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Viscosity controls humidity dependence of N₂O₅ uptake to citric acid aerosol

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Abstract

The heterogeneous loss of dinitrogen pentoxide (N_2O_5) to aerosol particles has a significant impact on the night time nitrogen oxide cycle and therefore the oxidative capacity in the troposphere. Using a ^{13}N short lived radioactive tracer method we studied the uptake kinetics of N_2O_5 on citric acid aerosol particles as a function of relative humidity (RH). The results show that citric acid exhibits lower reactivity than similar di- and polycarboxylic acids, with uptake coefficients between $\sim 3 \times 10^{-4}$ – $\sim 3 \times 10^{-3}$ depending on humidity (17–70 % RH). This humidity dependence can be explained by a changing viscosity and, hence, diffusivity in the organic matrix. Since the viscosity of highly concentrated citric acid solutions is not well established, we present four different parameterizations of N_2O_5 diffusivity based on the available literature data or estimates for viscosity and diffusivity. Above 50 % RH, uptake is consistent with the reacto-diffusive kinetic regime whereas below 50 % RH, the uptake coefficient is higher than expected from hydrolysis of N_2O_5 within the bulk of the particles, and the uptake kinetics may be limited by loss on the surface only. This study demonstrates the impact of viscosity in highly oxidized and highly functionalized secondary organic aerosol material on the heterogeneous chemistry of N_2O_5 and may explain some of the unexpectedly low loss rates to aerosol derived from field studies.

1 Introduction

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



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aerosols has thus received substantial interest over the past decades (Abbatt et al., 2012). The loss rate of N₂O₅ from the gas phase to aerosol particles is expressed in terms of the uptake coefficient, γ , which represents the probability that a gas kinetic collision of a N₂O₅ molecule leads to its uptake at the interface. Extensive studies on inorganic aerosols or corresponding proxy systems have shown that the primary factors influencing the uptake coefficient in the range of 0.0001 to 0.05 are relative humidity (RH), physical state, particle size and composition (Abbatt et al., 2012; Davis et al., 2008; George et al., 1994; Hallquist et al., 2003; Hanson and Ravishankara, 1991; Hu and Abbatt, 1997; Karagulian et al., 2006; Mozurkewich and Calvert, 1988; Vandoren et al., 1991; Wahner et al., 1998). Supersaturated liquid particles have shown uptake coefficients up to 1–2 orders of magnitude higher than corresponding solid particles at the same RH, pointing towards the importance of the hydrolysis reaction (Reactions R3–R7) of N₂O₅ with liquid water present in the bulk of aerosol particles (Hallquist et al., 2003; Thornton and Abbatt, 2005).

Recently, the focus of N₂O₅ uptake studies has shifted towards organic and mixed inorganic and organic aerosol particles (Anttila et al., 2006; Gaston et al., 2014; Griffiths et al., 2009; Gross et al., 2009; Thornton et al., 2003). Hydrophobic organics may rather form organic surface films or phase separated liquid coatings and thereby may suppress γ for N₂O₅ significantly compared to pure inorganic aerosols (Badger et al., 2006; Riemer et al., 2009; Thornton and Abbatt, 2005). In turn, particles composed of hygroscopic organics, such as polycarboxylic acids, show uptake coefficient values that in some cases approach those for inorganic aerosols due to their high water content (Griffiths et al., 2009; Thornton et al., 2003), and the humidity-dependent uptake can be understood in terms of the concentration of water as reactant (Ammann et al., 2013).

Organic aerosols account for a significant fraction of atmospheric particulate mass (Kanakidou et al., 2005). However there are still significant gaps in our knowledge regarding the chemistry and physical state of organic aerosols (De Gouw and Jimenez, 2009; Kanakidou et al., 2005; Zhang et al., 2007). Recent studies have shown that the previous assumptions of low-viscosity, well mixed liquid aerosol phases are not al-

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ways correct, but must be considered depending on environmental conditions such as humidity and temperature. Especially under cold or dry conditions, aerosol particles dominated by organic compounds can exhibit a highly viscous or even glassy state (Koop et al., 2011; Murray, 2008; Renbaum-Wolff et al., 2013; Virtanen et al., 2010; Zobrist et al., 2008). Diffusion in these particles is significantly retarded (Price et al., 2014; Zobrist et al., 2011), leading to severe kinetic limitations in gas-particle partitioning (Shiraiwa et al., 2013; Vaden et al., 2011).

Field measurements (Bertram et al., 2009; Brown et al., 2009) have shown that the observed reactivity of N₂O₅ on aerosol particles containing organics can be up to a factor of 10 lower than the values predicted by model parameterizations, which are based on laboratory measurements with organic compounds such as malonic acid. Also, a recent laboratory study has shown that uptake of N₂O₅ to laboratory SOA proxies does not only follow the expected trend with water content based on the correlation of the latter with O : C ratio (Gaston et al., 2014).

For this study we investigated the uptake of N₂O₅ on citric acid aerosol using the short-lived ¹³N radioactive tracer technique developed at the Paul Scherrer Institute (Ammann, 2001; Gržinić et al., 2014). This technique has been used before to study the uptake kinetics of other nitrogen oxides on aerosol particles (Guimbaud et al., 2002; Sosedova et al., 2009; Vlasenko et al., 2009), and we have recently developed a method to produce ¹³N labeled N₂O₅ for use in the kinetic experiments (Gržinić et al., 2014). Citric acid was used as a proxy for highly oxidized organic species found in secondary organic aerosol (SOA). It has well-known thermodynamic properties and new studies on viscosity and water diffusivity in citric acid have recently become available (Lienhard et al., 2012, 2014). In our study, measurements were conducted over a wide RH range and several methods were used to estimate the diffusivity of N₂O₅ in citric acid as a basis for the kinetic analysis.

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 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 $^{16}\text{O}(p, \alpha)^{13}\text{N}$ 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 $\sim 380^\circ\text{C}$) 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^{-1}) is mixed with nitrogen carrier gas and non-labeled NO ($\sim 2 \text{ mL min}^{-1}$) from a certified gas cylinder (10 ppm in N_2). O_3 at ~ 8 ppmv is produced by irradiating a flow (50 mL min^{-1}) 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).

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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. To avoid efflorescence of the aerosol particles, the sheath gas used in the diffusion drier has been humidified to 15–17 % RH. The resulting aerosol gas flow was passed through a homemade ⁸⁵Kr bipolar ion source to establish an equilibrium charge distribution on the aerosol, followed by an electrostatic precipitator to remove all charged particles. This was done to avoid uncontrollable wall losses of charged particles in the insulating aerosol flow tube. A homemade Gore-Tex membrane humidifier was placed behind the precipitator for precise adjustment of RH, followed by an elution volume with ~ 2 min residence time to assure gas – particle equilibrium. Measurements were conducted from 17 to 70.3 % RH.

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

2.3 Aerosol flow tube

The gas flows containing aerosol and N₂O₅, respectively, were mixed in a cylindrical flow tube reactor consisting of a PFA tube with an inner diameter of 7 cm. The inlet and outlet are cylindrical PTFE stops with inverse cones milled into. The stops are equipped with a pneumatic ring to seal the reactor. The inlet and outlet can be moved inside the reactor to vary reaction time. The N₂O₅ gas flow (102 mL min⁻¹) is introduced

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in the gas phase, cannot be separated from N₂O₅ by this technique and is likewise absorbed on the first denuder plate together with N₂O₅. The citric acid coating was prepared by applying a citric acid solution 2 % by weight in 50/50 % methanol/water to the plates and allowed to dry at room temperature. The following two denuders were coated with a 1 % N-(1-naphtyl) ethylene diamine dihydrochloride (NDA) solution in 1 % KOH and 10 % water in methanol. NDA reacts efficiently with NO₂ and the basic nature of the solution prevents the re-evaporation of the so formed nitrite. Since NDA is sensitive to O₃, which is present at around ~ 550 ppbv in our system, two sets of denuder plates were installed in series to extend the operating life. Fresh coatings were prepared and applied every day. An additional gamma detector was attached to the non-coated, 10 cm long, and trapezoidally shaped aluminium inlet to determine the amount of N₂O₅ trapped there.

The ¹³N containing species that were trapped on the denuder plates, inlet and particle filter were measured by monitoring the radioactive decay of ¹³N. A CsI scintillator crystal with integrated PIN diode detector (Carroll and Ramsey, USA) was placed on each of the traps. ¹³N, a well-known β⁺ emitter, decays with emission of a positron which, upon annihilation with an electron, emits two coincident γ rays in opposite directions. These γ rays are detected by the scintillators and the signal is converted to the flux of the ¹³N containing gaseous species into the respective traps using the inversion procedure reported elsewhere (Kalberer et al., 1996). The flux into a trap can be calculated using Eq. (1).

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

Where I_j is the flux into trap j , $A_{j(i-1)}$ and $A_{j(i)}$ are two consecutive activity measurements performed at times $t_{(i-1)}$ and $t_{(i)}$ and λ is the decay constant for ¹³N ($\lambda = 0.00116 \text{ s}^{-1}$). The measured flux is proportional to the gas phase concentration of the respective species. By comparing the value of the gas phase NO₂ concentration measured with the NO_x analyzer to the ¹³NO₂ and ¹³N₂O₅ signals measured at the

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denuder traps and the particle filter it is possible to calculate the concentration of N₂O₅ in the gas phase and its degradation products in the particle phase. The overall signal of N₂O₅ in the gas phase was obtained by adding the inlet and first citric acid coated denuder plate signals and subtracting the second citric acid denuder signal (NO₂ interference). To correct for the small amounts of NO₃ present in the gas phase the signal was multiplied with the N₂O₅/(NO₃ + N₂O₅) ratio obtained via the gas kinetic model described in our previous study (Gržinić et al., 2014).

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

3 Results and discussion

3.1 Uptake coefficient of N₂O₅ as a function of relative humidity

A typical experiment was performed as follows: after a period of stabilization, during which all flows were switched on, but the nebulizer switched off, the NO and NO₂ concentrations were measured via the NO_x analyzer connected to the system (in place of the SMPS), before turning on the O₃ generator. Concentrations around 9–10 ppbv of NO were obtained in the aerosol flow tube reactor. From the measured gamma-ray detector signals of N₂O₅ and NO₂, after switching on the O₃ generator, typically, a maximum initial concentration of ~5 ppbv of N₂O₅ was calculated. Next, a wall loss measurement was performed by changing the length of the aerosol flow tube and thus the reaction time, which is shown in the first part of the exemplary record of an experiment in Fig. 1. Typical pseudo-first order wall loss rate constants, k_w , were ~9 × 10⁻³ and ~3 × 10⁻² s⁻¹ for low and high humidity, respectively, indicating strong wall loss of the labeled N₂O₅ molecules. k_w was remaining constant over time after an initial passivation period. After the wall loss measurement was completed, the SMPS was

connected to the system and the reactor length was adjusted to enable a 60 s reaction time within the aerosol flow tube.

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

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

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

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 in the particle phase at the end of the reactor, $t = 60$ s, k_w is the wall loss rate constant, measured as described above, and k_p denotes the apparent first order rate coefficient for loss of N_2O_5 from the gas phase due to its heterogeneous reaction with the aerosol phase. Eq. (3) relates k_p to the uptake coefficient, γ :

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

where S_p is the total aerosol surface area to gas volume ratio obtained with the SMPS, ω is the mean thermal velocity of N_2O_5 , R is the gas constant, T is the absolute temperature and M is the molar weight of N_2O_5 . Equation (2) was then used to fit the experimental data as shown in Fig. 2 with γ being the only variable. Note that this procedure of varying the aerosol surface area to volume ratio gave better reproducibility and lower scatter than varying the interaction time. The resulting γ values ranged from 3×10^{-4} to $\sim 3 \times 10^{-3}$ over the RH range of 17 to 70 % as shown in Fig. 3.

The uncertainty in γ arises primarily from the fact that aerosol uptake rates (k_p) were smaller than wall loss rates (k_w) as well as from the systematic error associated with

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the measurements of surface to volume ratio of the aerosol by the SMPS (S_p), which amounts to $\sim 30\%$. The 95 % confidence interval from replication (as can be seen in Fig. 2) does not strongly influence the overall uncertainty for γ . There are a few factors that may have influenced the scatter among the measurements at different RH.

We have noticed that a small but variable number of very large particles fell outside the measurement range of the DMA, which for our settings was limited to particle diameters up to 806 nm. Additionally, two separate batches of citric acid (from the same manufacturer) have been used to prepare the solutions, and possible contaminations may have affected the physical properties of the resulting aerosol.

Compared to other aqueous polycarboxylic acids (Griffiths et al., 2009; Thornton et al., 2003) the uptake coefficient on citric acid is more than an order of magnitude lower. As mentioned in the experimental section, care was taken to avoid crystallization by equilibrating the solution droplets resulting from the nebulizer to the lowest RH used in the experiments. Therefore, the low uptake coefficients are unlikely to represent uptake to crystalline citric acid. With respect to the humidity range, the primary limitations were wall loss (at high RH) and potential efflorescence of the aqueous aerosol (at low RH).

As a consistency test we measured the uptake coefficient of N₂O₅ on deliquesced ammonium sulfate aerosol at 52 % RH as described by (Gržinić et al., 2014) and obtained an average value of $(1.4 \pm 0.4) \times 10^{-2}$, similar to other studies compiled in (Ammann et al., 2013).

3.2 Physical state, reaction mechanism and parameterization

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

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

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

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

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

$$q = \frac{l}{r} \quad (5)$$

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

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

The reacto-diffusive length is the characteristic distance that a molecule diffuses within a particle before reacting, which brings about a size dependence of γ when l is comparable to or larger than the radius of the particle ($q > 1$). Equation (5), in which the complex mechanism (Reactions R3–R7) is lumped into the net Reaction (R2) by treating only one dissolved N_2O_5 species undergoing a bimolecular reaction with liquid phase water, provides a reasonable parameterization to describe uptake of N_2O_5 to laboratory generated aerosol particles (Ammann et al., 2013). An analytical expression has been suggested to take into account the nitrate effect (Griffiths et al., 2009). Since we have worked at low N_2O_5 concentrations (5 ppbv), where the maximum HNO_3 concentration expected in the particle phase was $\sim 10^{-3}$ M, we could safely neglect this.

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

Since water is the main reactant for the hydrolysis of N_2O_5 , the parameterization relies heavily on the water concentration as a function of RH. Mass growth factor values

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(and consequently mass fractions) for citric acid and water were obtained from Zardini et al. (2008), while the citric acid solution densities have been obtained from several sources, each relating to the particular parameterization used for viscosity further below (Laguerie et al., 1976; Lienhard et al., 2012; Peng et al., 2001).

For the diffusion coefficient D_1 of N_2O_5 in an aqueous solution, previous studies were based 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., 2003; Thornton et al., 2003), independent of water activity. Together with the other parameters, this leads to a reasonable agreement of the parameterisation based on Eq. (4) with the measured data for malonic acid. However, as it turns out, the parameterisation would largely overpredict the reactivity for citric acid. Citric acid solutions exhibit a substantially higher viscosity, i.e. for a solution of 1.04 M, the reported viscosity (Laguerie et al., 1976) of 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, 2008), close to that of water ($0.91 \times 10^{-3} \text{ Pa s}$). It is therefore likely that the lower uptake coefficients of N_2O_5 in citric acid compared to those for malonic acid are caused by lower diffusivity in the more viscous solution. Since the diffusivity of N_2O_5 is not known in either medium, we used four methods for its estimation, based either on measured viscosities or on measured or estimated diffusivity of H_2O . If the viscosity is known, D_1 for N_2O_5 can be calculated by applying the Stokes–Einstein relation (Eq. (7)).

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

Where k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity and r is the radius of the N_2O_5 molecule assumed spherical (2.5 Å). Uncertainty remains with respect to the effective molecular radius to be used, since we don't know the identity of the solute for the rate limiting step (dissolved N_2O_5 or NO_2^+). Additionally, for high viscosity (at low RH), the use of the Stokes–Einstein relation may be questioned: Power et al. (2013) suggested that the diffusivity of water in sucrose droplets decouples from the viscosity at viscosities around 1 Pa s, and at 10 Pa s the diffusivity

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calculated by Eq. (7) departs from measured values already by an order of magnitude. For the cases, where the diffusivity of H_2O is known or estimated, we also used Eq. (7) to estimate the diffusivity of N_2O_5 by accounting for the change in molecular size.

The results are summarized in Fig. 4. The different parameterizations are represented by solid lines, and by dashed lines where the use of the Stokes–Einstein relation may not be granted. The first one (labeled “Laguerie”) is based on viscosity measurements by Laguerie et al. (1976). The viscosity parameterization in this case covers a range of citric acid concentrations up to ~ 4.3 M, which in our case corresponds to RH values $> 70\%$. More recent measurements of viscosity of citric acid were provided by C. Cai and J. Reid (personal communication, 2015) from a combination of optical tweezers and electrodynamic balance (EDB) experiments covering a range of 3 to 73% RH (labeled “Reid” in Fig. 4). The third method is based on an estimate of the diffusivity of H_2O in the organic matrix, which is in turn based on the principal parameterization for the one of H_2O in sucrose from Zobrist et al. (2011). This method uses the measured glass transition and hygroscopicity data to infer diffusion properties of a target substance (e.g. citric acid) by extrapolation from a known reference substance (e.g. sucrose) (Berkemeier et al., 2014) (labeled “Berkemeier” in Fig. 4). The same method has been used to estimate the diffusivity of N_2O_5 in malonic acid. Finally, Lienhard et al. (2014) determined the diffusivity of H_2O in citric acid solution droplets by measuring the kinetics of the size change in response to step changes in RH in an EDB. The data are parameterized via an empirical Vignes-type equation (Lienhard et al., 2012, 2014).

The result of calculating the uptake coefficient according to Eq. (4) and using diffusion coefficients estimated according to these four methods is presented in Fig. 5. The solid and dashed shape of the lines again indicate the validity of the Stokes–Einstein relation as a basis for diffusivity estimation. Figure 5 also shows data of malonic acid (Griffiths et al., 2009; Thornton et al., 2003) and its calculated uptake coefficient based on Eq. (4), using the corresponding estimate of N_2O_5 diffusivity.

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The parameterization based on the Lienhard et al. H₂O diffusivity data starts to deviate strongly from the rest as well as from the measured citric acid uptake coefficients above 30 % RH, overestimating the uptake by about a factor 3–4. We note that the Vignes type parameterization used by Lienhard et al. (2014) was constrained by measurements of the diffusivity of water below 40 % RH at max 281 K only. Since H₂O is much smaller than N₂O₅, the diffusivity of N₂O₅ may exhibit a different slope as a function of humidity. The parameterization based on the Laguerie viscosity data is limited by the small range of solution compositions covered by measurements (RH > 70 %). The other parameterizations (Berkemeier, Reid) follow the measured uptake values fairly well down to values of about 50 % RH, indicating that the changing viscosity and associated changes in diffusivity as a function of RH control the uptake coefficient of N₂O₅. At lower RH the measured data seem to level off, which may be related to the decoupling between viscosity and diffusivity below 10 Pa s, which would lead to underestimating the uptake coefficient (Debenedetti and Stillinger, 2001; Power et al., 2013).

In spite of the uncertainties related to the diffusivity estimates, the uptake coefficient parameterized by Eq. (4), while well describing the measurements at higher RH, clearly underestimates the measurements at low RH. To assess the validity of the reacto-diffusive regime, we consider the reacto-diffusive length (Table 1), which remains much smaller than 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 N₂O₅, remains well mixed. Even for 15 % RH, using the diffusivity parameterization closest to our measured results (Berkemeier), the diffusivity of H₂O is about $1.34 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, and the characteristic time for diffusion across a particle, $t = d_p^2 / D_{\text{H}_2\text{O}}$, becomes about 0.75 s, which is significantly shorter than the time-scale of our uptake experiment. Other effects, such as salting in of N₂O₅ (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 N₂O₅ becomes limited by its hydrolysis on the surface, which is not included in Eq. (4). The uptake coefficient in the 10^{-4} range is comparable to that 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 %) and high (70 %) RH. The results can be described under the assumption that citric acid remains a supersaturated liquid, even at low RH, and exhibits an increased viscosity at low water content. Reactive uptake is found to be governed by reacto-diffusive limitation with the reacto-diffusive length decreasing under the influence of increased viscosity (and thus decreased diffusivity) from a few nm to the sub-nanometer range. Thus, the decreasing uptake coefficients with decreasing RH are well explained by the decreasing diffusivity of N_2O_5 . However, because estimating the diffusivity of N_2O_5 from measured diffusivity of H_2O or measured viscosity is problematic due to the decoupling between viscosity and diffusivity at high viscosity, the parameterization of N_2O_5 uptake by the traditional bulk reacto-diffusive uptake regime alone becomes uncertain at low RH. It cannot be ruled out that a surface reaction contributes significantly to uptake at low relative humidity.

Secondary organic aerosol (SOA) is likely to exhibit a similar, or even higher viscosity compared to citric acid used here as model compound (Renbaum-Wolff et al., 2013). Thus high viscosity at low RH could explain the discrepancy between N_2O_5 reactivity in field measurements and model predictions based on laboratory measurements. A recent study (Gaston et al., 2014) suggested that the organic O : C ratio in mixed inorganic–organic aerosols may be used as an indicator of N_2O_5 reactivity, based on a trend of increasing uptake coefficient with increasing O : C ratio. However, citric acid and some high O : C mixtures containing citric acid and other highly functionalized ox-

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idized organic compounds were an exception to this trend. Hence, while O : C ratio can serve as an indicator for reactivity towards N₂O₅ at low O : C, this trend might be reversed for highly oxidized organic compounds forming high viscosity aqueous solutions. Parameterization of N₂O₅ reactivity in atmospheric models should thus not only rely on particle O : C, but should also have means to take into account high particle viscosity.

**The Supplement related to this article is available online at
doi:10.5194/acpd-15-21983-2015-supplement.**

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References

- Abbatt, J. P. D., Lee, A. K. Y., and Thornton, J. A.: Quantifying trace gas uptake to tropospheric aerosol: recent advances and remaining challenges, *Chem. Soc. Rev.*, 41, 6555–6581, 2012.
- Ammann, M.: Using ¹³N as tracer in heterogeneous atmospheric chemistry experiments, *Radiochim. Acta*, 89, 831–838, 2001.
- 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.

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Anttila, T., Kiendler-Scharr, A., Tillmann, R., and Mentel, T. F.: On the reactive uptake of gaseous compounds by organic-coated aqueous aerosols: theoretical analysis and application to the heterogeneous hydrolysis of N₂O₅, *J. Phys. Chem. A*, 110, 10435–10443, 2006.

Badger, C. L., Griffiths, P. T., George, I., Abbatt, J. P. D., and Cox, R. A.: Reactive uptake of N₂O₅ by aerosol particles containing mixtures of humic acid and ammonium sulfate, *J. Phys. Chem. A*, 110, 6986–6994, 2006.

Berkemeier, T., Shiraiwa, M., Pöschl, U., and Koop, T.: Competition between water uptake and ice nucleation by glassy organic aerosol particles, *Atmos. Chem. Phys.*, 14, 12513–12531, doi:10.5194/acp-14-12513-2014, 2014.

Bertram, T. H., Thornton, J. A., Riedel, T. P., Middlebrook, A. M., Bahreini, R., Bates, T. S., Quinn, P. K., and Coffman, D. J.: Direct observations of N₂O₅ reactivity on ambient aerosol particles, *Geophys. Res. Lett.*, 36, L19803, doi:10.1029/2009GL040248, 2009.

Brown, S. S., Dube, W. P., Fuchs, H., Ryerson, T. B., Wollny, A. G., Brock, C. A., Bahreini, R., Middlebrook, A. M., Neuman, J. A., Atlas, E., Roberts, J. M., Osthoff, H. D., Trainer, M., Fehsenfeld, F. C., and Ravishankara, A. R.: Reactive uptake coefficients for N₂O₅ determined from aircraft measurements during the second Texas air quality study: comparison to current model parameterizations, *J. Geophys. Res.-Atmos.*, 114, D00F10, doi:10.1029/2008JD011679, 2009.

Chang, W. L., Bhave, P. V., Brown, S. S., Riemer, N., Stutz, J., and Dabdub, D.: Heterogeneous atmospheric chemistry, ambient measurements, and model calculations of N₂O₅: a Review, *Aerosol Sci. Tech.*, 45, 665–695, 2011.

Chmielewska, A. and Bald, A.: Viscosimetric studies of aqueous solutions of dicarboxylic acids, *J. Mol. Liq.*, 137, 116–121, 2008.

Davidovits, P., Hu, J. H., Worsnop, D. R., Zahniser, M. S., and Kolb, C. E.: Entry of gas molecules into liquids, *Faraday Discuss.*, 100, 65–81, 1995.

Davis, J. M., Bhave, P. V., and Foley, K. M.: Parameterization of N₂O₅ reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate, *Atmos. Chem. Phys.*, 8, 5295–5311, doi:10.5194/acp-8-5295-2008, 2008.

Debenedetti, P. G. and Stillinger, F. H.: Supercooled liquids and the glass transition, *Nature*, 410, 259–267, 2001.

De Gouw, J. and Jimenez, J. L.: Organic aerosols in the Earth's atmosphere, *Environ. Sci. Technol.*, 43, 7614–7618, 2009.

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- Dentener, F. J. and Crutzen, P. J.: Reaction of N₂O₅ on tropospheric aerosols: impact on the global distributions of NO_x, O₃, and OH, *J. Geophys. Res.-Atmos.*, 98, 7149–7163, 1993.
- Gaston, C. J., Thornton, J. A., and Ng, N. L.: Reactive uptake of N₂O₅ to internally mixed inorganic and organic particles: the role of organic carbon oxidation state and inferred organic phase separations, *Atmos. Chem. Phys.*, 14, 5693–5707, doi:10.5194/acp-14-5693-2014, 2014.
- George, C., Ponche, J. L., Mirabel, P., Behnke, W., Scheer, V., and Zetzsch, C.: Study of the uptake of N₂O₅ by water and NaCl Solutions, *J. Phys. Chem.*, 98, 8780–8784, 1994.
- Griffiths, P. T., Badger, C. L., Cox, R. A., Folkers, M., Henk, H. H., and Mentel, T. F.: Reactive uptake of N₂O₅ by aerosols containing dicarboxylic acids, effect of particle phase, composition, and nitrate content, *J. Phys. Chem. A*, 113, 5082–5090, 2009.
- Gross, S., Iannone, R., Xiao, S., and Bertram, A. K.: Reactive uptake studies of NO₃ and N₂O₅ on alkenoic acid, alkanolate, and polyalcohol substrates to probe nighttime aerosol chemistry, *Phys. Chem. Chem. Phys.*, 11, 7792–7803, 2009.
- Gržinić, G., Bartels-Rausch, T., Birrer, M., Türler, A., and Ammann, M.: Production and use of ¹³N labeled N₂O₅ to determine gas–aerosol interaction kinetics, *Radiochim. Acta*, 102, 1025–1034, 2014.
- Guimbaud, C., Arens, F., Gutzwiller, L., Gäggeler, H. W., and Ammann, M.: Uptake of HNO₃ to deliquescent sea-salt particles: a study using the short-lived radioactive isotope tracer ¹³N, *Atmos. Chem. Phys.*, 2, 249–257, doi:10.5194/acp-2-249-2002, 2002.
- Hallquist, M., Stewart, D. J., Stephenson, S. K., and Cox, R. A.: Hydrolysis of N₂O₅ on sub-micron sulfate aerosols, *Phys. Chem. Chem. Phys.*, 5, 3453–3463, 2003.
- Hanson, D. R. and Ravishankara, A. R.: The reaction probabilities of ClONO₂ and N₂O₅ on 40 to 75 % sulfuric acid solutions, *J. Geophys. Res.-Atmos.*, 96, 17307–17314, 1991.
- Hu, J. H. and Abbatt, J. P. D.: Reaction probabilities for N₂O₅ hydrolysis on sulfuric acid and ammonium sulfate aerosols at room temperature, *J. Phys. Chem. A*, 101, 871–878, 1997.
- Kalberer, M., Tabor, K., Ammann, M., Parrat, Y., Weingartner, E., Piguet, D., Rössler, E., Jost, D. T., Turler, A., Gaggeler, H. W., and Baltensperger, U.: Heterogeneous chemical processing of (NO₂)-N-13 by monodisperse carbon aerosols at very low concentrations, *J. Phys. Chem.*, 100, 15487–15493, 1996.
- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K.,

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Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmos. Chem. Phys.*, 5, 1053–1123, doi:10.5194/acp-5-1053-2005, 2005.

Karagulian, F., Santschi, C., and Rossi, M. J.: The heterogeneous chemical kinetics of N₂O₅ on CaCO₃ and other atmospheric mineral dust surrogates, *Atmos. Chem. Phys.*, 6, 1373–1388, doi:10.5194/acp-6-1373-2006, 2006.

Koop, T., Bookhold, J., Shiraiwa, M., and Poschl, U.: Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere, *Phys. Chem. Chem. Phys.*, 13, 19238–19255, 2011.

Laguerie, C., Aubry, M., and Couderc, J. P.: Some physicochemical data on monohydrate citric acid solutions in water: solubility, density, viscosity, diffusivity, pH of standard solution, and refractive index, *J. Chem. Eng. Data.*, 21, 85–87, 1976.

Laskin, A., Moffet, R. C., Gilles, M. K., Fast, J. D., Zaveri, R. A., Wang, B., Nigge, P., and Shutthanandan, J.: Tropospheric chemistry of internally mixed sea salt and organic particles: surprising reactivity of NaCl with weak organic acids, *J. Geophys. Res.-Atmos.*, 117, D15302, doi:10.1029/2012JD017743, 2012.

Lienhard, D. M., Bones, D. L., Zuend, A., Krieger, U. K., Reid, J. P., and Peter, T.: Measurements of Thermodynamic and Optical Properties of Selected Aqueous Organic and Organic-Inorganic Mixtures of Atmospheric Relevance, *J. Phys. Chem. A*, 116, 9954–9968, 2012.

Lienhard, D. M., Huisman, A. J., Bones, D. L., Te, Y.-F., Luo, B. P., Krieger, U. K., and Reid, J. P.: Retrieving the translational diffusion coefficient of water from experiments on single levitated aerosol droplets, *Phys. Chem. Chem. Phys.*, 16, 16677–16683, 2014.

Mentel, T. F., Sohn, M., and Wahner, A.: Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, *Phys. Chem. Chem. Phys.*, 1, 5451–5457, 1999.

Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Pöschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, *Atmos. Chem. Phys.*, 9, 9491–9522, doi:10.5194/acp-9-9491-2009, 2009.

Mozurkewich, M. and Calvert, J. G.: Reaction probability of N₂O₅ on aqueous aerosols, *J. Geophys. Res.-Atmos.*, 93, 15889–15896, 1988.

Murray, B. J.: Inhibition of ice crystallisation in highly viscous aqueous organic acid droplets, *Atmos. Chem. Phys.*, 8, 5423–5433, doi:10.5194/acp-8-5423-2008, 2008.

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Peng, C., Chan, M. N., and Chan, C. K.: The hygroscopic properties of dicarboxylic and multi-functional acids: measurements and UNIFAC predictions, *Environ. Sci. Technol.*, 35, 4495–4501, 2001.

Power, R. M., Simpson, S. H., Reid, J. P., and Hudson, A. J.: The transition from liquid to solid-like behaviour in ultrahigh viscosity aerosol particles, *Chemical Science*, 4, 2597–2604, 2013.

Price, H. C., Murray, B. J., Mattsson, J., O'Sullivan, D., Wilson, T. W., Baustian, K. J., and Bening, L. G.: Quantifying water diffusion in high-viscosity and glassy aqueous solutions using a Raman isotope tracer method, *Atmos. Chem. Phys.*, 14, 3817–3830, doi:10.5194/acp-14-3817-2014, 2014.

Renbaum-Wolff, L., Grayson, J. W., Bateman, A. P., Kuwata, M., Sellier, M., Murray, B. J., Shilling, J. E., Martin, S. T., and Bertram, A. K.: Viscosity of α -pinene secondary organic material and implications for particle growth and reactivity, *P. Natl. Acad. Sci. USA*, 110, 8014–8019, 2013.

Riemer, N., Vogel, H., Vogel, B., Anttila, T., Kiendler-Scharr, A., and Mentel, T. F.: Relative importance of organic coatings for the heterogeneous hydrolysis of N₂O₅ during summer in Europe, *J. Geophys. Res.-Atmos.*, 114, D17307, doi:10.1029/2008JD011369, 2009.

Robinson, G. N., Worsnop, D. R., Jayne, J. T., Kolb, C. E., and Davidovits, P.: Heterogeneous uptake of ClONO₂ and N₂O₅ by sulfuric acid solutions, *J. Geophys. Res.-Atmos.*, 102, 3583–3601, 1997.

Shiraiwa, M., Yee, L. D., Schilling, K. A., Loza, C. L., Craven, J. S., Zuend, A., Ziemann, P. J., and Seinfeld, J. H.: Size distribution dynamics reveal particle-phase chemistry in organic aerosol formation, *P. Natl. Acad. Sci. USA*, 110, 11746–11750, 2013.

Sosedova, Y., Rouvière, A., Gäggeler, H. W., and Ammann, M.: Uptake of NO₂ to deliquesced dihydroxybenzoate aerosol particles, *J. Phys. Chem. A*, 113, 10979–10987, 2009.

Thornton, J. A. and Abbatt, J. P. D.: N₂O₅ reaction on submicron sea salt aerosol: kinetics, products, and the effect of surface active organics, *J. Phys. Chem. A*, 109, 10004–10012, 2005.

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.

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Table 1. Reacto-diffusive lengths calculated using diffusivity values obtained via the four 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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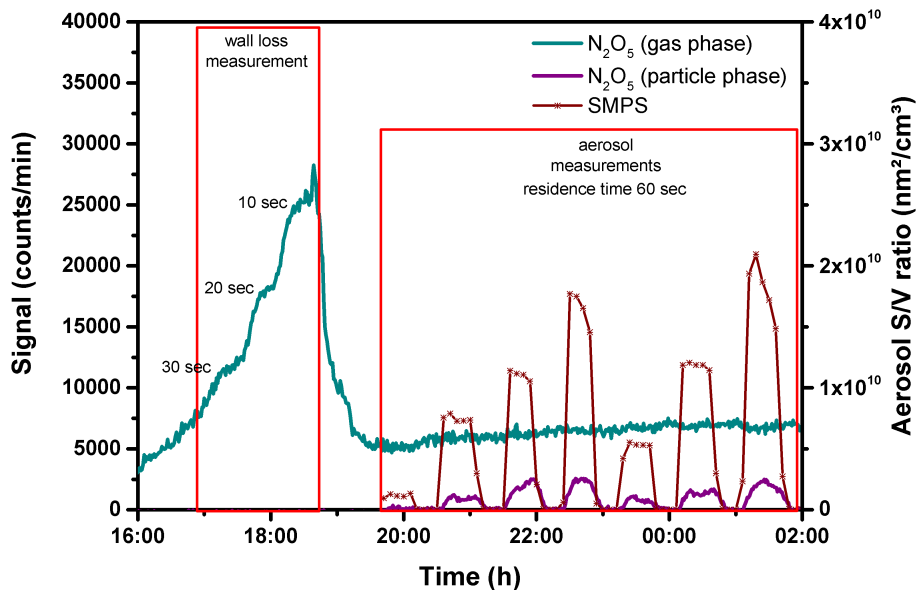


Figure 1. Exemplary traces of inverted detector signals for an experiment: teal: gas-phase $^{13}N_2O_5$ signal; purple: particle-phase ^{13}N signal; red: SMPS signal (aerosol surface/volume ratio).

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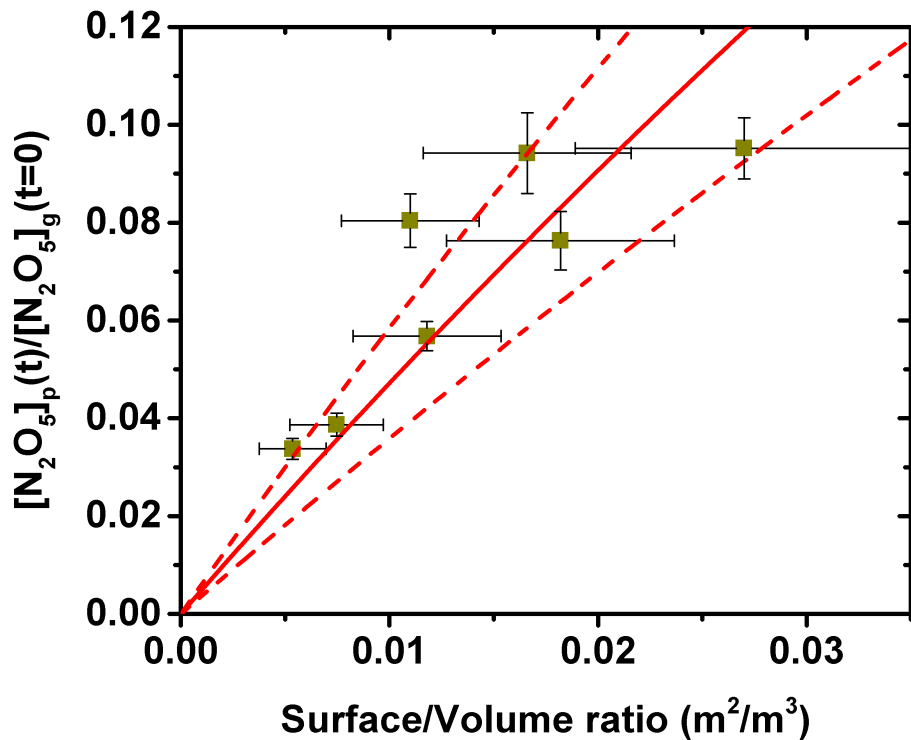


Figure 2. Normalized particle-phase N_2O_5 concentration vs. aerosol surface area to gas volume ratio for the experiment from Fig. 1. The data points represent experimental data; vertical error bars represent a 95 % confidence interval, horizontal error bars represent the S/V measurement error (30 %), the full red line is the fitted series determined by least-squares fitting of Eq. (2) to experimental data, the dashed red lines are 95 % confidence intervals.

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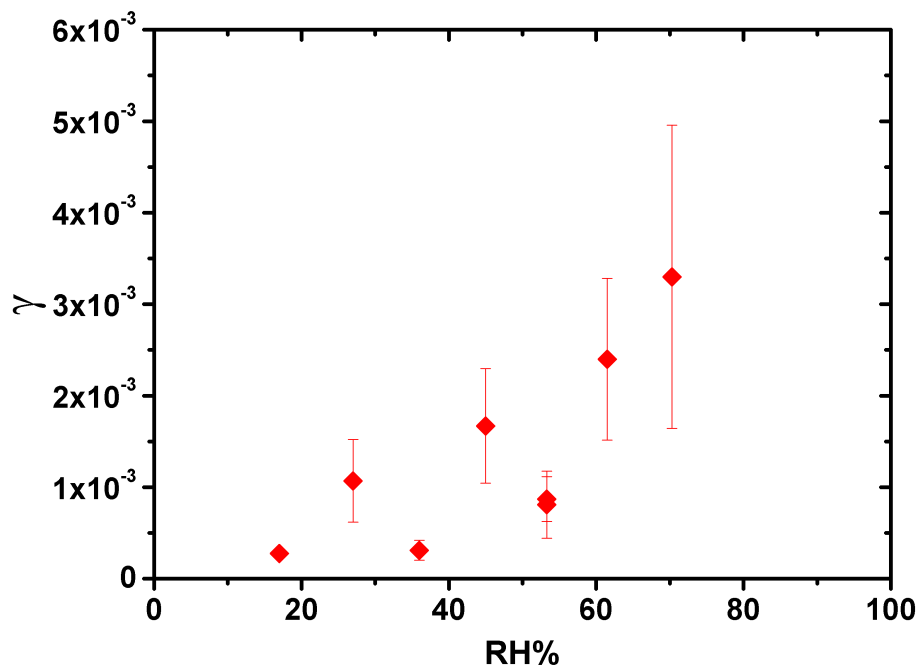
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Figure 3. Uptake coefficient of N_2O_5 on citric acid as a function of RH. Error bars represent 95 % confidence bounds. The measured values can be found in Table S1 of the Supplement.

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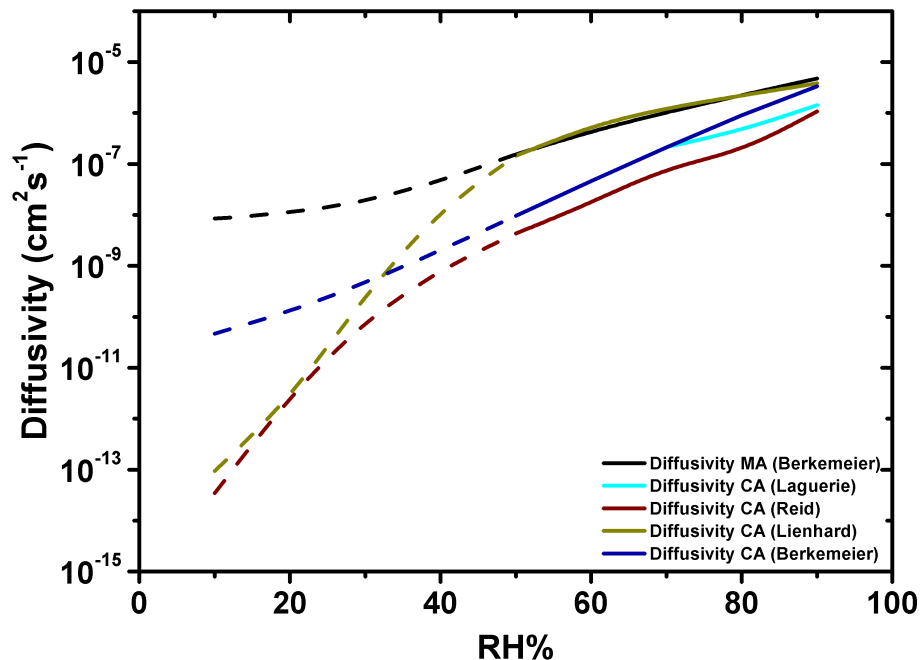


Figure 4. Diffusivity of N_2O_5 in malonic and citric acid solutions as calculated according to four parameterization methods: black: Berkemeier (for malonic acid); teal: Laguerie; red: Reid; green: Lienhard; blue: Berkemeier; see text for details. Calculated values for a RH range between 10 and 90 %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

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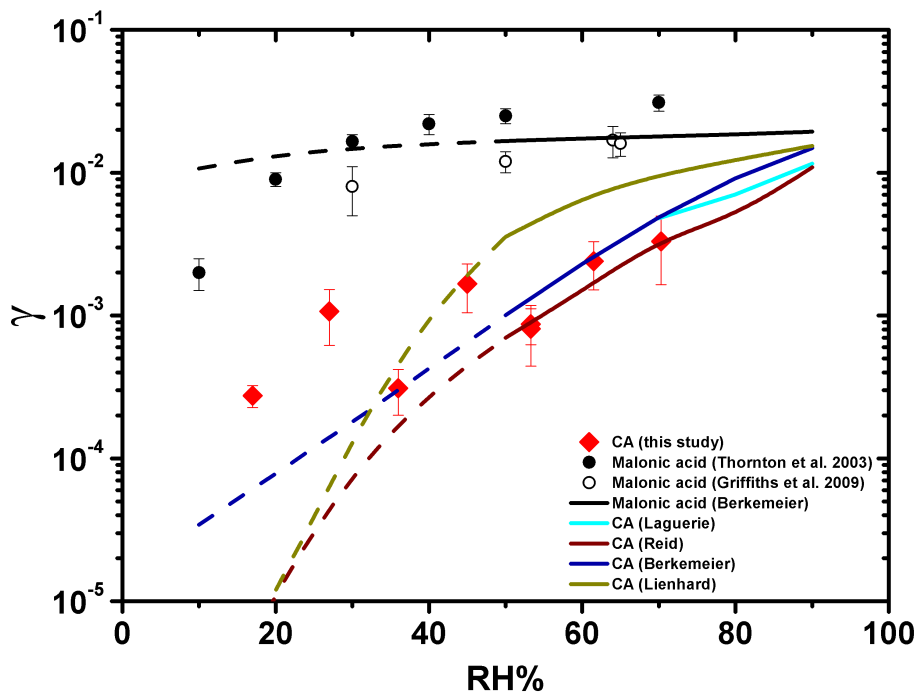


Figure 5. Parameterization of N_2O_5 uptake on citric acid aerosol based on diffusivities estimated by the four parameterization methods: teal: Laguerie; dark red: Reid; green: Lienhard; blue: Berkemeier; black: parameterization for malonic acid using the same kinetic parameters and diffusivity data estimated using the same method as Berkemeier; 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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