Production and use of $^{13}$N labeled N$_2$O$_5$ to determine gas–aerosol interaction kinetics

Abstract: Dinitrogen pentoxide has aroused significant interest in atmospheric chemistry because of its importance in the night time chemistry of nitrogen oxides to influence the tropospheric oxidation capacity. We have used an established method of $^{13}$N production to synthesize $^{13}$N labeled N$_2$O$_5$ for the first time in order to study N$_2$O$_5$ uptake kinetics on aerosol particles. $^{13}$N is produced via the $^{16}$O(p, α)$^{13}$N reaction in a gas target attached to the IP2 endstation of the Injector 2 cyclotron at PSI. The $^{13}$NO produced in the gas target is transported to a laboratory where it is mixed, under dry conditions, with non-labeled NO and O$_3$ in a gas reactor, giving $^{13}$NNO$_5$. The N$_2$O$_5$ thus produced is fed into an aerosol flow tube together with a humidified aerosol gas flow. The gaseous species present in the resulting gas flow are selectively separated via a narrow parallel plate diffusion denuder system, while aerosol particles can be trapped on a particle filter placed at the end of the denuder system. The activity of the $^{13}$N labeled species trapped on the denuder plates and in the particle filter can be monitored via scintillation counters. A system for the routine online production of $^{13}$N labeled N$_2$O$_5$ has been assembled and used to assess the conformity of the results by kinetic modeling of gas phase N$_2$O$_5$ chemistry, showing good agreement. A few exemplary experiments of uptake of labelled N$_2$O$_5$ to ammonium sulfate and citric acid particles are presented that are in good agreement with results obtained with other methods reported in the literature.

Keywords: N$_2$O$_5$, Nitrogen-13, Aerosols, Kinetics, Atmospheric Chemistry.

1 Introduction

During the last two decades the compound N$_2$O$_5$ has been the topic of many studies in the field of atmospheric chemistry due to its significant role in the nighttime tropospheric NO$_x$ chemistry. Its formation starts with oxidation of NO$_2$ to NO$_3$ radicals by ozone (R1) followed by a reaction with NO$_2$ that yields N$_2$O$_5$ (R2).

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad (\text{R1})$$

$$\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5 \quad (\text{R2})$$

Daytime formation of N$_2$O$_5$ is inefficient because of the short photolytic lifetime of NO$_3$ (~1 s); however, during the night N$_2$O$_5$ can reach concentrations of up to 10–15 ppb in polluted atmospheres and thus may play an important role in nighttime tropospheric chemistry [1]. During nighttime the concentration of N$_2$O$_5$ (as well as NO$_3$ and NO$_2$) is controlled by the equilibrium established between N$_2$O$_5$ formation and N$_2$O$_5$ loss due to thermal decomposition (R2).

The importance of N$_2$O$_5$ stems from its role as a NO$_3$ radical reservoir as well as being a major sink for NO$_3$ species due to the fast heterogeneous hydrolysis reaction with water molecules (R3) on aerosol and ice surfaces [2, 3].

$$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \quad (\text{R3})$$

Particle phase nitric acid formed via this heterogeneous reaction may then be removed from the atmospheric cycle via wet or dry deposition. Due to the equilibrium that exists between NO$_2$, NO$_3$ and N$_2$O$_5$, removal of the latter reduces the first two which leads to a reduction of tropospheric ozone, thus lowering the oxidizing capacity of the troposphere [1, 4, 5].

Because of the impact of N$_2$O$_5$ on ozone formation and the effect that removal via hydrolysis on aerosol particles has on the overall budget, uptake kinetics of N$_2$O$_5$ on aerosols have been an important topic of study. The
Mass Spectrometry (CIMS) [14] have been particularly popular. Down Spectroscopy (CRDS) [13] and Chemical Ionization Mass Spectrometry (CIMS) [14] have been particularly popular. CRDS is an optical method that uses a dye laser to inject a laser beam between two mirrors of high reflectivity placed in a cavity. The concentration of the analyte is proportional to the species concentration (in this case within the cavity with time, the decay rate being directly determined by monitoring the decay of the laser intensity). Various detection methods have been used; Cavity Ring-Down Spectroscopy (CRDS) [13] and Chemical Ionization Mass Spectrometry (CIMS) [14] have been particularly popular.

The method provides very low detection limits (down to the 1–5 pptv range), and allows for parallel measurements of NO$_3$ and N$_2$O$_5$. It can operate at ambient pressure and is relatively compact and thus suitable for field studies. CIMS is based on a selective ionization process resulting from a reaction between a reagent ion and the analyzed species followed by mass spectrometry of the resulting ions. Also this method is highly sensitive (10 pptv range) and the reagent ion used for N$_2$O$_5$ studies ($\Gamma^-$) is reasonably specific for either NO$_3$ or N$_2$O$_5$, ionizing both species to NO$_3^-$ detected at 62 amu. The principal drawback of the method is that it cannot differentiate between NO$_3$ and N$_2$O$_5$, and under typical operating conditions often non negligible background noise at 62 amu appears.

While the above mentioned measurement methods have many advantages, they still present some disadvantages that are non negligible, such as difficult operation under high relative humidity or the fact that in laboratory studies N$_2$O$_5$ uptake by aerosol particles can only be derived by following its loss from the gas phase. Instead, we have used the short lived $^{13}$N radioactive tracer technique developed at the Paul Scherrer Institute [15, 16]. This technique has been used already to study the uptake kinetics of other nitrogen oxides such as HNO$_3$ [17] and NO$_2$ [18] to aerosols and of NO$_3^-$ to ice surfaces [19–21], by labeling them with $^{13}$N, a short-lived isotope with a half-life of 10 min. $^{13}$N is well known as a positron emitter and also used in positron emission tomography (PET) for medical purposes [22]. In our application, we trace uptake in the particulate phase by monitoring the radioactive decay of $^{13}$N labeled N$_2$O$_5$ absorbed on aerosol particles while working under realistic ambient temperature and humidity conditions. In this study we will detail the method of production of $^{13}$N$_2$O$_5$ and the experimental setup to study the uptake kinetics on aerosol particles. The result-
ing flow is then directed into a parallel plate diffusion denuder system where the gaseous and particle phase products can be selectively separated and trapped on coated denuder plates and a particle filter, respectively. By monitoring the decay of \(^{13}\)N on each trap it is possible to derive simultaneously the concentration of the various \(^{13}\)N labeled species in the gas and particle phase. Figure 1 shows a schematic diagram of our experimental arrangement.

### 2.2 Production and transport of \(^{13}\)NO

At the Paul Scherrer Institute \(^{13}\)NO has been produced for the purpose of tracer experiments in atmospheric chemistry since about two decades. A detailed description of the method has been described earlier [15]. Briefly, \(^{13}\)N is produced via the \(^{16}\)O\((p,\alpha)^{13}\)N reaction in a gas-target by irradiating \(^{16}\)O with about 11 MeV protons at around 10 \(\mu\)A intensity. Developed from an earlier design [15], the gas-target is a conically shaped aluminium flow reactor attached to the Isotope Production Station IP2 at a branch of the Injector II cyclotron at PSI. The primary proton beam with an energy of 72 MeV is passed through a first de-grader to bring the energy down to 35 MeV. The window into the \(^{13}\)N target, consisting of two water cooled aluminium windows, is designed such that the energy of the protons at the entry into the gas volume is further degraded down to about 11 MeV. The further degradation within the gas target depends on pressure, which was kept at 2.5 bar, and a continuous 1 l/min STP flow of 20% \(^{18}\)O in He (all flow rates are given in volumetric flow normalized to standard temperature and pressure) is passed through the target. This pressure was also constrained by other boundary conditions of our experiments and not adjusted to optimize \(^{13}\)N production according to the detailed structure of the excitation function for the \(^{16}\)O\((p,\alpha)^{13}\)N reaction [23, 24]. Highly oxidized and reactive forms of nitrogen oxides are produced and chemically converted to \(^{13}\)NO over a Mo converter (at \(\sim 380 \, ^{\circ}\)C) connected to the gas-target in order to facilitate transport. As discussed in our earlier study [15], quantitative \(^{13}\)N output is difficult to achieve, likely due to chemical losses on surfaces before the Mo converter. Non-labeled nitrogen oxide species (at around 8 ppbv) are also produced from nitrogen impurities in the carrier gas and likewise converted to NO. Only a very small fraction of the overall NO produced contain the tracer atoms (below ppt levels), Additionally, trace amounts of carbon monoxide or carbon dioxide are formed from organic impurities present in the gas feed. The resulting \(^{13}\)NO containing gas is then continuously transported to the laboratory via a 580 m long PVDF tube (inner diameter 4 mm).

### 2.3 Production of \(^{13}\)N\(_2\)O\(_5\)

In the laboratory, selected amounts of the target gas flow (typically 50 ml/min) can be mixed with variable amounts of \(N_2\) and certified amounts (1 ml/min) of non-labeled NO from a gas cylinder (10 ppm in \(N_2\)) allowing to cover a wide range of NO concentrations in the ppb range. Possible traces of HONO are removed by using a \(Na_2CO_3\) trap. The \(^{13}\)NO gas flow is directed into the \(N_2\)O reactor where it is mixed with a flow (50 ml/min) containing ozone (\(\sim 4\) ppmv in this reactor) in order to generate \(^{13}\)N labeled \(N_2\)O\(_5\) via reactions (R1) and (R2). \(O_3\) is produced by passing a flow of 10% \(O_2\) in \(N_2\) over a UV lamp (185 nm wavelength). The \(N_2\)O\(_5\) reactor is covered with a shroud in order to prevent \(NO_3\) photolysis and thus loss of \(N_2\)O\(_5\). Additionally, in order to minimize losses due to heterogeneous hydrolysis on the walls, \(N_2\)O\(_5\) production is conducted under dry conditions, and the walls of the reactor are covered with PTFE foil. The resulting gas flow (101 ml/min) is then fed into the flow tube reactor, where it is mixed with the aerosol flow (720 ml/min).

### 2.4 Modeling of gas phase \(^{13}\)N\(_2\)O\(_5\) production

As a support tool for the design of the experiment and to address issues such as the slow formation of \(N_2\)O\(_5\) \textit{via} reactions (R4), (R1) and (R2) vs. the radioactive decay of \(^{13}\)N with a half-life of 10 min, a modeling study of gas phase \(N_2\)O\(_5\) formation has been carried out. The kinetics was based on the recommendations of the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation [25] and the NASA Panel for Data Evaluation [26]. Modeling work has been performed in Matlab using ODE (ordinary differential equation) solvers and using temperature, pressure, time, reactor geometry and starting concentrations for NO and \(O_3\) as input variables. Wall loss was also incorporated into the model. Overall 12 reactions have been included in the model (R4–R15). The rate coefficients listed beside the reactions are given at standard temperature and pressure. In the computer model pressure and temperature dependence of the rate coefficients as recommended in the above mentioned data bases has been included.

\[
NO + O_3 \rightarrow NO_2 + O_2
\]
\[
k = 1.8 \times 10^{-14} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}
\]  
(R4)
NO₂ + O₃ → NO₃ + O₂
k = 3.5 × 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹ (R5)

NO₂ + NO₃ → N₂O₅
k = 8.8 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ (R6)

N₂O₅ → NO₂ + NO₃
k = 6.9 × 10⁻² s⁻¹ (R7)

2NO + O₂ → 2NO₂
k = 2.0 × 10⁻³⁸ cm⁶ molecule⁻² s⁻¹ (R8)

NO + NO₂ → N₂O₃
k = 7.66 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ (R9)

N₂O₅ → NO + NO₂
k = 3.6 × 10⁸ s⁻¹ (R10)

NO + NO₃ → 2NO₂
k = 2.6 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ (R11)

2NO₂ → N₂O₄
k = 1.0 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ (R12)

N₂O₅ → 2NO₂
k = 4.4 × 10⁶ s⁻¹ (R13)

NO₂ + NO₃ → NO + NO₂ + O₂
k = 6.76 × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ (R14)

2NO₃ → 2NO₂ + O₂
k = 2.42 × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ (R15)

The model allowed us to analyze the influence of O₃ and NO concentrations on N₂O₅ production and its temperature dependence as well as estimating the N₂O₅/NO₃ ratio in the gas phase. The resulting estimates and predictions were used in the experimental design phase to optimize the production of N₂O₅ as well as to benchmark our N₂O₅ production process to the known gas phase kinetic data.

2.5 Aerosol generation and characterization

The aerosol was produced by nebulizing a 0.7% (by weight) solution of citric acid (HQ, Fluka, >99%) or of 0.69% wt. solution of ammonium sulfate in MilliQ water by means of an ultrasonic nebulizer. Citric acid was used as a proxy for a generic organic aerosol while ammonium sulfate was chosen because of the wealth of experimental data already available in the literature. The mist droplets formed were dried by passing the flow through a Nafion membrane diffusion dryer. The sheath gas out-
side the Nafion membrane was humidified such that the resulting aerosol flow had the relative humidity intended for the experiment by avoiding efflorescence of the particles in experiments below the deliquescence relative humidity. In order to avoid uncontrolled losses of charged aerosol particles to the insulating walls of tubing and the aerosol flow reactor, the aerosol flow was passed through a Kr source, to establish an equilibrium charge distribution, followed by an electrostatic precipitator removing all charged particles. After that the aerosol flow was fed into the aerosol flow tube.

When aerosol was used in the experiments, measurement of its surface area to gas volume ratio was performed with a Scanning Mobility Particle Sizer (SMPS). This system consists of a homemade Kr source to establish charge equilibrium of the aerosol, a differential mobility analyzer (DMA, TSI 3071) and a condensation particle counter (CPC, TSI 3022). Since the aerosol water content and consequently the particle diameter and aerosol surface to volume ratio strongly depend on relative humidity, filtered carrier gas from the flow tube was used as sheath gas in the DMA in order to keep the two flows in equilibrium. Aerosol sampling was conducted at an outlet directly behind the aerosol flow tube, where additionally other instruments such as NO₂ or O₃ analyzers could be connected as well.

2.6 Aerosol flow tube

The aerosol and N₂O₅ containing gas flow were mixed together in the cylindrical aerosol flow tube composed of a PFA tube with an inner diameter of 7 cm and a movable inlet and outlet that allow adjusting the length of the aerosol – gas interaction zone and thus the reaction time inside the flow tube. The gas flow is introduced via a conically shaped gas inlet along the axis of the flow tube. The aerosol flow is introduced into the flow tube via a fixed injector which protrudes from the side of the conical inlet. The injector is a 6 mm diameter Inox steel tube bent in such a way that the injector nozzles are equidistant from the reactor walls and the aerosol flow is injected perpendicularly to the gas flow. When the outlet is pushed all the way in to the minimum position inside the flow tube, the reaction time is minimum (~10 s), while pulling the outlet to the maximum position one can achieve a reaction time of 60 s. The flow tube is operated under laminar flow conditions and it is assumed that a laminar flow profile is established a few cm downstream of the aerosol injector. PFA has been chosen in an attempt to minimize N₂O₅ losses to the wall. While losses are lower than with a glass tube react-
tor, they are still substantial when operating under humid conditions.

2.7 Detection system

Following the aerosol flow tube, the combined gas flow was directed towards the parallel plate diffusion denuder system. A T-connector was placed between the two in order to allow connecting the SMPS system or a NO$_3$ or O$_3$ detector. Upon entering the denuder train the gaseous species (N$_2$O$_5$ and NO$_3$) are separated on different chemically selective coatings by lateral diffusion. The sub-micron aerosol particles have a small diffusivity and pass through the denuder unobstructed with almost 100% efficiency. Gaseous N$_2$O$_5$ (and the small amounts of NO$_3$ present) was collected on the first set of denuder plates coated with citric acid, prepared from a 2 wt% solution in 50% methanol/water. Citric acid has well documented hygroscopic properties [27] and mixes well with water, thus facilitating coating preparation. It also forms a solution down to low relative humidity and thus maintains reactivity also in experiments at low relative humidity. The citric acid coating was applied to the first and second denuder plate set; the former to capture N$_2$O$_5$, the latter to monitor the interference of NO$_2$ on the citric acid coating. The third and fourth sets of denuder plates were coated with NDA (N-(1-naphthyl) ethylene diamine dihydrochloride) mixed with KOH (1% solution with 1% KOH and 10% water in methanol). NDA absorbs NO$_3$ very efficiently and the basic coating assures that the nitrite product stays on the surface. Two denuder plate sets with NDA were used, because NDA is sensitive to ozone present in our system and is depleted rapidly, so the second denuder plate is used to extend the available experimental time. Fresh coatings were prepared and applied every day. After passing the denuder system, the aerosol particles were captured by a glass fiber filter. $^{13}$N decay results in the emission of a positron, which, upon annihilation with an electron, results in the coincident emission of two $\gamma$-rays in opposite directions. To each trap (the coatings and filter) a separate CsI scintillator crystal with integrated PIN diode detector was attached (Carroll and Ramsey, USA), which detects the gamma quanta emitted after decay of the $^{13}$N atoms. The detector signal is converted to the flux of the gaseous species into the trap using the inversion procedure reported earlier [16, 28]. This flux is proportional to the concentration of the species in the gas phase. The relative counting efficiency of the various $\gamma$-detectors was determined by exposing in turn each of the detectors to a glass fiber filter on which a drop of a $^{22}$NaI solution was deposited, in a way that closely mimics the geometrical configuration at each trap. Additional information about coating preparation, traps and measurement efficiencies can be found elsewhere [15, 16].

3 Results and discussion

3.1 Gas phase production of $^{13}$N$_2$O$_5$

Our experiments dealing with production of $^{13}$N$_2$O$_5$ were conducted with a 4 min residence time in the N$_2$O$_5$ reactor and 1 min residence time in the aerosol flow tube in order to simulate default operating settings also used for the aerosol experiments reported further below. These settings resulted in an NO concentration of 99 ppbv and an O$_3$ concentration of ~4 ppmv in the N$_2$O$_5$ reactor. The resulting gas flow was fed into the flow tube, together with the flow from the aerosol gas line. The ultrasonic nebulizer connected to this gas flow line was turned off (and thus no aerosol was generated) since only gas phase kinetics were studied in this step. The humidity inside the aerosol flow tube was kept at ~27% RH (humidified aerosol gas flow). Figure 2 shows the resulting N$_2$O$_5$ and NO$_2$ gas phase signals measured at the parallel plate diffusion denuder system.

N$_2$O$_5$ and NO$_3$ are absorbed on the first denuder plate set coated with citric acid. The second citric acid coated plate set, which is placed after the first, shows the NO$_2$ interference signal on the citric acid coating. Finally, the NDA coated denuder plate set gives the NO$_3$ signal. When $^{13}$NO and non labeled NO were fed into the system (12:46), the activity on all coatings increased. The signals originate from the background of $^{13}$NO decaying in the gas phase while passing through the denuder system and the filter and from small amounts of $^{15}$NO$_2$ and HO$^{15}$NO formed along the flow system that were trapped in the first citric acid coating. When O$_3$ was turned on for the first time a marked increase of the signal on the first citric acid denuder plate set occurred due to N$_2$O$_5$ (and NO$_3$, see below) that was formed. The signal derived from the second citric acid plate set shows a modest increase that is due to the NO$_2$ interference on the citric acid coating. Lastly, the NO$_2$ signal shows a significant increase due to its formation from NO and O$_3$. When O$_3$ was turned off, the N$_2$O$_5$ signal dropped rapidly while the other two signals did so gradually. The dynamic response of the NO$_2$ signal in between is discussed below. The certified NO flow was then doubled to 2 ml/min (14:23, 196 ppbv in N$_2$O$_5$ reactor) and O$_3$ was turned on again. The signals have a behavior similar to the earlier ones, but with an increase in lev-
els that can be attributed to the higher NO concentration (see model calculations below). The plotted signals also give some indication of the transient behavior of the gas phase system. In particular, peaks in the NO₂ signal can be noticed shortly after O₃ was turned on and off. This is due to the kinetics of the reactions involved and in particular (R1), (R2) and (R4). When O₃ was turned on we observed the fast titration of NO to yield NO₂ (R4). The subsequent reaction of NO₂ with O₃ to give NO₃ (R1) is about 3 orders of magnitude slower than (R4). As NO₂ was transformed into NO₃ the NO₂ signal diminished until it reached a steady-state level. When O₃ was turned off, the faster reaction R4 consumed the remaining O₃ to effectively suppress reaction R1 and thus NO₂ was no longer converted to NO₃. This brought about another increase of the NO₂ signal before it gradually decreased as the rest of the O₃ was consumed.

3.2 Comparison with model

In order to obtain a quantitative value for the N₂O₅ signal measured at the parallel plate denuder system we connected a NO₃ analyzer (ML 9841A) at the T connector behind the aerosol flow tube reactor. In this way we were able to measure the NO₂ concentration in the system and consequently calculate the N₂O₅ concentration in the gas and particle phase from the ¹³NO₂ and ¹⁵N₂O₅ signals observed on the denuder plates and particle filter. Thus we were able to calibrate the setup and assign a concentration value to the denuder plate and particle filter signals. The next step in the process was to evaluate the wall loss in the aerosol flow tube. The wall uptake represents the loss of gas phase N₂O₅ due to hydrolysis on the walls of the flow tube. Measurements were performed by varying the flow tube length (residence time) and measuring the gas phase N₂O₅ concentration in the reactor at each length. Flow tube lengths from 0 cm (10 s) to 20 cm (60 s) were evaluated, using the 10 s position as the starting point as shown in the resulting decay plot (Figure 3).

The measured, pseudo-first order loss rate constant k_wall was determined to be equal to 9.5 × 10⁻³ s⁻¹, giving an effective coefficient of uptake on the wall (𝛾_wall) of 2.8 × 10⁻⁶. A correction of the observed uptake rate for diffusion in the gas phase using the Cooney-Kim-Davis (CKD) method was applied [29], which yielded an uptake coefficient of 3.7 × 10⁻⁶.

Finally, a data comparison of N₂O₅ formation from NO and O₃ with the model calculation was performed. First, a model calculation was made for the N₂O₅ reactor using the initial NO and O₃ concentrations therein. The resulting gas phase concentrations obtained from the model (Figure 4a) were then corrected for dilution by the aerosol flow into the aerosol flow tube. The model calculations were then performed again, this time for the aerosol flow tube, taking into account the experimentally measured k_wall (Figure 4b). Thus the whole experimental system can be accounted for (N₂O₅ reactor+flow tube reactor) and modeled as a single entity. The experimental results appear in good agreement with the data obtained from model calculations, although the expected concentrations were slightly lower than the measured ones. Note that the slope was constrained by the k_wall measurement.

Fig. 2: Production of gas phase ¹³N₂O₅: dark blue: first citric acid denuder signal (gas phase N₂O₅); light blue: second citric acid denuder signal (NO₂ interference on citric acid denuder); red: NDA denuder signal (gas phase NO₂).

Fig. 3: Decay plot of N₂O₅ vs. reactor length fitted to the measured data using the CKD method.
and thus consistency of the modeled slope with the measured slope for N$_2$O$_5$ with time is not surprising. However, the model estimates the absolute concentration level fairly well. The difference between model and measurement is probably at least in part due to the value of $k_{wall}$ (and $\gamma_{wall}$ respectively) for the N$_2$O$_5$ reactor that we used in the model calculations and that remained an adjustable parameter. It should be noted that, as mentioned in the experimental section, it is not possible to distinguish between N$_2$O$_5$ and NO$_3$ in the gas phase since both are taken up efficiently on the denuder coating. The contribution of NO$_3$ to the overall signal depends primarily on temperature, since the decomposition of N$_2$O$_5$ to its precursors is a thermally driven process. At STP the NO$_3$ concentration is roughly one order of magnitude lower than that of N$_2$O$_5$.

Figure 4b shows this contribution.

The uptake coefficient on the wall for the N$_2$O$_5$ reactor was not measured; however, taking into consideration the values obtained for the aerosol flow tube and the fact that N$_2$O$_5$ synthesis is performed under dry conditions, a conservative value in the range of $1 - 5 \times 10^{-7}$ has been assumed by fitting the model to the experimental data. As mentioned above, this has given good results. Changing the value to $10^{-8}$ gives N$_2$O$_5$ levels slightly above those measured, while the NO$_2$ levels show negligible changes. On the other hand, when using a value of $10^{-6}$, the N$_2$O$_5$ level is lower by roughly a factor of two compared to measured results, while the NO$_2$ levels decrease as well, albeit not so strongly. As far as the aerosol flow tube is concerned, increases in $\gamma_{wall}$ and $k_{wall}$ (for example in cases of higher humidity) bring about a strong drop in N$_2$O$_5$ levels, while NO$_2$ levels show negligible changes.

### 3.3 Uptake by aerosol

An exemplary measurement of $^{13}$N labeled N$_2$O$_5$ uptake by citric acid aerosol particles at 27% relative humidity and an N$_2$O$_5$ concentration of $\sim 5$ ppbv is shown in Figure 5. When aerosol was fed into the system by switching on the ultrasonic nebulizer, uptake was observed by measuring an increase in activity on the particle filter. At the same time the gas phase N$_2$O$_5$ signal slightly decreased, corresponding to a drop in gas phase concentration by 0.31 ppbv. However the resulting aerosol signal accounts for only 0.16 ppbv lost from the gas phase. This is the result of the complex interplay of wall loss and uptake by the particles under conditions where the apparent wall loss is larger than the loss to the particles.

By applying the principles of gas-aerosol interaction kinetics (E1), we can analyze the net uptake kinetics from the signal in the aerosol phase and the measured wall loss rate constant in absence of aerosol.

\[
\frac{C_p(t)}{C_p(t=0)} = \frac{1 - e^{-(k_w + k_p)t}}{1 + \frac{k_w}{k_p}} \quad (E1)
\]

where $C_p(t=0)$ is the initial gas-phase concentration of N$_2$O$_5$ at time zero, $C_p(t)$ is the concentration of N$_2$O$_5$ in the particulate phase, $k_p$ is the constant for the heterogeneous reaction between gaseous N$_2$O$_5$ acid and aerosol...
The heterogeneous rate constant \( k_s \) in the presence of citric acid is defined as:

\[
\gamma = \frac{4k_{p}}{S_{p}\omega} \quad \omega = \sqrt{\frac{8RT}{\pi M}}
\]  

(\text{E2})

where \( S_p \) is the aerosol surface to volume ratio, \( \omega \) is the mean thermal velocity of \( \text{N}_2\text{O}_5 \), \( R \) is the gas constant, \( T \) is the absolute temperature and \( M \) is the molar weight of \( \text{N}_2\text{O}_5 \).

In the experiments that were conducted, the surface to volume ratio of the aerosol was varied by changing the settings at the ultrasonic nebulizer. From the obtained experimental data the value of the uptake coefficient for citric acid at 27% RH has been estimated at 1.4 ± 0.4 × 10\(^{-3}\). An experiment was also conducted using ammonium sulphate aerosol at 52% relative humidity (Figure 6). It becomes immediately apparent that the signal on the particles scales with the aerosol surface area. Since this experiment has been performed at higher humidity than the one with citric acid shown above, the background signal of \( \text{N}_2\text{O}_5 \) in absence of aerosol is lower due to a larger value of \( k_{\text{wall}} \). Surprisingly, we observe a small but significant increase in the \( \text{N}_2\text{O}_5 \) (g) signal in presence of aerosol. The characteristic gas–aerosol separation time in the denuder is about 30 ms per pair of coated plates. Since the time scale for diffusion of a dissolved species through the submicron particles is on the order of microseconds, there is enough time for any dissolved \( \text{N}_2\text{O}_5 \) to escape and being trapped. However, we also see a corresponding increase of the signal in the second pair of denuder plates we use for assessing the \( \text{NO}_3^- \) interference. This indicates that there is also a slow process leading to evaporation of \( \text{N}_2\text{O}_5 \). The fate of dissolved \( \text{N}_2\text{O}_5 \) is the disproportionation into \( \text{NO}_2^- \) and \( \text{NO}_3^- \). It is therefore likely that the slow evaporation of \( \text{N}_2\text{O}_5 \) out of the particles over time scales of about 100 ms or more may be limited by the kinetics of the back reaction of \( \text{NO}_2^+ \) and \( \text{NO}_3^- \). There is also the possibility that \( \text{HNO}_3 \), the product of \( \text{N}_2\text{O}_5 \) uptake, is evaporating from the particles [9, 30]. In spite of its strong degree of dissociation, a small amount of undissociated \( \text{HNO}_3 \) exists within the particles that remains in equilibrium with the gas phase. However, we would expect that stripping off excess \( \text{HNO}_3 \) would only be limited by the time scale of diffusion through the particles, which is on the order of microseconds. The fact that the increase in signal also occurs on the second citric acid coating could thus only result from additional \( \text{HNO}_3 \) formed from the reaction of \( \text{NO}_2^- \) with water after passing through the first denuder plate set, the extent of which is in turn again limited by how long \( \text{NO}_3^- \) remains available before being converted back to \( \text{N}_2\text{O}_5 \).

Using the data obtained we calculated the uptake coefficient for ammonium sulphate at 52% RH, which is equal to 1.45 ± 0.35 × 10\(^{-2}\). This is in excellent agreement with previously reported results [31].

As can be seen in Figure 6, the particle signal in the case of ammonium sulphate is stronger than in the case of citric acid. This is consistent with the increased water content in ammonium sulphate vs. citric acid aerosol (40 vs. 10 M) as calculated using the Extended AIM Aerosol Thermodynamics Model [32] and a parameterization of the hygroscopic studies of citric acid [33]. Assuming that the Henry’s Law coefficient (H) does not change with the ionic strength of the solution, the increased water content increases the amount of dissolved \( \text{N}_2\text{O}_5 \), and thus also the extent of the reversible disproportionation reaction of dissolved \( \text{N}_2\text{O}_5 \) with water to give \( \text{NO}_2^+ \) and \( \text{NO}_3^- \) in the aerosol phase. In turn, this leads to an increased extent of reaction of \( \text{NO}_2^+ \) with water and thus increased net uptake of \( \text{N}_2\text{O}_5 \) from the gas phase.

### 4 Conclusions and outlook

We have produced \( ^{13}\text{N} \) labeled \( \text{N}_2\text{O}_5 \) for the first time. An experimental setup has been assembled for the study of uptake kinetics of \( \text{N}_2\text{O}_5 \) on aerosol particles and has been successfully tested. Gas phase \( \text{N}_2\text{O}_5 \) production data has
showed good agreement with results obtained with a kinetic model. Measured data has shown that the experimental method also gives insight into the dynamics of the gas phase system. Routine production of N$_2$O$_5$ in the ppb range has been achieved, allowing for further studies involving $^{13}$N labeled N$_2$O$_5$.

Additionally, aerosol uptake experiments were conducted in order to test the experimental setup under realistic conditions. Uptake on citric acid aerosol has been observed and quantified. Uptake on ammonium sulphate aerosol has likewise been observed and an uptake coefficient has been measured that is consistent with that reported in the literature for deliquesced ammonium sulphate. Since the method allows tracing uptake in the particulate phase, this opens the way for further experiments with other types of aerosols at a wider range of humidities as well as temperatures. Of particular interest would be the possibility to monitor the exchange with the particulate nitrate pool in nitrate aerosols.

Overall the study has shown the viability of the proposed method to produce $^{13}$N labeled N$_2$O$_5$ for atmospheric science related experimental studies, and in particular the assembled setup and the related operating procedures will be used in future studies of N$_2$O$_5$ uptake kinetics on aerosol particles.

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**References**


