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Uptake of N_2O_5 on
dust

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Kinetics and mechanism of the uptake of N_2O_5 on mineral dust at 298 K

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Abstract

The heterogeneous reaction of N_2O_5 with mineral (Saharan) dust has been studied at $T=298\text{ K}$ using a combination of Knudsen and DRIFTS cell for kinetic and product investigations, respectively. The initial uptake coefficient has been determined to be $\gamma=(8.0\pm 0.3)\cdot 10^{-2}$. This uptake slowly saturates into a steady state uptake of $\gamma=(1.3\pm 0.3)10^{-2}$ suggesting that reaction of N_2O_5 with the mineral dust surface and hydrolysis of N_2O_5 on the surface take place simultaneously. Moreover, the product investigations suggest that N_2O_5 is irreversibly taken up forming nitrate on the surface. The uptake rates of N_2O_5 on Saharan dust are large enough to influence the photo-oxidant budget of the atmosphere.

1. Introduction

The mineral aerosol represents one of the largest natural mass fractions of the global aerosol with an estimated global atmospheric burden of 14 to 41 Tg (Houghton et al., 2001). Mineral dust particles smaller than $10\ \mu\text{m}$ may be transported over thousands of kilometers and are therefore found far away from their sources resulting in a global distribution of this aerosols (Husar et al., 2001). During dust storm events particle mass densities of up to $4650\ \mu\text{g m}^{-3}$ are measured in the lower troposphere (Alfaro et al., 2003). Even at altitudes of 10 to 12 km, up to 500 ppt of mineral ions can be found in aerosol samples, indicating that these particles are also transported into the upper troposphere (Tabazadeh et al., 1998).

The impact of mineral dust particles on the Earth's atmosphere is manifold. They are believed to have a direct and indirect effect on the radiation budget of the atmosphere and therefore are expected to impact on climate (Cziczo et al., 2004; Tegen and Lacis, 1996). In addition, the surface of such aerosol particles represents a site for heterogeneous reactions, the potential role of which has been emphasized in several modelling studies (Bauer et al., 2004; Dentener et al., 1996; Phadnis and

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Carmichael, 2000; Zhang and Carmichael, 1999). It was found, that the interaction of NO_y (HNO₃+NO₃+N₂O₅) species with mineral dust particles may lead to a global ozone reduction of approximately 5% (Bauer et al., 2004). Evidence for the occurrence of such reactions comes from field experiments as well as from laboratory studies (Hanke et al., 2003; Usher et al., 2003; Putaud et al., 2004; Seisel et al., 2004).

Roughly 1% of the ozone loss calculated in the above modelling studies is due to a heterogeneous loss of N₂O₅ to mineral dust which reduces thereby the atmospheric N₂O₅ concentrations by up to 20% (Bauer et al., 2004; Bian and Zender, 2003). Moreover, low NO₃ levels during dust storm events have been attributed to additional heterogeneous sinks of N₂O₅ (Shon et al., 2004). Although these studies suggest an impact of the heterogeneous reaction of N₂O₅ with mineral dust particles on the photo-oxidant budget of the atmosphere, laboratory studies are not yet available to confirm and quantify this process.

In the present study the uptake of N₂O₅ on Saharan dust samples has been investigated at 298 K using a Knudsen cell with mass-spectrometric detection to probe the gas-phase. In addition, the mineral dust surface has been probed by means of DRIFT spectroscopy. From these investigations uptake coefficients for N₂O₅ as well as condensed-phase products could be determined for the first time.

2. Experimental

2.1. Diffuse Reflectance Infrared Spectroscopy (DRIFTS)

Diffuse Reflectance FTIR Spectroscopy (DRIFTS) was used to probe the condensed phase during the heterogeneous reactions. The experimental set-up has been described in detail elsewhere (Börensén et al., 2000; Seisel et al., 2004) and only the most relevant features will be described here. The sample compartment of the FTIR-spectrometer houses the reaction cell equipped with a DRIFTS optic and a sample holder. The reaction cell was part of a flow system, where a mixture of N₂O₅ in Helium

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was added to a carrier gas stream of Helium. With the known mixing ratio and flow rate of the N₂O₅/Helium mixture the concentration of the reactive gas inside the reaction cell could be calculated. In order to make the experimental set-up suitable for fast heterogeneous reactions ($\gamma > 10^{-4}$) a glass plate placed into the focus of the DRIFTS optic served as a holder for the dust samples.

During the exposure of the dust sample to N₂O₅ vibrational spectra were recorded in the spectral range from 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹. To improve the signal to noise ratio 100 scans were co-added for each spectrum resulting in a time resolution of 1 min and in a sensitivity of approximately 3·10¹⁵ ions cm⁻² in the spectral range from 4000 to 1100 cm⁻¹.

The integrated absorption bands of the products were calibrated absolutely by analysing the sample by ion chromatography after reaction (Seisel et al., 2004). In order to account for a possible nitrate background in the mineral dust, reference samples have been analyzed where a nitrate background of 3.4·10¹⁷ molecules g⁻¹ has been found. The number of nitrate found in the samples after background correction was linearly correlated to the integrated absorbance of the corresponding nitrate absorption band. Using this calibration the formation rate of nitrate and thus the uptake coefficients for product formation on mineral dust could be calculated according to Börensén et al. (2000).

2.2. Knudsen cell reactor (KC)

The experiments were performed in a Teflon coated Knudsen flow reactor operating in the molecular flow regime (10^{-5} mbar < p < 10^{-3} mbar). The experiment has already been described in the literature (Seisel et al., 2004). In the present paper we will therefore only describe the main features of the technique as pertinent to the present study.

The apparatus consists of a gas handling system, the Knudsen reactor ($V=1950$ cm³) and a differentially pumped vacuum chamber housing the quadrupole mass spectrometer (QMS). N₂O₅ is introduced into the Knudsen reactor from the gas

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handling system and leaves the Knudsen reactor through an escape orifice of 12 mm diameter, which results in a residence time of N₂O₅ in the cell of $\tau=0.29$ s. The effusive beam formed behind the exit of the cell is detected by QMS with a detection limit of $5 \cdot 10^9$ molecules cm⁻³.

The Knudsen cell has been operated in two different modes. In the steady state operation a constant flow of N₂O₅ is introduced via a capillary while bypassing the reactive surface. After lifting the plunger, which separates the sample compartment from the reactor, N₂O₅ is exposed to the surface and a change in the steady state MS-signal is observed. For a surface reaction first-order in gas phase concentration from the difference in the two MS-signals the rate constant for the uptake k_{uni} can be inferred.

In the pulsed operation of the Knudsen cell a pulse of N₂O₅ of typically 5 ms duration is introduced via a solenoid valve. While the sample compartment is closed in a reference experiment the rate constant for effusive loss k_{esc} is obtained from the mono-exponential decay of the N₂O₅ concentration monitored by the QMS. By introducing a pulse of N₂O₅ while the sample compartment is open on the other hand the exponential decay is characterized by a different decay constant k_{dec} . From a comparison of the two decay constants the rate constant k_{uni} for the uptake of N₂O₅ is derived. By normalizing the rate constant k_{uni} with respect to the collision frequency ω (58.6 s⁻¹) of the gas with the geometric surface area of the sample holder, the dimensionless initial uptake coefficient $\gamma_{ini}=k_{uni}/\omega$ is obtained.

2.3. Sample preparation

Saharan dust collected at the Cap Verde Islands (Desboeufs et al., 1999) was used as mineral dust (Desboeufs, LISA Paris). The particles had a mean diameter of 15 μ m and the bulk density was determined to be $\rho_B=0.93$ g cm⁻³. The solid samples were prepared by suspending the dust in approximately 5 ml de-ionized water and subsequent spreading of the suspension on the sample holder. Glass plates of 9×9 mm and 49 mm diameter, respectively, served as sample holders for the DRIFTS cell and the

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Knudsen cell. A reference experiment performed in the Knudsen cell showed that the uptake of N₂O₅ onto the plate itself is negligible with an uptake coefficient of $\gamma \leq 1 \cdot 10^{-3}$.

All samples were dried under vacuum before each experiment. The extent of dryness of the samples was controlled by monitoring the water desorbing from the surface in the Knudsen cell. Samples were defined as “dry” if water was no longer observed to desorb from the surface upon opening the plunger. Although we can not exclude the presence of strongly adsorbed water, a more efficient drying procedure i.e. at higher temperatures has been rejected in order not to destroy the internal structure of the clay mineral.

N₂O₅ was synthesized by oxidation of NO₂ with O₃ described by Fenter et al. (1996). The quality of the produced N₂O₅ was checked routinely by means of mass spectrometry or FTIR-spectroscopy. Impurities of HNO₃ were less than 7%, NO₂ impurities have been found to be lower than 1%.

3. Results and discussion

3.1. Condensed-phase products

In order to identify the condensed phase products the interaction of N₂O₅ with mineral dust samples has been studied at $T=298$ K using the surface sensitive DRIFTS method. N₂O₅ gas phase concentrations have been varied between $3 \cdot 10^{11}$ and $4 \cdot 10^{12}$ molecules cm⁻³ and sample masses between 15 and 20 mg have been used. In all uptake experiments the DRIFT-spectrum of the unreacted mineral dust sample have been used as a background spectrum.

In Fig. 1 a typical time series monitored during the exposure of N₂O₅ to Saharan dust is shown. The most prominent feature in the spectra is the appearance of two strong absorption bands at 1350 cm⁻¹ and 1452 cm⁻¹ which can be assigned to a split of the double degenerated asymmetric stretch vibration (ν_3) of the nitrate ion. The split of this degeneration has been observed before, especially for nitrate in an adsorbed state. It

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is caused by a non-symmetric environment (Nakamoto, 1997) and due to the observed small split of 100 cm^{-1} the two adsorption peaks at 1350 cm^{-1} and 1452 cm^{-1} are clearly assigned to the nitrate ion (Seisel et al., 2004). Evacuating the reaction cell as well as heating the reacted sample to 470 K did not change the intensity of the absorption bands, indicating that strongly bounded nitrate is irreversibly formed during the uptake of N_2O_5 onto Saharan dust.

The absorption band at 3756 cm^{-1} and the shoulder at 3725 cm^{-1} can be attributed to the stretching vibration of free OH-groups located on the surface of the mineral dust sample (Little, 1966). The observed decrease in the absorption intensity indicates therefore a loss of surface OH-groups.

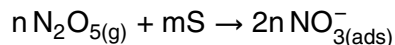
The growth of a broad absorption ranging from 1650 to 3100 cm^{-1} with a maximum around 2500 cm^{-1} is assigned to adsorbed water. Such unusual red-shifted band positions have already been observed before for water adsorbed on mineral dust (Seisel et al., 2004). The band positions as well as their shapes indicate the presence of strongly hydrogen bonded water assigning the broad absorption between 1800 cm^{-1} and 3100 cm^{-1} to the ν_1 , ν_3 -stretching vibration and the absorption at 1720 cm^{-1} to the ν_2 -bending mode of H_2O (Geiseler and Seidel, 1977; Hair, 1967).

The occurrence of strongly hydrogen bonded water may be explained by the fact that water is produced during the reaction of the mineral dust with N_2O_5 and remains attached to the surface. An additional contribution to the observed absorption bands may come from the stretching and bending vibrations of the hydronium ion (H_3O^+) which are observed around 2500 cm^{-1} and 1700 cm^{-1} , respectively, (Ritzhaupt and Devlin, 1991; Smith et al., 1991) and which may be produced by the hydrolysis of N_2O_5 . It should be noted, however, that water is not forming a quasi-liquid layer on the mineral dust surface, since no indications for solvated nitrate ions have been found in the IR-spectra.

3.2. Uptake coefficients

In addition to the study of the condensed products formed during the heterogeneous interaction, kinetic data can also be deduced from the DRIFTS experiments. In the insert in Fig. 1 the integrated absorbance of the ν_3 absorption band ($1600\text{--}1240\text{ cm}^{-1}$) of the nitrate formed during the reaction as a function of reaction time is shown. From the slope of that curve and the calibration factor derived by ion chromatography the rate of nitrate formation on the surface can be calculated. As can be seen from Fig. 1, the integrated absorbance increases linearly with time for the first 100 min. The linear region of this increase corresponds to a constant formation rate of nitrate ions on the surface, at longer reaction times the integrated absorbance starts to level off indicating that the formation rate slows down.

The reactive uptake coefficient can be calculated from the reaction rate for nitrate formation (Börensén et al., 2000). For a heterogeneous reaction of the type:



with S = surface site, and m and n being stoichiometric coefficients of the reactants, the reaction order in $\text{N}_2\text{O}_5(g)$ for nitrate formation can be determined via (Börensén et al., 2000):

$$\log \left(\frac{1}{2} \frac{d[\text{NO}_3^-]_{\text{ads}}}{dt} \right) = n \log [\text{N}_2\text{O}_5]_g + \log k + m \log [\text{S}] \quad (1)$$

where k is the rate constant for nitrate formation. In Fig. 2 the formation rate derived from the linear temporal increase of the integrated absorbance of experiments performed at different $\text{N}_2\text{O}_5(g)$ concentrations has been plotted against the corresponding N_2O_5 concentration on a double-logarithmic scale. As can be seen, the uptake follows a first order rate law in N_2O_5 . By dividing the reaction rate by the total number of collisions Z of $\text{N}_2\text{O}_5(g)$ with the geometric surface area of the sample, a reactive uptake coefficient of $\gamma = (9.1 \pm 0.7) \cdot 10^{-3}$ is obtained.

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In addition, the uptake coefficients of N₂O₅ on Saharan dust have been determined at $T=298$ K using the Knudsen cell reactor. N₂O₅ gas phase concentrations have been varied between $3 \cdot 10^{10}$ and $1 \cdot 10^{12}$ molecules cm⁻³. Mineral dust sample masses between 140 and 460 mg, corresponding to numbers of formal grain layers between 5 and 18, have been used. Figure 3 shows a typical temporal concentration profile for the uptake of N₂O₅ followed at its MS-signals m/e 46 and 30. After lifting the plunger at $t=0$ s a steep decrease in the N₂O₅ concentration due to the uptake on the surface is observed. This initial uptake (MS-Signal S_{*i*} for m/e 46) is followed by slow saturation and a time-dependent uptake of N₂O₅.

At the end of the uptake experiment, N₂O₅ has not been observed to desorb from the surface, indicating that the uptake is irreversible in agreement with the results of the DRIFTS experiments. The initial uptake coefficients of N₂O₅, which is determined from the minimum MS-signal just after lifting the plunger, are found to be independent of the N₂O₅ gas phase concentration that is the uptake follows a first order rate law in N₂O₅ (Fig. 2).

In addition to the concentration dependence the dependence of the initial uptake on the total mass of the dust sample has been investigated. Such studies are important in order to unravel whether or not the effectively available surface area is influenced by internal surface areas caused by interstitial voids between the individual dust grain particles. As can be seen in Fig. 4, the initial uptake coefficients determined are independent of the sample mass, which is proportional to the number of grain layers deposited on the sample holder. The result indicates that diffusion of N₂O₅ into the bulk of the mineral dust sample is too slow to influence the initial uptake kinetics on the time scale of our experiments. Therefore, the reactive surface available is the uppermost layer of the mineral dust sample and a diffusion correction of the initial uptake coefficients as proposed e.g. by Fenter et al. (1996) is not necessary.

Additional uptake experiments have been performed using the pulsed valve gas inlet with an improved response time (Seisel et al., 2005¹). In Fig. 5 a typical time profile for

¹Seisel, S., Keil, Th., Lian, Y., and Zellner, R.: Kinetics of the uptake of SO₂ on mineral
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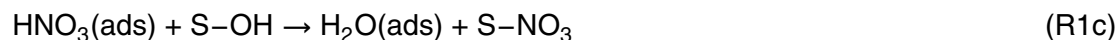
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the uptake of N₂O₅ on mineral dust is shown. Uptake coefficients obtained from pulsed and steady state experiments are in good agreement as shown in Fig. 4, indicating that the initial uptake coefficients are not influenced by saturation effects under our experimental conditions.

Consequently, at $T=298$ K the mean value for the initial uptake coefficient determined in the Knudsen cell experiments has been found to be of $\gamma=(8.0\pm 0.3)\cdot 10^{-2}$ on the basis of the projected (geometric) surface area of the solid samples. The uptake coefficients obtained from the two methods differs by roughly one order of magnitude, the possible reasons of which will be discussed in the next section.

3.3. Mechanism

During the uptake of N₂O₅ on Saharan dust the most intense absorption bands have been observed for ionic nitrate. Along with the formation of nitrate the loss of surface OH-groups has been observed, suggesting that N₂O₅ reacts with surface OH-groups to form nitrate via Reactions (1a) and (1b). The intermediate product HNO₃ could not be observed neither in the gas phase nor on the surface indicating that it is readily consumed via Reaction (1c) as already shown by Seisel et al. (2004a)



On the surface as well as in the gas phase free water molecules have not been found in contrast to the reaction of HNO₃ with mineral dust (Seisel et al., 2004). Instead, water was observed in a strongly hydrogen-bonded form or as hydronium ions which leads

oxides, Improved initial uptake coefficients at 298 K from pulsed Knudsen cell experiments, Int. J. Chem. Kin, in review, 2005.

to the conclusion that it is consumed in a hydrolysis of N_2O_5 (Reaction 2a) followed by dissociation of nitric acid (Reaction 2b).



5 By taking into account that mineral dust consists of clay minerals with interlamellar water the actual amount of water present in the mineral dust samples even under dry conditions may be large enough to induce an efficient hydrolysis of N_2O_5 . Consequently, the uptake of N_2O_5 on mineral dust surfaces proceeds simultaneously via reaction with surface OH-groups as well as hydrolysis, both channels leading to the formation of
10 nitrate ions on the surface.

The simultaneous occurrence of surface reaction and surface hydrolysis is also reflected by the uptake coefficients. In the beginning of the experiment, where a large number of surface-OH groups is still present, the loss rate of N_2O_5 is given by:

$$\frac{d [N_2O_5]_g}{dt} = - (k_{1a} [S-OH] + k_{2a} [H_2O]_{ads}) [N_2O_5]_g \quad (2)$$

15 with the units of all compounds in number of molecules. Dividing this expression by the collision number Z of N_2O_5 with the surface yields the overall (observed) uptake coefficient, which according to Eq. (3) is the sum of two terms:

$$\gamma_{obs} = \gamma_{reac} + \gamma_{hydr} \quad (3)$$

20 Whilst the reaction proceeds the number of surface-OH groups decreases and consequently a time-dependent uptake is observed. At longer exposure times the uptake is dominated by the hydrolysis of N_2O_5 and the determined uptake coefficient corresponds to γ_{hydr} . In Fig. 6 the temporal evolution of the uptake coefficient for N_2O_5 on mineral dust determined in a KC experiment is shown. It can be seen that the uptake coefficient decreases within 20 min to a value of approximately $\gamma = 2 \cdot 10^{-2}$. Analysing

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the experiments performed in more detail, the decay of the uptake coefficient can be described by the following mono-exponential expression:

$$\gamma = (1.7 \pm 0.3) \cdot 10^{-2} + (6.2 \pm 0.5) \cdot 10^{-2} \exp(-(1.8 \pm 0.5) \cdot 10^{-3} \text{s}^{-1} t) \quad (4)$$

where t is the exposure time of N₂O₅ to the mineral dust. Following the arguments above, the first term corresponds to the hydrolysis of N₂O₅ ($\gamma_{hydr} = (1.7 \pm 0.3) \cdot 10^{-2}$). The exponential term describes the time dependence of the surface reaction and gives an initial uptake coefficient for N₂O₅ of $\gamma_{react} = (6.2 \pm 0.5) \cdot 10^{-2}$.

In contrast to the KC experiment the uptake rate determined from the DRIFTS experiments remains time independent over approximately 100 min (Fig. 1). However, two important differences between the two experimental methods exist:

- The geometric surface area as well as the mineral dust masses used in the DRIFTS experiments is approximately 20 times smaller than in the KC experiment, resulting in a lower number of surface-OH groups.
- In the KC experiments an initial uptake coefficient has been determined whereas mean uptake coefficients are obtained from the DRIFTS experiments (Seisel et al., 2004).

Due to the lower number of surface OH-groups the rate of the surface reaction (Reaction 1a–c) will decrease faster in the DRIFTS experiments than in the KC experiments. This may lead – together with the low time resolution – to the fact that the initial period of the uptake where the surface reaction is dominating, is not observed in the DRIFTS experiments. Consequently, the observed nitrate formation is assumed to be caused by the hydrolysis of N₂O₅ (Reaction 2a and b) rather than surface reaction (Reaction 1a–c). Under this assumption the formation rate of nitrate can be described by:

$$\frac{d[\text{NO}_3^-]}{dt} = 2k_{2a} \cdot [\text{H}_2\text{O}]_{\text{ads}} \cdot [\text{N}_2\text{O}_5]_{\text{g}} \quad (5)$$

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According to this expression the formation rate of nitrate is first order in $[\text{N}_2\text{O}_5]_g$ as observed (Fig. 2) and constant as long as enough water is available. The uptake coefficient of $(9.1 \pm 0.7) \cdot 10^{-3}$ derived from the DRIFTS experiments corresponds then to γ_{hydr} , in agreement with the value determined from the KC experiments. From both experiments a mean value for the surface hydrolysis of N_2O_5 of $\gamma = (1.3 \pm 0.3) \cdot 10^{-2}$ is determined.

Moreover, the value of $\gamma_{hydr} = 1.3 \cdot 10^{-2}$ is close to the literature value for the hydrolysis of N_2O_5 on solid and liquid water surfaces (Atkinson et al., 2001) which once more supports the above proposed mechanism that the reaction of N_2O_5 with surface-OH groups and with adsorbed water are concurrent processes.

3.4. Atmospheric implications

As mentioned in the introduction, modelling studies show that roughly 1% of the ozone loss is due to a heterogeneous loss of N_2O_5 to mineral dust which reduces thereby the atmospheric N_2O_5 concentrations by up to 20% (Bauer et al., 2004; Bian and Zender, 2003). However, these results have been obtained for assumed values for the uptake coefficient of $2 \cdot 10^{-2}$ (Bauer et al., 2004) and $1 \cdot 10^{-3}$ (Bian and Zender, 2003) due to the fact that kinetic data for the reaction have not been available. These values are significant lower than the values determined in the present study which suggests that the heterogeneous reaction of N_2O_5 with mineral dust should indeed have an impact on the photo-oxidant budget of the atmosphere. However, two important aspects have to be discussed concerning the application of our results to atmospheric conditions, namely the time-dependent uptake of N_2O_5 and the influence of water on the uptake coefficient.

As has been discussed in the previous chapter, for the uptake of N_2O_5 on mineral dust these two aspects are closely related. The uptake of N_2O_5 proceeds via two reaction channels. The first one, the reaction of N_2O_5 with surface-OH groups has an high initial uptake coefficient of $\gamma_{reac} = (6.2 \pm 0.5) \cdot 10^{-2}$ and causes the time-dependence of

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the uptake by the depletion of surface-OH groups during uptake. The second reaction channel, the hydrolysis of N₂O₅, however, operates with a constant uptake coefficient of $\gamma_{hydr}=(1.3\pm 0.3)\cdot 10^{-2}$ as long as enough water is available. Therefore, under atmospheric conditions N₂O₅ should be taken up readily with an uptake coefficient between $8.0\cdot 10^{-2} > \gamma > 1.3\cdot 10^{-2}$ depending on the actual relative humidity and the age of the mineral dust particles. Since these values are at the upper limit of the values used in the above mentioned modelling calculations (Bauer et al., 2004; Bian and Zender, 2003) the heterogeneous loss of N₂O₅ may influence the photo-oxidant budget of the atmosphere. In addition, the observed formation of H₃O⁺ ions on the surface will lower the pH-value of the mineral dust particles upon uptake of N₂O₅. This might have consequences for other heterogeneous processes like the oxidation of SO₂, which should be addressed in a detailed modelling study.

4. Conclusions

In the study presented the heterogeneous reactions of N₂O₅ with mineral dust has been studied using DRIFT spectroscopy as surface-sensitive method and a Knudsen-cell coupled to a QMS for the analysis of the gas phase. It was found that N₂O₅ is readily and irreversibly taken up on Saharan dust with an initial uptake coefficient of $\gamma_{ini}=(8.0\pm 0.3)\cdot 10^{-2}$ forming nitrate on the surface. In addition, water and hydronium ions have been observed to be produced on the mineral dust surface which suggests that surface reaction and hydrolysis take place simultaneously. For the two reaction channels uptake coefficients of $\gamma_{reac}=(6.2\pm 0.5)\cdot 10^{-2}$ and $\gamma_{hydr}=(1.3\pm 0.3)\cdot 10^{-2}$ have been derived.

The uptake coefficients determined are high enough to influence the photo-oxidant budget of the atmosphere according to model calculation by Bauer et al. (2004) and Bian and Zneder (2003).

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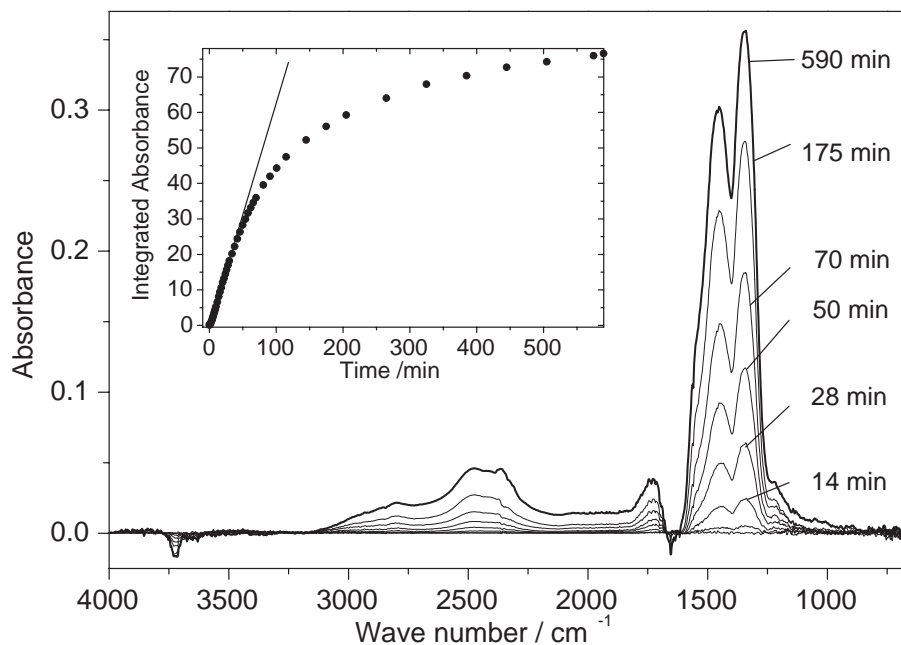


Fig. 1. Absorption spectra recorded during the reaction of N_2O_5 ($[\text{N}_2\text{O}_5]_0 = 1.7 \cdot 10^{12}$ molecules cm^{-3}) on Saharan dust. The insert shows the temporal evolution of the integrated absorbance of the nitrate absorption band ($1600\text{--}1240$ cm^{-1}).

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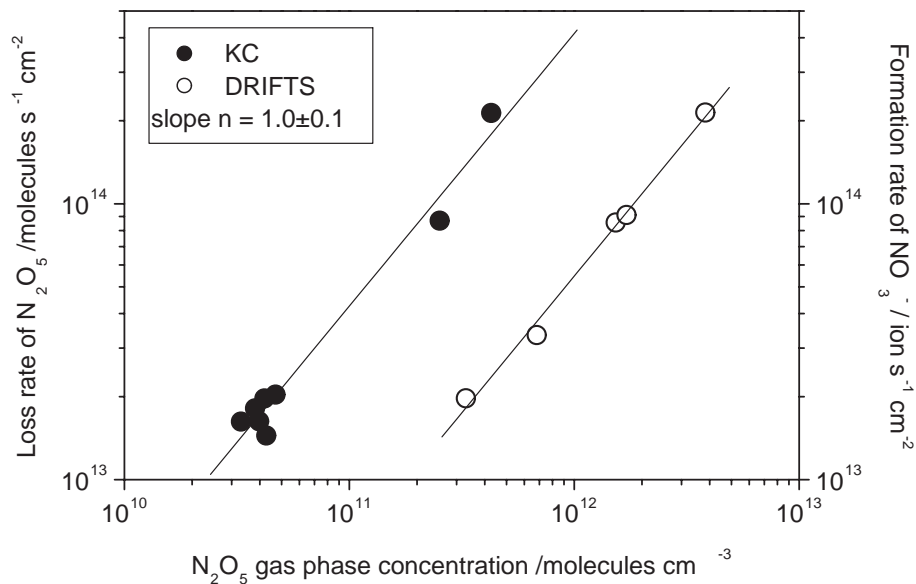


Fig. 2. Bilogarithmic plot of the loss rate of N_2O_5 and the formation rate of nitrate as a function of the N_2O_5 gas phase concentration. The solid lines have a slope of 1, indicating first order processes.

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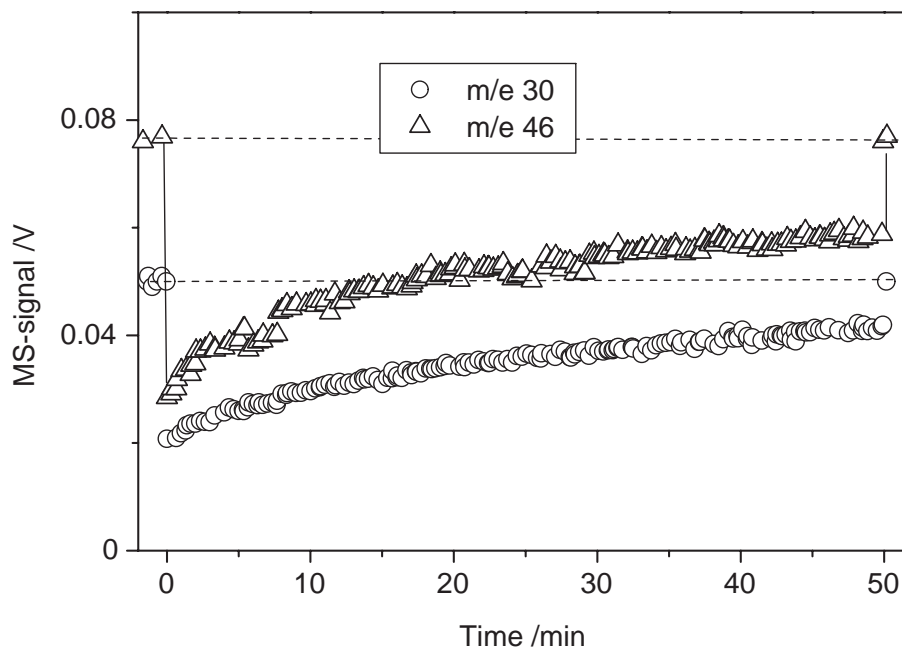


Fig. 3. Typical time profile for the gas phase concentrations of N_2O_5 (monitored at m/e 30 and 46) during the interaction N_2O_5 ($[N_2O_5]_0=7\cdot 10^{10}$ molecules cm^{-3}) with mineral dust ($m=437$ mg).

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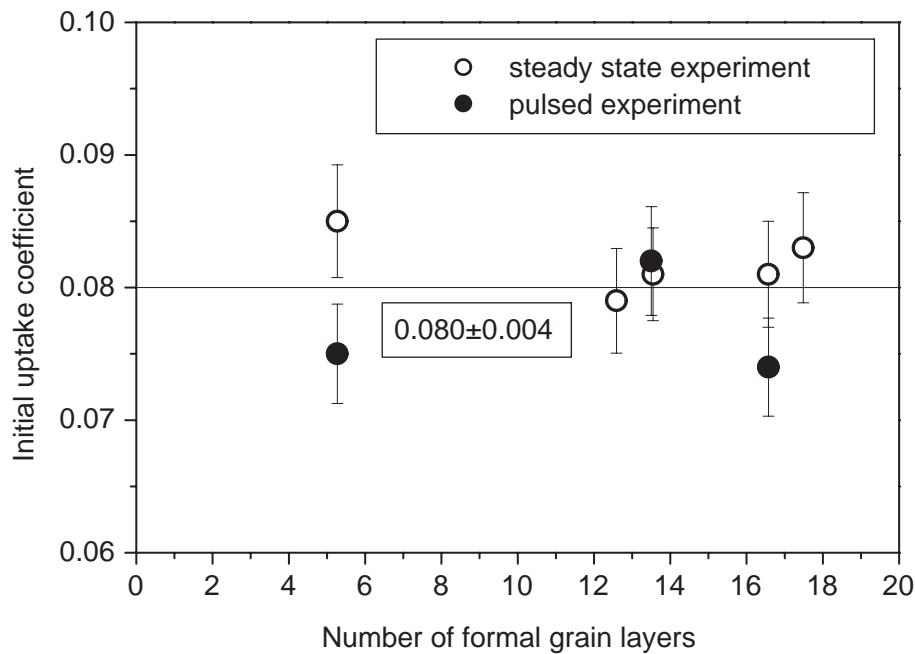


Fig. 4. Initial uptake coefficients of N_2O_5 on Saharan dust as a function of the number of formal grain layers (sample mass).

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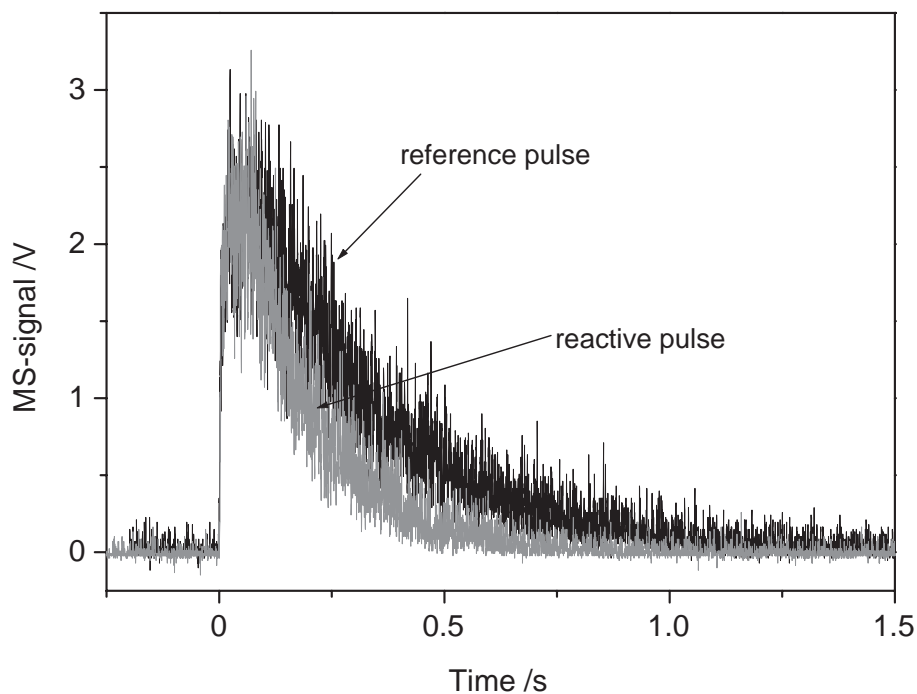


Fig. 5. Temporal traces for the uptake of N_2O_5 on mineral dust using the pulsed mode operation of the Knudsen cell ($m(\text{dust})=139$ mg). N_2O_5 has been monitored at its mass fragment m/e 46. During the reference experiment the plunger is kept closed. During the reactive experiment the plunger is kept open and N_2O_5 is exposed to the surface the entire time.

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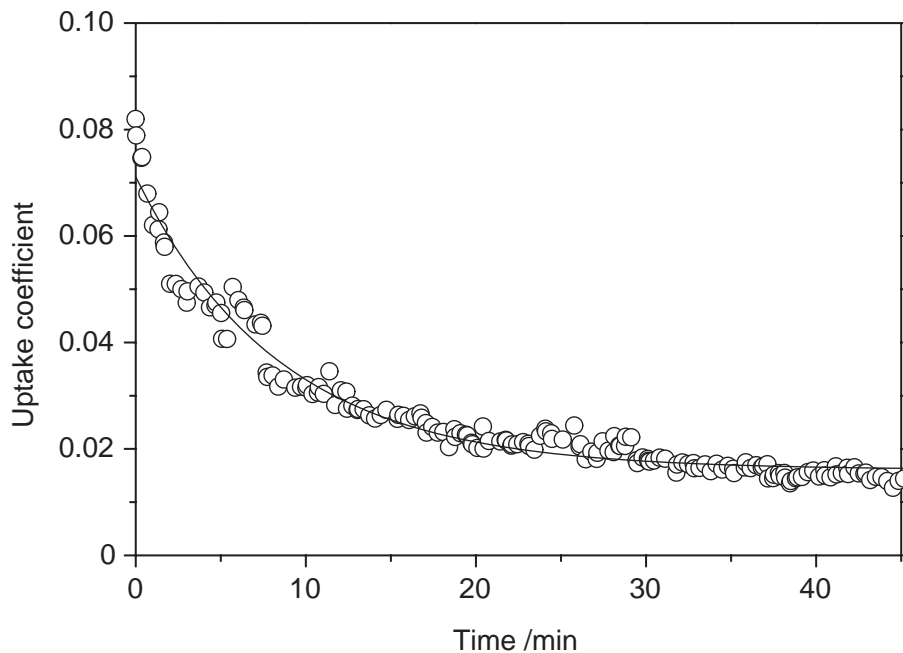


Fig. 6. Temporal evolution of the uptake coefficient of N_2O_5 ($[\text{N}_2\text{O}_5]_0 = 7 \cdot 10^{10} \text{ molecules cm}^{-3}$) on mineral dust ($m = 437 \text{ mg}$).

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