Referee 1

The presented work deals with experimental aspects of an important interfacial reaction of a NOy species for which considerable experimental backlog and remaining necessity exists regarding its role in numerical modeling of the troposphere. Definitive experimental results regarding the fundamental reactivity of “mineral dust” under tropospheric conditions are still outstanding and impatiently expected. The authors have investigated the reactions of N₂O₅ on the mineral dust proxies Illite and Arizona Test Dust (ATD) as a function of relative humidity at ambient temperature in order to discover a potential systematic trend of the uptake coefficient $\gamma$ with the goal to extract fundamental chemical kinetic laws applicable to mineral dust of a given provenience.

The authors have developed a superb, extremely sensitive and simple optical monitor of N₂O₅ and/or NO₃• free radical, namely cavity ring-down spectroscopy at 662 nm, that they have successfully applied to this laboratory study. I generally concur with the results and discussion by the authors but have a few remarks that I would like to see answered to the benefit of the readership of Atmospheric Chemistry and Physics.

We thank the referee for the detailed review and positive assessment of the topical nature of the work and quality of the experimental tools.

Pg. 24864, lines 9 to 16, and pg. 24865, lines 21 and following: authors claim an exponential rate law for the sum of $k_d + k_w$ as a consequence of the correlation between [N₂Os] and N₄ displayed in Figure 4, both for Illite and ATD. However, at a closer look, [N₂Os] visibly droops below the straight line that is heavily weighted towards the high values of [N₂Os] at the beginning (origin) of the plot (Figure 4). This is unusual, because in general the opposite is true owing to the increasing importance of the background as the signal decreases in amplitude. The measurement precision being what it is, and surmising that the authors do the best job they can, a slightly different interpretation may be proposed.

We write that the variation of the N₂O₅ signal with the number of dust particles is “consistent with” the expressions involving the terms $k_d$ and $k_w$ we have used to derive the uptake coefficient, which suggest an exponential dependence of N₂O₅ concentration on the dust numbers for a given interaction time.

We use the word “consistent” as we indeed recognise that the data no not extend over an extended variation in N₂O₅ signal (factor of 10) as would be the ideal case.

Within experimental scatter there is an exponential dependence between the N₂O₅ signal and the number of dust particles. The
One may claim that at these fairly large values of $[\text{N}_2\text{O}_5]$ partial saturation of uptake may occur at steady-state which would make the uptake rate constant $k_d$ faster at lower values of $[\text{N}_2\text{O}_5]$ under conditions of reversible and partial saturation of reactive surface sites. This “fall-off” effect of the apparently increasing value of $k_d$ with decreasing $[\text{N}_2\text{O}_5]$ may also be observed for $\text{N}_2\text{O}_5$/Saharan Dust in Figure 4 of the cited paper Tang et al. 2012 (PCCP, 2012, 14, 8551-85561). The authors gloss over the single-exponential rate law a bit fast for my taste in order to arrive at the probable, but perhaps debatable conclusion of “first-order” rate law for uptake.

Knudsen flow reactor studies have shown over and over again that the rate constants generally do not follow first-order behavior, but the authors are a bit quick to dismiss these studies as not “atmospherically relevant”. I in part agree – surprisingly - with this statement because the evidence is subtle. However, these studies teach one a lot about rate laws and reaction products that are not (yet) accessible using AFT’s owing to experimental complexities. I am not so sure about the statement on top of pg. 24864 that $\gamma$ is “in any case not dependent on the initial $\text{N}_2\text{O}_5$ concentration”. This rate law check is rarely performed, if at all, by flow tubers, more frequently by proponents of Knudsen flow reactor studies.

“droop” identified by the reviewer is present in only two of the six decays presented. In one case (Illite) it is not observed in the dataset taken at the longest interaction time (injector position), where a change in the uptake rate due to surface saturation should be most apparent.

In a revised version, we write:

“We are not entirely sure what the referee means when he says that, in Knudsen studies “rate constants generally do not follow first-order behavior”. We assume he refers to the fact that the loss rates are not independent of the initial trace-gas concentration and that the uptake coefficient derived from these loss rates are not independent of the surface area (or mass) of the bulk substrate.

There is no reason why an aerosol flow tube (which overcomes the problems with diffusion limited uptake experienced by coated wall flow tubes) cannot deliver the same information regarding rate laws as a Knudsen reactor. Likewise, detection of products (both gas and aerosol phase) is possible as described in Tang et al. 2012.

The uptake coefficients we derive here and elsewhere for $\text{N}_2\text{O}_5$ (Tang et al. 2012) are, within experimental uncertainty, independent of the initial concentration of $\text{N}_2\text{O}_5$. And show no systematic dependence on the surface area. There is nothing ambiguous about this statement.
A case in point related to the subject is made by Karagulian et al. (2006) cited by the authors where \(k_d\) (or \(\gamma_{ss}\)) decreases by a factor of three upon increasing \([N_2O_5]\) by a factor of ten at \(N_2O_5\) concentrations equal to or lower than used by the present authors. The same behavior of partial saturation of reactive surface sites has been observed for \(NO_3\) interacting with mineral dust (Karagulian et al., PCCP 2005, 7, 3150). Over the years I have not come across a single uptake process that was independent of the concentration of the gas phase species, with the exception of unitary systems, such as \(H_2O\) vapor on \(H_2O\) ice.

We refer the referee to our previous study (Tang et al. 2012) in which uptake coefficients of \(N_2O_5\) showed (within experimental scatter) no dependence on \(N_2O_5\) when the latter was varied by a factor of 60.

The gas-kinetic parameter \(Z_{11}\) (gas-wall collision rate) of a gaseous ensemble of molecules is proportional to the total surface area of the particles present. Figure 2 displays the distribution of the number concentration as a function of the aerodynamic diameter. A more appropriate display would be to plot the surface distribution as a function of Stokes (= geometrical) diameter in order to obtain an appropriately surface-weighted average value for \(A_d\) rather than the number concentration-weighted value.

The surface areas used were, of course, calculated from the surface weighted distribution. We already state this on page 24861. We did not derive an average surface area from the peak of the number distribution.

The relation between stokes and aerodynamic diameters is given on page 24861. We prefer to plot the distribution as measured rather than subsequent to the conversion factors and assumptions listed in the text.

We agree that the larger ATD particles will dominate the uptake. This will however not lead to a change in our calculated uptake coefficient as we have already used the correct surface area (see above). On page 24861 the average surface areas for ATD and Illite are listed. Due to the large diameter mode, the ATD particles have average surface areas a factor 6 larger than Illite even though the small modes are both at about 1.8 microns.

To clarify, we now write: “The average surface area were calculated by dividing the total surface area (per volume) of all the particles with the number (per volume) of the particles”.

I assume that the authors have taken Figure 2 in order to deduce the “average surface area of dust particles” (pg. 24864, line 7). It would be instructive to compare the absolute values of the so-derived \(\gamma\) with the procedure presented by the authors. I am sure that the surface-weighting of the distribution of Figure 2 leads to the inverse shown: large particles are more important than the smaller ones, which leads to the suppression of the mode at 1.8 mm and the emphasis of the mode at 8 mm for ATD. For illite there will be a shift of the mode towards higher values. As a result \(\gamma_{exp}\) may become smaller if \(A_d\) shifts to higher values owing to surface-weighting.
It is not quite clear how absolute concentrations of N$_2$O$_5$ have been obtained by the authors. Although this knowledge is not necessary in the present context if first-order behavior of the rate law is postulated, this question triggered my curiosity as the authors reveal the N$_2$O$_5$ concentration, on the order of (8-24) 10$^{12}$ molecule cm$^{-3}$ (Table 1).

The flow tube concentration of N$_2$O$_5$ is derived from the CRD measurement (which is absolute) and the dilution factor between flow tube and CRD. This is described on page 24862.

A first-order rate constant for disappearance of NO$_3$, $k_l = 0.6 \pm 0.27$ s$^{-1}$, was measured at ambient temperature by Karagulian et al. (2005, see above) for a FEP-coated Knudsen flow reactor. The authors measure $k_w$ that is approximately a factor of six lower than this value (Schuster et al., 2009) at ambient temperature.

However, caution needs to be exercised because N$_2$O$_5$ is undergoing dissociation at roughly 100°C such that the NO$_3$ disappearance may be faster. We routinely “sacrificed” about 50% of NO$_3$ in favor of NO$_2$ in our studies when we generate NO$_3$ from thermal dissociation of N$_2$O$_5$.

What is the HNO$_3$ level in your experiment? This is another pegpoint for the quality of the used N$_2$O$_5$.

It is unclear what comparing wall loss rates in a FEP coated Knudsen reactor (mTorr pressure) or a FEP coated glass tube tells us. The former is limited by surface reactivity, the latter by diffusion.

Knowledge of the first order loss of NO$_3$ in the cavity at 100 °C is important only for absolute determination of concentrations. As we measure relative changes in concentration of N$_2$O$_5$ here, cavity losses of N$_2$O$_5$ or NO$_3$ are not relevant.

The N$_2$O$_5$ crystals were carefully prepared using dried gases, and as N$_2$O$_5$ will strip H$_2$O from glass and Teflon walls of H$_2$O after a while. Also, eluting the N$_2$O$_5$ from a crystalline sample at -50 °C will favour transfer of N$_2$O$_5$ rather than HNO$_3$ to the gas-phase.

We have not measured the HNO$_3$ impurity in this study but do not expect it to be larger than the < 5 % reported previously from this lab (Wagner et al, Atmos. Chem. Phys. 8, 91, 2008)

We mention this in the revised manuscript.
Figure 2 conveys a fairly moderate aerosol number concentration for small diameters, and a reasonable one for larger particles. Nevertheless, the surface area of suspended particles is much smaller than the surface area of the vessel walls.

I do not get a feeling for the importance of $k_w$ vs. $k_d$ while reading the paper, which would be useful in view of the highly reactive nature of the dust-laden walls of the flow tube. It is a clever idea by the authors to make the wall-loss rate independent of fluctuations, but I am left with the question of the absolute values of both contributions to the total rate of $\text{N}_2\text{O}_5$ disappearance. Is it the extremely sensitive detection of $\text{NO}_3$ that enables the successful separation of $k_w$ and $k_d$? This point should be belabored a bit more by the authors.

It is not the sensitive detection of $\text{N}_2\text{O}_5$ that enables the “separation” of $k_w$ and $k_d$, but the stability of $k_w$. As the referee correctly indicates, $k_w$ is stable (“independent of fluctuations”) as it is diffusion limited.

As we state on page 24864, we do not need to know $k_w$ as long as relative changes in $\text{N}_2\text{O}_5$ concentrations induced by dust pulses are larger than fluctuations in $k_w$ on the same time scale.

However, we recognise that this information is useful and now write: “The wall loss constant, $k_w$, was about $0.04 \text{s}^{-1}$ which can be compared to a first-order loss rate constant due to uptake to illite of $k_d \approx 0.1$ when $N_d = 5000 \text{ cm}^3$. Note that it is the stability (rather than size) of $k_w$ during an experiment that limits the experimental accuracy.”

As we monitor only the gas-phase loss of $\text{N}_2\text{O}_5$, we cannot (and do not attempt to) derive detailed mechanistic information, but have simply shown that our RH dependences can be considered consistent with conclusions made in previous studies in which surface spectroscopy (Seisel et al., 2005) and theory (Messaoudi et al 2013) revealed an important role of OH groups for uptake of $\text{N}_2\text{O}_5$ to mineral substrates.

The two reaction mechanisms, e.g. reaction with OH groups and hydrolysis by surface adsorbed water, have been proposed, formulate, and detailed by Seisel et al (2005). Therefore, we have referred to original work of Seisel.

We do not see any gain in adding more speculative discussion of a mechanism on which we have no real handle in these experiments.

Pg. 24866, lines 24 and following regarding surface OH-groups and pg. 24868, line 26 and following: What are the alternatives between reaction of $\text{N}_2\text{O}_5$ with surface OH-groups and heterogeneous hydrolysis? It would be instructive to clearly formulate the different reaction paths.

First remark: $\text{N}_2\text{O}_5$ hydrolysis like any other organic or inorganic hydrolysis is either general acid- or base-catalyzed because both $\text{H}_2\text{O}$ and $\text{N}_2\text{O}_5$ are closed shell compounds and react only slowly in the absence of a catalyst. A second remark concerns the surface OH-groups which either behave as acids or bases. In the presence of adsorbed $\text{H}_2\text{O}$ (which is seldom absent) it is probably immaterial (and impossible) to distinguish between hydrolysis and acid/base-catalyzed (hydrolysis) reaction. For instance, $\text{TiO}_2$(rutile, boehmite or anatase) have surface OH-groups ranging from very acidic to very basic all at once! I can think of the following in this regard: acidic OH group: $\text{M}^+\text{OH}^- + \text{NO}_2^+\text{NO}_3^- \rightarrow \text{MO}^- + \text{HNO}_3$(or...
nitrate after neutralization) + NO₂⁺

basic OH group:

M⁺OH⁻ + NO₂⁻NO₃⁻ → M⁺ + HNO₃ + NO₃⁻

In my view the basic pathway is favored because it generates the stable nitrate anion compared to the unstable nitronium ion. But surprises do happen: remember the heterogeneous reaction of N₂O₅ on deliquescent sea salt particles...There the nitronium ion was surprisingly stable.

Pg. 24867, line 14 and following: This is the first time I hear that quartz does not have (intrinsic? What is that?) surface OH-groups. Fused and crystalline quartz and Pyrex (75% fused SiO₂) are slightly acidic just because of surface OH-groups. You may even titrate them as a function of rh. All inorganic oxide surfaces have surface OH-groups capping (terminating) the surface. But perhaps the authors address a distinctly different point that I did not get.

This is true. We have revised the text as below. As we are blind to the surface, this discussion is not intended to be more than speculative / qualitative in nature.

The results for ATD reveal a rather different picture, with lower uptake coefficients (factor ~10 lower than illite at 0 % RH) and (at most) a weak dependence on RH. The lower uptake coefficients may be related to the mineral composition of ATD which consists mainly of feldspar and quartz (Broadley et al., 2012), which may have less (and/or less reactive) surface OH groups. The weak dependence on RH is probably related to the fact that the hygroscopic growth of ATD particles is very small (Gustafsson et al., 2005; Vlasenko et al., 2005) and therefore even at high RH, the amount of adsorbed water on the surface does not contribute significantly to N₂O₅ solvation/ionisation but may still result in deactivation of surface OH groups as shown by Goodman et al. (2001). Surface sensitive methods would be required to confirm this postulate.

The equilibrium between N₂O₅, NO₃ and NO₂ should perhaps make reference to the additional and irreversible pathway NO₂+ NO₃ → NO + NO₂ + O₂ which is responsible for the slow N₂O₅ degradation to NO₂ in static or long-residence time (= slow flow) laboratory experiments, especially at elevated temperatures where the forward reaction of N₂O₅ decomposition is fast.

This reaction has never been firmly established as the source of N₂O₅ loss (see Sander, S. P., et al.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17," JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, http://jpldataeval.jpl.nasa.gov., 2011.

It might not be a gas-phase process and is usually ignored.

Pg. 24857, line 15 and following: laboratory experiments established the existence and properties of ClNO₂ long before they were detected in the field!

We have added a reference to the pioneering laboratory study (Finlayson-Pitts, 1989).

Pg. 24861, line 24: "bin" instead of "pin" correction will be made
| Pg. 24867, line 3: “...uptake coefficient (0.04) on illite is similar to....” | correction will be made |
| Pg. 24867, line 26: “Bulk samples”. | correction will be made |
| Pg. 24868, line 12: “studying”; line 26: “...that under these....” | corrections will be made |
| Pg. 24869, line 24: “deserts” | correction will be made |

### Amendment from Referee 1

I would like to post an amendment to the third "bullet" in my referee comment: (a) the length scale of the average size of the mineral dust particles (illite, ATD) are micrometers, not millimeters; (b) I stand by my point on surface-weighting of the size distribution function in terms of number concentration: at constant mass the total surface area decreases as does the gas-wall collision frequency "omega" on all particles considered in the volume. This should make "gamma" larger, not smaller, at a given (measured) value of the rate constant k according to: $k = \gamma \times \omega$.

This comment has been answered as described above.