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Interactive comment on “Kinetics and mechanism of the uptake of N_2O_5 on mineral dust at 298 K” *by* S. Seisel et al.

S. Seisel et al.

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We thank the referee for the critical review of the manuscript. He/she raised a number of interesting points which we will respond to. Most of the arguments given below will also be included in the revised version of the manuscript.

Major Comment

1) As already mentioned in the short comment 140 mg of dust correspond to 5.3 formal grain layers (calculated on the basis of the bulk density, particle diameter, sample mass and diameter of the sample holder). However, one formal monolayer, as defined above, will not be sufficient to cover the sample holder completely. Using instead the true density of 2.86 g cm^{-3} 140 mg dust corresponds to 1.7 layers which is close to one

layer. From this calculation it is obvious that we will observe a mass dependence if we use sample masses below 100 mg (81 mg). However, this is due to an incomplete coverage of the sample holder and not to diffusion of N_2O_5 into the bulk of the sample. Nevertheless, if smaller sample holders and/or samples with much smaller particle diameters as reported by e.g. Underwood et al. (2000) are used it is even possible to observe diffusion into the bulk at sample masses far below 100 mg.

The observed absence of a mass dependence together with the pulsed valve experiments lead us to conclude, that N_2O_5 is not diffusing into the bulk of the mineral dust sample and only the first layer is involved. We decided to use the geometric surface area as the reference for our uptake coefficients for the following reasons. The geometric surface area represents the lower limit of the reactive surface area and the determined uptake coefficient has therefore to be regarded as an upper limit. In contrast, the BET surface area of 50 m^2 g^{-1} represents the upper limit of the reactive surface area. A complete coverage of the sample holder with mineral dust would need 81 mg of dust, resulting in a surface area of 2 m^2 and an lower limit for the uptake coefficient of $\gamma = 7.5 * 10^{-5}$.

In atmospheric models, however, the surface area of aerosol particles are usually calculated on the basis of the particle diameter which results in a geometric surface area (e.g. Bauer et al., 2004; Dentener et al., 1996; Pöschl et al., 2005; Underwood et al., 2001). In order to make our uptake coefficients directly applicable to atmospheric models, we therefore decided to report all values on the basis of the geometric surface area. Nevertheless, we agree with the referee that our values may still be overestimated due to the roughness of the surface by a factor of 2-3 and will report our values as upper limits throughout the manuscript.

A point which we will also stress in the revised version of the manuscript is that all these considerations are only valid for the initial uptake coefficient. If we extent our experiments to longer time scales diffusion into the bulk could not be excluded anymore.

2) Although the experiments were performed under similar conditions some differences between the two methods exist:

a) The geometric surface area as well as the mineral dust masses used in the DRIFTS experiments are approximately 20 times smaller than in the KC experiment, resulting in a lower absolute number of reactive surfaces sites at the top layer of the sample as well as in the entire sample.

b)Although there is a certain overlap in the gas phase concentrations used in both studies the ones in the DRIFTS experiment are usually higher due to the lower sensitivity of the technique.

c) In the KC experiments a time-resolved uptake coefficients have been determined whereas mean uptake coefficients are obtained from the DRIFTS experiments, which are less sensitive to variations (Seisel et al., 2004a). These differences lead to the assumption that under our experimental conditions different processes were measured in the KC and in the DRIFTS experiment. The initial period of the uptake where the surface reaction (reaction 1a-c) is dominating, is observed in the KC experiments. In contrast, the hydrolysis of N_2O_5 is measured in the DRIFTS experiments and in this case the saturation of the uptake is due to the vanishing amount of water and not of S-OH. For both processes the rate is constant and the derived rate constant is independent of the N_2O_5 gas concentration as long as the number of surface site (S-OH or water) is large enough to establish pseudo-first order condition. In addition, it has to be noted that the concentrations given in Figure 2 are the N_2O_5 concentrations at the time where the uptake coefficient has been determined. In this sense the concentration given for the DRIFTS data are also mean concentrations during uptake and not initial ones.

As proposed by the referee, the uptake coefficients derived in the KC experiments have been implemented into a simple kinetic model including reactions 1 and 2. With a number of S-OH groups of 2*10^{16} cm^{-2} the time profiles observed in the KC experiments

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could be reproduced. This value is 10 times higher than the value expected from the geometric surface area but 3 orders of magnitude lower than expected from the BET surface area of the upper-most layer. This finding strengthened also the arguments given under 1). The geometric surface area gives a lower limit for the reactive surface and the BET surface area an upper limit for the surface area. In addition, the number is similar to the number of reactive sites estimated for the uptake of water on mineral dust (Seisel et al., 2004b).

Under the conditions of the DRIFTS experiment, the S-OH groups were consumed within 1 min reaction time and the uptake was controlled by reaction 2 resulting in a constant uptake rate, which supports again the arguments given above. In principal the referee is right, if we would lower the N_2O_5 concentration in the DRIFTS experiment the same time dependence of the uptake coefficient should be observed. However, the method is not sensitive enough, to detect such low nitrate concentrations.

Diffusion of N_2O_5 into the bulk on a longer time scale is not considered in this simple model. However, we performed long time experiments with the KC for different sample masses and did not found any significant difference in the time dependence of the uptake coefficient. This also supports the idea of a hydrolysis which takes place at the surface of the mineral dust.

3) We will consider recent publications concerning the uptake of N_2O_5 on aqueous/solid surfaces in the revised version of the manuscript. In all studies cited by the referee a humidity dependence of the uptake coefficient has been observed. One set of studies has been performed with aerosols containing at least several tens of wt

4) Taking into account the complex structure and composition of mineral dust the proposed mechanism may be an oversimplification, neglecting the heterogeneities of the surface. Nevertheless, the temporal evolution of the uptake coefficient clearly shows that two different processes are operating. A slow time-independent (on the time scale of our experiment) uptake superimposed by a faster time-dependent process which

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suggest that N_2O_5 is reacting with two different surface sites. Water is ubiquitous present in the mineral dust samples. We observed the disappearance of surface OH-groups and the formation of H_3O^+.

We assume that diffusion into the bulk is not responsible for the decrease of the uptake coefficient (KC experiments), since we did not observe a mass dependence in the long time experiments.

As mentioned above we also ruled out a nitrate effect, since at these low nitrate coverages according to the literature a nitrate effect should not be observed.

Consequently we assumed that S-OH and water represent the reactive sites for N_2O_5 uptake, but it has to be noted that we have no direct evidence for the exact nature of these sites.

5) The time scale for complete saturation is on the order of hours as seen from Figure 3. However, this saturation process does not influence the initial uptake coefficient for the following reasons: a) the uptake coefficients of the pulsed and steady state experiments agree, as reported in the manuscript. b) the decay of the reactive pulse is mono-exponential. If saturation would occur on the time scale of a pulsed-valve experiment a deviation from the mono-exponential decay would be observed. We will add this information into the discussion of Figure 4 (see under 1).

6) We will discuss the calculations in detail in the manuscript.

Minor comments: 1) The paragraph will be clarified in the revised version of the manuscript.

2) Yes, it will be done in the revised version.

3) Yes, it is simple the difference. However, the complete expression will be added to the manuscript.

4) The sentence will be changed.

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5) The indication for solvated nitrate is the disappearance of the split of the double degenerated ν_3-vibration ((1600 - 1240 cm^{-1}). From our experiments it is not possible to give a detection limit for this species.

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