

## ***Interactive comment on* “Kinetics and mechanism of the uptake of N<sub>2</sub>O<sub>5</sub> on mineral dust at 298 K” by S. Seisel et al.**

### **Anonymous Referee #2**

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Note "g" = gamma (reaction probability)

First, I find it somewhat strange that Referee 1 has provided a response to my comments before the actual authors have responded, but the editor can address that issue offline.

Referee #1 states the following: “Referee # 2 misses the point made by the authors regarding the justification of the geometric surface area used for the evaluation of the uptake coefficient. The essence of the argument lies in the fact that the pulsed valve admission experiment yields results for the uptake coefficient virtually identical to continuous flow admission. . .”

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Let us first consult what the authors actually wrote concerning their justification of the geometric surface area and Figure 4: “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. . .As can be seen in Figure 4, the initial uptake coefficients determined are independent of sample mass, which is proportional to the number of grain layers. . .The result indicates that diffusion of N<sub>2</sub>O<sub>5</sub> 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. . .”

Nowhere in this description of Figure 4 are the pulsed valve results mentioned. And yet they have already concluded that the reactive surface available is the uppermost layer. It was this statement that was troubling me. In direct response to Referee 1: How could I miss a point which was not even attempted by the authors?

The authors continue in a new paragraph to discuss the pulsed valve results: “Additional uptake experiments have been performed using the pulsed valve. . .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.”

Nowhere in this description of the pulsed valve results do the authors mention their connection to the available surface area. These two sections are essentially the only discussion of Figure 4 the authors make. After re-reading this section I still feel their conclusions, as written, are not adequately supported by the data alone. No attempt is made by the authors to connect the degree of “saturation effects” to accessible surface area. Nor do they provide a typical surface area per mass of their sample to make an argument that Referee 1 does. Referee 1 uses a number by Hanisch and Crowley, but certainly all dust are not the same in this regard and so this manuscript cannot be read and interpreted as a stand-alone document.

I appreciate the argument presented by Referee 1, but there is still some hand-waving to this argument and it does not completely remove the possibility that even on short times scales N<sub>2</sub>O<sub>5</sub> diffuses deeper than the upper most layer and “sees” more surface area than presented by the top layer alone. Does Referee 1 believe that not even 10% of N<sub>2</sub>O<sub>5</sub> by pure chance make it past the first layer? I simply find this smearing of the dust surface into distinct layers a bit unrealistic. But, I need to stress that I don't think this issue impacts the results much, except that the measured  $g$  are very likely upper limits to the true value! A point which Referee 1 agrees with, and which I further comment on below.

For the record, I feel Referee 1 has made some unjustified criticisms of my comments as containing “several confusing statements” or “missing the point.”

So that there's no more confusion, I will repeat my most important comment: regardless of whether only the top layer is accessed or not, the measured reaction probabilities must be upper limits. Referee 1 states that the reaction probabilities may at most be a factor of 2 too high due to underestimating the true surface area. The current manuscript makes no mention of this possibility. I don't know where Referee 1 gets the factor 2 estimate, is this a rigorous estimate? A factor of 2 bias should not be ignored, especially if it is a bias that is expected. The burden is on the authors to ensure that these biases are clearly stated in the abstract and conclusions, and preferably discussed in the discussion section. A factor of 2 is very important with respect to the atmospheric importance of N<sub>2</sub>O<sub>5</sub> reaction on dust.

I'm not sure what Referee 1 is getting at regarding the definition of  $k = gvS/4$ . Yes, this is obvious, and yes I agree that at some point  $k$  should scale linearly with mass. I think this was the point I was trying to make. There's no observed mass dependence because they did not use a low enough sample mass, this is obvious. However, if N<sub>2</sub>O<sub>5</sub> is truly only accessing the “top layer” then the initial  $g$  should be constant to about 25 mg (my estimate of the mass of 1 dust layer in their experiment). If the  $k$  remained independent of mass all the way down to “1 layer”, then this would have been

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additional compelling observational evidence that indeed only the upper most layer was being accessed.

Reviewer 1 comments that a reaction probability of 0.01 is not unreasonable given that such a value has been inferred from recent in situ measurements. I have no problem with the value of 0.01. I too think it is reasonable. But I'll point out that other measurements made in Europe using DOAS (I believe by the Plane group) show that the reaction probability is variable and at times less than 0.01. So I don't see how this particular comment is all that relevant to current manuscript. The in situ measurements referenced were made in an urban area on the west coast of the U.S. where dust plays no role.

The current manuscript actually states on page 5658: . . . "under atmospheric conditions, N<sub>2</sub>O<sub>5</sub>, should be taken up readily with an uptake coefficient between 0.08 > g > 0.013". This is perhaps the most troubling statement in the manuscript as it implies the measured steady state value for g is greater than 0.01 and therefore that it is not biased high at all, but that it is biased low!

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Interactive comment on Atmos. Chem. Phys. Discuss., 5, 5645, 2005.

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