

## ***Interactive comment on “Effect of humidity on nitric acid uptake to mineral dust aerosol particles” by A. Vlasenko et al.***

### **Anonymous Referee #3**

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I fully agree with referee 1 and 2 that this study addresses important aspects of the heterogeneous interaction of nitric acid with mineral dust particles. The use of an aerosol flow tube together with the variation of the relative humidity is novel and improves the knowledge of the kinetics of this reaction. I recommend publication in Atmospheric Chemistry and Physics after revision of the manuscript. In addition to the comments made by referee 1 and 2 I will only stress one point again, which I would like the authors to consider in a revised version of the manuscript.

My main concern lies in the discussion of the uptake coefficients and the comparison with the literature values. The authors report a dependence of the uptake coefficient on RH. The extrapolation of their values to RH below 1% yielded a low value of  $\gamma = 1 \cdot 10^{-3}$

and therefore they concluded that their values are in better agreement with the uptake coefficients determined by Goodman et al. [2000, 2001], Johnson et al. [2005] and Underwood et al. [2001] as with the values reported by Hanisch and Crowley [2001], Fenter et al. [1995] and Seisel et al. [2004]. In my opinion this conclusion is wrong as I will point out in detail:

1) The only difference in the works cited is the surface area to which the rate constant for uptake is normalized. The first 4 studies used the BET-surface area of the samples whereas in the last 3 studies the geometric surface area of the sample holder has been used. In the original papers of Goodman et al. [2001] and Underwood et al. [2001], uptake coefficients normalized to the geometric surface area of the sample holder are also reported and are found to be in the same order of magnitude as the one determined by Hanisch and Crowley [2001], Fenter et al. [1995] and Seisel et al. [2004]. Therefore, it is not a question, which uptake coefficient is correct; rather it is a question, which is the correct surface area to use. The BET surface area represents an upper limit for the surface area since it includes all kind of pores which are probably not accessible on a short time scale. The geometric surface area, in contrast, represents a lower limit, since it neglects the roughness of the surface completely. Therefore, neither of the values reported so far in the literature is comparable to the uptake coefficients determined in this study since the present values have been normalized to a surface area which neglects the pores of the sample but considers the roughness of the surface by using individual particles. Consequently the surface area used in this work lies between the two extreme cases of BET and geometric surface area and so do the determined uptake coefficients.

I agree with referee 2 that the values determined from an aerosol flow tube are well suited to application to atmospheric conditions.

2) Furthermore, the aerosol flow tube provides the unique possibility to test which surface area better describes the real surface area. The BET surface area increases with the mass of the particles whereas the geometric surface area with their size. Experi-

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ments where the size of the aerosols is varied but the total aerosol mass is held constant (or vice versa) can therefore give an idea if the BET surface area or the geometric surface is more close to the reactive surface.

3) The authors observed a concentration dependence of the uptake coefficient in agreement with previous studies. However, they used only two different concentrations. Could it be, that even at the lower concentration the uptake coefficients are underestimated due to an onset of saturation?

4) As referee 1 pointed out, the adsorption isotherm of water given in Figure 8 fits not necessarily the uptake coefficients. The data can be represented by a linear dependence or even be independent of RH up to RH of 40 % followed by an increase in the uptake at higher RH. Such an interpretation would also be in agreement with the hygroscopic growth experiments shown in Figure 9 where an increase in the hygroscopic growth is only observed after reaction at 85% RH.

5) Finally, Seisel et al. [2004] showed that  $\text{HNO}_3$  is reacting on dry mineral dust with the surface-OH groups and formed coordinated nitrate. If water is present on the surface the mechanism must not necessarily be the same. It may well be that some kind of solvated nitrate (as observed by Goodman et al. [2001]) is formed which results in different uptake kinetics.

Some minor comments and questions:

1) The reference Seisel et al., 2004 is missing in the reference list.

2) p. 11835: What is the accuracy for detection of nitrate in the aerosol phase and the gas phase.

3) p. 11835, 3. paragraph: The results given in Figure 6 and Table 2.

4) Is the mass balance for  $\text{HNO}_3$  closed?

5) Table 2: Could the authors include values for  $k_p$  derived from gas-phase  $\text{HNO}_3$  for

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comparison, even if the accuracy is lower?

6) Figure 5: To what volume refers “HNO<sub>3</sub> on aerosol [molecules cm<sup>-3</sup>]”, could the values perhaps been given in molecule cm<sup>-2</sup>?

References:

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