

Interactive comment on “DRIFTS and Knudsen cell study of the heterogeneous reactivity of SO₂ and NO₂ on mineral dust” by M. Ullerstam, et al.

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It is true that the presence of NO₂ did not influence the total uptake coefficient for the Knudsen experiment but this is not the case for the reactive uptake coefficient measured in the DRIFTS experiments. Without the NO₂ present there would be no quantitative formation of sulfate on the surface. Knudsen measures the rate of one fundamental process, the loss rate from the gas phase. What we see is physisorption, but a strong long lasting physic- (not chemi-) sorption i.e. "surface trapping". It is precisely what one needs to define the lifetime of gas phase NO₂ and SO₂, which is how we use the number later in Fig. 8. However, we have included a sentence at the end of the discussion stating that it is more likely that the SO₂ will desorb rather than forming sulfate, as evidenced by the different values of uptake coefficients determined by the two techniques.

The difference in uptake coefficient from our work compared to coefficients found in the

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literature is more likely to be due to the difference in substance than in experimental artefacts. In the paper from Underwood et al. 2001, an uptake coefficient for NO_2 on Saharan sand is reported. This sample has a BET surface area of $31 \text{ cm}^2 \text{ mg}^{-1}$ and a particle diameter of $250 \mu\text{m}$ compared to our mineral dust sample which has a BET surface area of $500 \text{ cm}^2 \text{ mg}^{-1}$ and diameter of $<20 \mu\text{m}$. The China loess sample, which has a different composition than Saharan sand, used by Underwood et al. 2001 and Usher et al. 2002 has a BET surface area of $110 \text{ cm}^2 \text{ mg}^{-1}$. It is not unlikely that different natural mineral samples will have different reactivities.

We agree that it would be very interesting to study the effect of RH on the uptake but it has not been in the scope of this paper.

Figure 1; We have added the reaction times for NO_2 and SO_2/NO_2 experiments in the figure text under (a) and (b). Under (c) it now reads "residue from subtraction of final spectrum of NO_2 experiment in (a) from the final spectrum of SO_2/NO_2 experiment in (b)".

For clarification a sentence on Page 4075, line 12 has also been added. "It should be noted that spectra shown in Figure 1b and 2b are identical spectra from the same experiment."

Figure 2; We have added the reaction times in the figure text for the SO_2/NO_2 experiment under (b). For clarification we have removed the spectra that were not used for the subtraction in (a). Under (c) in figure text it now reads "residue from subtraction of reference spectrum (a) from the final spectrum of SO_2/NO_2 experiment in (b)".

Page 4075, line 3; It is clear that water will affect the thermodynamics and kinetics of reactions involving ions. In doing DRIFTS and Knudsen, the requirements of the technique (e.g. vacuum, and range of T) limit our ability to either completely remove all water, or to work in conditions of high relative humidity. We made a good compromise, which was to remove excess water in a way that gives us a reproducible experiment, allowing us to look for the interaction of NO_2 and SO_2 . The effect of water vapor is

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outside the scope of our work.

We have added one sentence on page 4079, line 20 "The surface adsorbed water present during the experiment has not been quantified." Further discussion about the effect of surface water is also included in the discussion page 4081, line 19.

Page 4076, eq. 7; We agree that this needed some clarification. "The initial drop in the signal is used to obtain SR" has been included on page 4076, line 23.

For further comments see below at ("page 4080, line 15").

Page 4078, line 4; It is true that the entire sample from the DRIFTS experiment is used for the ion chromatography analysis. With the present procedure this is the best estimate we can make.

Page 4080, line 15; We have removed two sentences (page 4080, line 18-20) in the discussion that had no real value of information. We believe that this will make the discussion easier to read.

Page 4083, line 7; We agree that the word "dominant" might be a little too strong a word so we have now changed it to "competitive".

Figure 3; we have added error bars to Figure 3. It is not necessary to know where the saturation point is in order to be certain that the experiment is performed in the linear mass regime (LMR). In this regime of "trivial linear mass dependence" you avoid having to make a correction for incomplete penetration of the gas into underlying layers. In the regime of LMR, all you need is the sample mass and the BET area (see Grassian 2002).

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