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Atmospheric
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Discussions

Interactive comment on “DRIFTS and Knudsen cell study of the heterogeneous reactivity of SO_2 and NO_2 on mineral dust” *by* M. Ullerstam, et al.

Anonymous Referee #1

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General:

This experimental work examines the interaction of mineral dust with the traces gases NO2 and SO2. Studies of mineral dust interactions with trace gases are topical, and should provide the tools for modellers to assess the role of mineral dust in modifying the NOx and SOx chemistry of the free troposphere. The use of both surface sensitive and gas-phase detection is an important extension of the conventional analysis of only the gas-phase. Despite this, I am concerned that important questions have been left unanswered, and the usefulness of these results in terms of understanding mineral dust / trace gas interactions is thereby impaired. As is frequently the case, the use of powdery, bulk samples to derive parameters for modelling trace gas uptake to airborne atmospheric particles has not delivered unambiguous results.

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Specific:

The results indicate a weak uptake of both species, essentially confirming what was already known. NO2 was found not to influence the SO2 uptake coefficient, and vice versa, which given the weak interaction of both components, one would have intuitively expected. The experiments were carried out using trace gas concentrations orders of magnitude larger than found in the atmosphere, though the lack of dependence of gamma on this parameter is taken to assume that extrapolation of the results to the atmosphere is allowed. The present work does not explain why there are differences of up to a factor 10 in uptake coefficients of NO2 found in the literature. One presumes that experimental artefacts or simply a lack of characterisation of the sample and its "available" surface area are responsible. This seems to be confirmed by the great divergence in results derived from the experiments using the DRIFTS cell and the Knudsen reactor which deviate by orders of magnitude. Clearly the gamma derived in DRIFTS has little to do with the gamma derived in Knudsen and it remains unclear which (if any) is the appropriate one for modelling dust particles in the atmosphere. If the authors wish to argue that the high gammas from the Knudsen reactor experiments represent the rate of physi-adsorption and not reaction (page 4080), which implies reversibility, the numbers derived in these experiments are not relevant for the atmosphere where time scales are such that desorption will also take place. Despite this, the authors use the larger value obtained in the Knudsen reactor experiments to draw implications for the atmosphere. In addition, the authors have concentrated on the kinetic aspects of uptake, and have made no effort to assess the capacity of dust to remove SO2 from the gas phase, although there appear to be experiments which may contain this information. Specific points are addressed below. The role of water, even if not explored in these experiments, needs to addressed. The authors should also mention the effect of O3 which they have themselves explored in a previous publication.

Figure 1 and 2. These figures show IR absorption features from DRIFTS experiments. There are several traces per spectrum which I assume to be either spectra taken at different times of exposure for a fixed concentration, or at different trace gas concentrations at a fixed time. I have been unable to find this information.

Page 4075, Line3. The SO2 appears to adsorb preferentially to the OH groups on the surface. This would appear to indicate that SO2 uptake is possibly dependent on humidity, which has been assumed to be the case in models. The authors experiments are carried out at extremely low relative humidity, and may therefore have no relevance for an atmospheric dust particles which will be in equilibrium with water vapour. The authors should comment on this.

Page 4076, Eqn (7). The parameter SR is not independent of exposure time, as Figure 5 reveals. What part of the profile is used to calculate gamma ?. My guess is that the gamma is derived from the initial drop in the signal (i.e. the maximum value). The authors should clarify this, and also try to describe what causes the time dependence in the SO2 and NO2 uptake coefficients. The uptake of SO2 appears to be quasi-catalytic at t $>$ 350 s (or is this a case of bad baseline drift ?) It would have been interesting to see the effect of changing the concentration of SO2 on its uptake profile, as information on its capacity to take up SO2 is contained here.

Page 4078, Line 4. It appears that ion chromatography was used to derive the surface concentration of sulphate. I assume that the complete sample was washed to do this, and the resultant aqueous phase sulphate analysed. The DRIFTS IR features were then calibrated by comparison. How can the authors be sure that the part of the sample analysed by DRIFTS had the same (average) surface coverage of sulphate as the whole sample, or this simply assumed ?

Page 4080, Line 15. The discussion of the differences between the uptake coefficients gained from the Knudsen reactor work and the DRIFTS cell is rather hand waving and unconvincing. If the difference is to be attributed to physisorption contributing to the Knudsen reactor then most of the trace gas is initially taken up reversibly. I see no evidence for this in Figure 5. At the large concentrations used in these experiments

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it would likely have been possible to see the large amount of "physisorbed" SO2 on the surface. If the authors analyse the data in terms of amount of gas taken up to the surface over the entire exposure period they might find an answer to this problem. At the same time they will be able to say something about the capacity of the dust to take up the trace gases. I do not expect that the lifetime of SO2 on a dust surface (before desorption or reaction) is hundreds of seconds, as these authors appear to be claiming.

Page 4083, Line 7. The authors claim that loss of SO2 to dust will be its dominant loss process at high dust loading. As they have already derived a lifetime for loss by reaction with OH of 13 days, and present gammas that (according to their own calculations) result in similar lifetimes in a "dust storm" the term dominant would appear to be inappropriate, especially considering that their Knudsen reactor numbers are at the high end of uptake coefficients measured for this process, and the DRIFTS numbers are orders of magnitude lower.

Figures 3 and 6 need errors bars on each data point, which indicate both errors in sample mass and also in gamma. The authors should indicate if the data points are the results of single experiments or the average of many. In the case of Figure 3, I agree with the comments of the other reviewer that the applicability of the BET surface area to calculate gamma is not proven in this work. Only with correctly assessed error bars and an extended sample mass range is this possible.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 4069, 2003.