

## ***Interactive comment on “The uptake of SO<sub>2</sub> on Saharan dust: a flow tube study” by J. W. Adams et al.***

**Anonymous Referee #1**

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Report on “The uptake of SO<sub>2</sub> on Saharan Dust: a flow tube study” by J. W. Adams, D. Rodriguez and R. A. Cox.

This laboratory study complements several other studies performed on nominally identical Saharan Dust substrates obtained using other experimental methods such as Knudsen flow reactors, static reactors and DRIFTS cells. This work deals with an important trace gas whose concentration in the free troposphere varies significantly from pristine to polluted environments. Moreover, the work goes beyond a purely descriptive approach of collecting experimental kinetic parameters by making use of a simple model for the adsorption/desorption process. The paper is written in a clear and concise style, yet it gives sufficient information to the reader to be able to follow

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the arguments. I am therefore in favor of publication of this work in ACP. However, in the interest of clarity and understanding the following questions should be specifically answered before a final decision on publication may be made. - The use of the total (external and internal) surface area  $A(\text{BET})$  in the evaluation of the initial uptake coefficient  $\gamma_{0,\text{BET}}$  implies that the probe gas,  $\text{SO}_2$ , explores the total surface area within the contact time of 50-100 ms, thereby giving rise to the maximum rate of uptake observed at  $t = 0$  when the injector is pushed back, unless I misunderstand. Naturally, the modeled rate of adsorption results in the same situation as the rate constant  $k_{\text{ads}}$  has been chosen accordingly. I would like to raise the question whether this is reasonable. Taking as an example the measurement of BET isotherms of nitrogen on  $\text{Al}_2\text{O}_3$  of comparable BET surface area as Saharan dust one invariably observes a pressure relaxation period of 9 to 12 minutes after every new addition of nitrogen starting at a fraction of a mbar up to one atmosphere of nitrogen. During this time the pressure drops continuously because  $\text{N}_2$  is undergoing pore diffusion until equilibration is reached. This seems to be in conflict to the assumption made by the authors on the bottom of pg. 2649 (“If we assume the  $\text{SO}_2$  gas can access the whole of the BET surface area instantly, then  $\tilde{E}$ ”). The question here is one of time scale of pore diffusion. - In order to solve this dilemma I would encourage the authors to emphasize that the initial uptake coefficient  $\gamma_{0,\text{BET}}$  is certainly a lower limit to the “true” uptake coefficient. In this case one cannot speak of the “true” value. In uptake experiments of  $\text{HNO}_3$  on mineral dust aerosol one observes that the resulting uptake coefficient is much closer to  $\gamma_{0,\text{geom}}$  than to  $\gamma_{0,\text{BET}}$ . - When talking about “unhumidified” Saharan dust could the authors give an indication of the amount of adsorbed water? - An alternative, potentially more instructive way of describing the amount of adsorbed  $\text{SO}_2$  molecules (pg. 2654) would be to evaluate this quantity at an equal number of collisions with the dust substrate as a function of initial partial pressure of  $\text{SO}_2$  rather than upon integration over 200s which seems a bit arbitrary. - The data plotted in Figure 7 at low initial  $\text{SO}_2$  concentration do not appear to lie on a straight line with the data at higher concentration. I understand the reasons for wanting to preserve the simple

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Langmuir adsorption model discussed on page 2657, however, allowance should be made for curvature potentially owing to mechanistic complications at low SO<sub>2</sub> initial concentration which is of atmospheric relevance. - Concerning the “presence of ozone on the mineral dust surface” (pg. 2657, line14): do the authors have proof that ozone is in fact adsorbed on dust and may therefore partake in a Langmuir-Hinshelwood mechanism, or is it simply O<sub>3</sub> and SO<sub>2</sub> co-flowing? On pg. 2655, line 15, the authors talk about the “presence” of O<sub>3</sub> which I understand as a co-flow experiment. - If one calculates the rate of adsorption (R<sub>1</sub>), namely, rate = k<sub>ads</sub>(SO<sub>2</sub>), where (SO<sub>2</sub>) is the SO<sub>2</sub> concentration given in molecule cm<sup>-3</sup> using the expression for k<sub>ads</sub> given in equation (4), I end up with unphysical units of cm<sup>-1</sup>s<sup>-1</sup> for a chemical rate. Instead, it should be either molecule s<sup>-1</sup> or molecule cm<sup>-3</sup>s<sup>-1</sup> (pg. 2660). Please explain! - What is the physical basis of using equation (6) (Pg. 2660) for the kinetics of pore diffusion? This expression is borrowed from solubility-limited uptake of trace gases into fluid media implying a t<sup>-0.5</sup> dependence. Has such a dependence been observed for pore diffusion before? If yes, please provide the proper reference. - I understand that the parameter (D(L))<sup>0.5</sup>/L has been used as an adjustable parameter. What is a typical value for D(L) at a reasonable choice of L? Is it compatible with free molecular flow (Knudsen diffusion) inside the pores as one would expect? This question is related to the point made above.

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