

Replies to comments for article “Efficient bulk mass accommodation of N₂O₅ into neutral aqueous aerosol” by G. Gržinić et al.

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Anonymous Referee #1

1. I am a bit confused by the nomenclature. In Figure 2 (and Equation 3) there is a [N₂O₅(p)] term. What is meant by that? It is clearly not the dissolved concentration of N₂O₅ in the particle. Is it instead the concentration of N* in the particle (as stated in line 37)? But this would be orders of magnitude lower than the level of dissolved unlabeled N. So, how do the authors scale N* concentrations to indicate the amount of N₂O₅ that has been taken up to the particle, which is what I believe this term represents? Also please use either C or [] nomenclature for concentration but not both.

Response: Thank you for pointing this out. Since the observables of the present experiment are gas phase labelled N₂O₅ and labelled product, thus labelled nitrate, in the aerosol phase, Equation (3) should more clearly refer to the fate of labelled molecules. We will choose a more clear notation and explain it more explicitly in the text to avoid confusion.

2. I must be missing a very important point in the paper, and would like the authors to explain this to make the paper clearer. In particular, I understand that the kinetics experiments with nitrate particles indicate a large uptake coefficient that can be interpreted as a large mass accommodation coefficient. But, I am at a loss to understand why the results with sulfate particles, that show roughly an order of magnitude smaller uptake, cannot also be interpreted as a mass accommodation coefficient measurement. If the reaction proceeds half through the left channel in Figure 3, then the labelled nitrate so formed should stay in solution. If the mass accommodation coefficient is really larger than 0.1 on aqueous droplets then the uptake coefficient in these experiments should have been at least this large. But the observations show much smaller uptake kinetics. Does this not imply that the mass accommodation coefficient on sulfate must not be as large as on nitrate?

Response: This is indeed an important point of the manuscript, and obviously we need to clarify this better. In absence of aerosol phase nitrate, labelled nitronium not undergoing hydrolysis will react with non-labelled nitrate coming into the aqueous phase as well and reform N₂O₅ and equilibrate with the gas phase again. Therefore, in absence of nitrate, uptake of labelled N₂O₅ is exactly following the fate of non-labelled N₂O₅. The fast accommodation and dissociation of labelled and non-labelled N₂O₅ into the aqueous phase is not becoming rate limiting. The amount of aqueous phase N₂O₅, nitronium and nitrate is in effective Henry’s law equilibrium with gas phase N₂O₅, nitrate from the reaction of nitronium with

water is only slowly building up. We will show some box model simulations to show this behavior in the revised version.

3. The results are interpreted in terms of bulk processes. With very high concentrations of nitrate, could the chemistry for those particles be happening on the particle surface? In this case the kinetics would be surface-uptake controlled and not bulk-controlled, and then this would not be a measurement of the bulk mass accommodation coefficient. Overall, is it possible that the observations are consistent with (fast) surface uptake for the nitrate experiments and with (slower) bulk uptake for the sulfate experiments?

Response: In principle, we cannot exclude a surface contribution. Since also the suggested bulk accommodation is followed via obviously very fast dissociation into nitronium and nitrate, this process will occur close to the surface anyhow, with a short reacto-diffusive length (in contrast to the much slower hydrolysis reaction of nitronium with H₂O). Therefore, for instance, varying the surface to volume ratio of the aerosol would not allow differentiating bulk from surface accommodation. Though, we would prefer not invoking a surface process if bulk phase processing explains the observation. But we will place a caveat on this in the revised version.

4. It is stated a few times that nitric acid does not volatilize under the conditions of the experiments (and this was the reason to use neutral particles and not acidic ones). Can the authors confirm that this is the case for their conditions?

Response: it is correct that progressing uptake of non-labelled N₂O₅ during the residence time in the flow tube leads to acidification of the particles. However, with non-labelled N₂O₅ being in the low ppb range, the maximum HNO₃ concentration in the aqueous phase becomes about 10⁻³ M leading to a pH of around 3 so that evaporation should not play a role. As explained in Grzinic et al. (2014), measurable evaporation could be observed in the denuder detection system on the traps following that for N₂O₅ but was not observed in the present study. Though, unambiguous differentiation of that signal between HNO₃ evaporating from the particles and N₂O₅ formed from the back reaction of nitrate with nitronium would not be possible.

5. Table 1: Please list how many experiments were conducted per experimental condition.

Response: Each experiment involved 15-20 activity measurements, each averaged over 60 s, for each injector position. Overall, replicates from several different experiment series performed on several different operation days of the ¹³N delivering facilities were averaged to obtain values and standard deviations reported in the table. This is due to the often only limited periods of stable ¹³N production. This will be added to the experimental section.