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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Efficient bulk mass accommodation of N_2O_5 into neutral aqueous aerosol” *by* Goran Gržinić et al.

Anonymous Referee #3

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This paper describes a novel experiment to probe the mass accommodation coefficient of N2O5 on deliquesced sodium sulfate and sodium nitrate aerosol particles. The mass accommodation coefficient is a fundamental parameter needed to describe and understand the reactive uptake of N2O5 and its conversion to products such as nitrate and nitryl halides on atmospheric aerosol particles. The experiment relies on using radioactive 13N2O5, and pH neutral (aqueous) aerosol particles, followed by collection of the particles and measurement of the 13N nitrate products. Overall this is an interesting experiment, and I recommend publication if some fairly significant issues can be clarified or addressed.

If I understand correctly, the net uptake is determined by measuring the gas-phase 13N and the particle phase 13N, where it is assumed particle phase 13N was only derived from 13N N2O5, and that any 13N nitrate produced from N2O5 stays in the particle

phase.

Lines 25 on – what are the relative amounts of NO2 and N2O5. NO2 is known to undergo slow disproportionation to HNO3. Is this a concern here? What about wall production of 13HNO3 and its incorporation into the particles due to revolatilization?

I’m not sure that the net reaction probabilities and their interpretation is correct or at least well explained. I can see why the net uptake measured in this 13N system on nitrate containing particles would be higher than that for unlabeled N2O5 on nitrate containing particles, due to the added channel of "isotope exchange" (for short). But I do not see why there would be an order of magnitude larger net reactive uptake of 13N N2O5 on nitrate containing particles compared to 13N N2O5 reacting on sulfate particles. I think a simple box model using the ratio of k5/k7 and nitrate and water molalities might help.

Or the description of the results and their interpretation needs to be clearer. I don’t see where the limitation in the sulfate system is to produce that much lower of a net reaction probability, if there is equal probability of 13N N2O5 becoming 13NO3- and 13NO2+. What would be the limitation to 13NO2+ in the sulfate particles that doesn’t exist in the nitrate particles?

Lines 10 onward, page 2 – I don’t think all previous estimates of bulk accommodation were as low as implied here, only that net reactive uptake was lower. In other papers, a typical assumption was also that the accommodation coefficient was not limiting net uptake, see for e.g. Bertram and Thornton ACP 2009 and others.

Line 23, page 5 – sentence that starts here as a double negative at the end, making it difficult to interpret the meaning. Suggest: Thus, in this branch, all 13N labels remain in the aqueous phase given that HNO3 evaporation from neutral aerosol is unlikely.

Line 7, page 6 – this paragraph is interesting. In the Bertram and Thornton parameterization, there is a dependence of the equilibrium between N2O5(aq) = NO3-(aq)

+ NO2+(aq) on the water activity (molar concentration in that paper) that was inferred from the behavior of observed uptake coefficients. This dependence was in addition to that inferred for the fate of the NO2+. Seems this presents a possible physical explanation.

Conclusions, last sentence: "The absence of accommodation limitation also helps rationalizing results from field experiments (Phillips et al., 2016; Wagner et al., 2013), where under some conditions uptake coefficients constrained by combined N2O5 and aerosol measurements are larger than those suggested by laboratory studies available to date."

I'm not sure I completely agree with this conclusion. Do the measurements presented herein actually help explain field determinations of the reaction probability being larger than those measured in the laboratory? A few lines above, it was noted that the net reaction probability from this set of measurements was similar to previous values (at least for sulfate particles). The field observations are not deriving accommodation coefficients, but net reaction probabilities. I agree that if some previous laboratory studies concluded mass accommodation coefficients were <0.04, then field observations of net reaction probability greater than 0.04 would not be supported by such a conclusion (or vice versa).

However, other laboratory studies and even parameterizations for similar aerosol systems as those used here, have concluded or assumed mass accommodation is not limiting (e.g. Bertram and Thornton, ACP 2009 and references therein), and thus that the limitations are in the chemistry and diffusion.

Thus, I would argue that for the reaction probabilities derived from field measurements that are larger than some laboratory measurements (pretty small fraction) are because of three possible reasons: (1) laboratory measurements have an additional limitation to net uptake not present (or reduced) in the atmosphere (could be salting out as suggested), (2) there are additional faster reaction pathways for N2O5 in ambient aerosol

particles not yet probed in the laboratory, or (3) because the assumptions required in deriving the reaction probabilities from field observations are flawed.

It is hard to imagine there is something that reacts with NO2+ much faster than Chloride in solution (though it is possible), and in aqueous sea salt particles, the reaction probability is still only measured to be similar to that on aqueous sulfate particles. That to me suggest the limitation that seems to keep reaction probabilities < 0.05 at room temperature is less likely the NO2+ chemistry and instead the solubility, dissociation, and diffusion beforehand. Anyway, that is a long winded way of saying that I don't think there is support for that conclusion as written.

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