

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 #2

1) Most of the discussion centers on the uptake of N₂O₅ to nitrate aerosol. The conclusions drawn suggest large values for alpha and supports N₂O₅ ionization at the particle interface. What is less clear is if this is a general result for all aerosol at the same water activity. In the case of sulfate particles, labelled N₂O₅ likely evaporates from the interfacial region wo/the opportunity for exchange with unlabeled nitrate. The upper limit of 0.03 is achieved that is likely a combination of alpha, KH, and the reaction rates described. If KH and the hydrolysis rates are the same for sulfate and nitrate aerosol, is it correct to generalize the mass accommodation results derived from the nitrate aerosol experiments to all aqueous aerosol of comparable interfacial water activity? It would be helpful for the authors to provide some discussion on these points and the generality of the derived mass accommodation coefficient. I would find it very helpful if there was a second panel to Figure 3, which showed the processes for the sulfate particles.

Response: we agree that the present results are strictly valid only for the compositions used in the present experiments. Since the observed gamma values for the pure sodium sulfate case follow that expected for non-labelled N₂O₅, labelled N₂O₅ seems to follow the fate of non-labelled N₂O₅, since not enough non-labelled nitrate is building up to allow exchange with that pool and larger uptake for labelled N₂O₅. Therefore, in fact, strictly speaking we are unable to prove that alpha and dissociation in aqueous aerosol devoid of nitrate is as fast as in presence of nitrate. Nevertheless, it is reasonable to assume (and all other laboratory studies support this) that water activity drives the reactivity with N₂O₅ apart from the nitrate effect and the particle physical properties. Instead of a second panel to Figure 3, we will provide some results of box model simulations to demonstrate the different behavior of labelled and non-labelled N₂O₅ for the two cases. Unfortunately, the dataset is not large enough in terms of nitrate concentration range to more precisely constrain the individual rate coefficients as a function of water activity.

2) Most of the aerosol flow reactor community is familiar with the kinetic equations shown, for unlabeled reactants. Are there any special considerations that need to be accounted for regarding single, vs multiple collisions of the labelled N₂O₅ with aerosol and the walls? Or rather, in Fig. 3, how many times would you expect a labelled N₂O₅ to cycle through a particle or the wall of the flow tube over the time constant of the flow reactor? Is this important to the analysis or derivation of the equations presented?

Response: no it is not important, since we integrate over many labelled molecules arriving in the detection system, and we statistically evaluate in what chemical form they are at the moment of detection. Thus the first order loss rate coefficient is correctly derived from the observed net loss or appearance rates, independent of the number of molecules contributing to these, as long as counting statistics is not limiting the error. In fact, the condensed phase cycling of N₂O₅ is very fast, and so is evaporation back to the gas phase, and the number of times an individual molecule (labelled or non-labelled) is entering the particle phase is limited by the collision rate with the particles, which is on the order of one per second for the aerosol conditions used. Since the number density of labelled molecules in the gas phase is of the same order of magnitude as that of the number density of particles, each particle receives at most one labelled N₂O₅ molecule during the residence time in the flow tube.

3) What is the effect of labelled HNO₃ that is generated in the source region? How would this be interpreted in the experiment. It is not uncommon for N₂O₅ sources to be 10:1 HNO₃ to N₂O₅. What is the expected ratio in this experiment?

Response: The citric acid coating used to trap N₂O₅ would not be able to differentiate from HNO₃, in that sense the detection system is not able to resolve this. Though, the wall loss rate coefficient of labelled HNO₃ is so large that for the present flow tube surface to volume ratio the dominant fraction of it would deposit at the entrance of the flow tube (Guimbaud et al., 2002), which was not observed; the uptake coefficient for labelled N₂O₅ on the reactor walls was in the range of 10⁻⁷, which would also not lead to substantial HNO₃ production.. We will add a note on this in the revised version.

4) Like reviewer #1, I am also confused by the notation of [N₂O₅]p. It would be helpful if equation 3 and Figure 2 were consistent in notation. It would also be helpful to denote between labelled and unlabeled here, as the unlabeled N₂O₅ uptake coefficient to nitrate aerosol could be pretty small even at high labeled N₂O₅ uptake coefficients, correct?

Response: as already mentioned in the response to Referee #1, we will adapt the notation and make clear that the quantities in equation refer to labelled molecules (which were the only direct observables of the experiment). Yes, the net uptake of non-labelled N₂O₅ to nitrate containing aerosol is very low (Table 1, lowest row).