

Interactive comment on “The effect of viscosity on the HO₂ uptake by sucrose and secondary organic aerosol particles” by Pascale S. J. Lakey et al.

Anonymous Referee #1

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The manuscript entitled, “The effect of viscosity on the HO₂ uptake by sucrose and secondary organic aerosol particles,” by Lakey et. al. describes new measurement of the uptake coefficient of HO₂ onto model organic aerosol surfaces (sucrose and SOA). The HO₂ loss rate onto aerosol surfaces may have important ramifications for the HO_x cycle in the atmosphere. The experimental measurements are interpreted using a kinetic multi-layer model. The experimental measurements are carefully done with the appropriate checks and associated error analysis. The following aspects should be addressed by the authors in a revised manuscript.

1. There are a number of studies not cited in the manuscript that have generally discussed and observed the evolution of uptake coefficients with particle viscosity. These should be included and discussed in light of their relevance for the present study. For example, Slade and Knopf (Geophys. Res. Lett., 41, 5297–5306), Davies and Wilson

(Chem Sci, 2015,6, 7020-7027) Houle et al. (Phys. Chem. Chem. Phys., 2015, 17, 4412), observed similar relationships as shown in Fig. 5 albeit for OH radical uptake. All of these studies interpret the relationship between gamma and viscosity mathematically using diffusoreactive lengths and such an analysis should be conducted in order to connect the present study with the larger body of literature on the subject.

2. On lines 275-279 the authors say that the Henry's law constant and HO₂ diffusion constant are both terms contained within the bulk HO₂ bulk accommodation coefficient. This statement should be clarified in the manuscript. Does this mean that the two quantities cannot be separated independently in the model?
3. The authors should clarify the geometry of the simulation, spherical shells?
4. As diffusion becomes slower as RH decreases for sucrose, will any of the rate coefficients for R4-R10 be limited by this slow diffusion. In other words, while diffusion of species between shells decreases with RH, do the reactions occurring within a single shell have to be slowed due to diffusion? This should be clarified why this is or is not needed to accurately simulate the experimental data.
5. The desorption lifetime of HO₂ appears unphysically long (1.5 ms) compared to MD simulations results presented in Vieceli et al. (J. Phys. Chem. B 2005, 109, 15876-15892). The desorption lifetimes from MD for OH, O₃ and H₂O range from 35-140 ps, orders of magnitude faster than the HO₂ value used in the present study. While these are different species, I can't imagine a molecular reason for such a large difference for HO₂. The value used here for the desorption lifetime of HO₂ (Shiraiwa, 2010) is from a previous simulation study of ozone + oleic acid and appears to be a fit parameter, which is also orders of magnitude different than the MD results of Vieceli et al. for the ozone desorption lifetime. The reason for this discrepancy should be addressed and if possible simulations be run with a more realistic value for t_d.
6. To account for the finite value of the gamma at low RH the authors invoke a surface reaction (R11) catalyzed by Cu⁺². It is unclear what the rate law is for this catalyzed



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reaction, the authors should make this clear in the manuscript. Furthermore, why would this reaction only occur at the surface? This assumes that HO₂, which is fairly unreactive will not diffuse even into the subsurface region. It seems more reasonable to me, since surface rate coefficients are rarely measured, to allow this reaction to occur in the subsurface with a rate coefficient that has bulk units. This will allow the reader to more closely evaluate the magnitude of the rate coefficient needed to account for the measurements.

7. The authors interpret their data solely in terms of the diffusion of HO₂ into sucrose. However, it is not clear whether this captures the complete picture. Wouldn't the diffusion of Cu⁺², and O₂⁻ to the surface be equally important as HO₂ diffusion at low RH for determining gamma? The authors should include these diffusing species in the simulation or clearly justify why it is not necessary to explicitly include the diffusion of all species (including sucrose) in their simulation.

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