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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurements of the timescales for the mass transfer of water in glassy aerosol at low relative humidity and ambient temperature" *by* H.-J. Tong et al.

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Tong et al. present an experimental study of the timescales for the uptake or loss of water from aqueous solution droplets when RH is changed. They show that when the solution droplets are in a liquid state their water content responds promptly to changes in RH, whereas when the droplets are expected to exist in a glassy state the diffusion of water is slowed to such an extent that the droplets remain out of equilibrium for at least many hours. This is an important study which adds to our quantitative understanding of the role of glassy aerosol in the Earth's atmosphere and suitable for publication in Atmospheric Chemistry and Physics once the following minor comments

are addressed.

Scientific comments

1) P4845. In the discussion of why it is important to understand the response of aerosol to temperature and RH the role of aerosols in cloud formation is omitted. For example, the water activity criterion for homogeneous freezing (Koop et al., Nature, 2000) relies on the assumption that droplets are in equilibrium with their surroundings which may not be the case if they exist in a glassy state or ultra-viscous state (e.g. Murray, ACP, 2008; Murray et al. Nature Geoscience, 3, 233-237, 2010).

2) P4856. Ln 1-7. Given the raman spectra show small amount of water in the droplets, can you rule out the presence of one or more crystalline hydrates? Slow recrystallisation from a dihydrate to a monohydrate might result in the slow loss of water observed over long time periods

3) P4857, ln 29. The agreement between model and measurement isn't very good above $\sim$70 % either.

4) P 4859 ln 10-14. Murray et al. (Nature Geoscience, 2010) observed heterogeneous nucleation on increasing the RH when citric acid droplets were in a glassy state. In Murray's figure 2, there was heterogeneous nucleation at low RH, but there was also a burst of ice particles at high humidity consistent with homogeneous nucleation (although perhaps a little delayed). This suggests that these glassy citric acid droplets transformed to a liquid on increasing RH (hence they apparently froze homogeneously) on the timescale of the experiment (a few minutes). This seems to be consistent with Tong et al's finding that the timescale for devitrification is 10-100 s and should be discussed. It is less clear if this happens in experiments at lower temperature where the rise in RH is limited by strong heterogeneous nucleation and the RH may not have been sufficiently high for homogeneous nucleation.

5) P4860, ln1-5. This discussion is confusing. I thought the fit between model and

experiment in fig 5b looked very good, so I do not see why the authors think that their diffusion coefficient is too large.

6) Figure 8. There appears to be a slight discontinuity at ~5000 s, is this significant? Might one expect a discontinuity when the droplets become glassy?

7) Abstract: Also state the result that when going from low RH to above the glass transition the droplets respond in 10-100 s. This is important since there is some disagreement in the literature on this. Murray (2008) suggested water uptake would be inhibited; Zobrist et al. (2008) expected it to be like crystal to liquid deliquescence at the RH of the glass transition (i.e. prompt) and Mikhailov (2009) suggested this transition would be more gradual. It looks like Mikhailov et al. were closest to the mark.

Technical comments

1) P4854, ln 1. The use of 'we' here doesn't really make sense – the two papers only have two authors in common

2) P4854, ln 2. 'be' is missing after 'equilibrium can'.

3) P4855, ln 11. 'more than < 10'. Delete either words or symbol.

4) P4856, ln 1-5. It isn't clear which spectra are being referred to here. Label the spectra in the figure.

5) P4856, ln 3, Insert word 'liquid' to be clear here that you are referring to a liquid rather than glassy solution droplet.

6) Fig 4. I found this figure difficult to read. I suggest making fig 4a into two separate figures one focussed on the initial large step in RH and the second focused on the incremental changes in RH. It took a while before I saw the green line at the earliest time. Also, the images are too small and the raman spectra need to be labelled.

7) P4861, ln 12. 'balance' Delete?

8) P4862, ln17. 'this water activity' . State the water activity you are referring to.

9) Fig 7. In the caption or figure indicate what the shaded regions are referring to.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 4843, 2011.