**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "The optical, physical and chemical properties of the products of glyoxal uptake on ammonium sulfate seed aerosols" *by* M. Trainic et al.

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Received and published: 6 September 2011

Reply to referee #1:

We thank the Reviewer for the positive assessment of our paper and for the thoughtful comments. The corrections and replies to all the issues are given below, each of the comments is followed by our reply (highlighted in bold letters).

1. I do not like the sentence 'The observed increase in the ratio of the investigated absorbing substances is slightly indicated in the RI values found by the model, as the imaginary part of the product RI increases from 0.01 to 0.02 with increasing RH.', particularly the use of the word 'slightly'.

Agreed. The wording was changed accordingly. Changed to: 'The observed increase in the ratio of the absorbing substances is indicated in the RI values found by the model, as the imaginary part of the product RI increased from 0.01 to 0.02 with increasing RH. However, the observed increase at this wavelength is within the error range of the model calculations.'

2. However, I suspect that this is close to the lower limit that can be measured by this technique (it may then be considered to be slight) and the reader is left questioning what the level of reported error should be. The authors should include an error with this value and this should also be discussed in greater depth later in the manuscript.

The range of the RIs retrieved is given in section 3.1 (Optical and physical properties) and in table 2, and is shown that this increase is indeed within reported error.

3. The phrase 'leads to more optically active aerosols' could be misleading, based purely on the extinction cross-section. I would prefer the change in size to be normalized out to give the extinction efficiency change, as the authors do later in the paper. Although the geometric cross-section increases by only a factor of 1.35, the extinction cross-section increases by 2.64.

The reason why in this section the change in size is not normalized to give extinction efficiency is that we are interested in showing the total effect of the reaction on the extinction by reacted aerosols. The total effect is not just the change in RI as demonstrated by change in extinction efficiency, but also the change in size, which contributes to the change in the optical effect of the reacted particle due to the steep rise in the Mie curve (see figure 1 below for demonstration). This point is highlighted in this section. In following sections, when we focus on the RI of the new compounds, we eliminate the effect of size and use extinction efficiency. See also our answer to comment #11.

4. Generally, I don't like the use of the phrase 'optically active aerosols'. All aerosols are 'active' at some level, by scattering or absorbing light. It is just that their extinction cross-section may be too low to be significant.

We agree with this statement, all particles are optically active. This is the reason why we write 'more optically active' and not just 'optically active'. There is an increase in the optical activity from a smaller value due to the steep increase in the Mie scattering at these size parameters.

5. The reasons why reaction is seen at an RH below the deliquescence point of AS seem to be quite tenuous. Given that the particles are dried and the deliquescence RH is not reached until 80 % where the particles will become solution droplets, they attribute the growth in size entirely to a monolayer of water, which is thought to occur above 20 % RH. If this reason is correct, why is no growth seen above 20 % RH, but only at 35 % and above?

The text was changed to be clearer. We changed the old text to: ' Mikhailov et al. [2009] (Figure 5b in their paper) showed that approximately 2 water monolayers are formed on the surface of AS particle at low RH values. The authors suggest that from approximately $\sim$20% RH up to 45% RH there might be adsorption of water monolayers or restructuring at the surface of the AS particles, and from 45% RH their measurements are much more robust and are attributed to water adsorption only. Their conclusions are consistent with earlier measurements and estimations [Galloway et al., 2009; Kroll et al., 2005; Liggio et al., 2005a; b]. Therefore, we suggest that the reaction we observe under low RH conditions may proceed through water adsorption onto the AS particles by forming a thin aqueous or partially dissolved layer on the particle. Our findings that there is no reaction at low RH values of 20-35% RH are in agreement with Mikhailov et al. [2009] assumption that any observed changes in particle size at these RH values are attributed to restructuring rather than water uptake. However, while their findings show certain water uptake only at 45% RH, our results indicate that water uptake occurs at 35% RH already, when a reaction is observed.'

6. The authors talk about the monolayer as being like a bulk solution phase saying: 'The aqueous conditions allow for the dissolution of the AS and the glyoxal gas into the outer layer of the particle, leading to a highly concentrated aqueous component around

the particle.' This seems inconsistent with the description of a monolayer of adsorbed water and more consistent with a particle that is undergoing dissolution/deliquescence.

In order to clarify this point in the paper we changed the sentence to: 'The water monolayers enable partial dissolution of the glyoxal gas and of a small amount of AS at the outer layer of the particle, leading to a highly concentrated component around the particle.'

7. Following this sentence the authors state: 'This may also explain why the change in the optical and physical cross sections of the product aerosol is enhanced with decreasing RH values in the reaction.' It is not clear why this sentence follows logically from the preceding one and more explanation is required.

To clarify this point we changed the sentence: 'This may also explain why the change in the optical and physical cross sections of the product aerosol is enhanced with decreasing RH values in the reaction.' To: 'Mikhailov et al. [2009] observed an increase from $\sim$2 monolayers at 50% RH to $\sim$6 monlayers at 75% RH and deliquescence after $\sim$80% RH. This may also explain why the change in the optical and physical cross sections of the product aerosol is smaller with increasing RH values from 50% to 90%, since at this RH range increasing RH values yield higher water content in the outer layer of the AS particles, which in turn leads to a less concentrated aqueous component in the outer layer of the particle, where the reaction takes place, and by that decreasing the reaction rate.'

8. To what extent must gas phase reaction be considered with the deposition of water soluble secondary organics on the particle surface which then behave then as a true solution phase? In general, I find the consideration of the phase of the aerosol and the phase in which the different components are residing to be rather ill-defined. This may be with good purpose as it may not be known, but there does appear to be confusion in the way the manuscript is written.

We hope the changes we made based on the comments have helped clarify the matter.

More detailed studies of water adsorption on inorganic particles are obviously needed but are beyond the scope of this study.

9. For the smallest size (100 nm) can the authors give some estimate of the uncertainty in the extinction cross-section for the pre-reacted particles?

Standard deviation values are given in table 1 of the paper.

10. How sensitive is the CRD technique to such smaller particles and what concentrations are required to measure such a small cross-section?

The sensitivity of the CRD technique that we use is up to 2×10-9 cm-1. We refer the reader to Riziq et al 2007 (Optical properties of absorbing and non-absorbing aerosols retrieved by cavity ring down (CRD) spectroscopy) for more information. The value of extinction coefficient of AS 100nm at the concentrations that we used ($\sim$6,000 cm-3) is 1.59×10-9 cm-1 which is within the sensitivity of the CRD system.

11. I presume that the dramatic increase in the extinction cross-section for these very small particles when compared with the larger particles is just due to the region of the extinction efficiency curve that they fall on. I do not feel that this is ever adequately explained.

We agree, and therefore we added the following text to clarify this point: 'This substantial increase in optical cross section is mostly due to the fact that 100nm particles at a wavelength of λ=355nm have a size parameter of 0.88, yielding near-zero Qext values due to the shape of the Mie curve. When the particles grow to larger sizes due to the reactive uptake of glyoxal, the resulting size parameter is at the sharpest increase of the Mie curve and therefore leads to a very substantial increase in Qext and consequently in σext values.'

12. If some of the ammonium has been used up by reaction, given the considerable increase in the particle size due to reaction, is there not a potential significant error in assuming that the core size has not changed or even changed in refractive index?

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This is a good point. However, we do not think that there is a significant error in the calculation because: A. AS is not consumed in the main reaction, which is glyoxal oligomerization. It only acts as a catalyst for this reaction. B. Only a very small amount of AS is dissolved in the outer layer of the particle in the case of RH values of 50% and 75%, which are below the deliquescence point of AS, and therefore the core size estimation is reasonable.

13. The real parts of the refractive indices retrieved for the two shells are considerably different (1.67 and 1.71) and much larger than the value of 1.61 for HULIS compounds reported previously – I do not understand the phrase 'qualitatively consistent', do they just mean the refractive index has increased on aging?

Thank you for the comment. After further consideration we decided that HULIS is probably not a good choice for comparison. The sentence in P. 19235, lines 14-18 has been deleted.

14. The final sentence states: 'This suggests that under the same RH conditions (in the 40–80% range), the reaction of an evaporating AS droplet will be slower than for the reaction under hydration conditions, due to the higher water content of the dehydrating particles compared to the hydrating ones.' This clearly depends on other factors such as particle size. Are the authors comparing rates for particles of the same dry AS size, the same total size etc.? I feel this is a poor sentence on which to finish section 3 without suitable clarification.

We thank the Reviewer for this comment. We changed the sentence to: 'This suggests that under the same RH conditions (in the 40-80% range), the reaction of an evaporating AS droplet with the same dry diameter will be slower than for the reaction under hydration conditions, due to the higher water content of the dehydrating particles compared to the hydrating ones. '
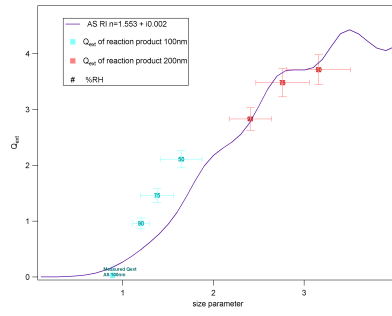
Fig. 1. Figure 1. The final measured Qext values versus size parameter for AS particles with initial diameters of 100nm (light-blue squares) and 200nm (red squares) after the ~1 hour heterogeneous reaction wi

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