**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.

M. Trainic et al.

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Reply to referee #3:

We thank the Reviewer for the thoughtful review of our paper and for raising important issues. 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. Does drying the particles after reaction have any effect on the measurements? This has implications for the discussion provided on p. 19238, line 10.

This is indeed an important issue. Thank you for the comment. The observed behavior

is a result of the process of a reaction occurring under hydrated conditions and the consequent drying. This entire process leads to the observed results. With the current setup it is impossible to separate the effect of drying on the entire process. Such effects could lead to acceleration of the reaction or evaporation of products. The residence time of the particles in the dryers is very short compared to the residence time in the reactor (approximately 20 sec vs. 1 hour), and another 10 sec until they reach the CRD and SMPS systems, which may limit the effect of the drying process. However, we do not rule out that the drying process does play a part in the results. Therefore, the measurements describe an atmospheric condition of a hydrated aerosol reacting with glyoxal and then dried. This is now clarified in the text:

(a) Line 5 page 19224 has been changed to: 'Our experiments imitate an atmospheric scenario of a dry particle hydration at ambient RH conditions in the presence of glyoxal gas followed by efflorescence due to decrease of the ambient RH. The reactions were studied under different relative humidity (RH) conditions, starting from dry conditions (∼20% RH) and up to 90% RH, covering conditions prevalent in many atmospheric environments, and followed by consequent drying of the reacted particles before their analysis by the aerosol mass spectrometer (AMS), cavity ring down (CRD) and scanning mobility particle sizer (SMPS) systems.' (b) Line 10 page 19229 describes the entire process: '...after which the nearly monodisperse aerosol flow is directed into a humidification stage consisting of a nafion humidifier with a temperature controlled bath. This setup allows control of the aerosol flow RH by varying the bath temperature. The hydrated aerosol flow enters a 30L reaction vessel into which gas phase glyoxal is introduced. The residence time in the reactor is approximately 1 hour, after which the aerosol population is dried by two additional silica gel diffusion dryer columns. The RH at the exit of the dryers was measured to be 5%(±3%). ' (c) Line 10 page 19238 was changed to: 'Our experiments were conducted for the hydration process of AS aerosols (i.e. while increasing the RH), followed by drying and consequent efflorescence of the reacted particles.' In addition, we changed line 22 page 19238 to: 'Due to reaction on hydrated AS particles followed by drying and efflorescence, there is formation of sec-

ondary organic material composed of glyoxal oligomers and C-N containing products that result in particle growth.'

2. Regarding the optical property measurements, were the cross-sections corrected for contributions of doubly-charged particles, the contribution and importance of which likely vary as a function of particle size?

We are aware of the issue of doubly charged particles and therefore we work with very diluted solutions (see Methodology section line 5 p. 19229), and the particle concentration in the CRD did not exceed $\sim$800 p/cc. SMPS measurements we conducted in this study as well as our results from our previous studies at similar concentrations of particles show negligible contribution from doubly charged particles.

3. The authors should provide a deﬁnition of what they speciﬁcally mean by "optically active." What is the criterion used?

We agree with the statement that in principle all particles are optically active. This is the reason why we write 'more optically active' and not just 'optically active'. Especially for the smaller particles, there is a substantial increase in the optical activity from a smaller value due to the steep increase in the Mie scattering at small size parameters. This issue has also been brought to our attention by the two other reviewers and we added the following text regarding the 130nm AS particles to the paper for clarification: '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 size parameters due to the reactive uptake of glyoxal, the resulting size parameter is at the steepest increase of the Mie curve and therefore leads to a very substantial increase in Qext and consequently in σext values.'

4. The authors should determine mean RI values for the combination of AS and their glyoxal reaction products for the deliquesced particles (i.e. for the reactions above 85% RH). If the particles are internal mixtures, as opposed to core-shell, the RI should be a

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combination of the pure AS and coating RI's, weighted appropriately (by volume?). This seems an important self-consistency check with the core-coat results. Unfortunately, I think the authors will ﬁnd that the use of a weighted average RI, where the glyoxal reaction product RI is based on the lower RH core-coat particles, will not reproduce the observations, especially if all of the different size particles are included.

The issue can be demonstrated using the data presented in table 2 and figure 5 of our paper. It is shown in table 2 that the RI changes with RH value from 1.67 + 0.01i at 50% RH to 1.71 + 0.02i at 75% RH. This is supported and may be explained by the evidence from AMS analysis (figure 5), which clearly demonstrates that the extent of absorbing substances formation relative to non-absorbing is RH dependant. Therefore, it is impossible to conclude that the RI obtained from the core/shell model for the products of the reaction at 50% and 75% RH can be used for the reaction products at 90% RH.

5. The authors use 1.552 + 0.002i for the RI of the ammonium sulfate seed particles. However, their dry particle measurements appear to be more consistent with a real part of the RI closer to 1.5; use of 1.55 with Mie theory over-predicts the measured Qext values for the dry particles for the 200 nm and 300 nm particles, in particular. How much does the choice of the core RI affect the deduced coating RI?

Our dry particle measurements are always consistent for 1.552 + 0.002i at λ=355nm, which is the wavelength that we used in this work. The RI value of 1.5 is more suitable for λ=532nm.

6. As the authors note, the uncertainties associated with ﬁtting a single data point can be very large. The authors should instead rely on the simultaneous ﬁt to all data points to determine their best ﬁt RI value for the coating. Further, I do not understand why the ﬁt was limited to the 300 nm AS particle data-set only. Why not use the 250 nm data set, where there are many more data points? Or better yet, all of the available data. It would be much better if the authors were to do a global ﬁt to all of their data

at all sizes (excluding, perhaps, the deliquesced particles). I am guessing the authors' argument against this might be that the RIs of the coatings may actually be different for the different RH's because the composition is different. However, I think that the use of single data points is insufﬁciently constrained (see next paragraph), and thus the merging of the data is the less problematic choice.

This is indeed an important comment. We made the following changes according to the suggestion. Table 2 has been altered and the calculated mean is discussed in the paper. The mean RIs are separate for 50% and 75% since AMS results indicate different products for the different RH values. We have made numerous changes that are scattered in the paper to account for this point.

The discussion has been changed accordingly.

7. Related to the previous point, the ranges reported by the authors for the RI values of the coating (p. 19235) seem to be insufﬁciently broad and possibly incorrect. For example, I ﬁnd that, without even considering the uncertainties, an RI of 1.81 + 0.02i gives perfect agreement with the 378 nm data point, as does RI = 1.75 + 0.04i or RI = 2.1 + 0.09i. These are somewhat arbitrary choices: again, using a single data point does not really constrain the possible range of values, which the authors acknowledge, but do not seem to fully appreciate. If uncertainties are taken into account, an even larger range of values is possible.

An RI retrieval using one data point and no constraints can obviously provide many values, which are somewhat arbitrary. The core/shell model, however, provides additional constraint due to the known RI of the core together with the thickness of the shell and the total Qext of the particle. Because the amount of products, and hence the shell's refractive index, change with RH, we have no choice but to use the single point retrieval, and accept the inherent and unavoidable associated errors.

8. The uncertainties in the Qext values given in Table 2 are inconsistent with the uncertainties in Table 1. If the relative error in the diameter is around +/- 10% (approximately

what is shown in the table), then the uncertainties in the Qext values must be at least as large, given the nature of error propagation upon division. This does not seem to be the case. Presumably the 'uncertainties' in the diameter are not really uncertainties, but more of a speciﬁcation of the width of the size-selected mode?

The uncertainties related to the aerosol size are indeed from the width of the distribution around the mode as measured by the SMPS. We use the mode value for the Qext calculations and that is the reason for the observed apparent discrepancy in the error values.

9. The authors were using a high resolution AMS. Presumably, this instrument is capable of determining the atomic composition of the aerosol. Why do the authors instead rely on the unit mass resolution analysis procedure of Galloway et al. (2009)? Why not try and utilize the full capabilities of the instrument? What sort of bias is possible by using the UMR data?

For the AMS analysis we focused on two main issues. One, for validation of the products in these experiments we compared the peaks of the products with the peaks observed by Galloway et al. 2009. The second issue was to obtain the ratio of absorbing to non-absorbing compounds according to the findings that were already obtained by previous studies (Galloway et al. 2009 and Liggio et al. 2005). For consistency we used the same AMS assignment as Galloway et al. (2009) and Liggio et al (2005). The possible bias in the UMR data can lead to differences in sub-unit mass resolution, which was not used in our data analysis.

10. Figure 3 is un-necessary, in my opinion. It would be better to replace it with a ﬁgure that shows the measured Q_extinction values as a function of particle size along with the best ﬁt curves.

The total effect of this reaction is the combined growth in size and change in optical properties, both leading to higher extinction cross section values. While the Qext values provide information on the efficiency of light extinction, the cross section pro-

vides information on the actual extinction of the light by the particles. The atmospheric implications of this reaction involve both, hence we chose to focus on the growth in extinction cross section, shown in figure 3.

11. I do not believe that the authors can make any claims as to an increase in the imaginary RI with RH, as they do on p. 19237, line 14. This goes well beyond the uncertainties of the measurements, especially given that the authors have done their fitting for single data points (which inherently have large uncertainties). The authors state specifically that "Although the increase is within the model error, we cannot rule out that it indicates a trend of growth in the imaginary part of the RI with increasing RH." This is misleading: just as they cannot rule it out, neither can they rule it in. Their data provide absolutely no support in either direction, given the uncertainties. This discussion should be re-moved from the manuscript. If they wish to even attempt to make such a conclusion, then they must, at the very least, include the data from all of the measurements (i.e. all AS particle sizes below deliquescence).

Thank you for this comment. We agree with the referee's statement and changed the text in page 19237 lines 11-19 accordingly to: 'The observed increase in the ratio of the absorbing substances (C-N compounds, including imidazoles) to the glyoxal oligomers with increasing RH values is not indicated in the change from RH 50% to 75%. A further increase in the ratio of absorbing substances and a resulting increase in the imaginary part of the RI at higher RH values is expected, and may become even more substantial after longer reaction times (possibly in cloud or fog droplets). However, the sensitivity of the CRD system and the small change in absorption (at least on these time scales and this wavelength) does not enable to detect changes in absorption.

12. Page 19237, Line 20: The authors compare their results to the literature (specifically Liggio et al. 2005), but seem to restrict their comparison to the 300 nm AS particle results. It is not clear to me why they exclude their 100, 200 and 250 nm particles from the discussion, especially given that Liggio et al. used 125 nm particles. I also do not see where the authors have actually shown that they "found in this study that the

reaction is enhanced with decreasing initial particle size." They did show that the optical growth is larger for the smaller particles, but this says nothing about whether the reaction is enhanced or not. The authors also do not justify (or even discuss) their "linear reaction rate" assumption to extend their results to 4 hrs (Table 3). Overall, I find the discussion in this paragraph to be weak. No AMS measurements were made with AS particles at sizes 100-250nm in this study. We compared our obtained results for AS 300nm to the AMS results from Liggio et al. (at 125 nm) and Galloway et al. 2009. The comparison was restricted by many differences in the experiments apart from initial size. This work is the first to demonstrate that initial size has an impact on the final product. Table 1 and figure 3 demonstrate this effect. Figure three shows the size dependence of the extent of change in final size and extinction after $\sim$1 hour of reaction on RH. Table 1 shows all the data and is less specific but clearly shows this dependence. Since Galloway et al. 2009 used polydisperse aerosol distribution and since we found that the reaction is size-dependent the comparison with their results is difficult. This is explained in the paper in p. 19238 lines 2-9.

Regarding the comment about the reaction enhancement, we changed the phrase to: 'Our value of 13.30$\pm$0.79 is slightly smaller than their value of 16, and our calculated mass growth rate is one order of magnitude smaller. Since we found in this study that the observed relative size change due to the reaction is greater with decreasing initial particle size (see table 1), and our initial seed aerosol size is approximately twice the size used by Liggio et al [2005b] this difference can be expected.' Regarding the linear reaction rate, the following sentence has been added to the comments in table 3:'Based on the findings of Liggio et al. [2005a; b] that the reaction rate is linear in the first 4 hours of their measurements.'

Table 2. The average shell RIs for the reacted particles of the AS at two RH values, retrieved from the core/shell model.

RH	Average RI calculated using the core/shell model for AS 250nm and 300nm particles	
	Real part	Imaginary part
50%	1.68±0.10	0.01±0.02
75%	1.65±0.06	0.02±0.01

Fig. 1. Table #2

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