

## ***Interactive comment on “Light-absorbing secondary organic material formed by glyoxal in aqueous aerosol mimics” by E. L. Shapiro et al.***

### **Anonymous Referee #1**

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This manuscript describes the optical properties of aqueous glyoxal solutions acting as surrogates for secondary organic aerosol. The authors provide evidence for glyoxal and ammonium sulfate reacting to form products with conjugated pi-bonding and perform DFT calculations to support their findings. In addition, they perform basic surface tension and mass spectrometry measurements. The manuscript is well written and within the scope of ACP. However, the manuscript should be revised to address the following concerns.

1. As the authors are probably well aware, two papers studying the glyoxal/ammonium sulfate system have been published while this manuscript was in the submission process. The first is Nozière et al., 2008 which addresses the reaction kinetics of aqueous glyoxal and ammonium ions. Using UV absorption and LC-HRMS, they find the reac-

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tion occurring in their solutions to be second order and propose an iminium pathway to form larger glyoxal oligomers. Nozière et al. were also able to determine the effect of pH and the counterion on the reaction rate. How does this study compare with Nozière et al., 2008, considering both use similar experimental techniques? Can the authors determine the reaction order or propose reaction products with the given data? Can the conclusions of this study be applied to field investigations such as Volkamer et al., 2007?

2. The second publication is Galloway et al., 2008, a chamber study which finds that the glyoxal sulfates proposed by Liggio et al., 2005 are not formed in uptake experiments in the absence of light and were not measured by the Aerodyne Aerosol Mass Spectrometer. The current study should be revised to acknowledge this. Galloway et al. found, however, that organosulfates were formed in the presence of UV light. How much light were the samples exposed to before measurement?

3. The authors need to state the duration at which the control solutions were analyzed with the UV/Vis spectrophotometer to allow comparison to the glyoxal/ $(\text{NH}_4)_2\text{SO}_4$  solutions since both absorb at 277 nm.

4. The authors note that absorbance at 277 nm can be attributed to a  $\pi \rightarrow \pi^*$  transition and propose molecules (g) and (h) in Table 1 that can undergo this transition. Low level DFT calculations support this claim. However, to the reviewers knowledge, there is no evidence to suggest a glyoxal/ $(\text{NH}_4)_2\text{SO}_4$  solution can form these products. Mechanisms should be referenced to lend support to these structures.

5. When the authors state glyoxal can form "ester products," I believe they mean "acetal products."

6. In Figure 3, a MALDI-MS shows the possible masses of products formed in solution. It is odd though that the peaks start at 500 amu and only go as far as 600 amu. This distribution suggests that the products consist of many glyoxal units and only vary within 1 or 2 glyoxal units. Mass spectra from the AMS (Liggio et al., 2005; Galloway

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et al., 2008) show peaks as high as 175 to 192 amu, and Nozière et al., using a much softer ionization method, identify compounds at 228 amu. Can the authors identify the peaks that occur in Figure 3 to at least unit mass resolution? Do the differences in the mass spectrum peaks suggest losses of monomer units? Does the spectrum vary with glyoxal or  $(\text{NH}_4)_2\text{SO}_4$  concentrations? Does the spectrum vary with how long the solution sits before measurement? Answers to these questions could provide insight into the kinetics of the reactions occurring in solution and possible reaction products.

#### References:

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