January 6, 2021

Dear Editor,

Thank you for your comments on our manuscript. Please find below our responses to your comments.

p. 1 line 10 I think it should be "indicating that XAS in the" rather than "indicating that the XAS in the"

Thank you, we have corrected the text in line 10.

p. 2 line 35, for ammonia please also cite Galloway et al. 2009

We have added the reference in line 35.

p. 2 line 41 I think this should be "has a lower value" and not "has lower value"

We have corrected the text in line 41.

p. 3. Line 61-62 Can a statement be made on the purity of the glyoxal and methylglyoxal solutions?

It is stated that the aqueous solution of glyoxal has acidity due to CHOCOOH while we cannot provide a statement about the solution of methylglyoxal. We modify the text in lines 61–62: "Glyoxal and methylglyoxal were delivered as 40 wt% aqueous solutions. Stated acidity of the aqueous glyoxal (glyoxylic acid, CHOCOOH) is maximum 2%. Glycerol was a viscous liquid of 99.5% purity."

p. 3 line 76 Perhaps better "pumped through the liquid cell with a flow rate . . . "

Thank you for the suggestion. We have changed the text in lines 75–76 to: "The liquid sample can be pumped through the liquid cell with adjustable flow rate (Cole–Parmer Masterflex L/S pump system)."

p. 4 Table 1. Could the authors please double check the solubility of NaCl. It seems a little high, as I thought it was around 36g of NaCl per 100g of water with little temperature dependence.

We agree that the given solubility of NaCl is high and we change the value to 36 g/100g [1].

p. 5 line 96. Perhaps better "The C K-edge spectra of pure water were subtracted from the C K-edge spectra of the samples to . . . "

Thank you, we rephrase the sentence in line 96 as you have suggested.

p. 9 figure 3. What are the energies for the oligomeric C-O-C acetal. This could have a high enough concentration for glyoxal to be observed see figure S9 in Yu et al. 2011 especially as those were only 1M solutions?

p. 10 line 182-183. Regarding the absorption edge energy increase with decreasing concentration of glyoxal (2M to 1M) and with addition of salt. Could this be explained by a decrease of the oligomer to monomer ratio with decreasing glyoxal concentration and increasing salt concentration as hypothesized by Yu et al. 2011? I think this is consistent with the results presented here?

Unfortunately, the absorption energies of oligomers have not been calculated. However, we agree that this should be discussed further and that the changes on the absorption edge energies could be related to the abundance of oligomers. We have changed the text in line 181 to: "Kua et al. (2008) [2] and Yu et al. (2011) [3] identified potential oligomers containing acetal groups in aqueous glyoxal. Here, we did not calculate absorption energies of oligomers but based on the C 1s absorption energies of similar O-C-OH functional groups found in saccharides (Gainar et al., 2015 [4]), we estimate that in oligomers acetal moieties would have higher absorption energies compared to C-OH moieties. Their contribution would therefore be embedded in the broad continuum part of the XAS spectrum. The observed increase in absorption edge energy with decreasing concentration of glyoxal and addition of salts could be related to changes in the degree of oligomerisation. This is in line with the study of Yu et al. (2011) [3] who observed deoligomerization with addition of Na_2SO_4 and NaCl."

p. 15 line 270 -271 p. 16 line 299-300. Yu et al. did not conclude that glyoxal exists entirely in its fully hydrated form, as they were able to observe aldehyde 1H NMR signals. The NMR intensities of the aldehydic hydrogen was very low but the authors were able to show that upon addition of salts the dihydrate to monohydrate signal increased, see Table 1 in their paper.

Thank you very much for pointing this out. We have changed the text in lines 270–271 to: "Here, we confirm experimentally that glyoxal, to the sensitivity of our measurements, exists strongly in its fully hydrated form in aqueous solution, in agreement with previous studies [3, 5, 2]" and we remove the sentence in lines 299–300: "However, our finding that glyoxal exists entirely in its covalently bond dihydrate form in aqueous solution is in line with the results of Yu et al. (2011)."

p. 16 line 288, please add "to the sensitivity of our measurements"

Thank you, we have added the text in line 288.

Supplement p 1. Line 28. Should this be aldehydic rather than ketonic for glyoxal, as it has only aldehyde groups and no keto groups? What is the purity of the solution. Glyoxal has a very high Henry's law constant, could contaminations of higher vapor pressure glyoxylic or glycolic acid cause the feature at 288.7eV?

Thank you for bringing the typo in our attention. We change the word "ketonic" to "aldehydic" in line 28 of the Supporting Information. It is estimated that the solution acidity due to glyoxylic acid is maximum 2%. We add in line 33 of the SI: "indicating possible presence of acid (as CHOCOOH, $\sim$ 2% according to manufacturer Wako) impurities in the solution."

Sincerely, on the behalf of the authors,

Georgia Michailoudi

*References

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[3] G. Yu, A. R. Bayer, M. M. Galloway, K. J. Korshavn, C. G. Fry, and F. N. Keutsch. Glyoxal in aqueous ammonium sulfate solutions: Products, kinetics and hydration effects. *Environ. Sci. Technol.*, 45(15):6336–6342, 2011.

[4] A. Gainar, J. S. Stevens, C. Jaye, D. A. Fischer, and S. L. M. Schroeder. Nexafs sensitivity to bond lengths in complex molecular materials: a study of crystalline saccharides. *J. Phys. Chem. B*, 119(45):14373–14381, 2015.

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