Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-393-RC1, 2020

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Aqueous phase behavior of glyoxal and methylglyoxal observed with carbon and oxygen K-edge X-ray absorption spectroscopy" *by* Georgia Michailoudi et al.

Anonymous Referee #3

Received and published: 26 August 2020

This work describes the use of X-ray absorption spectroscopy to study solutions of glyoxal and methylglyoxal mixed with NaCl or Na2SO4, in order to simulate aqueous aerosol environments. While the method turned out to be too insensitive to observe the effects of organic – inorganic interactions (between, for example, glyoxal and sulfate), which seem to have been the original goal of the study, it did produce clear observations of enol forms of methylglyoxal in solution, the main new result. Glyoxal's tendency to be fully hydrated was also observed in the lack of any C=O signal, consistent with the results of several other studies using different spectroscopic methods. Together, these observations confirm the ability of glyoxal and methylglyoxal to hydrate and react in other ways when dissolved in water, and therefore form aqueous SOA in the atmosphere.

Specific comments:

Line 7: The abstract suggests that the X-ray spectra of methylglyoxal imply the presence of the dihydrate form, but there is little evidence of this form according to Figure 5. Any dihydrate transitions appear to be buried in the ionization peak. I think the data does not imply the dihydrate's presence or absence.

Line 10: Since organic - inorganic interactions have been observed for these species by other methods, a statement about a lack of method sensitivity would be more appropriate than one about the weakness of these interactions. They are evidently strong enough to greatly increase measured Henry's law coefficients. (Kampf, Waxman et al. 2013)

Figure 3: Are the decreases in the C-OH ionization peak sizes caused by salt addition evidence of a chemical change? If so, this would be the opposite of what was observed for Na2SO4 by Yu et al. (Yu, Bayer et al. 2011). Could the authors address this?

Figure 4: Are the decreases in the size of the A and B peaks caused by salt addition (especially for NaCl) evidence of a shift away from enol forms?

Line 274: This sentence states that C=O and C-H functional groups are found in the dihydrate form of methylglyoxal. For C=O this statement is false.

Technical Corrections:

Table 3: Why are excitation energies not listed for dehydrated methylglyoxal? The text states that they were calculated in line 136.

Line 159: Are these differences of 0.1 – 0.2 eV significant, given that they are "within the photon energy resolution"? Or are they just random variation? If random, Table 4 should be moved to the SI section or eliminated from discussion.

In Table 5, the functional group entry for peak B should also be labelled "enol", if I

Printer-friendly version

Discussion paper

understand Figure 5 correctly. Also, no oscillator appears to line up with the C3 peak, so the origin of its assignment in Table 5 is unclear.

Figures 6-8 have two deep pink lines in the legend that look identical, but not in the figure itself.

Line 276: This sentence calls 1 – 2 M “low solute concentrations,” which is somewhat misleading. It seems like the issue is rather the large signals of water.

Cited references:

Kampf, C. J., E. M. Waxman, J. G. Slowik, J. Dommen, L. Pfaffenberger, A. P. Praplan, A. S. H. Prévôt, U. Baltensperger, T. Hoffmann and R. Volkamer (2013). "Effective Henry’s Law Partitioning and the Salting Constant of Glyoxal in Aerosols Containing Sulfate." Environmental Science & Technology 47(9): 4236-4244.

Yu, G., A. R. Bayer, M. M. Galloway, K. J. Korshavn, C. G. Fry and F. N. Keutsch (2011). "Glyoxal in aqueous ammonium sulfate solutions: products, kinetics, and hydration effects." Environmental Science and Technology 45: 6336-6342.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-393, 2020.