

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 #4

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The authors use XAS to study the structure of glyoxal and methylglyoxal in aqueous solutions with varying levels of inorganic salts. Quantum chemical calculations (that include electron correlation effects) are used to estimate ionization and excitation energies for hypothesized molecules in the gas-phase with appropriate discussion of uncertainties in using them to interpret condensed-phase spectra. From the C K-edge spectra, glyoxal is found to be completely hydrated due to observation of COH and lack of C=O, while products of enol structures and aldol condensation products that include C=C bonds are observed for methylglyoxal (in addition to hydrated forms suggested by C=C and COH bonds). The O K-edge is found to be generally insensitive for examining the structure of these organic molecules in these systems. The manuscript

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is clearly written and interpretations are sensible. The work is of interest to the Atmospheric Chemistry and Physics community and is recommended for publication with minor changes.

Minor comments:

In the Introduction, there is no mention of relevant literature with regards to characterizing molecular structure and electrolyte-nonelectrolyte interactions in relevant systems. This is actually partially covered later in the discussion, but the work should be placed in context of prior art up front.

These ionic strengths are quite low by atmospheric standards so there should be a caveat regarding the limitations of this study.

The authors introduce the "NEXAFS" later in the manuscript as if it were a different technique, but it's not clear that this is actually different from the technique used by the authors referred under broader term, "XAS".

Apart from studying water (as cited by the authors), the O K-edge has generally not been found to be useful for characterizing specific structures of organic compounds (apart from indicating total oxygen content) in past work, and also seems to be the case here. The O K-edge does not really make a contribution to the main findings of the manuscript and should probably be summarized in a few sentence and removed otherwise (or placed in supplemental).

Table 4 also seems superfluous and can be moved to the supplemental since it can be summed up concisely in the text.

Can the authors elaborate on how the measured absolute intensity or optical density calibration is used in the experiments?

The way the units is presented is not entirely clear since the authors talk about measured beam intensity and absorption intensity (abs. = absorbance units?). Can authors clarify in one of the Figure captions?

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The inline equation at the top of pg. 5 should be the Lambert formula since Beer's contribution comes from introducing the molar or number concentration to the linear attenuation coefficient of the material.

The authors seem to use the term "salting in/out" to generally refer to nonideal electrolyte-nonelectrolyte interactions instead of the consequence of their interactions, unless they are expecting a specific type of change in the spectra that was not made explicit in the manuscript.

Fig. 3: One of the vertical lines appear red while the other appears purple. It should be specified that it's these vertical lines that are scaled according to oscillator strengths and not the spectra (which are also drawn as lines).

Fig. 5. Since the overall fit is shown, can the authors display all the curves that are fitted (not just the Gaussian peaks)?

The authors talk about "IP of the C=O sites" (and for other groups) but would maybe more naturally be referred to as the "IP of the C=O moiety" in this context?

"SCF" is not defined.

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