We thank the reviewers for the constructive comments and feedback. Please find below the response to the comments and questions.

Referee #1

1. *The authors could stress more that the technique applied in this paper is not limited to only aqueous phase processing.*

   - This point was stressed in the conclusion of the original manuscript (P6167 line 25 - P6168 line 2): "while it was convenient for us to monitor change occurring during aqueous phase oxidation in the laboratory, we stress that the same general behavior is likely to be observed from chemical change being driven by gas phase or heterogeneous OH oxidation".

   - This point was also mentioned in the introduction of the original manuscript (P6152 line 26-28): "We treat this complex organic mixture and its subsequent aqueous photo-oxidation components as models to highlight the capabilities of high resolution aerosol-CI-ToFMS to study organic aerosol composition and processing".

   - As requested, this sentence was added in the introduction of the revised version (Page 5, line 3-5) "while this study focuses on the aqueous phase chemistry, the technique and the approach discussed here can be pursued for other systems and phases (i.e. gas and heterogeneous phases)".

   - Also, the title of the paper was changed to "High Resolution Chemical Ionization Mass Spectrometry (ToF-CIMS): Application to Study SOA Composition and Processing" in order to emphasize how the approach discussed in the paper is general to any type of study.

2. *I suggest removing "focus on" from the title, and possibly moving the "application to" in it's place.*

   The title was changed to "High Resolution Chemical Ionization Mass Spectrometry (ToF-CIMS): Application to Study SOA Composition and Processing"

3. *The introduction is a bit lengthy, and could be more focused on the issues discussed in this paper. For example, the ability to detect single molecules is high-lighted in the introduction, but actual molecular results seem to be awaiting a subsequent publication.*

P6149 line 23 – P6150 line 20 paragraph in the original manuscript was removed.

4. *Many of the most intriguing results in this paper arise from the use of several different reagent ions, but hardly any background is given on the importance of choosing the "correct" reagent ion when doing CIMS. I would in general like to see some more discussion on the different reagent ions.*

   The authors agree with the referee and the following was added in the revised manuscript (Page 3, line 31-Page 4, line 10) “For instance, protonated water clusters $(H_2O)_nH^+$ have been used for the detection of oxygen, nitrogen and sulfur containing organic compounds for decades (Sunner et al., 1988, Lindinger et al., 1998). Iodide water cluster $I(H_2O)_n^-$ reagent ions have been employed in several lab and field studies that targeted oxygenated organic compounds and nitrogenous inorganic species such as N_2O_5 and $ClNO_2$ (Caldwell et al., 1989, Bertram et al., 2009; Kercher et al., 2009, Le Breton et al., 2012). In addition, the use of acetate reagent ions has recently been emphasized for the detection of organic, halo-organic (e.g. trichloroacetic acid), inorganic acids (e.g. HCl, HNO_3 and H_2SO_4) as well as nitrophenols (Veres et al., 2008). Gas phase H_2SO_4 and its neutral ambient clusters have also been detected with CIMS using nitrate reagent ions (Mauldin et al., 1999, Kurten et al., 2011, Jokinen et al., 2012).”

5. *Are the authors able to recommend one reagent ion over the others, in situations where switching is not an option?*

   The best reagent ion depends on the system used and the compounds targeted. The paper illustrates the selectivity of the three reagent ions towards different types of organic compounds that are oxygenated. Sectional 3.1 presents a detailed discussion on the instrument selectivity for the three reagent ions.

6. *Is it important to always use several [reagent ions] to detect "all" compounds?*

   The use of multiple reagent ions is required if a full composition elucidation is required. In particular, the results from the paper indicate the selectivity of the reagent ions is dependent to some degree of the degree of oxygenation of the species being studied. However, in cases where only a few compounds are targeted, then one reagent ion may be sufficient.

7. *And what fraction of the SOA is believed to be detected with the reagent ions used here? Maybe all compounds still weren’t measured, and other reagent ions should be considered?*

This is a very good point that is raised by the referee. The authors do not have the ability to measure the fraction of SOA being detected by the CIMS. The need for other reagent ions might be required to fully elucidate the composition. For instance, assuming the AMS captures the majority of the SOA composition and referring to figure 8b, the AMS region between O/C 0.7 and O/C 0.8 does not seem to be covered by the CIMS acetate and iodide traces. As a result, a more selective reagent ion might be required for the detection of these highly oxygenated organics that give rise to the high O/C measured by the AMS.

8. *Section 2.2: It sounds like the oxidation takes place for 4h, and the sampling occurs later. Only in Fig.3 does it become clear that the solution is actually sampled throughout the oxidation process. This should be noted already in this section for clarity.*

   This was fixed in the revised manuscript as of the following:

   Point 3 in Page 5, line 24-25 was changed to "(3) on-line detection of photo-oxidation products using high resolution ToF-CIMS and AMS (Aerodyne Inc.)."

   Page 7, line 19-22: "The WSOC solution was continuously atomized using a TSI constant output atomizer (model 3076). A fraction of the droplets was diluted by a factor of 4 with nitrogen gas (BOC, grade 4.8) or air (Linde, grade 0.1) before entering the high resolution ToF-CIMS (Aerodyne Inc.) (Figure 3) for on-line detection."

   Section 2.3 was renamed to "On-line detection of WSOC and the photo-oxidation products".

9. *Page 6168, lines 14-15: Were the three reagents switched continuously, or were experiments made with different samples? The only reference to how the switching was done in practice seems to be in the caption of Fig. 4 that states "One reagent ion was used at a time.", but this is not very helpful. The switching should be explained in the methods section, especially as the simplicity of the switching is high-lighted in the conclusions.*

   This was fixed. "One reagent ion was used at a time." was added to Page 8, line 18 in the revised manuscript.

   The SOA was generated for all three experiments under the same chamber conditions. The difference is that the water extracts of three filters were combined for one reagent ion experiments (OH oxidation and control experiments).

10. *6151, 1-8: Several Canagaratna references are not needed here. The last two can be removed.*

Fixed

11. *6151, 9: First "ESI" can be removed.*

    Fixed

12. *6154, 18: "spectrometer"*

    Fixed

13. *6157, 16-17: "Protonated water clusters and iodide water clusters reagent ions experiments..." is confusing and should be reformulated.*

    The sentence was changed to "The ToF-CIMS was operated in weak-field mode during the experiments where $(H_2O)_nH^+$ and $I(H_2O)_n^-$ were used as the reagent ions."

14. *6158, 4: "ions"*

    Fixed

15. *6158, 5-6: I have never seen such exact resolution numbers quoted, and doubt that these were this exact even between two consecutive spectra. Regardless, the authors should rather state that the resolution was 4100-4300 or "just above 4000" for all experiments instead.*

    Fixed

16. *6158, 14: Fix parenthesis in citation.*

    Fixed

17. *6161, 12: "analogue". Also, it is not clear in which way it is analogous.*

    Fixed. They are similar in structure. Pyruvic acid has an extra methyl group.

18. *6161, 24-26: "To illustrate, it was observed (not shown) in the sensitivity test (Sect. 3.1) the presence of ions for (H2O)nH+ and in CH3C(O)O reagent ions, which was not expected based on Reactions (R1) and (R2)." This sentence is very confusing and should be reformulated.*

It was fixed to “To illustrate, it was observed (not shown) in the $(H_2O)_nH^+$ and in $CH_3C(O)O^-$ sensitivity test (Section 3.1) that some of the ions detected did not form by a proton transfer reaction from/to the reagent ions as in R1 and R2”

19. *6167, 1: "compared to"*

    Fixed

20. *Fig. 8: AMS symbol is "water"?*

    The black circles represent the AMS data from the $(H_2O)_nH^+$ (or water) experiments. The iodide and acetate experiments showed similar results as for the water experiment. Thus the AMS results from the two latter reagent ions were not shown. The caption of the figure was adjusted to address that. “Note that although AMS measurements were conducted for each reagent ion experiment, for clarity sake only one set of data (i.e. AMS data collected during the Water or $(H_2O)_nH^+$ runs) is plotted here; the other experiments gave similar results.”

21. *Fig. 9: The average OSc point seems to be missing. Also, I think the light vs dark dots are explained differently in the text and in the figure.*

    The authors are not sure which average OSc point is missing.

    The light vs. dark dots error was fixed.

Referee #2

1. *Abstract: "In the bulk O/C and H/C space, i.e. in a Van Krevelen plot, there is a remarkable agreement in both absolute magnitude and oxidation trajectory between CIToFMS data and those from a high resolution aerosol mass spectrometer (HR-AMS). This indicates that the CI-ToFMS data captures much of the chemical change occurring in the particle and that gas phase species, which are not detected by the HR-AMS, do not dominate the overall ion signal." The bulk elemental ratios (O/C and H/C) referred to here are averages weighted by the ion intensity (section 3.2.2). As shown from the calibration experiments presented in this manuscript (section 3.1), the sensitivity of the instrument to different organic species can differ by orders of magnitude. Thus, the intensity averaged elemental ratios could be significantly different from mass or mole-averaged elemental ratios. Thus, the comparison of elemental ratios from the HRToF-CIMS and HR-AMS is not rigorous, and it is not clear whether scientific conclusions can or should be drawn from such a comparison (e.g. that the gas phase species do not dominate the ion signal). This issue should be discussed in the revised manuscript.*

   We understand the point that the Reviewer is making. Indeed, when we started this work we did not anticipate that a comparison of CIMS and AMS data in a Van Krevelen space would show such good agreement for just the reasons pointed out in the review, i.e. there would be differing sensitivities to different species as measured by CIMS, and we are not able to distinguish between gas and particle-based species. While we cannot rule out the agreement as being fortuitous, what this more likely implies is that the gas phase species do not contribute substantially and that the CIMS sensitivities do not exhibit a lot of variability for the major components of the particles. Indeed, we showed in Section 3.1 how the sensitivities of several organics differ from one another when they are detected with the three reagent ions used in this work. The data clearly show that only with the $(H_2O)_nH^+$ reagent ions that the sensitivities differ by orders of magnitude. Acetate and iodide reagent ions experiments show that the sensitivities of the organics are only small factors different from each other with few exceptions that are discussed in text. Thus, as a first-cut, we feel that the similarities between the two instruments is noteworthy. We note that a comparison with the AMS allows one to see if the majority of the chemical composition is indeed captured by the CIMS (ie., the AMS is a reference instrument as it is well established technique).

   That all being said, we have now included in Section 3.2.3, a short section that makes the point that a comparison of this type should ideally be made when sensitivity-weighted CIMS signals are used, but that this is difficult to do when not all species have been calibrated for. Rather, the close agreement between the CIMS and AMS data when acetate and iodide are used is likely due to similar sensitivities that make up the bulk composition of the aerosol, as indicated by the data in Section 3.1. The following short paragraph has been added to the first paragraph in Section 3.2.3 (Page 15, line 13-18 in the revised manuscript):

"Ideally this comparison would be made using sensitivities that are tied to molecular composition, with the gas and particle signals separated. The fact that the CIMS and AMS data agree so closely with each other suggests that the CIMS sensitivities are similar to each other for major, highly oxygenated components of the aerosol, especially when using the iodide and acetate reagent ions. To some degree, with is consistent with the conclusions drawn above from the work done with standards."

As well we have deleted the wording "*and that gas phase species, which are not detected by the HR-AMS, do not dominate the overall ion signal.*" from the Abstract because we agree that we can not unambiguously make this conclusion, and we have altered the wording in the Abstract to some degree also.

Abstract: "Despite not using a sensitivity-weighted response for the ToF-CIMS data, the CIMS approach appears to capture much of the chemical change occurring. As demonstrated by the calibration experiments with standards, this is likely because there is not a large variability in sensitivities from one highly oxygenated species to another, particularly for the $CH_3C(O)O^-$ and $I(H_2O)_n^-$ reagent ions."

2. *Pg. 6163, lines 11-12: "Peaks higher than 300 u cannot be unambiguously assigned for the* $(H_2O)_nH^+$*,* $CH_3C(O)O^-$ *reagent ions." The authors seem to imply that peaks lower than 300 amu can be unambiguously assigned. Considering the quantity of peaks identified some of the mass spectra must be quite crowded, and it is not clear that the peaks could be unambiguously identified. The authors should comment on this and perhaps show a figure or two – one in which the peaks can; another in which they cannot be unambiguously identified.*

   We thank for the reviewer's suggestion. New figures have been added to the supplementary information to show the peak fitting in different m/z region for demonstration. Also, the related sentence has been revised as following (Page 13, line 26-27 of the revised manuscript):

   "Peaks higher than 300 u cannot be assigned for the $(H_2O)_nH^+$, $CH_3C(O)O^-$ reagent ions with high confidence (see supplementary information)."

3. *Pg. 6163, lines 15-18: "Elements other than C, H and O were not considered in the formula predictions as it was assumed that those elements were absent from the reagents (WSOC and H2O2) and purified water." This assumption implies that there was no contamination in this system, which is unlikely for any experimental system. Purified water is often not as pure as one might expect. Especially since the HRToF-CIMS has such different sensitivities to different ions, low levels of contamination can result in significant peaks. I worry that some of*

these peaks may have been erroneously attributed to an organic species of a similar molecular mass. One way to check this is to conduct a control experiment – purified water, H2O2 and UV lights – and comment on the resulting mass spectrum in the HRToF-CIMS

Control experiments were conducted but were not explicitly discussed in the manuscript. The results from the control experiments have shown negligible contamination from purified water, H_2O_2 and UV lights. The background peaks that were present were stable and small in intensity compared to the peaks that arise from the sample. Thus, we believe that the contribution of elements other than C, H and O is minor and can be ignored in this work. This is a good point, which is now addressed in Section 3.2 (page 12, line 21-23 of the revised manuscript).

"As well, we note that the intensity of the CIMS peaks in the control experiments conducted with H_2O_2, water and light (but no WSOC) were minor compared to the peaks that were associated with the WSOC."