On behalf of all of the co-authors, I would like to thank all of the reviewers for their extremely thoughtful and comprehensive reviews. Unless specifically indicated, table and figure numbers refer to the ACPD verison. The reviewers' comments are reproduced in black, our responses are detailed below in red:

**Comments on the manuscript entitled "**Direct photolysis of carbonyl compounds dissolved in cloud and fog droplets**" by S.A. Epstein, E. Tapavicza, F. Furche, and S.A. Nizkorodov**
**Review by Anne Monod**

**General comments:**

This paper is of high interest, as it provides a thorough analysis of the importance of direct photolysis reactions of carbonyl compounds in cloud and fog droplets, compared to aqueous phase OH-oxidation, and gas phase photolysis and OH-oxidation. This paper can be regarded as the companion paper of the one published in 2012 (Epstein and Nizkorodov, ACP, 2012), but the present one focusses on carbonyl compounds. This class of compounds is in fact of high atmospheric relevance for this investigation as i) they can partly hydrate in the aqueous phase, thus inducing different reactivity compared to the gas phase; ii) they are able to oligomerize in the aqueous phase (Tan et al., 2012; Lim et al., 2010; Renard et al., 2013); iii) their photolysis can initiate totally different chemical mechanisms in the aqueous phase compared to the gas phase (Guzman et al., 2006; Griffith et al., 2013). All these reasons fully justify a new study on the subject, and this should be underlined in the introduction.

We are glad to hear that the paper will be of high interest to the community. We agree that carbonyls represent a very important group of oxidized organics, and this is why we decided to dedicate the entire paper to this group of compounds. We added a few sentences in the introduction further justifying our choice to study carbonyls.

The paper highlights the current lack of experimental data concerning aqueous phase photolysis (in particular extinction coefficients and quantum yields), and the results obtained are extremely useful to determine what compounds are of atmospheric relevance for further experimental investigations. The results are significant and fully appropriate for the journal, the paper is well written, and I recommend its publication after minor revisions. I have several specific comments that are mentioned below, among which are my 3 main concerns:

1- For the predictions of aqueous OH rate constants: it would be certainly worth using the up-to-date version of the SAR which is dedicated to carbonyl compounds: Doussin and Monod, 2013.

We recalculated all of the aqueous OH rate constants using Doussin and Monod, 2013. The revised version will contain only the results obtained with the up-to-date SAR.

2- Unsaturated carbonyl compounds are not clearly treated in the manuscript (see detailed comments)

We cleared up this analysis in multiple places in the text, and added more unsaturated carbonyl compounds to the figures and tables.

3- Figure 5 could be modified in a much more useful way (see detailed comments)

We incorporated your suggestions regarding modification of Figure 5.

**Detailed comments:**

**Abstract**: the last sentence is confusing: the reader may understand that the paper shows that for all alpha, beta conjugated carbonyls, aqueous phase direct photolysis is of importance.

We slightly modified the last sentence to avoid this confusion.

**Introduction**:

p. 10907 line 10: the reference to Sander et al (2011) is missing in the references.

Added.

p. 10908 lines 19-22: this phrase is too long and confusing. The goal of investigating these 2 compounds in particular should be more clearly explained here. Furthermore, the reader needs a reference to Figure 1 at this point.

We rearranged the entire paragraph to be more readable and less confusing. Figure 1 is now referenced when glyceraldehyde and dihydroxyacetone are introduced.

p. 10909 lines 2-5: same remark as in the abstract

We modified this sentence to avoid this confusion.

**Material and methods**:

p. 10909 lines 17-19: rephrase "to filter out light outside the actinic wavelength range" as this is not correct for the higher wavelengths.

Changed to read "…to filter out higher energy UV light outside of the actinic wavelength range…"

**Modelling approach**:

The calculation of Z implies that the kinetics of hydration is much faster than that of the studied reactions. The author should mention this, and refer to Doussin and Monod (2013) and Ervens and Volkamer (2010) and possibly the older references included in these papers.

We added the following sentence to address this "Consistent with previous researchers, we assume that the kinetics of hydration is faster than aqueous photolysis and aqueous oxidation by OH (Doussin and Monod, 2013;Ervens and Volkamer, 2010)."

p. 10911 line 3: replace "the Henry's law constant" by "the effective Henry's law constant"

Changed.

p. 10911 lines 9-12: effective Henry's Law predictions: how does the HENRYWIN compares to the SAR developed by Raventos-Duran et al. (2010)?

HENRYWIN and the GHROMHE method developed in Raventos-Duran et al. have similar predictive abilities for the molecules we are interested in: mono-functional, di-functional, and compounds with $k_H^{eff}$ exceeding $10^3$ M atm$^{-1}$. There are many other Henry's law SAR models. (Dearden and Schüürmann, 2003) and (Raventos-Duran et al.) evaluate their performance. We added the following sentence to the text to address this: "Several other models designed to predict Henry's law constants exist in the literature; (Dearden and Schüürmann, 2003) and (Raventos-Duran et al.) provide thorough comparisons of these methods."

p. 10911 lines 22-26: predictions of hydration equilibrium constants: also refer to Gomez-Bombarelli et al. (2009). Also, the reference to Karickoff et al. (2011) is missing in the references.

We would prefer to not add additional references for other predictions of hydration equilibrium because we want to avoid giving an impression that we have a comprehensive list of references cited. We added Karickoff's reference to the reference list.

p. 10912 lines 7-11: predictions of aqueous OH rate constants: it would be certainly worth using the up-to-date version of the SAR which is dedicated to carbonyl compounds: Doussin and Monod, 2013.

This is a great suggestion. We updated all of the calculations to use the up-to-date version.

p. 10912 lines 14-16: I fully agree that alkenes or cyclic compounds are potentially important compounds in the authors' analysis. However, the paper is not quite consistent on this issue: it states here that these classes of compounds were not included in this study, but some of them are considered further in the results (Figure 3, Figure 4, Figure S11). It should be worth considering the compounds of atmospherically relevance, for which experimental data exist. For instance, for α, β unsaturated carbonyls, aqueous phase extinction coefficients and OH-oxidation rate constants can be found in Liu et al., 2009, Szeremeta et al., 2009, Liu et al., 2012 and Renard et al., 2013 and references therein.

We agree. Two atmospherically relevant unsaturated compounds were added to the analysis: methacrolein and methylvinylketone. This supplements the current form of the paper that addresses acrolein, 4-hydroxybut-3-en-2-one, 4-hydroxy-3-methyl-but-2-enal, and 1-hydroxy-3-methylbut-3-en-2-one. We changed these lines to read "We were unable to make rate constant predictions of saturated compounds because they were absent in the training data set." The potential importance of aromatic compounds is discussed in the Atmospheric Implications section. We also added a paragraph to the results section about the OH oxidation rates of unsaturated compounds relative to their saturated analogues.

p. 10912 lines 17-20: it is true that the relative fraction of anion and undissociated acid is a function of droplet pH, and that the undissociated form is less reactive towards OH-oxidation. However, the photolysis reaction should also be affected, both in terms of extinction coefficients and quantum yields (Leermakers and Vesley, 1963). This should be clarified in the text, giving an example.

We addressed this with a new paragraph in the text: "For specific carboxylic acids, changes in pH may modify molar extinction coefficients and quantum yields. Pyruvic acid, an α-keto carboxylic acid with interaction between the dissociating acid and absorbing carbonyl group, does not exhibit a significant change in absorption between the acid and anion form (Fischer and Warneck, 1991). On the contrary, the quantum yields of pyruvic acid and pyruvate are drastically different (Leermakers and Vesley, 1963), but this fact does not affect our analysis designed to calculate the upper limit of aqueous photolysis with $\Phi_{max} = 1$."

**Results and discussion**:

p. 10917 lines 22-25: this phrase is too long and confusing.

We modified the phase to read: “However, a low value of Z does not necessarily imply that photolysis is the primary sink in the aqueous-phase; the photolysis lifetime might be too long to be atmospherically relevant and/or it may not be able to compete with oxidation by OH.”

p. 10918 lines 11-15: the comparison between propanal and acrolein is very interesting and relevant. One would like to see on that figure other similar comparisons, especially with α, β unsaturated carbonyls, such as methacrolein and methylvinyl ketone, which are atmospherically relevant as the primary reaction products of isoprene. One would also like to see the α, β unsaturated carbonyls mentioned in Fig. 3.

We added methacrolein, methyl vinyl ketone, and crotonaldehyde to Figures 4 and 5 for additional comparison between unsaturated carbonyls and their (α, β) unsaturated analogs. We have also modified the text to reflect this change. We are unable to include all of the unsaturated carbonyls mentioned in Fig. 3 (pyruvic acid and methyl glyoxal are already on Figures 4 and 5) because of uncertainties in predicting the $\lambda_{max}$ and $\varepsilon_{max}$ values with TDDFT.

p. 10918 lines 23-29 and p. 10919 lines 1-4: Figure 5 is very interesting and potentially show clearly the relative importance of aqueous phase photolysis compared to OH-oxidation. However, as it is presented, very little can be ruled out from it, and the corresponding text is not clear. I suggest modifying the figure showing the actual compounds with 2 points for each (one for $k_{OH}$ and one for $<\varphi>.\varepsilon_{max}$) linked with an arrow pointing towards kOH, and modifying the text accordingly. The resulting figure should show clearly the compounds for which photolysis matters (descending arrows). In the new figure, again, the α, β unsaturated carbonyls should be of high interest!

This is a great suggestion. We incorporated points representing $k_{OH}$ values and connected them with arrows to their corresponding point on the plot. We also replaced the letters with shapes and included a legend.

p. 10919 line 14: replace “Z” by “Q”

changed

p. 10919 line 15: replace “Q” by “Z”

changed

p. 10919 line 28: replace “3-oxopropanoic acid” by “3-oxopropanal”

Recalculation of Figure 6 with the up-to-date SAR values slightly shifted around some molecules. Now there is no reason to call out 3-oxopropanal in the text.

p. 10920 line 7: the up-to-date version of the SAR by Doussin and Monod, 2013 would give the following values for the rate constants of OH-oxidation in the aqueous phase: 2.16 x 108 M-1s-1, 1.83 x 108 M-1s-1 and 1.09 x 109 M-1s-1 for pyruvic acid, 3-oxobutanoic acid and 3-oxopropanoic acid respectively (using hydration constants of 1.4, 0.2 and 28.8 respectively).

We recalculated all of the values with the up-to-date version.

**Tables and Figures**: in general, the terminology used for molecule names are not always consistent, see for example levulinic acid, which should be replaced by 4-oxopentanoic acid.

In our attempts to make many of the molecules we studied recognizable, we used common names in our figures and in the text. In order to be more consistent, where possible, we modified the text to include both IUPAC and common names.

**Table 1**:
It should help the reader to add 1 column with the molecular structures.

We are worried that adding an additional column to figure 1 will make it too wide to fit on the page. However, the molecular structures have been added to the supplementary material plots with the calculated spectra.

The experimental $\lambda_{max}$ are not always consistent with the values indicated in Table S1 (especially for aqueous acetone and for aqueous pyruvic acid)

Upon a closer examination of Table 1, we found several unreliable gas and aqueous phase extinction coefficient parameters. Table 1 has been modified to be consistent with the values used in main analysis (Table S1 values).

Add in the legend: see references indicated in Table S3 for each compound.
We added the references as subscripts directly into the table.

**Fig. 2**:
In the legend, replace “Henry’s law constants” by “hydration equilibrium” and vise et versa
We reconfigured the axis of Fig 2. The phrase “hydration equilibrium” now does not appear on the plot.

Try to make all the points readable (zoom out the top right of the figure).
We added an additional zoomed in plot examining the top right section.

**Fig. 3**: for compound 4-hydroxybut-3-en-2-one, was the keto-enolic equilibrium considered in the calculations ?

We recalculated this compound in the more dominant keto form and noted this in the figure caption.

**Fig. 5**: as mentioned above, Figure 5 is very interesting and potentially shows clearly the relative importance of aqueous phase photolysis compared to OH-oxidation. It should be very useful for experimentalists. However, as it is presented, very little can be ruled out from it. I suggest modifying the figure showing the actual compounds with 2 points for each (one for $k_{OH}$ and one for $<\varphi>\varepsilon_{max}$) linked with an arrow pointing towards $k_{OH}$. The resulting Figure should show clearly the compounds for which photolysis matters (descending arrows). In the new Figure, it would be useful to show the intermediate values for $k_{OH}$. Finally, showing on that Figure α, β unsaturated carbonyls for which experimental $k_{OH}$ are available should be of high interest.
See response above

**Fig. 6**: some points are hidden such as oxoacetic acid (hidden by the legend). Figures S9 and S10 explore the sensitivity of the results to the very relevant parameters SZA and [OHaq]. I suggest

to add also a sensitivity study to LWC, which is known as a very sensitive parameter to air/water mass transfers.

We made sure that the legend did not obscure any points on the recalculated version of figure 6. We added an additional figure in the supporting information addressing sensitivity in LWC and another figure addressing sensitivity in pH. Figure 6 was also reproduced with error bars assessing the uncertainty resulting in the property predictions.

**Supplementary material**:

**Fig**. **S4**: is water vapour interfering on this region of FTIR spectra ?

Water vapor does not strongly absorb between 2100 and 2400, the limits of Figure S4. Here is a gas-phase FTIR spectrum of water obtained from the NIST Chemistry WebBook (http://webbook.nist.gov/chemistry/):

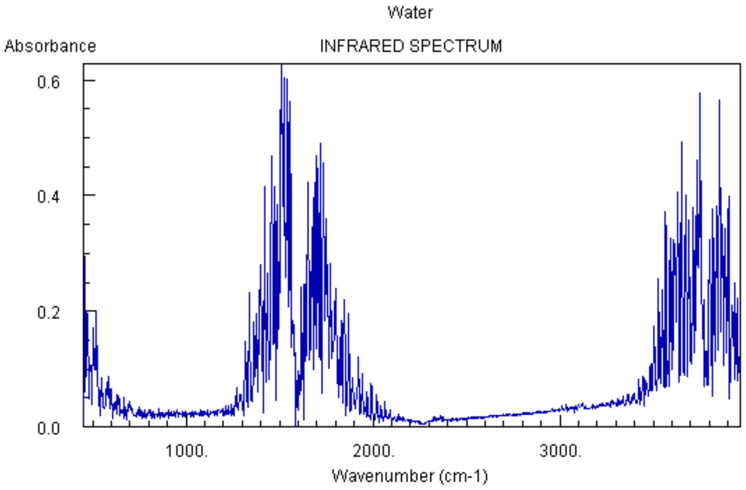

**Fig. S5**: below the figure, the text should read “hyperchromic” instead of “hypochromic” (?)

This is correct. Changed.

**Fig**. **S6**: below the figure, “small aliquots” should be more precise : the reader would like to see the ratio between glyceraldehyde and derivatisation agent concentrations needed.

We edited the text to be more specific: “25 µL aliquots of the glyceraldehyde solution were diluted with 10 mL of a solution containing 0.89 mM GT and 54 µM tetraethylammonium chloride”.

**Fig**. S7: the figure lacks a legend. Why is it so difficult to quantify the derivatized products with ESI-MS?

We added a legend to the figure. We tried running samples on two different ESI-MS instruments before and after a complete renovation of one of them, and could not improve the quantification. We are not exactly sure why this is the case.

**Fig**. S8: what is the reaction time investigated?

We added the photolysis time of 125 minutes to the text

**Tables S1 to S4**: it should be worth adding a table with the molecular structures of all the molecules investigated in the study.
We added several tables showing the molecular structures used in the study.

**References Supplied by the Reviewer:**

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