

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 version. The reviewers' comments are reproduced in black; our responses are detailed below in red:

Major Comments

1. As described above, the science in the manuscript is very interesting, but the presentation and explanation of the science is often too short. Here are some examples:

(a) The discussion of Figure 2 could be improved. Under the assumption that $J(\text{aq}) = J(\text{gas})$, the position of a given compound on Figure 2 is determined by the product $X(\text{aq}) F(\text{Carb})$, where $X(\text{aq})$ is the fraction of total (carbonyl and hydrated) compound present in the aqueous phase and $F(\text{Carb})$ is the fraction of aqueous compound present as carbonyl. The $Z = 1$ line represents $X(\text{aq}) F(\text{Carb}) = 0.5$; for compounds with $X(\text{aq})F(\text{Carb}) > 0.5$ (i.e., to the right of the $Z = 1$ line) aqueous photolysis might be significant. Given the primary importance of $X(\text{aq})$ on Z , I recommend that a line for $X(\text{aq})$ be included on the graph and the idea be incorporated into the discussion.

We agree that looking at Figure 2 as a product of the fraction of free carbonyl and the fraction present in the aqueous phase is much more intuitive. In light of this, we fully reconstructed figures 2 and 3 as a function of these parameters with a secondary X-axis containing the logarithmic Henry's law constants. This idea was added to the methods and discussion section.

(b) There is almost no discussion of Fig. 4. What are the main points from this figure? The propanal/acrolein couple is suggested as an example of the impact of alpha-beta carbonyl-alkene unsaturation, but nothing is said about the actual result from the Figure.

We expanded the discussion of Fig. 4 in the text. The main point of Fig. 4 is that aqueous photolysis may occur on atmospherically relevant timescales. This leads to the observation that even though aqueous photolysis may be fast, it must compete with other gas and aqueous phase processes to be important.

(c) Literally nothing is said about Fig. 7 in the text. The Figure is called out, but that's the full extent. This figure gives some important information about the uncertainty in the computed absorption spectra so it should be kept, but it needs to be discussed.

A discussion of Figure 7 was added to the text.

(d) Table 1. Some of the SP and MD calculated values for $\lambda(\text{max})$ are similar to measured values, but a few are significantly blue-shifted (e.g., aqueous pyruvic acid), which will greatly lower $j(\text{aq})$. The impact of this underestimate of $\lambda(\text{max})$ on the results should be quantified.

We were reporting secondary (higher-energy) absorption peaks of pyruvic acid. A peak in the actinic range, evident in Figure S16 has been reported instead.

(e) Overall, some of the manuscript is well written, but many parts appear to have been hastily prepared. (See examples above, and under Minor Comments below.) I encourage the authors to re-read the entire manuscript with the goal of improving the writing.

The manuscript underwent significant changes in response to the comments of all four reviewers. In addition to addressing reviewers' comments, we made a significant effort to improve the readability of the manuscript. The revised version is considerably more polished than the initially submitted version.

2. The authors should add some information about gas-phase OH as a sink. If it is not a significant sink, this should be discussed. If it is a significant sink, this should be indicated for specific compounds. The main focus is on aqueous photolysis, but of course readers will also want to know the dominant sink for a given carbonyl.

We computed rates of gas phase oxidation by OH using published measurements and Atkinson's structure activity relationships. We notated molecules for which OH oxidation is the most significant sink by underlining their carbon number in the plot.

3. More data should be provided in the Supplement, analogous to the spectral data in Tables S1 and S2. This should include: (a) Henry's law constants, (b) Hydration constants, and (c) second-order rate constants with OH. It would be useful to include both experimental and predicted data (e.g., for Henry's law constants) to assess the skill of the predictions since they were used for many of the compounds.

We added tables to the supplement that contain Henry's law constants, hydration equilibrium constants, aqueous OH rate constants, gaseous OH rate constants and pK_A values for the acidic carbonyls. We also included a reproduction of Figure 6 with error-bars in Q and Z that arise from using predictions of these parameters. We added a sentence referring the reader to (Dearden and Schüürmann, 2003) and (Raventos-Duran et al., 2010) for an evaluation of Henry's law prediction methods.

4. The manuscript has very little treatment or discussion of uncertainties in each model parameter or in the resulting rates and ratios Q and Z. It makes clear that the results are order-of-magnitude estimates, but it would be useful to give a semi-quantitative estimate of the typical uncertainty in each parameter and the propagated uncertainties in the ratios Q and Z. Where are the largest uncertainties? The uncertainty caused by parameterizing the carbonyl peak(s) (eq. 4) should be included in this discussion. For compounds with measured spectra, how different is the parameterized spectra when compared as the integral of actinic flux times absorption coefficient in equation (5)?

We included a reproduction of Figure 6 in the supplement with error-bars in Q and Z that arise from using predictions of these parameters and referenced it in the main manuscript. We also evaluated the uncertainties in using the parameterized spectra as compared to the measured spectra for eight compounds with published extinction coefficients. This is presented as a figure in the supplement and is referenced in the main manuscript. We added the following paragraph to the paper: “Uncertainties in the prediction of Z and Q arise from using estimates of K_H , K_{hyd} , k_{OH} , and pK_A where experimental data was not available. The uncertainties in Z and Q for the carbonyl compounds examined in Figure 6 are represented as error bars in new Figure S13. While some compounds have large uncertainty bounds, the majority of compounds have uncertainties that are less than an order of magnitude in Z and Q. None of the compounds have uncertainty bounds large enough to alter the conclusions that we draw from Figure 6. Uncertainties also arise from parameterizing the extinction coefficients as a function of λ_{max} and ϵ_{max} . A comparison of Q calculated with published extinction coefficients and Q calculated with our parameterization is presented in new Figure S14. For compounds without published extinction coefficients, estimates of λ_{max} and ϵ_{max} from compounds with similar functionality are another source of uncertainty. We used upper-bound estimates to continue with the theme of calculating maximum aqueous photolysis rates to eliminate compounds with uncompetitive rates.”

5. Section 3.3 is confusing and appears to be out of place.

We changed the title of section 3.3 to be more revealing and revised the text to avoid the confusion.

(a) It is not clear why the TDDFT modeling was performed. The first sentence indicates that the modeling was used "To predict the importance of aqueous photolysis for compounds where no spectroscopic data is available..." but data for all the compounds in Fig. 6 was either from the literature (for a few) or assumed (for most), as described in Supplemental Table S1. For which figures were the modeled spectra used to determine aqueous- and gas-phase photolysis rates? Fig. 3? For other figures but not Fig. 6? Only for the d-limonene and isoprene SOA? This needs to be clearly explained and consistent with the supplemental figures of the TDDFT results.

The TDDFT results were only used to estimate aqueous photolysis for the d-limonene and isoprene SOA products. We clarified this in the methods and results section and added a section addressing this in the introduction

(b) If the TDDFT results are only to estimate aqueous photolysis for the d-limonene and isoprene SOA products, then this section should be renamed (e.g., 3.3 d-limonene and isoprene SOA) and more clearly explained. (If the TDDFT results were used more broadly, then this section should be moved to earlier in the manuscript, before the photolysis results are discussed.) Procedural information (e.g., sentences 3-5 of the first paragraph in section 3.3 and the first 3 sentences of the second paragraph) should be put in the Methods section. Details on TDDFT (e.g., lines 18-21) should be put as footnotes in Table 1.

We moved the procedural information related to the Gaussian Broadening to the methods section where we elaborate how the broadening is determined. We also moved the additional procedural information to the methods section. We have also renamed section 3.3 to read “Computational Chemistry Predictions of Spectroscopic Properties of Compounds in d-Limonene and Isoprene SOA”

(c) Page 10921, lines 2-3. The sentence “In solution, MAE amount to...” glosses over the significant blue-shifting of λ_{\max} by the SP and MD calculations for acetone and pyruvic acid. This needs to be pointed out and discussed, as it has important implications for photolysis lifetimes. I believe that measured (and not computed) absorption values were used for both of these compounds; either way, the source of their spectral data should be indicated.

The measured absorption values were used for both of these compounds. We added an emphasis on this in the text. We also added a discussion of the blue shifting of λ_{\max} to the text: “As in the case of acetone (Fig. 7), we observe a blue shift for all compounds except for pyruvaldehyde when the solvent is included in the calculation. In most cases, inclusion of the solvent leads to decreased aqueous photolysis rate because of the decreased overlap between the absorption band and the actinic flux. The selected FWHM values also affect the calculated rates...”

6. Fig. 6. This is a very interesting figure that is the heart of the manuscript, but it takes significant time for a reader to understand. Additional explanation on the figure would help.

(a) It would be very helpful to have clear, explicit definitions of Q and Z on the figure. The current caption description has this information, but not in a way that makes it clear which quantity is in the numerator and denominator.

We added explicit definitions in the form of an equation in the caption.

(b) Adding text to the unlabelled axes would help the reader understand the figure much more quickly; e.g., on the right-hand y-axis there could be a dividing line at $Q = 0$, with text above the

line indicating “Aq. OH > Aq. h” and text below the line indicating the opposite. A similar demarcation and analogous text would go along the top of the figure to explain Z.

We added this text on the right hand y-axis and on the top of the figure.

(c) The figure is not easy to read because the lines are too faint and axis numbers and all fonts are too small.

The figure will be significantly bigger in the ACP version of the paper (7 inches wide by 4 inches tall, i.e., the full page width). This should increase the readability of the lines and fonts. Increasing the font size relative to the size of the axis makes the figure essentially unreadable as marker labels merge into adjacent marker labels.

(d) It would be useful to distinguish the relative importance of gas-phase photolysis and aqueous-phase OH in the upper-right hand quadrant by including (and discussing) a $Q = Z$ line. It’s interesting that there is a fairly clear distinction between the more soluble, more functionalized compounds in this quadrant (e.g., dialdehydes and ketoaldehydes), which are destroyed mostly by aqueous OH, and the mono-aldehydes and ketones, which are destroyed mostly by gas-phase photolysis.

A $Q = Z$ line was added to Figure 6 and a discussion was added to the text. “The $Q = Z$ line is shown as a dashed line in the upper-right quadrant. Molecules to the right of this line have gas-phase photolysis rates that exceed rates of aqueous oxidation by OH. The mono-aldehydes and mono-ketones lie completely in this region along with some of the smaller multi-functional compounds. The small Henry’s law constants and/or hydration equilibrium constants of these molecules ensure that gas phase processes will dominate. Molecules to the left of the $Q = Z$ line have rates of aqueous oxidation by OH that exceed the gas-phase photolysis rates. The majority of the multifunctional compounds lie in this region. These multi-functional compounds generally have enhanced Henry’s law constants that increase solubility and encourage aqueous processing.”

(e) It would be useful to understand how important gas-phase OH is as a sink for the compounds with $Z > 1$. I recommend that compounds where gas-phase OH is the dominant sink be denoted in the figure (e.g., by adding a prime character on the number).

We identified these molecules by underlining the marker number on the figure.

(f) The symbol for the 2-carbon aldehydic acid is hidden under the legend box.

This compound moved slightly after using the updated aqueous OH reactivity structure activity relationships in (Doussin and Monod, 2013).

Minor Comments

1. There are numerous instances where the writing is unclear, repetitive, or contains typographical errors:

(a) Abstract, page 10906, lines 10 – 12. This sentence essentially repeats a portion of the previous sentence and could be deleted.

We believe that this sentence regarding our MD simulations elaborates on the previous sentence and is an important part of the abstract. We want to mention our MD simulations in the abstract as to appeal to readers interested in these calculations.

(b) Page 10908, line 19 through first line of next page. This is too much information about the glyceraldehyde quantum yield and other details, especially since you later decide not to try to estimate quantum yields for each compound. This text should be moved to the discussion of the glyceraldehyde results.

Corrected.

(c) Page 10918, line 13: a dash is missing after “acrolein” (to complete the dash before the word).

The sentence has been modified to read: “One can compare the lifetime of propanal and its (α , β) unsaturated analog—acrolein, butanal and its (α , β) unsaturated analog—crotonaldehyde, and 2-butanone and its (α , β) unsaturated analog—methyl vinyl ketone to investigate this effect.”

(d) Page 10918, line 24: “and a larger photolysis quantum yields”. Delete “a”.

Changed.

(e) Page 10920, lines 3-4. This sentence essentially repeats the text that was 2 sentences earlier. Rearrange the paragraph structure to avoid this repetition.

Changed.

(f) Page 10921, line 24. Period should be after parentheses (not before).

Changed.

(g) Page 10922, line 8. Problem with the citation: “see Refs. (Leermakers and Vesley 1963; Larsen and Vaida, 2012; Guzman et al., 2006, 2007).”

This indicates that there are two papers assigned to Guzman et al.

(h) Page 10923, line 6. A second citation problem: "...suggested in Ref. in Vione et al. (2006)...".

Changed.

(i) Page 10923, line 20. "clouds" should be singular.

Changed.

(j) Page 10923, line 23. k(hyd) should be K(hyd).

Changed.

(k) Page 10923, line 24. "...if quantum yield experiments will product pertinent results...". QY experiments will certainly produce pertinent results (i.e., that pertain to the issue of the atmospheric fate of carbonyls). Whether they're important is a different matter, as you imply in the last part of this sentence. Fix the wording of this sentence.

Changed "pertinent" to "significant"

2. Page 10906, Abstract. Adding a one-sentence summary of Figure 2 would be helpful for readers.

We tried to keep the content of the abstract focused on the big picture ideas of the paper. We feel that a summary of figure 2 would involve a level of detail and explanation inconsistent with the rest of the abstract.

3. Page 10906 and throughout the manuscript. When "gas-phase" or "aqueous-phase" (or any other two-noun phrase) is used as an adjective it should be hyphenated. Thus it is "gas-phase compound" rather than "gas phase compound".

Changed.

4. Page 10907, lines 26-30. (a) Define "hypsochromic" or use a more self-explanatory term. (b) All of the reference compounds in Table 1 show a red shift for the aqueous spectrum relative to the gaseous data, which is the opposite of the Xu et al. (1993) result cited in the introduction. Certainly some compounds show a blue shift in solution, but perhaps for many of the carbonyls examined here this is not significant? This part of the introduction should be modified, as it might overly downplay aqueous-phase photolysis relative to gas-phase photolysis.

We defined hypsochromic in text

Upon a closer examination of Table 1, we found several unreliable gas and aqueous phase extinction coefficient parameters. After replacing them with more reliable sources, all of the compounds with aqueous and gaseous exhibit a neutral or blue shift, consistent with Xu et al. (1993). The extinction coefficients of 3-oxobutanal were eliminated as the Reaxys database where we obtained the original values presented the λ_{\max} and ϵ_{\max} of a similarly named compound.

5. Page 10908, line 5. More recent data indicates the in-drop actinic flux is enhanced by a factor of 1.5 compared to the surrounding gas-phase. See Mayer and Madronich, ACP, 4, 2241, 2004.

This sentence has been changed to read “Even though the actinic flux may be enhanced slightly inside a water droplet, the enhancement factor is thought to be relatively small, 1.5 to 2 (Nissenon et al., 2006;Mayer and Madronich, 2004), and therefore easily outweighed by the above effects.”

6. Page 10908, line 8. O₃ + O₂⁻ is generally a minor source of OH in cloud and fog drops that are acidic. See modeling work by Herrmann and co-workers.

We eliminated this from the text.

7. Page 10909, line 24. Actinometry was performed before and after photolysis. How different were the two determinations on a given day?

We added the following sentence to the text: “Actinometer measurements revealed lamp intensities that varied by less than 10% during a given experiment.”

8. Page 10910, equation (1).

(a) It should be made clear that K(H) is the effective Henry’s law constant. It would be good to distinguish it from the physical Henry’s law constant, e.g., by including an asterisk on the effective value.

We defined all instances of the Henry’s law constant as the effective Henry’s law constant.

(b) The equation accounts for the hydrated carbonyl in the gas-aqueous partitioning by using the effective Henry’s law constant, but then the hydrated form of the carbonyl is "removed" from

consideration by the term $(K(\text{hyd}) + 1)$ in the numerator. A simpler, equivalent formulation of equation (1) replaces the effective $K^*(\text{H})$ with the physical Henry's Law constant and removes the factor of $(K(\text{hyd}) + 1)$ from the numerator. I recommend that this alternate form of the equation be added to the manuscript as it is often simpler to determine, requiring only the physical $K(\text{H})$ (which is sometimes easier to find than the effective value) but not the hydration constant.

We prefer to keep our parameterization in terms of the effective Henry's law constant because predicted values obtained from Henry's law constant predictors such as HENRYWIN, SPARC, and GROMHE produce effective values. In addition, hydration equilibrium constants are still needed for the di-carbonyls because we take into account the photochemistry of the partially hydrated form.

(c) The authors should examine whether a similar simplification could be accomplished for the dicarbonyl equation in the supplement.

See above.

(d) It would help the reader understand equation (1) if it was first shown as an equality with the aqueous-phase and gas-phase rate constants shown explicitly. Then the assumption that $J(\text{gas}) \geq J(\text{aq})$ should be explicitly stated, leading to the current form of equation (1).

We added this inequality to the text before arriving at our equation for Z.

(e) As formulated in eqn (1), $LWC(v)$ is the volumetric liquid water content (e.g., Laqueous/L-air) and not the mass-based LWC as stated. 9. Page 10912, line 6. It should be indicated that $k(\text{OH})$ is a second-order rate constant.

We corrected the definition of LWC_v . We added "second-order" to the text.

10. Page 10913, lines 10-11. The wording "As an approximation, we treat the photolysis quantum yield as an average value over all relevant wavelengths:" is somewhat misleading since there is little treatment of quantum yields in the subsequent text. In most cases it is assumed that $\text{PHI} = 1$.

This wording has been changed to read: "As an approximation, we write the photolysis quantum yield as an average value over all relevant wavelengths"

11. Page 10916, line 18. The authors assume that $\text{PHI} = 1$. They should add a few sentences of discussion here about literature values for aqueous carbonyls beyond hydroxyacetone and glyceraldehyde. Is this assumption better for certain classes of carbonyls?

We agree that wording of our sentence is misleading. We do not mean to “assume” that $\Phi = 1$ for all molecules included in this study. We use $\Phi = 1$ as an upper limit for the actual (unknown) values of Φ because we want to calculate the maximum extent of aqueous photolysis. We changed the sentence to read: “To determine the potential importance of aqueous photolysis processes from the parameters Z and Q defined above, we use the maximum value of the photolysis yield, $\Phi = \Phi_{\max} = 1$.”

Experimental measurements of non-cyclic carbonyl compounds at atmospherically relevant wavelengths are extremely limited. Here is a quote addressing this issue from our previous paper (Epstein and Nizkorodov, 2012): “The photochemistry treatise by (Calvert and Pitts, 1966) describes a few early aqueous photolysis studies of organic compounds, most of which were done under 254 nm irradiation. Only a handful of additional photolysis quantum yield studies in aqueous solutions under irradiation conditions that are relevant for the lower atmosphere (> 280 nm) have appeared since then. Examples include photolysis of a number of organic pesticides(Vione et al., 2006;Wan et al., 1994), aromatic carbonyls(Ledger and Porter, 1972), substituted phenols (Czaplicka, 2006;Albinet et al., 2010) , substituted benzyl derivatives(Zimmerman and Sandel, 1963), small aldehydes without correction for hydration (Hirshberg and Farkas, 1937) dicarbonyls such as biacetyl (Faust et al., 1997), hydrogen peroxide(Chu and Anastasio, 2005;Goldstein et al., 2007), methyl peroxide (Epstein et al., 2012), and pyruvic acid (Leermakers and Vesley, 1963;Larsen and Vaida, 2012;Guzmán et al., 2006;Guzmán et al., 2007). This data set is too meager for the development of a conceptual treatment of quantum yields or even an educated estimation for the selected atmospherically relevant compounds.”

12. Page 10917, line 7. “maximum” here should be “minimum” (since the lifetime was calculated with $\text{PHI} = 1$).

Changed.

13. Page 10919, lines 8 – 10. Indicate the number of compounds where an upper estimate for the maximum molar absorptivity was used. Also indicate the total number of carbonyl compounds considered.

We changed this sentence to read: “For simple mono- and di-carbonyl compounds without published λ_{\max} and ϵ_{\max} values (76 out of 92 total compounds), we made educated upper-estimates based on the values of compounds with similar functionality.”

14. Page 10919, lines 20-21. “Reproductions of Fig. 6 under other relevant atmospheric conditions are presented in the Supplement.” This is too vague to be very helpful. It would be better to explicitly list the different conditions considered and the corresponding supplemental figure number.

We added the following paragraph to the text: “We also investigated the sensitivity of Z and Q under different atmospheric conditions. Figs. S11 details the effects of a lower LWC of 0.05 g m^{-3} , Fig. S9 uses a SZA of 0° , Fig S12 shows how pH affects Z and Q values, and Fig. S10 was calculated at a lower-limit aqueous OH concentration of 10^{-14} M . (A full discussion of these figures is presented in the SM.)”

15. Page 10919, line 28. It doesn't appear that 3-oxopropanoic acid is the correct compound. Based on the symbol type this should be the 3-carbon ketoaldehyde (2-oxopropanal, aka, methylglyoxal), rather than the 3-carbon ketoacid (which was already called out in the bottom left quadrant).

The compounds in the bottom right quadrant have changed since the updated OH rate constants were used.

16. Page 10922, lines 13-15, “The same functional groups that allow for photolysis at actinic radiation and increased solubility in water can also increase the rate of hydrogen abstraction in the molecule.” Specifically, which functional groups do you mean? Given that this paper didn't consider unsaturated carbonyls, I assume it's referring to additional carbonyls and/or alcohols. But does the addition of a carbonyl to a molecule increase its OH rate constant? Does the addition of an alcohol group increase absorption of solar radiation appreciably?

We eliminated this phrase because it was misleading and confusing. We changed this paragraph to read: “OH oxidation rate constants typically increase for larger compounds as there are more hydrogen atoms available for abstraction. Figs. S16 and S17 show predicted $k_{\text{OH}}^{\text{aq}}$ of each chemical family investigated as a function of carbon and hydrogen number, respectively. Only photolabile carbonyls with enough oxygen functionality to enhance solubility and deactivating ketone and/or acid groups, but few hydrogen atoms for abstraction by OH, may have significant rates of aqueous photolysis.”

We also included two additional figures in the supplementary material that go into further details about how chemical functionality affects the $k_{\text{OH}}^{\text{aq}}$.

17. Page 10923, line 1. “higher” should instead be “lower”, i.e., lower solar zenith angle, which corresponds to a higher actinic flux.

Changed.

18. Page 10923, line 8. (a) The supplemental figure should be S10, not S6 as stated in the text. (b) The caption for Figure S10 indicates that the aqueous OH concentration is 1E-14M, while the text here lists the concentration as 2.5 E-14M. Which is it? (I’m guessing the latter based on the S10 results, which are not consistent with the stated concentration.)

The figure labels have been corrected. The OH concentration should be 2.5×10^{-14} M. This has been changed in the text.

19. Fig. 3. It would be helpful to have the names of the compounds included in the caption or in the supplemental material.

The names of the compounds have been added to the caption. We put additional details such as names, hydration equilibrium constants, Henry’s law constants, structures, and references in the Supplementary Material.

20. Fig. 4. (a) I believe the photolysis lifetime calculation assumes a constant actinic flux. If so, 10 days of this condition is more than 20 days of actual time. Either way, this should be explained in the text. (b) The acetone symbol (A) in the figure is not consistent with Figure 7. $\lambda(\text{max})$ in Fig. 4 is 265 nm, while the Fig. 7 value is at least 10 nm larger. Also, $\text{PHI} \cdot \epsilon$ is nearly 20 in Fig. 4, while the Fig. 7 molar absorptivity sets an upper bound of 14. (c) “ethanol” in the caption (line 5) is not correct. Should it be ethanal?

We added the following sentence to clear up this issue: “Note that since photolysis can only occur during daylight hours, these photolysis lifetimes are in terms of sunlight irradiation time.”

We accidentally used a different data set to construct Figure 7. We modified Figure 7 to include extinction coefficients from (Xu et al., 1993).

“Ethanol” should be ethanal. We removed this part of the caption and inserted a legend instead.

21. Fig. 5. I believe each line corresponds to $Q = 1$ for a given value of $k(\text{OH})$. If so, this should be indicated in the text and/or figure caption.

This was added to the figure caption. In addition, Fig. 5 has been enhanced to eliminate this ambiguity.

22. Fig. 7. (a) This figure (and the implications of the MD underestimation of light absorption by acetone) needs to be discussed in the text. (b) The actinic flux for SZA = 20 deg should be included in the figure to show the importance of $\lambda(\text{max})$. (c) The blue-shift in $\lambda(\text{max})$ for the MD simulated spectra relative to measured values for acetone is troubling since this will lead to an underestimate of the photolysis lifetimes. The aqueous shift makes a huge difference: while the measured molar absorptivities modestly overlap with the solar spectrum, the MD result has essentially no overlap. (d) To make the curves more visible, I recommend that you restrict the y-axis range to 0 - 14.

- a) We added a complete discussion of Figure 7 to the text.
- b) We added the actinic flux for SZA = 20° to the figure.
- c) We found errors in the MD simulation of acetone. Recalculation with Gaussian broadenings on 0.1 and 0.4 eV produces computational absorption spectra that have much better agreement with experimental data. The predicted blue shift from the gas to aqueous-phase spectra is consistent with the magnitude of the blue shift seen in experimental measurements.
- d) We modified the limits of Figure 7 to better capture the data.

23. Table 1. References for the measured data in Table 1 should be moved from Table S3 to the main text.

References were moved to Table 1 as superscripts.

24. Supplemental Table S1. As I understand it, this approach was only used to calculate rates of aqueous photolysis, but not gas-phase photolysis. This should be made clear.

That is correct. We added this to the figure caption.

25. (a) It would help the reader wade through the sea of names if the authors added a supplemental table with IUPAC and common names for the compounds in Table S1, at least up to carbon number 4 or 5. (b) Structures should be shown for the compounds in Table S4. (c) Structures should be included on Figures S12 – S21. (d) If you really want to help the reader navigate the sea of organic compounds, adding a figure with the structures corresponding to the names in Table S1 would be a great help.

We included IUPAC and common names for all of the compounds in Table S1 to a table with all of the experimental and predicted parameters used in the analysis. See new Table S9.

We added structures to Table S4. See new Table S7.

We added structures on new Figures S18-S27.

We added a table with the first three structures of each series corresponding to Table S1. See new Table S2.

26. (a) Far too many significant figures are presented in the molar absorptivity values and uncertainties in Table S6. (b) What does the uncertainty represent? 1 standard error?

We reduced the amount of significant figures

The uncertainties arise from the linear least-squares regression of concentration versus absorbance when determining the extinction coefficient. This has been added to caption of new Table S4 and new Table S5.

Overall Assessment

This manuscript makes an important contribution to our understanding of the atmospheric fate of carbonyls. The concepts in the manuscript are interesting and the results are comprehensive. Once the text is expanded and clarified this has the potential to be a great paper.

References Used in the Response

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