Review of "Characterization of a chemical modulation reactor (CMR) for the measurement of atmospheric concentrations of hydroxyl radicals with a laser-induced fluorescence instrument" by Cho et al.

This paper presents information on the use of a pre-reactor designed to minimize interferences in the measurements of hydroxyl radicals (OH) by the technique of laser-induced fluorescence (LIF). The use of such reactors has become common-place since the recognition of interferences in LIF OH measurements that are not accounted for by spectral modulation (on-line/off-line). This so-called chemical background has been found to be systematically and sometimes significantly larger than the spectroscopic background.

This paper points out that there is known and correctable interference from the production of OH within the instrument from the photolysis of ozone by the laser in the presence of water vapor. In principle, this interference will be captured by the chemical method of background determination.

Important in the use of an external reactor, when working with highly reactive radical species such as OH, is the impact of the reactor surfaces on ambient OH and whether the effect of the surfaces that are contacted by the sample changes between the signal plus background and the background measurement modes. Also, it is important to evaluate the impacts of gases added to ambient air on the performance of the LIF detection.

These issues were covered quite well in this paper and are presented in an understandable fashion.

General comments.

The CMR was presented as a design with a configuration that was considered optimum and final. Did the researchers consider other configurations of the CMR, including (1) reduced pressure at say 100-200 mbar to optimize mixing, (2) switching the addition of propane between the front location and near the end of the reaction zone to provide constant composition entering the LIF detection cell (like the OH CIMS technique), (3) test various diameters and lengths of reaction, and various materials for the reactor walls, and (4) examine impacts of flow rate on mixing and CMR performance? Such tests, if performed, should be discussed in the paper. If not performed, their possible impacts should be presented

While some instruments have apparently not seen significant interferences beyond the impact of ozone photolysis by the probe laser, is it possible that it is because of the atmospheric environments in which the tests were done. Indeed, even in the present study, there doesn't appear to be a significant impact of biogenic VOCs on OH reactivity. Previous studies have indicated that forested environments, presumable with significant BVOC emission, have the largest measured interferences. This possibility should be added to discussion, including in the middle of page 3.

This reviewer found the use the various Greek symbols (α, β) with multiple superscripts and subscripts not clearly defined. While Figure 2 was helpful in this regard, not all of the symbols are included. It might be easier for the reader if the symbols were more mnemonic. In other words, use T for transmission of radicals (as on page 12) throughout the paper with a clear definition (the fraction of radicals successfully transported through the CMR), and another symbol (perhaps R) for the reverse of transmission, which is referred to as the residual factor (suggest a different term) and definition (the fraction of radicals lost during transport through the CMR). This way it is easier for the reader to remember what the various symbols stand for. This reviewer suggests the authors consider a table with the symbols used in the paper to aid the reader.

This reviewer tried to reproduce the plots in Figure 7 based on information in the paper. It was not possible arrive at the exactly the same figures. Suggest that you carefully check the calculations (perhaps by at least two people independently) to ensure that these calculations are correct.

Specific comments.

Page 1, lines 11 & 12. Suggest replacing the word "how" used twice in this first sentence. For example, "…are essential to investigate mechanisms for oxidation and transformation of trace gases..." and "…and processes leading to the formation of secondary pollutants…"

Page 1, line14. The use of chemical modulation has been utilized in most LIF instruments "recently". Somewhere, if possible, give a reference to the first suggestion, or a recent suggestion, that this is how such measurements should be performed.

Page 1, line 17. While this reviewer agrees that this paper describes the application and characterization of the CMR, it is not obvious that it has been validated. Suggest adding text, perhaps near the end of the Introduction that demonstrates the CMR has been validated. Later, on page 3, the words "introduced, described, and characterized" are used, which might be better here as well.

Page 1, line 20. Suggest rewording "It allowed performing OH…". Perhaps "enabled" instead of "allowed" or a reorganization of the sentence.

Page 1, line 22. Suggest removing "A" to read "Good agreement was obtained…".

Page 1, line 22. Suggest a "-" or "/" or "vs" in "LIF-DOAS".

Page 1, lines 22-23. This reviewer takes issue that good agreement between LIF and DOAS confirms that the CMR provides interference-free OH measurements. It depends on whether the comparison was performed in conditions that cause interference, and it assumes that there is no possibility of interference in DOAS. While the latter seems unlikely, it cannot be ruled out completely. In fact, the statement on line 30, indicates that the situation of JULIAC did not include unexplained interference. Thus, it might not be suitable to use the setup described in a forested environment with large BVOC emissions. This should be discussed somewhere in the paper, and perhaps the case made not quite to strong in the abstract.

Page 1, lines 27-28. The description of the medium diurnal variation of the interference could be misleading. I think you mean that the maximum value of 0.8×10^6 occurs during daytime, and the minimum value occurs at night, but it could be interpreted other ways. Suggest rewording the sentence.

Page 1, lines 33-37. The models described in the paper do not seem to be chemical kinetic models (nor kinetic chemical models). Also, the language could be improved in these sentences. For example, "A kinetical chemical model of the chemical modulation reactor was developed…". Suggest substituting a different word to avoid using "chemical" twice or rearranging the sentence. In the next sentence, "reactions" and "reactor' are used close together that makes the sentence a bit awkward. This reviewer prefers "photolytic" to "photolytical", but which one the author uses is their choice.

Page 1, lines 40-41. This conclusion that chemical modulation can be subject to interferences while attempting to correct for other interferences is an important finding. It should be clearly stressed (maybe with a bit more detail) here and elsewhere in the paper.

Page 2, line 14. The Stone et al., 2012 reference discussing OH measurements is good, but now a bit out of date. Suggest adding one or two more recent references.

Page 2, lines15-16. Suggest rewording part of this sentence "…which helped in the investigation of the atmospheric OH radical budget."

Page 2, lines 28-29. Suggest rewording "…in atmospheric chemical models increases the predicted concentrations of OH considerably for some conditions, for example…"

Page 2, line 33. It might make sense to add discussion of measurements of OH by other techniques and the relationship between measurements and models. There is indication, for example, that CIMS could be prone to interferences but it is believed that they are accounted for by the way propane is used in the inlet.

Page 2, line 37. Suggest adding one or more reference to "Previous studies" that are mentioned, again including measurements of from CIMS as well as LIF.

Page 3, lines 1-2. The Hofzumahaus and Heard reference does not suggest that use of chemical modulation necessarily leads to OH measurements that are interference free. Suggest rewording this sentence.

Page 3, lines 10-11. Again, while some instruments see large interferences, it may because of where they were deployed rather than the configuration of the instrument (or a combination). Suggest rewording and/or adding text to make this clear.

Page 3, line 8. Again, the term "interference-free" is used. This has not been unequivocally demonstrated. Indeed, the FZJ use of the CMR leads to a reduction of the interference, but not complete removal as shown later in the paper.

Page 3, lines 16-17. Suggest rewording "…but nighttime observations were similar to those found in forested environments."

Page 3, line 24. Suggest changing "avoid" to "minimize".

Page 3, line 30. Suggest "…is developed that provides estimates of the possible interferences…".

Page 3, line 36. Suggest "…a large range of chemical…".

Page 4, lines 5-6. Suggest rewording "…the excitation wavelength is modulated on and off the peak of the OH absorption line…".

Page 4, line 8. Could you describe why the timing of on-line and off-line signal measurements are not the same? Normally, optimum signal to noise is achieved when they are the same, unless the noise of the background (off-line) is very small.

Page 4, line 13. Suggest adding text to indicate that the intensity of the mercury lamp radiation must be known, and is determined by actinometry.

Page 4, line 17. Suggest rewording "Hydroxyl radicals originating not from ambient air but formed within the detection cell…".

Page 4, line 19. The physical location of the CMR is said to be "on top". While this may be true, up or down do not really apply to gas flows. Suggest using "in front" instead.

Page 4, line 20 and following. The dimensions and details of the CMR are described, but it doesn't say why these parameters were selected. Suggest adding text describing the method by which the current design was arrived at.

Page 4, line 21. The injectors are 1/8" OD tubes, with 50 µm ID, correct? Suggest rewording.

Page 4, line 25. For CIMS measurements, it was found that the purity of the propane is very important. Even small amounts of impurities can cause problems. Please give the purity of the propane use to make the propane/N_2 mixture. Indicate whether experiments with different sources (vendors) of propane have been performed. This is very important.

Page 4, line 30. Why are the measurement cycles so much longer with the CMR in place?

Page 4, line 33. Why do you do on-line and off-line measurements while using the CMR? This should not be necessary in normal measurement mode (but perhaps useful when doing tests). Equations 4 and 5 show that it isn't necessary to measure S_i.

Page 5, line 8. Suggest "…the OH cell with the CMR in place…".

Page 5, lines 10-13. This conclusion may not be valid if there are contaminants in the propane.

Page 5, line 17. The DOAS does not require calibration, but it does depend on knowledge of the absorption cross section for the pressure and temperature conditions of the measurement, and the absorption path length. Please add this information to this section.

Page 5, line 22. It is probably better to say "…experiments an NO concentration…", since the reader is likely to read "an en oh" rather than "a nitric oxide".

Page 6, line 1-2. Suggest "…which has a light transmission of greater than 0.8 over the complete solar spectral range…".

Page 6, line 3. Suggest "…to prevent contamination from…".

Page 6, line 6. The beginning of this section says that comprehensive tests were performed, but that is not clear from what is written. Did you do any tests with biogenic VOCs and ozone added to synthetic air to see if other interferences showed up? How about NO_3 oxidation experiments of BVOCs? These are situations that could produce additional interferences and should be investigated and discussed.

Page 6, line 9. Suggest "…measurements in SAPHIR during which ambient air was…".

Page 6, line 11. Suggest "…located close to the city of Julich."

Page 6, line 8-25. It is not clear why the experiments were performed in the SAPHIR chamber rather than just by sampling ambient air. Please add a sentence or two of explanation.

Page 6, line 21. Suggest "The total OH reactivity…".

Page 6, line 23. Suggest "range" instead of "suite".

Page 6, line 24. JULIAC indeed allowed potential interferences to be investigated, but only within the range of conditions found in Julich. There are other conditions throughout the world that are different and could present other interferences. This should be stated either here or elsewhere in the paper.

Page 6, line 35. It is not clear why the term "laminar flow tube" is used immediately followed by stating that it exhibits plug flow conditions. While it is possible to experience approximate plug flow in a tube, this is usually found at low pressures (< a few mbar) and in the entrance region (before the full flow regime is established). It is likely with the calibrator to be due to the latter. It would be useful to state the Reynolds number and remind the reader of the flow regime, both in the calibrator and the CMR. Then indicate why the calibrator might exhibit plug flow.

Page 7, line 1. Suggest "…(Reynold number, R_e = 2800)…". This value of R_e is actually in the transition regime (2300-2900), so the flow cannot be clearly classified as turbulent. Also, there is an transition

region of up to tube diameters to establish the condition of a given R_e. Finally, the injectors generate turbulent (to enhance mixing), so that has an effect as well.

Page 7, line 7. The experiment to measure transmission without the injectors is useful, but it would be interesting to see how it varies with flow rate and tube diameter. Were such experiments done?

Page 7, line 9. Since the radical calibrator produces both OH and HO_2, is there evidence of loss (or do you expect it from the kinetics) from the reaction of OH with HO_2. It would be helpful to give the range of OH concentrations employed in the various tests performed, including this one.

Page 7, line 12. Suggest "The rate coefficient, k_w, that was obtained can be used…"

Page 7, line 20. Was the concentration of CO in the CMR varied to see whether it had an effect? Are you concerned that if there was surface conversion of HO_2 to OH that could be released into the gas-phase, it would be masked by the presence of CO. It seems that the HO_2 loss experiment could be conducted without addition of CO, assuming reaction between HO_2 and OH was not an issue (comment earlier).

Page 7, line 27. There is a comma at the beginning of the line. Suggest rewording the text before and after equation (11) so this is not needed.

Page 7, line 33. Perhaps remind the reader that the following discussion is for clean air, in other words $k_{OH} = 0$. You also might want to use the superscript 0 to indicate this in all the terms being presented. It is also not clear the superscripts "e" and "r" were defined on the previous page.

Page 8, line 3. Suggest "where k_{sc} is the pseudo first-order rate constant for reaction between OH and propane."

Page 8, line 5. Suggest "The fraction of ambient OH remaining that subsequently enters the detection cell…".

Page 8, line 12. Suggest "…as expected from Equation 16, whose derivation assumes homogeneous mixing…".

Page 8, line 27. This reviewer disagrees that further increases in the propane concentration gives only small improvements in α. Looking at the data rather than the red line, there is little indication that the curve is flattening. The y-axis on this plot is logarithmic with magnitude orders of magnitude. Perhaps four symbol diameters correspond to a factor of two change in the residual amount remaining. Because of the issues with too much propane in the detection cell, experiments should be performed with longer length reactor tubes. It may be that a 50% increase is sufficient to bring α close to zero. This reviewer suggests performing such tests before publication of this paper.

Page 8, line 33. Is it also possible that ultraviolet light, either from the radical source or ambient sunlight enters the CMR and affects the conversion chemistry? This possibility should be discussed along with data collected using the apparatus.

Page 9, Line 9. Suggest "As employed in the HO_2 transmission tests…"

Page 9, line 5-25. It appears to this reviewer that higher amounts of propane could be used in the CMR with minor impacts in the detection cell. For reasons that are not clear, a 3% effect is considered negligible, where a 5% effect is unacceptable. It is excellent that this range of propane levels was tested to measure this affect. This reviewer suggests such range for the scavenging efficiency tests.

Page 9, line 33. "photolytical" is used again.

Page 9, line 35. Suggest “The instruments agreed to well within the combined 1σ accuracies…”. Can you demonstrate this numerically, for example by providing the mean and standard deviation of the differences between the two measurements (or some other metric)?

Page 10, line 1. When regression is mentioned throughout the paper, please indicate whether it is standard least squares or, as mentioned in one case, a bivariate technique such as fixexy in Press.

Page 10, line 8. This was mentioned before, but why is it necessary to do the on- and off-resonance measurements when using the CMR?

Page 10, line 15. Suggest “…when air pollutants influence the chemistry in…”

Page 10, line 15. Indicate the level of uncertainty (1σ?) for the accuracy statement (here and other places in the paper).

Page 10, line 19. Suggest “…known interferences (ozone photolysis and NO_3 radicals)…”

Page 10. Line 21. Suggest “…interferences from other sources.” This is because there could be sources other than chemical compounds, perhaps.

Page 10, line 28. Suggest “…and water vapour were varied up to 450 ppbv and 1.8%...”

Page 10, line 34. It is stated that the ozone photolysis interference is linear with the product of ozone and water vapor, but the parameterization in Figure 13 is not linear. Please give more information.

Page 10, lines 30-32. Why are the measurement techniques in this experiment different from Table 2?

Page 11, line 8. Suggest “…chamber using the thermal decomposition of N_2O_5 added from a condensed source which produces NO_3 radicals. Indicate measurement technique for NO_3 in these experiments. Can you explain the large amount of scatter in the Figure 6 plot?

Page 11, line 19. Suggest “This section describes studies of the application….”.

Page 11, line 33. As mentioned earlier, how do you know that there is no photolysis in the CMR? Suggest not using “inner darkness”, but use a more precise term.

Page 12, line 2. Suggest “…is the dominate non-photolytic source…”. (This reviewer agrees that photolytic is the correct term here).

Page 12, line 6. It should be recognized that in the normal atmosphere, the ratio of HO_2 to OH can be quite large, perhaps 100 or much more. In that case, a conversion of a small fraction of HO_2 to OH could greatly change the amount. Suggest reworking the discussion to reflect this.

Page 12, line 8. It is not true that NO is determined primarily NO reaction with ozone. This could be true, but there are also situations when the reaction of NO with peroxy radicals (HO_2 and RO_2) is comparable or even larger than $NO+O_3$. Suggest rewording this sentence.

Page 12. As a reader, I was confused by this section of equations. It was not clear how the terms and symbols used earlier applied to this section. This is why this reviewer suggests a table or figure to present all the various symbols and terms used. It is also not clear why there are two terms for transmission, β and T. With the correct corresponding subscripts and superscripts, one should be enough.

Page 13, line 1. It should be noted that k_{OH} is never 0. It can be as low as 0.5 s^{-1} for very clean air, but all air has methane and CO.

Page 13, line 5. Suggest reminding the reader why the minimum value is 0.042. Also, after using β values up to this point, why are the plots of α values?

Page 13, first paragraph. Mention that Figure 7b will be discussed later, in Section xx.

Page 13, line 8. Suggest "…the production P_d exceeds the photolysis-based OH production…"

Page 13, line 13. Suggest removing comma "…would be obtained if the influence…"

Page 13, line 15. Suggest "…signal S_i* is similarly :"

Page 13, line 18. Instead of "all kinds of" give the range of values over which it applies. It could be for the full range of values studied.

Page 13, line 28. Suggest "The result presented in Figure 8a is very similar to the homogeneous mixing case shown in Figure 7a."

Page 13 line 36 and page 14, line 1. What is meant by "uncertainty of the model". Suggest being clearer here or remove this assertion. It seems that real differences are expected between the two models.

Page 14, line 6. It is not clear why the inverse of the term in equation 31 is plotted in Figure 7b.

Page 14, line 12-13. This is a very important point that needs to be clearly stated in the abstract and the summary.

Page 14, line 17. Suggest "…OH production continues when the air enters…".

Page 14, line 18. Suggest "…When k_{OH} is much larger than…".

Page 14, line 21. Suggest "…causes a relatively small…".

Page 14, line 29. Suggest "…measured by DOAS for some of the JULIAC periods…".

Page 14, lines 30-31. Suggest "…the campaign afforded the opportunity to test the chemical…".

Page 14, line 32-33. Suggest "For only a short time between 1 to 11 February 2019, OH detection was done…".

Page 15, line 12. Suggest "…is only weakly dependent on k_{OH} and…".

Page 15, line 14. What does "…and otherwise add up" mean? This needs some more explanation.

Page 15, line 14. It seems that the average correction is not so important, but rather the size and frequency of larger corrections. If the corrections are always small, there is no need to use the CMR. If they are are sometimes big, and you don't know when, then it is important to have the CMR capability. Suggest rewording this part

Page 15, line 19. Is this better for "The combined OH summer dataset measured…"?

Page 15, line23. Can the authors provide some metric to indicate that the two LIF measurements indeed agree within their combined uncertainties?

Page 15, line 23. It should be noted that the differences between the two OH measurements were during the heatwave.

Page 15, line 24. Suggest "… systematically higher than the DOAS measurements by about 25%."

Page 15, line 26. See earlier comment about regression and fixexy.

Page 16, line 6. Is it meant to refer to equation 19 rather than equation 12?

Page 16, line 11. Has the limit of detection versus averaging time been explored? It would be good to calculate the Allan-Werle variance for the LIF-CMR instrument and discuss in this paper. The data in Figure 13 have hours of data included, so the uncertainties could potentially be much smaller.

Figure 1. Some suggestions to the body of the paper also apply to the figure caption. Suggest "Schematic drawing" rather than Technical drawing. Suggest "in front" rather than "on top". Suggest providing the mixing ratio rather than "traces of propane".

Figure 2. Possibly include other symbols in this figure (see suggestions made earlier).

Figure 4. Suggest "The data shown are…".

Figure 5. Suggest using the same x=axis on this figure and Figure 13.

Figure 7. In the body of the paper, it would be good to describe why these various terms are being plotted. What are each of these factors meant to show to the reader?

Figure 9. The values in the plots do not seem to agree with the measurement period averages in Table 3. For example, for winter compared to summer, the value of $j(O^1D)$ is about 10 times larger in summer, while NO is about 3 times higher in winter. This seems to indicate that the fraction of OH from photolysis should be about three times higher in summer than winter. But the figure seems to indicate than the photolysis fraction is about twice as high in the winter as the summer. Suggest checking the calculations for this figure and Table 3.

Figure 13. Suggest giving the equation number for the parameterization. Adjust text as appropriate based on earlier comment.

Table S1. Note that the detection limit depends on the averaging time (see earlier comment), so provide averaging time corresponding to the detection limit shown.

Figures S1, S2 and S3. Suggest "Dashed lines denote midnight."