Interactive comment on: *"Pressure dependent calibration of the OH and HO$_x$ channels of a FAGE HO$_x$ instrument using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC)"*

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We would like to thank the reviewer for their thorough appraisal and constructive comments on the submitted manuscript. We have addressed the points raised in order (highlighted in blue).

The authors describe the pressure dependent calibration of an OH/HO$_2$ FAGE instrument. This is done by using different inlet pinholes which results in a change of the internal cell pressure and by changing the "ambient" pressure in the HIRAC simulation chamber, which also results in a change of the internal FAGE cell pressure while using a fixed pinhole. For the second method the chamber is used as an alternative calibration procedure, using the decay of hydrocarbons (for OH) and HO2-HO2 recombination after photolysis of HCHO (for HO2).

It is shown, that the standard H2O photolysis calibration is consistent with the alternative HC and HCHO method respectively. Additionally it is shown, that the pressure dependence of the sensitivity is the same, independent of the way how the internal cell pressure is changed. Both results have a significant relevance for the data evaluation of HOx measurements performed with LIF-FAGE instruments, especially for flight applications. But it needs to be stated, that these results may strongly depend on the exact design of a specific FAGE instrument.

This is an important point which has been emphasised in the conclusion section, p. 7990 l. 24:

"…FAGE cell pressures. It should be emphasised that, strictly speaking, this validation applies only to these particular FAGE instruments, but suggest that the agreement between the different techniques will translate to FAGE instrument designs of similar designs. As the calibration…"

The main results and data discussion are presented in a good way, but there is, from my point of view, one major issue in the understanding of the paper by using the terms of "two FAGE instruments": "HIRAC FAGE" and "aircraft FAGE". From the information in the paper it's not clear to me if there are really two different instruments (e.g. with different cells/tubes/electronics etc…) or if there is one set of OH cell and HO2 cell, that can be used with different laser systems and the names "HIRAC FAGE" and "aircraft FAGE" are related to the used laser (like Table 1 is suggesting). From the cited paper it looks like the two instruments are the same except of the laser system and the pumps. The use of the names "HIRAC FAGE" and "aircraft FAGE" and the fact that e.g. the "HIRAC FAGE" was used with the 200 Hz and the 5 kHz laser system (page 7976) is confusing. Especially because different cells and inlets could lead to differences in the discussed results. For example in Table 1 it's stated that the H2O photolysis calibration was done with both instruments, but on page 7976, after describing the H2O photolysis method, only the HIRAC instrument is mentioned (but with both laser systems). In contrast to that figure 10 shows CHO2 from H2O photolysis for, as the caption says, the HIRAC (200 Hz) and aircraft (5 kHz) instrument. Therefore it would be very helpful if the authors add a more precise description of the differences between the two instruments in chapter 2.2 and choose a more conclusive usage of the names in the text and the figures.

This was a comment also raised by the other reviewer (see separate reply for details) and we have attempted to address this by adding some instrumental parameters to Table 1, as well as further clarifications in section 2.2 and throughout the manuscript.

Two other general points:

In the supplement the water vapour dependence of the sensitivity is discussed. The result of this discussion is that the water dependence is smaller than the uncertainty of the calibration. Therefore the authors decide not to correct the measured sensitivity with respect to the water

vapour. I would suggest to add this conclusion in chapter 5 before the comparison of the H2O photolysis measurements (which were performed under high [H2O]) with the HC decay method (performed under low [H2O]) and not only later in the text.

The manuscript has been updated to include this conclusion in-line with the reviewer's comment (p. 7985, l. 27):

"...the supplementary information. The change in instrument sensitivity over $[H_2O]$ between 200 and 4500 ppmv was observed to be within the uncertainty of the calibration (35% at 2σ) and was therefore considered negligible. For this reason no correction for sensitivity to $[H_2O]$ was applied to the date taken in the alternative calibration method where $[H_2O] < 10$ ppmv"

The uncertainty is in some figures given as the total uncertainty and sometimes only as the precision. For me it is not conclusive how/why this is chosen.

There are some parts of the analysis procedure that use the uncertainty in the regression to give an estimate of the precision, and hence the error bars represent the standard error in a measurement. Other figures that display instrument sensitivity as a function of pressure (for example) use the total determined uncertainty (sum in quadrature of the accuracy and precision terms) in an attempt to better compare results. Clarifications of this point have been made in the text, where appropriate.

Special comments:

-      p. 7974, line 23: If I understand this right the argument is, that "if" there is any OH generated by the laser, this would be probed within the same laser pulse because the air is exchanged between two pulses at 200 Hz PRF and that this OH would not be affected by the addition of iso-butane because of the short time for the reaction. But would there be any signal expected from the OH which is probed in the same pulse it was generated from? I think that this signal would be very small, at least much smaller than the interference signal given on page 7980. Do you have an explanation for this relatively high interference there?

We would expect to see OH probed in the same laser pulse from which it was generated, in line with the research from (Zeng, Heard et al. 1998) into the interference from O_3 photolysis in the presence of H_2O vapour. Using a 'back-of-the-envelope calculation', we can get a reasonable estimate of the [OH] generated in the laser pulse. Assuming a standard laser power in the FAGE cell of 8 mW (40 µJ pulse[-1] at 200 Hz PRF), the number of photons per pulse is (λ = 308 nm): ~6.2×10^{13} photons pulse[-1].

$$E = \frac{hc}{\lambda} = 6.4 \times 10^{-19} \text{ J}$$

Using the typical beam diameter of ~0.5 cm, we can calculate a photon density of ~1.2×10^{14} photons pulse[-1] cm^{-2}. Based on the [TBHP] introduced into HIRAC during a typical experiment (~3×10^{13} molecule cm^{-3}), the pressure differential between HIRAC and the FAGE cell creates a dilution factor of 4×10^{-3} (4 mbar internal cell pressure, 1000 mbar HIRAC pressure, =4/1000), or [TBHP] = 1.2×10^{11} molecule cm^{-3} in FAGE. Using the relationship:

[OH] = [TBHP] $\sigma_\lambda \Phi_\lambda F_\lambda$

where Φ_λ is the quantum yield of OH from photolysis at 308 nm (= 1), σ_λ is the absorption cross section for TBHP at 308 nm (~2.25×10^{14} cm[2] molecule[-1], based on the measurement by (Baasandorj, Papanastasiou et al. 2010)) and F_λ is the photon density (or flux), [OH] can be approximated. Using these values, [OH] = 3×10^4 molecule cm^{-3}, equivalent to 8×10^6 molecule cm^{-3} sampled at the inlet (after applying the pressure differential). This approximate concentration is in agreement with the interference concentration observed before the hydrocarbon decay calibration experiments.

If the 5 kHz laser is used, the air is not exchanged between two pulses. Is there any closer analysis for the interference with the 5 kHz laser? On page 7980 you give the information that you don't see any interference signal during the HC measurements with the 5 kHz laser. Is this just due to lower pulse energy?

We had only tested the 5 kHz instrument insofar as looking for an enhanced signal upon introduction of TBHP into HIRAC (under the same conditions as the 200 Hz laser system). However, TBHP is intended to be used as a low NOx source of OH in HIRAC in future, and a more comprehensive study into the interference with a 5 kHz laser system will be presented in a further publication. In the literature, Zeng et al (1998) illustrated that for a 5 kHz PRF laser system at 308 nm there was very little calculated OH signal from photolysis and fluorescence in

the same or subsequent laser pulse. Also, a detailed experimental investigation into laser generated interference using a range of different potential OH precursors was conducted by (Ren, Harder et al. 2004). By flowing precursors through their H_2O vapour photolysis calibrator and no laser generated interference was observed using a 5 kHz PRF laser system, which supports our observations. As the reviewer has noted, the absence of interference was most likely due to much lower laser pulse energies for the 5 kHz system (1.6 µJ pulse^{-1} compared to 40 µJ pulse^{-1} at 200 Hz PRF), and this will be clarified.

Unfortunately, we were unable to identify a unique absorption to analyse FTIR data taken for *n*-pentane and cyclohexane, as overlapping peaks from reactants and products made assignment difficult. For this reason we are unable to comment further.

The HC decay work presented in this manuscript has only been performed using the 200 Hz. However, a 5 kHz PRF laser system was briefly borrowed and used with the HIRAC FAGE instrument to test for any interference, aiding in the determination of the source of the interference. This has been clarified.

The reviewer asks an important question which we now feel warrants more explanation to clarify our conclusions. We had originally left this section short so as not to lengthen the manuscript, however, p. 7985 line 19 now reads:

'When [M]→0, the product becomes χ[M], and C_{OH} is directly proportional to pressure ([M]). At higher pressures when kq[M]>>A (at 18mbar the ratio is ~10) the product becomes ~χA/kq and C_{OH} is independent of [M], and thus depends only on the mixing ratio of OH.

However, FAGE is an on-resonance technique and therefore it is not possible to achieve the limit fgate = 1, because it is necessary to gate off the CPM during the laser pulse in order to

avoid saturation of the detector. Thus, in these experiments fgate was always <1, and depended nonlinearly on pressure because the photon counting gate remained the same whilst the fraction of the total fluorescence collected within this gate (fgate) changed as a result of changes in the total fluorescence lifetime of the excited state OH radicals. Thus the effective area of integration under the fluorescence decay curve reduced with increasing pressure such that fgate reduced non-linearly as pressure increased. For the conditions used in these experiments fgate = 0.79 – 0.63 (between 1.3–3.8 mbar). Hence the observation that C_{OH} increased non-linearly over pressures between 1.3–3.8 mbar in this study is consistent with the expected behaviour based purely on the balance between OH number density and the total fluorescence collected.

The inherent complexity that results from the multiple factors which control the sensitivity of FAGE instruments, and which also change with a variety of conditions (i.e. pressure, [H_2O], laser power) and instrumental factors (e.g. time take for CPM to reach maximum gain) require that FAGE instruments are frequently and carefully calibrated."

- P. 7985, line 23: shouldn't it be linearly?!

Yes. Corrected.

- P. 7986, line 5-8 and supplement: COH=2.1 given here for the HC experiment at 1000mbar with iso-butene is not represented in table S1 in the supplement and differs quite a lot from the two COH values given there for pChamber=1000 mbar (COH=4.02 and 3.08). Is this an additional measurement and why is it so different? Also it is a bit confusing that in the main text the total uncertainty is given with 1sigma and in the graph the precision with 2sigma. (see also comment below, Suppl. Fig 5 / Tab1)

We are grateful for the careful proof reading of the reviewer. On further inspection of the data, the values and associated uncertainties presented in the table are correct and the text is at fault. The value that was presented as *iso*-butene was actually from cyclohexane (see Table 1). As for the uncertainties, we had originally designed the manuscript to quote all uncertainties to 1sigma, and some were overlooked when updating the errors to 2sigma. The values has been updated to match those in the table provided in the supplementary material.

- P. 7987, line 7: how is [OH]inf defined? I don't understand how this is related to the dilution and an increase in the decay.

$[OH]_{inf}$ is the [OH] calculated from the hydrocarbon decay as in equation 4. Based on the rate of decay of the HC, a faster decay leads to more $[OH]_{inf}$, and therefore a slower decay leads

to less $[OH]_{inf}$. If we have accurately measured the decay in these experiments, but the dilution rate was faster than we have calculated (due to wall loss or some other unexplained extra loss), then $[OH]_{inf}$ could be smaller. This, in turn, could increase the C_{OH} calculated from the calibration, as $C_{OH} = S_{OH}/[OH]$. We are happy to include a more thorough description if requested.

- P. 7990, line 6, uncertainty of the initial SHO2: could you explain that a little bit more? Wouldn't it be possible to use the mean variation of the "approximately steady state HO2 concentration"?

Determining the accurate $S(HO_2)_0$ is hard as HO_2 does not fully reach steady state before the photolysis lamps are switched off, therefore there is a certain amount of subjective choice in the value of $S(HO_2)_0$. The uncertainty associated with this parameter was derived, as the reviewer has pointed out, from the mean variation of the approximately steady state HO_2 signal. A similar description will be added to the manuscript to clarify this.

- Fig 10: Data for the HIRAC 200 Hz and aircraft 5 kHz FAGE instrument are shown. If there is a difference between the HIRAC and aircraft instrument except the laser system, are there any data for CHO2 from H2O photolysis with the HIRAC instrument with 5 kHz laser, as mentioned on page 7976?

Differences in the aircraft and HIRAC based FAGE instruments have now been clarified as per the previous requests of both reviewers. The original draft for this manuscript had included some temperature dependent calibration data for the HIRAC FAGE instrument using a 5 kHz PRF laser source. However we decided to focus on measurements conducted at ambient temperatures, and the temperature dependent material will be presented at a later date. This misleading sentence has therefore been removed.

Supplement

- P.2 / Fig S1: The measured COH is normalized to 2900ppmv H2O but in the text on p. 2 and the caption of Fig S1 it's stated that the calculated values are normalized to 200ppmv. Is that really the case and if so, why? Shouldn't the dashed line in S1 then cross COH=1 at 200ppmv (or 2900ppmv if it's normalized to 2900ppmv)?

The reviewer makes a good point. The original decision was to normalise all data in this plot to the modal $[H_2O]vap$ (~3000 ppmv) used for the majority of the calibrations conducted

here. However, the $[H_2O]_{vap}$ quenching effect was calculated relative to 0 ppmv, so therefore we have now corrected the plot to reflect all points relative to 0 ppmv (see below).
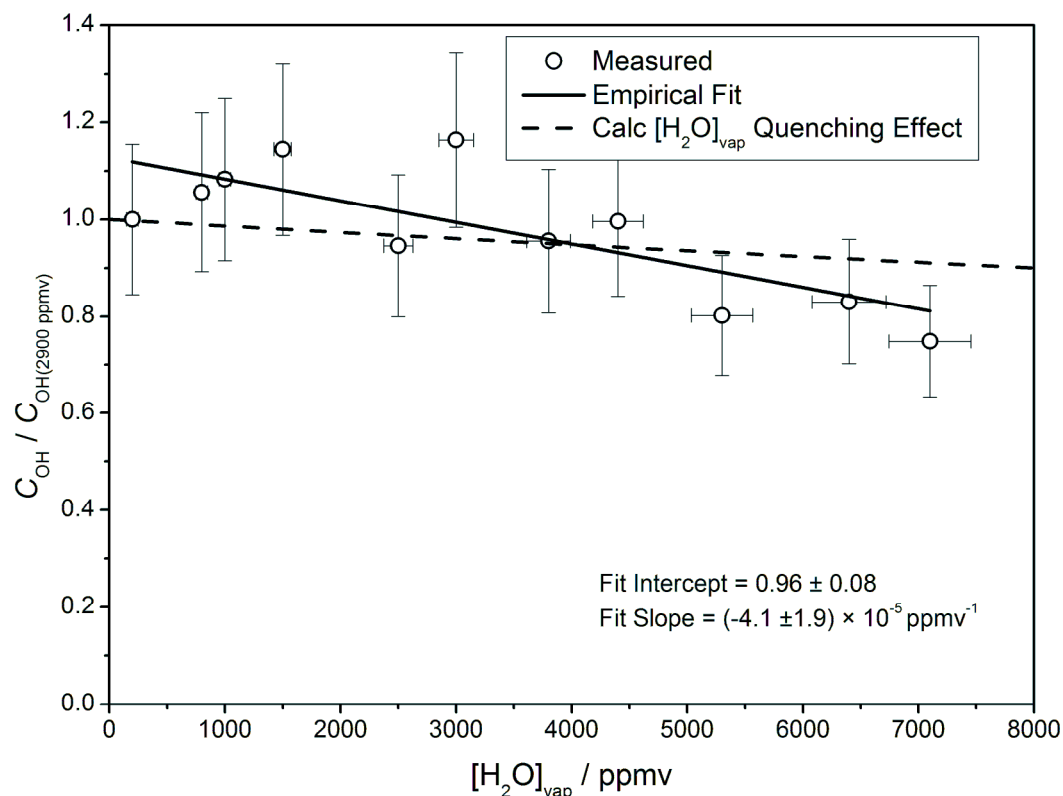
- Fig 5 / Tab S1: The slope for n-pentane = 3.42 +/- 0.85 is exactly the same as for iso-butene at 1000 mbar chamber pressure in the graphs but in table 1 COH from iso-butene is 3.08 and 4.02. Also the slope from the iso-butene graph in the main text doesn't correspond to these numbers (see comment above).

As with the response above, there has been an error in transferring the correct numbers from the up to date table across to the figures and text, and this will be corrected.

- Tab S2: Could you also add a table for the data of the aircraft 5 kHz calibration measurements (Fig10 b)?

A table showing the data from the aircraft FAGE instrument has been added to the manuscript.

Technical comments

- p. 7976, line 24: a table with the reaction coefficients and literature would give an additional (and more convenient) overview

We feel that whilst the reviewer's intentions are helpful, we do not see the need to a table for the rate coefficients used here as it would expand an already lengthy manuscript. However, we are happy to include this if requested by the Editor.

All other technical comments will be corrected as reported by the reviewer.

References

Baasandorj, M., D. K. Papanastasiou, R. K. Talukdar, A. S. Hasson and J. B. Burkholder (2010). "Tert-butyl hydroperoxide: OH reaction rate coefficients between 206 and 375 K and the OH photolysis quantum yield at 248 nm." Physical Chemistry Chemical Physics **12**(38): 12101-12111.

Ren, X. R., H. Harder, M. Martinez, I. C. Faloona, D. Tan, R. L. Lesher, P. Di Carlo, J. B. Simpas and W. H. Brune (2004). "Interference testing for atmospheric HOx measurements by laser-induced fluorescence." Journal of Atmospheric Chemistry **47**(2): 169-190.

Zeng, G., D. E. Heard, M. J. Pilling and S. H. Robertson (1998). "A master equation study of laser-generated interference in the detection of hydroxyl radicals using laser-induced fluorescence." Geophysical Research Letters **25**(24): 4497-4500.