

The paper is an interesting one, and suggests that ROOOH, present in the atmosphere from the reaction of RO<sub>2</sub> with OH, can somehow generate OH within the inlets and fluorescence chambers of instruments that use laser-induced fluorescence to determine OH levels in the atmosphere. Results are shown for the Lille system, where a signal is seen from a mixture of isoprene and an OH precursor (O<sub>3</sub>/H<sub>2</sub>O/hv) when the RO<sub>2</sub> + OH reaction is initiated within a flow-tube that is sampled by the FAGE instrument. The paper then discusses that ROOOH present in the atmosphere may act as a source of interference for OH measurements in order to explain some previous model/measurement discrepancies.

The results are interesting, and I agree that ROOOH decomposition within the inlet or cell of the instrument should certainly be considered as a possibility for generating some artificial OH signal. Nowadays FAGE instruments by some groups are operated with a scavenger inlet, which would enable any OH from ROOOH to be allowed for, so this finding is more relevant to previous field measurements without a scavenger inlet where the signal may partly be from an interfering species.

The range of experiments performed certainly seems to show that there is OH signal at long times (which grows after exposure of the OH reactivity flow tube to multiple photolysis laser shots) which is only present for the longer chain RO<sub>2</sub> (butane and also isoprene as the VOCs) where the ROOOH yield is expected to be larger. The RO<sub>2</sub> + OH reaction until recently was largely overlooked as important in the atmosphere, but work by the Lille group, and more recently from a US group, have measured the rate coefficient. For R=CH<sub>3</sub> there is still a significant disagreement in the rate coefficient (the disagreement was initially worse, but a revised rate coefficient from Lille brought the values closer to each other). Lille have studied RO<sub>2</sub>+OH now for a number of R, and have measured the HO<sub>2</sub> yield, which decreases for larger R (Assaf et al., IJCK 2018), providing evidence that the yield of ROOOH increases as R gets bigger. Recently the yield of CH<sub>3</sub>OH from CH<sub>3</sub>O<sub>2</sub>+OH was quantified experimentally to be small (there had been some theory on this reaction regarding the CH<sub>3</sub>OH yield).

Although there is clearly a signal in the Lille FAGE system at long times which grows further with the number of photolysis shots and which may derive from the ROOOH product of RO<sub>2</sub>+OH, it is surely a considerable stretch to say that this constitutes convincing evidence that the disagreement between model and measurements seen in previous field campaigns (under relevant conditions like low NO<sub>x</sub> forests where ROOOH is expected to have higher concentrations) is due to interference by the decomposition of ROOOH, and that ROOOH reflects the missing piece of the puzzle. There are several parameters which are unknown or poorly known, the most important of which is the concentration of ROOOH in the atmosphere, another is the fraction of ROOOH which may decompose within the fluorescence inlet/cell (which will be instrument dependent). In order for the atmospheric model in this paper to generate something that would generate a relevant level of OH, a decomposition fraction is assumed (based on an estimate from the Lille lab. data) and the loss rate of ROOOH was varied over 3 orders of magnitude and a value chosen to give a level of OH similar to atmospheric levels.

Another major point is even if ROOOH in the atmosphere were to constitute an interference that needed consideration, different FAGE instruments behave differently when it comes to interference formed in the inlet / fluorescence cell. This depends on a variety of factors including the residence time inside the instrument, inlet length from sampling pinhole to fluorescence cell, cell geometry (size, distance from walls), fluorescence imaging volume (e.g. single pass or multi-pass as the case here) and others like the pumping rate. For the case of HO<sub>2</sub> interference from RO<sub>2</sub> for example, the residence time and the geometry of the sampling/cell system has been shown to control the level of interference shown. This needs to be stated in the paper.

We completely agree that the effect might be very different in different FAGE systems. It was already mentioned in the beginning of the discussion that the results are only valid for the UL-FAGE (Page 10: If occurring also with a comparable intensity in other FAGE instruments, it.....), but we have now emphasized this fact on several occasions (Page 4, line 9ff and Page 7, line 26ff) as well as in the abstract.

Concerning the mechanism of the decomposition of ROOOH within the low-pressure FAGE cell, it is not clear what the mechanism is? It is colder (initially in the expansion) and the number density is low so what is the source of the energy? Is it a homogeneous or a heterogeneous process? For a gas phase process the energetics (Assaf et al., IJCK 2018) seem to suggest if decomposition occurs this would be via  $RO + HO_2$  rather than  $RO_2 + OH$ ? As the energetics are known can the ratio of  $RO_2 + OH$  to  $RO + HO_2$  be calculated? Is the ROOOH decomposing at all in the OH reactivity flow-tube (which is at atmospheric pressure – presumably any OH is then very quickly removed but could decomposition sustain a small steady-state level).

Indeed, we do not know how exactly the ROOOH leads to formation of OH radicals in our FAGE system. We have shown that it is NOT due to photolysis, but for the rest, we don't know. It could be thermal decomposition within the shock front, however one would expect mostly (or even exclusively) a decomposition to  $HO_2$  and  $RO$ , given that this decomposition path is around  $10 \text{ kJ mol}^{-1}$  more energetically favourable. According to Müller et al (in their supplementary data), the thermal decomposition of ROOOH is very slow and not a major fate of this species under atmospheric conditions. Also, they estimate the exclusive reaction products being  $CH_3O + HO_2$  and  $CH_3OH + O_2$ . It is therefore rather unlikely that the ROOOH decomposes thermally within the shockwave, or even in the photolysis reactor, leading to a low steady-state concentration. Maybe the decomposition is heterogeneous, either on the nozzle or on the wall of the FAGE cell. This would mean of course even more that different FAGE instruments would show different sensitivity to ROOOH. We have added at the end of the experimental part:

*No clear explanation can be given on the mechanism of this OH formation: a homogeneous decomposition within the shock wave of the expansion is unlikely, because the pathway leading to  $CH_3O$  and  $HO_2$  is thermodynamically more favoured (Assaf et al., 2018a). Therefore a heterogeneous decomposition on the walls of the FAGE cell or the entrance nozzle are more likely. The residence time of the gas mixture between entrance nozzle and detection beam can be calculated from the volume of the cell (0.25 l) and the gas flow ( $3 \text{ l min}^{-1}$  STP) to around 1 sec, leaving ample time for collisions with the reactor walls.*

There will be mixing in of non-photolysed gas where 266 nm is not present – and so not all of the gas will have been illuminated by the same number of pulses? Also, would the 266 nm radiation generate any OH from hitting the metal pinhole at the end of the flow-tube?

The diameter of the photolysis beam is 2.5 cm while the reactor has a diameter of 5 cm. We have not considered in our model that a part of the mixture will not be illuminated and that diffusion will dilute the mixture. This will add to the uncertainty of the estimated ROOOH concentration and lead to an overestimation, given that the key reaction is a radical-radical reaction and relies on the concentration of  $RO_2$  generated in the previous laser pulse, which will have time between two pulses to diffuse into the non-illuminated volume.

Generation of OH from 266nm light hitting the pinhole would probably have no impact on the signal at long reaction times and only influence the signal shortly after the laser pulse.

The OH signal does not decay to zero at long times for the isoprene (and to a lesser extent butane) and the long time signal (plateau signal) increases for the number of 266 nm laser shots – and this is the main evidence that OH (signal in the FAGE cell) builds up with time as more ROOOH is made in the OH reactivity flowtube for longer exposure as the isoprene gets used up. Monitoring the OH reactivity with the number of photolysis shots is a clever idea, and it clearly decreases as the isoprene gets used up. It would be nice to see the  $t < 0$  baseline level to compare with the long time plateau signal. The  $t < 0$  signal is not shown for any of the plots. For Figure S8 for methane, there is no build up of the long time signal with the number of pulses (evidence for no ROOOH being formed for  $R = CH_3$ ), but the signal is not zero? Presumably the  $t < 0$  signal should be zero? Why is there a “constant” underlying signal at long times, even for just 1 photolysis pulse there seems to be a long time signal, i.e. for Figure 2, for 1 photolysis pulse the plateau value is around 0.05 or so (right axis) and it only increases to 0.055 or so after 40 pulses?

The  $t < 0$  signal is not zero due to stray light from the excitation laser as well as some ambient laboratory light entering through the photolysis window and the nozzle. This has now been explained on Page 4. The conclusion of this work is based on the fact that we observe an increase in this background signal only under conditions where  $RO_2$  will partially react with OH; under any other condition the background is stable. We have now zoomed in Figure 2 onto the background, and have also shown the  $t < 0$  signal (we measure 15 ms before the laser pulse), even though this signal is at 2 Hz repetition rate nearly equivalent to the data points at long reaction time: there are only 100 ms without data points between the end of one trace and the beginning of the next one.

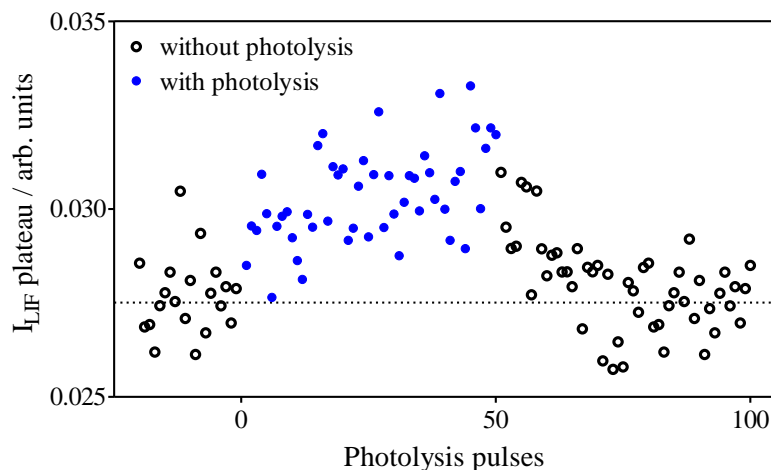
There are some processes not considered in the model, namely  $RO_2$ , isoprene (products) and ROOOH photolysis at 266 nm, which will generate products that may undergo secondary chemistry (e.g. second order isoprene oxidation products?) and build up something which makes OH in the FAGE cell?

Except for the photolysis of ROOOH all other processes will also take place in the same way when we do the experiments with higher VOC concentrations. And one of the main evidences of our hypothesis is the fact that we do NOT observe an increase in the background when we work under conditions (high VOC concentration) where all  $RO_2$  chemistry is the same except for the competition between  $RO_2$  and OH. Also, any OH generated through photolysis would react within the photolysis reactor and would not be detected as a signal at long reaction times.

If the photolysis is stopped after say 20 shots, could the loss of ROOOH from the flowtube be monitored in some way?

Yes, we did such experiments. The signal was recorded for 20 shots before uncovering the photolysis laser, then the mixture was photolysed for 50 shots and then the laser was covered again for 50 shots: open black symbols are traces with photolysis laser covered and represent the average of all data points of that trace; full blue symbols represent traces with photolysis and have been obtained as the plateau from a mono exponential fit between 20 ms and the end of the trace. The dotted line is a guidance for the eye and shows the average of all data points for the first and last 20 shots.

The result for an isoprene experiment under conditions comparable to Figure 1 is shown in the following figure:



For the determination of the OH reactivity, was the same fitting window used for all of the decays, i.e. was it the same for the Pulse 1 decay as for the Pulse 40 decay? Or was a different start and end time used?

The same time window has been used for all traces: the full trace has been fitted, only the first 20 ms, showing some stray light from the photolysis laser as well as the rise of the OH signal, have been discarded.

There is no doubt that the work is interesting, and the idea that ROOOH decomposing to OH and hence constituting a potential interference for OH instruments is worthwhile, and needs further exploration. However, it is unknown what the mechanism of decomposition might be, and it is a complex chemical system and the model used to explain the laboratory results has many assumptions/simplifications – and there may be other species generated in the system which could release OH once inside the FAGE cell. There is likely to be a cascade of chemistry over the 40 photolysis shots generating many species (some of the products and intermediates formed will be different to the real atmosphere owing to the conditions and wavelength of light present).

We agree that we have not attempted to precisely understand what is going on in the photolysis volume. Again, one of the major pieces of evidence for our hypothesis is the fact that we see a clear difference in experiments with low and high VOC concentrations, i.e. under conditions where RO<sub>2</sub> react or not with OH radicals. Indeed, if the reaction of ROOOH with OH or its photolysis leads to rather stable species that in turns leads to OH signal in our FAGE, we would not be able to distinguish it. On the other hand, if something like this happens, it might also happen in remote environments.

The language in the paper needs moderating considerably regarding extrapolating the laboratory observations to the conclusion that the work presents convincing evidence that previous model-measurement uncertainties in low NO<sub>x</sub> environments containing isoprene is due to ROOOH (R from isoprene or similar) decomposition. Our knowledge of ROOOH abundance and removal processes is virtually non-existent, and the model has been optimised using adjustable parameters so as to give a level of OH in the instrument which becomes important compared with atmospheric levels. The wording over the implications of the work, and also the title of the paper, needs changing.

We have removed the word “convincing” from the manuscript and have also more often used the subjunctive form. We are fully aware that our work does not present a final proof that the disagreement between modeling and measurement can be resolved by taking into account ROOOH. Unfortunately,

we do not have any datasets with our FAGE system from remote environments that would allow us to test our hypothesis; this now could only be done by the corresponding groups that have these data sets.

We have also changed the title by adding an “a” and changing it to a question:

**ROOOH: a missing piece of puzzle for OH measurements in low NO environments?**

Other points:

Title, abstract and conclusions – these need to be toned down to report the observations made, that ROOOH needs to be considered as a potential source of OH inside instruments. Any implication that the puzzle is solved is going too far and is rather premature. The title cannot remain as is. The abstract and conclusion also need to make it clear that any OH from ROOOH would be highly dependent upon the instrument design, and make implicit any assumptions made in the model.

Words such as “convincing” are of course subjective – and should be toned down or removed completely.

The title has been changed (see above), we have removed “convincing”, we have used several times the subjunctive form. We have also changed the abstract to the following:

**Abstract.** *Field campaigns have been carried out with the FAGE technique in remote biogenic environments in the last decade to quantify the in situ concentrations of OH, the main oxidant in the atmosphere. These data have revealed concentrations of OH radicals up to a factor of 10 higher than predicted by models, whereby the disagreement increases with decreasing NO concentration. This was interpreted as a major lack in our understanding of the chemistry of biogenic VOCs, particularly isoprene, which are dominant in remote pristine conditions. But interferences in these measurements of unknown origin have also been discovered for some FAGE instruments: using a pre-injector all ambient OH is removed by fast reaction before entering the FAGE cell, and any remaining OH signal can be attributed to an interference. This technique is now systematically used for FAGE measurements, allowing the reliable quantification of ambient OH concentrations along with the background OH. However, the disagreement between modelled and measured high OH concentrations of earlier field campaigns as well as the origin of the now-quantifiable background-OH is still not understood. We present in this paper the compelling idea that this interference, and thus the disagreement between model and measurement in earlier field campaigns, might be at least partially due to the unexpected decomposition of a new class of molecule, ROOOH, within the FAGE instruments. This idea is based on experiments, obtained with the FAGE set-up of University Lille, and supported by a modelling study. Even though the occurrence of this interference will be highly dependent on the design and measurement conditions of different FAGE instruments, including ROOOH in atmospheric chemistry models might reflect a missing piece of the puzzle in our understanding of OH in clean atmospheres.*

The balance of the main paper and the supplementary information seems skewed. There is information in the SI which really ought to be in the main paper (there is no compelling reason this has to be done for space reasons). e.g. Figures S1 and S4, S6 (this seems central to show) and probably one panel for butane and methane.

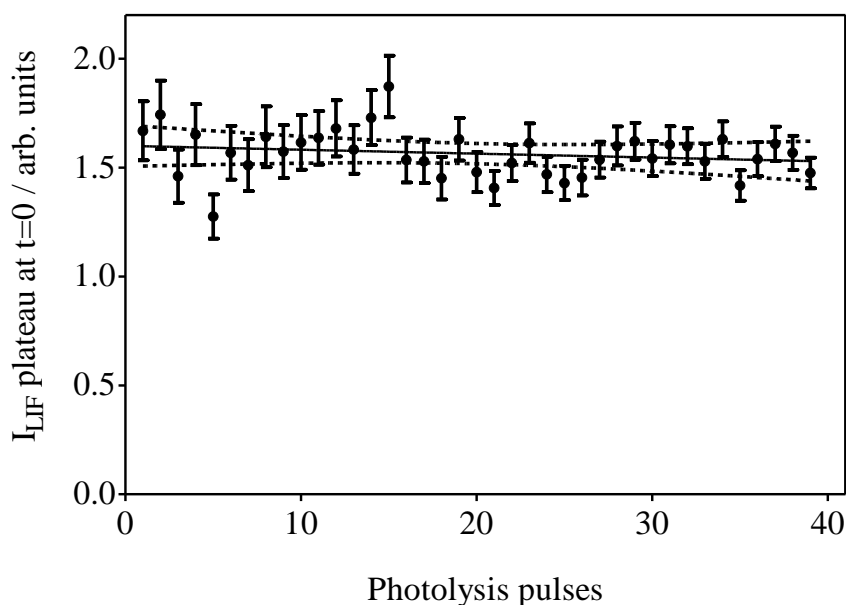
We have shifted a large part of the supplementary data into the main manuscript, notably the modelling of the chemistry in the photolysis reactor, all experiments and figures concerning the different tests with laser energy, different isoprene concentration and the tests with butane and CH<sub>4</sub>.

Page 4, line 18, it should be 200 microseconds (not ms).

Has been corrected.

Figure 1. It is not clear how the t=0 maximum in OH signal varies with the number of shots? Does this change with pulse 1 to 40 in any systematic way?

The LIF intensity at time 0 decreases slightly, probably due to the slow depletion of O<sub>3</sub> within the photolysis volume. The following figure shows the LIF intensity at time 0 for the experiments from Figure 1 (note that the fit to Figure 1 has been changed compared to the initial manuscript after close inspection of the data with respect to this question, now taking only data from 20 msec on, while before it was 10 msec. This has a slight influence as well on the decay rate and the plateau, therefore Figure 2 has also slightly changed). From pure photolysis one would expect at each photolysis shot a decrease of the signal of :  $\text{OH} / \text{O}_3 \approx 1.4 \times 10^{10} / 1.5 \times 10^{13} \approx 1 \times 10^{-3}$ , in good agreement with the decrease of the OH signal at time 0 :  $(1.8 \pm 1.5) \times 10^{-3}$ .



Also what does “data analysis is carried out with raw data” mean?

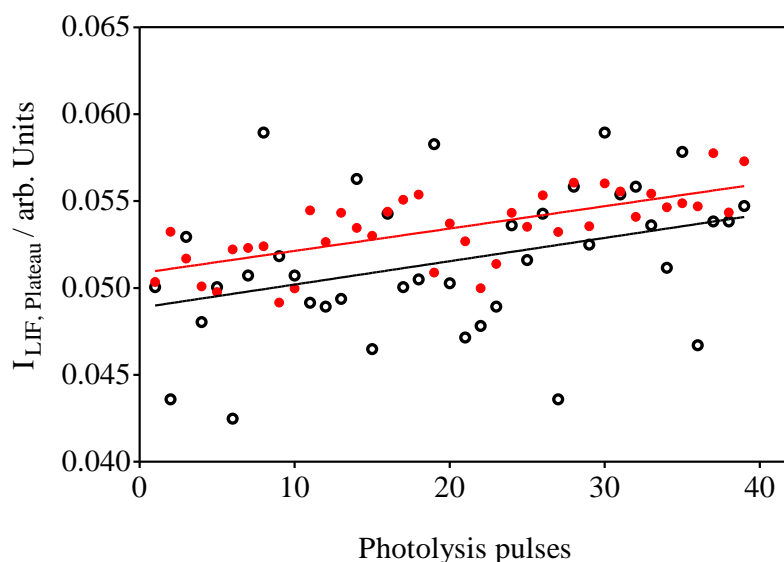
We wanted to express that the averaging is just done for better visualisation: “raw data” has been replaced by “non-averaged” data.

Figure 2. The red line shows the plateau OH signal from the fit, gradually increasing with the number of photolysis pulses. Given the very small magnitude of the plateau OH compared with the initial OH signal the accuracy of the fit at long time is very important. Could Figure 1 at long times be plotted on a very expanded vertical scale (perhaps from y=0 to y=0.15) and the fits be shown with it? The results are very dependent on how well things fit at long times. Related to this point I would like to see Figure 2 plotted when the plateau is averaged using the data at later times. As the OH reactivity becomes smaller

with the number of photolysis pulses, it takes longer for the signal to reach the plateau, so does this slower decay promote the increasing baseline signal in any way? There are certainly some decays in the SI that do not seem to have reached the baseline before the averaging window to obtain the plateau signal begins.

We agree that the increase of the signal is very small compared to the initial signal, and also compared to the scatter and the uncertainty. However, we are confident that the results really show an increase in OH signal, because consistently we always observe this increase only when we are in conditions where RO<sub>2</sub> reacts with OH, at any other experiments the background is stable within the uncertainty.

We have now plotted the data from Figure 2 in the manuscript (former Figure 1) with an inset showing the pre-photolysis signal as well as the first and the last trace blown up vertically, together with their fits. It can be seen that even for the slowest decay (shot 40) the fit has reached the plateau value at around 0.3 sec. In the figure below we show the data from Figure 4 (former Figure 2, without error bars) together with the raw data averaged from 0.35 to 0.41 sec. While the scatter is much larger using the averaged values, the overall trend of an increasing background with increasing photolysis pulses is the same.



Page 6, lines 5-15. Excitation laser energy and photolysis energy are both used here – be clearer about which pulse energy was changed. Clearly Fig S2 and S3 are for probe (excitation) laser energies, but unclear if photolysis (266 nm) energy was changed also?

Everything else was kept constant, only the probe laser was varied. This has been clarified in the manuscript. This part has also been moved from the supplementary data to the main manuscript.

The error in [ROOOH] from the model after 40 shots (figure S6 model) needs to be stated.

The error in [ROOOH] is very large, the model just serves to get a rough estimate. As we state, there are many processes that are not taken into account in the model (diffusion into unphotolysed volume, wall loss, photolysis of ROOOH, reaction of OH with several products, inhomogeneous photolysis beam (this can make a large error for radical-radical reactions, but is very difficult to quantify) etc.). So we think that the uncertainty is at least a factor of 10, but rather over- than underestimated (most of the neglected processes would either consume or produce less ROOOH).

Why was  $10^{-4} \text{ s}^{-1}$  chosen as the loss rate for ROOOH in the atmosphere? Presumably as this gave an OH concentration of around  $1 \times 10^6$ ? There is a very large uncertainty in [ROOOH], and so the statement on page 9, line 8 that [ROOOH] is predicted to be of the order of 50-200 pptv seems very optimistic in terms of the range of concentrations? For Figure 4, were there RO<sub>2</sub> measurements made in the field to constrain the model, or was modelled RO<sub>2</sub> used?

We agree with the reviewer that there is very large uncertainty in the atmospheric abundance of ROOOH. As we state on page 4 line 15 of the manuscript, the removal rate (and dominant process) is unknown at present. The use of a loss rate of  $10^{-4} \text{ s}^{-1}$  was chosen as an educated guess of a lifetime. This is on the order of the lifetime of ROOH (which is typically  $> 1$  hour) and much longer than RO<sub>2</sub> (which is typically  $< 10$  seconds). As we state on page 115 line 9 of the manuscript, we evaluated a range of 3 orders of magnitude in the loss rate of ROOOH in our modelling but for space reasons and to focus the discussion we opted to discuss the intermediate loss rate of  $10^{-4} \text{ s}^{-1}$ . We proposed the manuscript to make this clearer:

*As neither the removal rate nor the dominant process of these ROOOH species are currently known, different removal rates were tested, ranging from  $10^{-5}$  to  $10^{-2} \text{ s}^{-1}$ .*

*Figure 3 shows the average diurnal peak concentration of ROOOH in the Boreal (left) and Austral (right) summer obtained using a removal rate of  $10^{-4} \text{ s}^{-1}$ , leading to ROOOH lifetimes of around 3 hours, on the same order as the lifetime of ROOH species. Peak concentrations of several 100 ppt are reached in this scenario, especially at tropical latitudes, which would lead to an interference in the UL-FAGE system of the order of  $1 \times 10^6 \text{ cm}^{-3}$ . However, we would like to insist on the fact that both, the modelled concentration of ROOOH in the atmosphere as well as the sensitivity of the UL-FAGE against ROOOH species, bear currently an uncertainty of at least a factor of 10,*

For Figure 4 (Figure 10 in the revised manuscript) we did not constrain RO<sub>2</sub> but have made clearer in the text which species were constrained to the data reported in Feiner et al (2016)}

## Discussion

Page 10, line 6.

It is stated that the product of the RO<sub>2</sub>+OH reaction leads to an OH interference. The signal may originate from that, but there may be other origins of the signal also, and so the wording needs to be more flexible. This is also where a statement about the different FAGE designs is needed.

We think that the results of the different experiments carried out in this work show clearly that the increase in OH signal in the UL-FAGE does indeed originate from the products of the reaction of RO<sub>2</sub> + OH, so the wording seems suitable to us. There was already a (small) statement that other FAGE systems might behave differently (if occurring also with a comparable intensity in other FAGE instruments....), but we emphasized this fact by adding:

*The intensity or even the occurrence at all can depend on the design and working conditions of the FAGE set-up, which is different for different groups. However, if occurring also with a comparable intensity in other FAGE instruments, this interference might be high enough to explain numerous observations obtained with FAGE instruments from other research groups including: .....*



Supplementary material.

I think much of section 1 on the FAGE and probe system needs to go in the main paper.

We have added the Figure of the set-up into the main manuscript as well as a few details, but have preferred to leave most details of the set-up in the sup data.

What is the residence time of the FAGE detection cell (inlet from the pinhole and fluorescence cell)? There is no discussion of this and it is an important point. Was the pumping rate of the cell changed to change the residence time?

The volume of the FAGE cell between the inlet nozzle and the excitation laser beam is 0.25 l, the pumping into the FAGE is 3 l, this leads at 2 Torr to a residence time of the gas of around 1 sec. No, pumping rate was not changed in these experiments. Such experiment would indeed have been a good idea, but we did not do and now the experiment is in a different configuration.

Figure S2 – in the caption add a line saying what the black line is.

Has been done.

Line 187 of SI – “is consistent with” is better than “is indeed due to”

Has been done.

For all of the OH signal versus time plots the y axis ends at zero. Are there any negative points, or is the “baseline” some value a bit above zero?

There are never negative values, because the signal is obtained by counting photons. Therefore, it is either zero (if no photon occurred at that time window during any of the 20 individual decays) or above.

Figure S6. The concentrations versus no of photolysis pulses. This seems central and should be in the main paper.

Has been done

Line 220, reword “very basically”

Has been done.