

The paper « Measurement of OH reactivity by laser flash photolysis coupled with laser-induced fluorescence spectroscopy » by Stone et al. describes the pump-probe instrument such as used by the University Leeds. Laser photolysis coupled to FAGE has been described first by Sadanaga et al. in 2004 and has since been used and further developed by several groups. In this context, the paper, which is well presented, provides general information and does not give a very detailed view of the specificities of the Leeds' instrument.

The paper starts with a good introduction to OH reactivity and the description of different measurement methods currently used by the scientific community. It also gives an overview of results on OH reactivity measurements obtained during field campaigns until today by different groups and techniques. In section 2, the instrument is described, as well as how the OH reactivity is obtained and validated. Finally 2 types of application of this instrument are presented : use during two field campaigns and first measurements of a coupling of this instrument with the HIRAC chamber. I think such a paper with the detailed description of this instrument, data acquisition procedure and validation is very interesting. However, all sections are kept very general and contain only little detail, this should be completed before considering publication in AMT.

Here are suggestions on what could/should be described in more detail:

- I'm not sure if it is necessary to show the set-up in configuration with the reaction cell in 90° to the FAGE cell. Either you show more detailed results to make it clear and visible why the straight version is better than the 90° version (for example by showing zero air decays from both set-ups) or you just mention it in the manuscript, but a Figure is not needed.
- If I understand right, the entire system (photolysis cell including the laser and FAGE cell) are located on the roof of the container. Why do you not install it within the container? Is it to save space or to avoid tubing which would be necessary for connecting the photolysis cell if located inside the container? Being on the roof, the temperature in the photolysis cell can vary a lot, I guess you take this into account when calculating the OH reactivity? Please mention somewhere.
- What is the repetition rate of the photolysis laser used during normal running conditions?
- line 228, it is written that for the 90 ° configuration "the observed OH decays in such a configuration displayed biexponential behaviour, comprising a fast initial decay followed by a slower decay representative of the expected OH reactivity, as observed in previously described instruments (Sadanaga et al., 2004a; Lou et al., 2010)." The reason for the biexponential decay is explained as following (line 237) : Once mixing of the air having experienced the photolysis laser with that outside the beam diameter has occurred sufficiently to give uniform OH concentrations in the reaction cell the observed OH decay will result from the chemical losses in the instrument, leading to biexponential decays. Later you mention that in your end on configuration "biexponential decays can still be obtained if the photolysis laser is not correctly aligned along the axis of the reaction cell". Could you give more comments about the respective effect on the decay profile of the beam size (tested ?) and alignment for both configurations ?
- In the section 2.1, you say you draw 12 to 14 slm through the cell of which around 4slm is drawn into the FAGE cell? Can you be more precise on the design of the outlets? Is there just one outlet connected to the fan or several or is the cell designed in a way to pump evenly over the full circumference of the cell in order to maintain the laminar flow and to probe only air from the center of the photolysis cell into the FAGE? I would imagine that with just one outlet for the overflow you would draw gas from the reactor wall opposite of the

overflow outlet towards the FAGE inlet orifice, which should have some impact on the $k(\text{phys})$. Also, please give the model of the fan and the fan speed used for extraction. Line 475 you say that a total gas flow between 10 and 22 slm did not have any impact on the obtained rate constant of n-C₄H₉OH. Did you test the instrument without any extra outlet? If yes, what was the difference? I am wondering, if the flow rate has an impact on the intercept, i.e. the $k(\text{phys})$? I could imagine that higher flow rates create higher turbulences and thus higher $k(\text{phys})$? Can you comment on that? Maybe you could show a figure with $k(\text{phys})$ obtained with 10 and with 22 slm.

- How exactly do you determine your $k(\text{obs})$, does the exponential fit goes always over the same time period? At what delay after the photolysis laser do you start the fit and how did you decide on the starting point? When does it end and how did you decide? If the fit lengths changes depending on $k(\text{obs})$, then do you deduce the same $k(\text{phys})$ for all $k(\text{obs})$ or do you fit $k(\text{phys})$ over the same time interval? Please give more details on the data evaluation.
- In Figure 4, the intercept seems to be very close to zero for CH₄ and C₄H₉OH: did you deduce $k(\text{phys})$? For OH + CO it is clearly not zero: why?
- Did you estimate the potential bias due to RO₂ radicals within the cell as this could impact the OH decay in two different ways: OH recycling from the reaction of RO₂ in presence of NO can slow down the decays while reaction of OH with RO₂ can accelerate the decays. Indeed, the rate constant for the reaction of peroxy radicals with OH has recently been measured and has been found to be very fast (Bossolasco et al, Chemical Physics Letters, 593, 7-13 (2014), and Farago et al, Chemical Physics Letters, 619, 196 (2015) for CH₃O₂ and C₂H₅O₂, respectively), From this work, a tentative rate constant of $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for the reaction of all peroxy radicals with OH can probably be considered for a rough estimation of the possible impact. Therefore each 10^{10} cm^{-3} RO₂ would lead to an increase of the OH reactivity of 1 s^{-1} while the deceleration due to NO will depend on the NO concentration. The concentration of RO₂ radicals in the volume entering the FAGE system might be quite high for several reasons:
 - (a) You have a very short inlet line to the reaction cell, so peroxy radicals present in the atmosphere probably reach your cell: from your MCM models you should be able to estimate the RO₂ concentration present outside, which could be taken as an upper limit for the RO₂ concentration entering the FAGE cell. Even under moderate NO_x concentrations, a large fraction of these RO₂ radicals will probably survive the 7 sec before reaching the FAGE inlet.
 - (b) Peroxy radicals will be produced in the reaction cell due to reactions of VOCs with the photolytically generated OH radicals. You estimate that you produce a concentration of 10^9 cm^{-3} OH-radicals per photolysis shot (line 350). These OH radicals will produce a concentration of RO₂ radicals on the same order of magnitude. As the residence time of the gas in the reaction cell is 7 to 8 sec (line 190), the gas is probably photolysed 7 to 8 times before reaching the FAGE intake. Accumulation of reaction products over several laser shots can therefore increase the concentration of RO₂ to near 10^{10} cm^{-3} .
 - (c) Peroxy radicals could be produced by the direct photolysis of the ambient VOCs at 266nm. You use 50 mJ / pulse, with a 10mm diameter $\approx 60 \text{ mJ} / \text{cm}^2$. Taking acetone as an example, $\approx 0.4\%$ will be photolysed at each laser shot. Accumulation over several laser shots can add up to a total photolysis yield of 2 or 3%, which can lead each to 2 peroxy radicals. With 20 ppb as an example ($\approx 5 \times 10^{11} \text{ cm}^{-3}$) this could lead to up to $3 \times 10^{10} \text{ cm}^{-3}$ of peroxy radicals.

Summing up all these possible RO₂ sources, the OH reactivity might be increased by a few s⁻¹ due to the reaction RO₂ + OH, while it might be at the same time decelerated depending on NO concentration. Of course there is diffusion between two laser shots, decreasing the concentration of laser-made RO₂ radicals, but this process is probably rather slow, given you have laminar flow at ambient pressure. With k(phys) ≈ 1 s⁻¹ for OH radicals, 36% are still present after 1 s; RO₂ radicals being bigger, they have a smaller diffusion coefficient and the residual concentration after 1 s is probably higher than 36%. Line 312 you say that you have varied the photolysis energy between 1 and 0.1 Hz, which in principle is a good test on the influence of laser made interferences. However, I am doubtful about the feasibility of such experiments in the field: acquiring OH decays good enough to test for such interferences with a repetition rate of 0.1 Hz needs a long averaging time and hence the air mass might have changed in-between a measurement at 0.1 and 1 Hz. I think the coupling to the HIRAC chamber would be a good test as conditions can be kept stable: maybe you have done this already? If yes, could you show some more detailed results?

The possible influence of RO₂ radicals on the OH decays has already been mentioned in a recent intercomparison of OH lifetime instruments (Hansen et al. Atmos. Meas. Tech., 8, 4243–4264, 2015), but a much lower pulse energy at a larger beam diameter was used for estimation. Also; no further modelling has been carried out in that work to estimate the converse influence of NO. The current paper might be a good opportunity to go into more detail into this question.

- In section 7 you say, decays of up to 150 s⁻¹ are scattered (what is the standard deviation ?), but can nevertheless be fitted reliably. It would be interesting to see such a decay with the corresponding fit.
- Line 233: you say the air that has not experience the photolysis laser, contains only ambient OH concentration: I doubt that ambient OH radicals survive very long within the reaction cell. I think the sentence in line 439 is not complete.