Author response to anonymous referee #3 on “An intercomparison of CH_3O_2 measurements by Fluorescence Assay by Gas Expansion and Cavity Ring–Down Spectroscopy within HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry)” by L. Onel et al.

Minor comments:

P2-P3: Several techniques are discussed for the measurement of peroxy radicals. The authors should also briefly discuss the use of chemical ionization mass spectrometry methods such as published in Noziere and Hanson (2017), Noziere and Vereecken (2019), Hansel et al. (2018), Jokinen et al. (2014), etc.

We thank the referee for pointing out these additional references to include in the MS. We have now extended the introduction to discuss briefly the use of CIMS for the detection of speciated RO_2 radicals. The following text has been added to the MS after line 34, page 2:

“CIMS methods using reagent ions such as $H_3O^+(H_2O)n$, NO_3^- and NH_4^+ have been employed in the simultaneous and selective detection of RO_2 in a number of recent studies (Noziere and Hanson, 2017; Noziere and Vereecken, 2019; Hansel et al., 2018; Jokinen et al., 2014). Volatile small RO_2 radicals such as CH_3O_2 have been selectively measured in CIMS laboratory experiments with detection limits between $\sim 1 \times 10^8 - 1 \times 10^9$ molecule cm^{-3} (Noziere and Hanson, 2017; Noziere and Vereecken, 2019). CIMS with NO_3^- reagent ion has been employed in field measurements to record diurnal profiles of some highly oxygenated low–vapour pressure RO_2 radicals produced in the ozonolysis of monoterpenes peaking at a few 10^7 molecule cm^{-3} (Jokinen et al., 2014). ”

P4 L16 & P5 L19: CH4 is used during calibration experiments as a precursor for CH3O2 and is added in the Water-photolysis calibrator and the HIRAC chamber at concentrations as high as 2.5E17 molecule/cm3. Can the authors comment on the potential impact of CH4 on the quenching of CH3O in the detection cell?

The answer to this question is given in the response to the first specific question asked by referee 1, where no quenching effect of the $CH_3O(A)$ fluorescence by CH_4 was found in the present experiments. Experiments were performed at several $[CH_4]$ and no difference in the sensitivity factor for CH_3O_2 was observed. At the small mixing ratios of CH_4 used, and following expansion to low pressure in the FAGE fluorescence chamber, the quenching of $CH_3O(A)$ by CH_4 is expected to be very minor compared with that of O_2 or N_2.

P7 Eq. 6: Please define kloss

An explanation about kloss were added in lines 4–5, page 7:

“…the potential for a loss of CH_3O_2 to the walls was investigated. As circulation fans were used during all the experiments, the ‘movement’ of CH_3O_2 radicals within the chamber is in part molecular diffusion and in part convection. Therefore, the parameter k_{loss} is controlled by both convection and diffusion processes. By incorporating the wall loss…”

P6 L9-13 & P12 L4-6: What were the fitted values for kloss? Are the values inferred from the two experiments consistent with each other?

FAGE was sampling from a point close to the chamber centre while CRDS measured CH_3O_2 right across the HIRAC diameter (Fig. 2 in the main text). However, the kinetic decay analysis demonstrated that wall losses were negligible in both FAGE and CRDS measurements.
The analysis of the kinetic decays monitored by the two instruments has been done in the same way for both $[CH_3O_2]_{FAGE}$ and $[CH_3O_2]_{FAGE}$ decays. The upper limit for k_{loss} in the FAGE measurements was added to the text as shown in the answer to the first referee's comments:

"… the small values extracted for k_{loss} (upper limit of ~ 1×10^{-5} s^{-1}) fitting Eq. (6) to the FAGE data demonstrates that wall losses can be neglected…" was added on page 7, lines 11-12."

The same upper limit was obtained for k_{loss} by analysing the kinetic decays measured by CRDS. The result was added in line 6, page 12:

"…are statistical uncertainties. The values extracted for k_{loss} by fitting Eq. (9) to the CRDS data were small and similar to the values obtained by fitting Eq. (6) to the kinetic decays monitored by FAGE. An upper limit of ~ 1×10^{-5} s^{-1} was obtained for k_{loss} in both FAGE and CRDS measurements, showing that wall losses are negligible. From fitting…"

P6 L22: "1E-10" should read "1E-9"
"1E-10" was corrected to "1E-9"

P15 L9-12 & L17-18 & L21-22: The authors show that correlation plots between FAGE and CRDS exhibit slopes that are close to unity. However, the y-intercepts of the regression lines are not discussed. Were the intercepts not statistically significant?

The *y*-intercepts of the FAGE – CRDS correlation plots (Figs. 6b, 7b and 8b) have either a small negative value (Fig. 6b) or a positive value (Fig. 7b and 8b). We believe that the main source for the *y*-intercept values derived by the linear fit to the data is the method used to determine the background of the CRDS measurements. The background ring-down time (the ring-down time in the CH_3O_2 absence, τ_0) increased slightly during the time intervals with the lamps on due to the slow depletion of the reagents (methane or acetone). However, τ_0 could not be measured simultaneously with the ring-down time in the presence of the CH_3O_2 radicals, τ. Therefore, the background was regularly monitored by turning the lamps off, as explained in lines 9 – 10, page 10:

"As it is not possible to measure τ_0 and τ simultaneously, the background was monitored regularly during each experiment by switching off the photolysis lamps and allowing the signal to return to the baseline."

We also added a new paragraph describing the impact of the acetone and methane absorption on τ_0 to the main text (see the answer to the first specific comment of the referee 1).

The background in the FAGE measurements could not also be recorded simultaneously with the CH_3O_2 FAGE signal as it required the FAGE instrument measured off-line. Therefore, the off-line measurement was taken at the end of each on-line measurement. However, the FAGE measurement background was independent on any changes in the composition of the HIRAC gas mixture. Therefore, we believe that the source of the linear regression intercepts mentioned by the referee comes from the uncertainties associated with the determination of the CRDS measurement background as explained above. The intercepts are not significant as their values are only a few percent from the largest $[CH_3O_2]$ shown in each correlation plot.

P16 Figures 6-7: When the lamps are turned off, (1) the CRDS measurements seem to decrease to lower values than FAGE and (2) the FAGE measurements seem to reach a plateau more rapidly than the CRDS. Could the authors comment on this?

As it was not possible to measure τ_0 and τ simultaneously the background ring-down time was recorded regularly by turning off the chamber lamps to account for the slow decrease in the reagent (methane or acetone) concentrations (*vide supra*). The method led to typical small deviations of the baseline of the CRDS kinetic decays from zero and to the slight differences between the baselines of the $[CH_3O_2]_{FAGE}$ decay and $[CH_3O_2]_{CRDS}$ decay mentioned by the referee.

The two referee's observations are coupled to each other – the $[CH_3O_2]_{CRDS}$ continuing to go down, and $[CH_3O_2]_{FAGE}$ levelling off quicker. The FAGE measurement levelling is due to the second order kinetics going to a constant value, $[CH_3O_2] = 0$ whereas $[CH_3O_2]_{CRDS}$ continues to go down as some reaction products absorbing at the measuring wavenumber (7488 cm^{-1}) are changing with time. This in turn slightly changes the absorption even when the CH_3O_2 has reached zero concentration. Both these effects are more evident at 80 and 100 mbar than at 1000 mbar. The better FAGE – CRDS agreement at longer times at 1000 mbar than at 80 and 100 mbar could be due to a greater wall loss of the absorbing products at reduced pressures, where diffusion becomes more significant. However, even at 80 and 100 mbar the discrepancies noticed by the referee are minor and the FAGE – CRDS correlation plots, which incorporate all the temporal decay data show a good agreement under all conditions.