

Author response to anonymous referee #1 on “An intercomparison of CH₃O₂ 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.

General comments

Regarding the calibration of the FAGE, it was surprising that the water vapour photolysis method was not used at all conditions studied. This instrument has been deployed on aircraft, so sensitivities for OH and HO₂ were surely determined as a function of sample pressure.

The HIRAC FAGE instrument has not been deployed on an aircraft, although the Leeds aircraft FAGE instrument (Commane et al., 2010) does have fluorescence cells of a similar design to those used in HIRAC for this CH₃O₂ work. The sensitivity towards OH and HO₂ as a function of pressure of the fluorescence cell was determined for the HIRAC FAGE instrument (Winiberg et al., 2015), and also for the aircraft instrument (Commane et al., 2010). However, in both cases the sample pressure was not changed, rather the pressure in the fluorescence cell was altered by using different sized pinholes to reflect the same pressure as whilst sampling from reduced pressure (either at different altitudes on the aircraft or from HIRAC operating at reduced pressure). For the aircraft instrument there was very little dependence of the sensitivity with cell pressure for the range of altitudes encountered for both OH and HO₂ (Commane et al., 2010). For HIRAC, a small increase in the sensitivity for OH was seen, and a larger change for HO₂ was seen over the range of cell pressures used (Winiberg et al., 2015), although the experiments were performed at a range of pulse repetition frequencies, and different pumps were used for the aircraft and HIRAC pressure dependencies. This approach, which assumes there is no change in any losses at the pinhole across a changing pressure differential, was validated by another group for an aircraft instrument using different materials for the pinhole (Faloona et al., 2004). In HIRAC, we validated the approach by employing the decay of a hydrocarbon in HIRAC at different pressures in the presence of OH which was measured using FAGE, or that of HO₂ by its kinetic decay followed production via the photolysis of HCHO at different pressures, and obtained the same result as using the water vapour calibration method.

References

Commane, R., Floquet, C. F. A., Ingham, T., Stone, D., Evans, M. J., and Heard, D. E.: Observations of OH and HO₂ radicals over West Africa, *Atmos. Chem. Phys.*, 10, 8783–8801, 2010.

Winiberg, F. A. F., Smith, S. C., Bejan, I., Brumby, C. A., Ingham, T., Malkin, T. L., Orr, S. C., Heard, D. E., and Seakins, P. W.: Pressure-dependent calibration of the OH and HO₂ channels of a FAGE HO_x instrument using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC), *Atmos. Meas. Tech.*, 8, 523–540, 2015.

Faloona, I. C., Tan, D., Leshner, R. L., Hazen, N. L., Frame, C. L., Simpas, J. B., Harder, H., Martinez, M., Di Carlo, P., Ren, X. R., and Brune, W. H.: A laser-induced fluorescence instrument for detecting tropospheric OH and HO₂: Characteristics and calibration, *J. Atmos. Chem.*, 47, 139–167, 2004

It is straightforward to make use of this calibration procedure at reduced pressures for methylperoxy radicals. The paper would be greatly improved by performing such calibrations for the two other chamber conditions.

In this paper, rather than validating the water vapour method for the calibration of CH_3O_2 sensitivity as a function of pressure (using a known OH which is converted to CH_3O_2 , followed by conversion to CH_3O by NO, and the CH_3O formed detected (Onel et al. 2017b in the list of references of the manuscript), the main aim was to compare two distinct techniques (FAGE and CRDS) for a range of sampling conditions. Also, it is felt that because the sample pressure cannot be reduced in these experiments during the calibration (rather a change in pinhole is used or a change in pumping capacity is used to change the cell pressure, which would change the residence time from sampling to the laser-excitation axis), that additional uncertainties would arise in determining the sensitivity of FAGE to CH_3O_2 as a function of pressure using the water vapour calibration method, so it was used at atmospheric pressure to calibrate CH_3O_2 .

On the other hand, since there is a systematic difference between the two methods of calibrations at 1000 torr, and that the authors favor the water vapour photolysis method (indicating that perhaps the rate coefficient for methylperoxy radical decay, k_{obs} , should be reduced by 25-30%), it appears to this reviewer that perhaps the FAGE calibration factors for the 80 mbar and 100 mbar should be scaled by the ratio of the calibration factors for the two methods performed at 1000 mbar. If the rate coefficient is indeed in error, the CRDS calibrations should also be adjusted by the same factor. As stated in the paper, though, if both instruments rely on methylperoxy radical decay for their calibration, then the accuracy of the value for k_{obs} does not matter, if the same value is used for both.

The referee is correct, the same value is used for both and so the accuracy of the value for k_{obs} does not matter. The kinetic method used for the determination of the CH_3O_2 absorption cross-section, $\sigma_{\text{CH}_3\text{O}_2}$ relies on the value for the rate coefficient of the CH_3O_2 self-reaction. However, as the previous studies at a range of pressures typically used the CH_3O_2 kinetic decay to determine $\sigma_{\text{CH}_3\text{O}_2}$, the kinetic method of calibration was chosen in this work for comparisons of the value of $\sigma_{\text{CH}_3\text{O}_2}$ obtained in this work with the values for $\sigma_{\text{CH}_3\text{O}_2}$ reported previously.

The water vapour photolysis method of calibration is a well-established method for FAGE calibration (*vide supra*), routinely used in calibrations at atmospheric pressure. Therefore, both methods of FAGE calibration, the water vapour photolysis method and the kinetic method, were employed in this work at atmospheric pressure. As noted by the referee, a systematic 25–30% discrepancy was found between the FAGE sensitivities factors, $C_{\text{CH}_3\text{O}_2}$ obtained by the two methods at atmospheric pressure (this work and Onel et al. 2017b in the list of references of the manuscript). As the water vapour photolysis method is known to be an accurate and reliable method of calibration, the discrepancy at atmospheric pressure would seem to indicate that the value of k_{obs} (Atkinson et al. 2006) is overestimated by 25–30%. This is already discussed in detail in the main text (see lines 24 – 30, page 15 and lines 19 – 30, page 17).

It was also not obvious from the paper what k_{obs} referred to, so suggest adding some text to indicate that it refers to the effective rate coefficient for second order methylperoxy radical decay that includes contributions from methylperoxy radicals reacting with HO₂, which is produced from R5b followed by the rapid reaction of methoxy radicals with oxygen. It is possible that this is what lines 31-34 on page 6 were trying to say, but it was not clear to this reviewer. Suggest rewriting this text and/or adding more information. Note that without radical wall loss, $k_{\text{obs}} = k_5a + 2k_5b$. It would be useful to add discussion on the impact of HO₂ wall loss on k_{obs} both in the present experiments, and in those used by IUPAC to arrive at their kinetic recommendations.

Following the suggestions of the referees the paragraph in the MS corresponding to lines 26-33 on page 6 was changed and now includes both the expression used for the observed rate coefficient in line with IUPAC recommendation: $k_{\text{obs}} = k_5(1 + r_{5b})$, where r_{5b} is the branching ratio for the channel R5b, and the rationale behind this expression (see also the response to the other comment regarding line 26 on page 6, see below):

“As each HO₂ radical consumes rapidly one CH₃O₂ species on the time scale of the reaction R5, the CH₃O₂ decay is described by second order kinetics, with $k_{\text{obs}} = k_5(1 + r_{5b})$, where r_{5b} is the branching ratio for the channel R5b. By using the IUPAC recommendations (Atkinson et al., 2006): $k_5 = (3.5 \pm 1.0) \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ and $r_{5b} = 0.37 \pm 0.06$, a value of $4.8 \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ is obtained for k_{obs} .

Modelling of the decay process with a variety of CH₃O₂ and HO₂ concentrations after the lamps were switched off and following the establishment of steady state conditions showed that Eq. (3) was valid within experimental error. With $k_5 = 3.5 \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Atkinson et al., 2006), a faster observed rate constant (defined by Eq. (3)) was obtained from the model with a value, $4.9 \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ consistent with that recommended by IUPAC, $(4.8 \pm 0.6) \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (1σ uncertainty; Atkinson et al., 2006). Substituting ...”

Details of the experiments which investigated the potential impact of the HO₂ wall loss on the value of k_{obs} are included in the response to the comment regarding line 12 on page 7 and described in a paragraph added above Fig. 1, and included in the same response (*vide infra*).

Regarding the three conditions for the intercomparison: why were these selected? Would it have made sense to perform experiments in air at a variety of pressures (say five) between 100 and 1000 mbar? It is not apparent why helium/oxygen mixtures were used. Suggest adding some more discussion of the reasoning for the selection of chamber conditions for the intercomparisons.

The pressure of 1000 mbar of synthetic air was chosen to perform measurements under atmospheric conditions. To the best of our knowledge this is the first study of the CH₃O₂ absorption feature centred around 7488 cm⁻¹ at a relatively high pressure. The previous studies were performed at reduced pressures, in the range ~30 – 200 mbar (see the introduction of the main text). In order to enable comparison with the reported studies of the CH₃O₂ spectrum and also test the performance of both instruments (FAGE and CRDS) at reduced pressure part of the experiments were performed at 100 mbar of synthetic air. The pressure of 80 mbar He/O₂ mixture was chosen as the most recent reported CH₃O₂ absorption spectrum (Faragó et al. 2013) was obtained at reduced pressures (70 and 133 mbar) of He/O₂ mixtures. The text

describes all the conditions used previously in the studies of the CH₃O₂ absorption spectrum, so already provides some reasoning for why these conditions were chosen.

Clearly, analytical techniques for methylperoxy radicals are going to be useful in application to reactions of these radicals, such as R5 and R12. This paper states that studies of R5 kinetics will be reported in another paper. The authors may wish to consider publishing the other paper first, since such results could have direct bearing on the results of this paper.

The purpose of the present study is to provide a validation of the LIF method for CH₃O₂ measurements. As mentioned by the referee, even if the value of $\sigma_{\text{CH}_3\text{O}_2}$ does rely on the kinetics of the CH₃O₂ self-reaction, the $\sigma_{\text{CH}_3\text{O}_2}$ value obtained does not affect the results of the FAGE – CRDS intercomparison (as the same value for k_{obs} is used for both) and, hence the validation of the FAGE method. We would like to publish the present results first, which provide a validation of the newly LIF method for CH₃O₂ before reporting kinetic studies of CH₃O₂ reactions employing the method. A detailed paper describing extensive studies of kinetics of the CH₃O₂ self-reaction over a range of temperatures is in preparation. This publication will enable to scale the value of $\sigma_{\text{CH}_3\text{O}_2}$ based on any change value of k_{obs} for the CH₃O₂ self-reaction, as noted by the referee in the general comments (see above). The current paper is written to be consistent with the detailed kinetics paper to follow. We also mention that referee 2 notes this comment by referee 1, but did not feel that the kinetics paper needed to be published first.

Specific comments

Page 4, line 24, 31-33. Very high concentrations of chlorine, methane and acetone were used in these experiments. Have you verified that these high amounts do not affect the performance of the instruments through interferences or artifacts? If so, suggest adding a discussion of the tests that were performed.

We respond on this comment first for the CRDS instrument, then for the FAGE instrument.

CRDS instrument

The concentrations of the reagents were chosen to generate a range of CH₃O₂ concentrations above the detection limit of CRDS at each pressure (Table 2, page 14 in the main manuscript). The molecular chlorine delivery did not result in a change in the ring-down time. However, the methane and acetone delivery led to a decrease in the ring down time due to their absorbance in the range ~7486–7491 cm⁻¹ used in the CRDS measurements. The absorption coefficient of acetone in a typical concentration of $\sim 9 \times 10^{14}$ molecule cm⁻³ was measured in the absence of CH₃O₂ (before to turn the HIRAC lamps on to generate CH₃O₂) to obtain a value of $\sim 8 \times 10^{-9}$ cm⁻¹ at 7487.98 cm⁻¹. Similar measurements, in the absence CH₃O₂ were performed to determine the CH₄ absorption coefficient, α_{CH_4} . For the typical concentrations of CH₄, in the range of $(1.2\text{--}2.5) \times 10^{16}$ molecule cm⁻³, $\alpha_{\text{CH}_4, 7487.98 \text{ cm}^{-1}} \approx (0.7\text{--}1.4) \times 10^{-8}$ cm⁻¹. The absorption of acetone and methane in the background of the CRDS measurements of CH₃O₂ was taken into account in the determination of the [CH₃O₂]_{CRDS}. We have modified the wording in the MS as described in the paragraph below, added after line 10, page 10:

“The molecular chlorine delivery did not result in a change in the measured ring-down time. However, the delivery of the methane and acetone reagents led to a decrease in the ring-down time indicating that, in the concentrations delivered to the chamber, methane and acetone absorbed in the wavenumber range used in the present work, $\sim 7486\text{--}7491\text{ cm}^{-1}$. An absorption coefficient of $\sim 8 \times 10^{-9}\text{ cm}^{-1}$ was measured for [acetone] $\approx 9 \times 10^{14}\text{ molecule cm}^{-3}$ at the typical measurement point of 7487.98 cm^{-1} (*vide infra*). An absorption coefficient in the range $(0.7\text{--}1.4) \times 10^{-8}\text{ cm}^{-1}$ was determined at 7487.98 cm^{-1} for CH_4 in typical concentrations in the FAGE–CRDS intercomparison experiments in the range $(1.2\text{--}2.5) \times 10^{16}\text{ molecule cm}^{-3}$. The background ring-down time τ_0 (Eq. 7) contained the contributions of the reagents, methane or acetone, and was monitored regularly during the experiments by turning off the chamber lamps (*vide supra*).”

FAGE instrument

The concentrations of the reagents were a few orders of magnitude smaller in the fluorescence detection cell than in the HIRAC chamber as the gas mixture was sampled into the FAGE instrument through a 1.0 mm diameter pinhole nozzle resulting in the pressure in the FAGE detection cell being a few orders of magnitude lower than the pressure in HIRAC. The concentrations of the reagents were changed with no discernible change in the FAGE sensitivity factor – this is now mentioned in the text, see below.

The lines 39- 40, page 4 in Sect 2.2 were changed to ...:

“...The interior of the tube is held at a low pressure (3.3 mbar for a HIRAC pressure, p_{HIRAC} of 1000 mbar of synthetic air and 0.9 mbar for $p_{\text{HIRAC}} = 100$ mbar synthetic air and $p_{\text{HIRAC}} = 80$ mbar mixture of $\text{He}:\text{O}_2 = 3:1$) and...”

The investigations described below showed that there was no effect of the concentrations of the reagents (Cl_2 , methane and acetone) on the sensitivity factor of FAGE.

The following text was added after line 17, page 8 in the section 2.2.2:

“As the pressure in the FAGE detection cell was 2-3 orders of magnitude lower than the corresponding pressure in HIRAC (*vide supra* in Sect. 2.2) the concentrations of the reagents (Cl_2 , methane and acetone) were also 2-3 orders of magnitude lower in the fluorescence cells than the reagent concentrations in HIRAC. However, a potential effect of the reagents (Cl_2 , methane and acetone) on the FAGE sensitivity factor in the HIRAC experiments was investigated. Two different concentrations of CH_4 were used in the kinetic method for FAGE calibration at 80 mbar of $\text{He} + \text{O}_2$ in HIRAC to find practically the same sensitivity factor: $(3.80 \pm 0.50) \times 10^{-9}\text{ counts cm}^3\text{ molecule}^{-1}\text{ s}^{-1}\text{ mW}^{-1}$ for $2.5 \times 10^{16}\text{ molecule cm}^{-3}$ CH_4 ($2.8 \times 10^{14}\text{ molecule cm}^{-3}$ in the fluorescence cell) and $(3.86 \pm 0.50) \times 10^{-9}\text{ counts cm}^3\text{ molecule}^{-1}\text{ s}^{-1}\text{ mW}^{-1}$ for $2.5 \times 10^{17}\text{ molecule cm}^{-3}$ CH_4 ($2.8 \times 10^{15}\text{ molecule cm}^{-3}$ in the fluorescence cell).

As shown in Fig. S1 in the Supplement there is a good agreement between the laser excitation scans of CH_3O obtained from the CH_3O_2 generated in HIRAC using the two methods: acetone photolysis and Cl_2 photolysis in the presence of CH_4 and O_2 . In addition, a good agreement has been previously found between the laser excitation spectra of CH_3O generated using the reaction of CH_4 with OH (generated by the 254 nm photolysis of water) in the presence of O_2 and directly, through the 254 nm photolysis of CH_3OH . Therefore, no effect of the used reagents on the laser excitation spectrum of CH_3O was found.”

Page 4, line 38 to page 5, line 5. Suggest giving the transit times in addition to the distances in describing the sample moving through the FAGE.

Line 41, page 4: The value given for the flow rate of the gas sampled through the FAGE pinhole was corrected:

“...on one end of the tube at a rate of ~3 SLM.”

A sentence was added in the line 4 at page 5:

“... CH₃O₂ measurements detailed here. The CH₃O₂ radicals sampled through the FAGE pinhole at 1000 mbar in HIRAC reached the detection region in about 85 ms.”

Page 5, line 11-12. Suggest giving units for C_{CH3O2} and S_{CH3O2} factors.

The units were included in the text.

Page 6, equations 3, 4, and 5. Suggest using Δt instead of t in these equations.

t was changed to Δt in the equations.

Page 6, line 26. Suggest rewording “...does not stop the decay analysis...” and page 6, lines 30-34. Suggest rewording (mentioned earlier) this discussion.

Lines 26-33 on page 6 were reworded:

“As each HO₂ radical consumes rapidly one CH₃O₂ species on the time scale of the reaction R5, the CH₃O₂ decay is described by second order kinetics, with $k_{\text{obs}} = k_5(1 + r_{5b})$, where r_{5b} is the branching ratio for the channel R5b. By using the IUPAC recommendations (Atkinson et al., 2006): $k_5 = (3.5 \pm 1.0) \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ and $r_{5b} = 0.37 \pm 0.06$, a value of $4.8 \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ is obtained for k_{obs} .”

Modelling of the decay process with a variety of CH₃O₂ and HO₂ concentrations after the lamps were switched off and following the establishment of steady state conditions showed that Eq. (3) was valid within experimental error. With $k_5 = 3.5 \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Atkinson et al., 2006), a faster observed rate constant (defined by Eq. (3)) was obtained from the model with a value, $4.9 \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ consistent with that recommended by IUPAC, $(4.8 \pm 0.6) \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (1σ uncertainty; Atkinson et al., 2006). Substituting ...”

Page 7, lines 1 and 3. Suggest adding discussion of the fitting procedure used in this paper, both for the radical signal decays and the instrument comparisons.

The fitting algorithm was included in line 2, page 7: “which is then used to fit to the experimental data with k_{obs} fixed to the value recommended by IUPAC for 298 K, $4.8 \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$, using the Levenberg-Marquardt algorithm.”

Lines 20-22, page 7 (caption of figure 1): The value given for $C_{\text{CH}_3\text{O}_2}$ was corrected and the used fitting algorithm was included: “The data were fitted to Eq. (5) (excluding the wall loss rate, k_{loss} ; red line) and Eq. (6) (including k_{loss} ; blue dashed line) using the Levenberg-Marquardt algorithm. The obtained value for the sensitivity factor was the same by both fits: $C_{\text{CH}_3\text{O}_2} = (1.17 \pm 0.04) \times 10^{-9} \text{ counts cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ mW}^{-1}$.”

The discussion of the fitting procedure used in the FAGE-CRDS correlation plots was added to the text (*vide infra*).

Page 7, line 12. It is stated that “...wall losses are very small and can be neglected.” Suggest adding an upper limit for the wall loss of CH₃O₂ and for HO₂ (since this bears on the decay of CH₃O₂).

The upper limit for the wall loss rate coefficient of CH₃O₂ was added (lines 11-12 on page7): “... the small values extracted for k_{loss} (upper limit of $\sim 1 \times 10^{-5} \text{ s}^{-1}$) fitting Eq. (6) demonstrates that wall losses can be neglected.”

A paragraph regarding investigations into a potential impact of the wall loss of HO₂ on the analysis was added above figure 1:

“Modelling the CH₃O₂ decays including a wall loss for HO₂ in the range of measured values 0.03 – 0.09 s⁻¹ (Onel et al. 2017a in the MS), showed an minor impact of the wall loss of HO₂ on k_{obs} , i.e. k_{obs} within 98 – 95 % agreement with the IUPAC preferred value, $(4.8 \pm 0.6) \times 10^{13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (1σ uncertainty; Atkinson et al., 2006).”

Page 7, line 21-22. It appears that the exponent for the sensitivity should be “-9” rather than “-10” as shown.

The power was changed to “-9”.

Page 8, line 9. Suggest “...S2 and S3, respectively.”

A comma was added after S3.

Page 8, line 30. Does the large amount of ozone affect the instrument performance?

No effect of O₃ on the instrument was encountered. Note that due to the lower pressure in the FAGE detection cell (3.3 mbar) compared to the pressure in the chamber (1000 mbar) in these experiments $[\text{O}_3]_{\text{FAGE}} = 8.3 \times 10^{10} \text{ molecule cm}^{-3}$ for $[\text{O}_3]_{\text{HIRAC}} = 2.5 \times 10^{13} \text{ molecule cm}^{-3}$.

Page 10, line 14. Is it not possible to keep the radical concentration stable for more than 5 minutes? Perhaps this sentence needs rewording.

The result was revised and the time was changed from 5 min to 10 min.

Page 10, line 35. Suggest rewording “...potential small difference in wavelength compared to λ in the spectrum...”. The meaning is not clear as written.

Due to the difference in the resolution of the two CH₃O₂ spectra – the spectrum obtained in this work and the spectrum reported by Faragó et al. (2013) – it is difficult to realise if there are any slight shifts of the spectrum found by Faragó et al. (2013) relative to the spectrum reported in this study.

Therefore the words “potential small difference in wavelength compared to λ in the spectrum” on line 35, page 10 were removed and therefore, the lines 33 – 35, page 10 are changed to: “The peaks at the top of the spectral feature reported by Faragó et al. (2013) are not reproduced in this work owing to the method of generating the spectrum, which did not allow for a high spectral resolution (Sect. 2.3). Previously Pushkarsky et al. (2000)...”

Page 12, line 28. It is not clear where the term “Allan-Werle deviation plots” originated. As this reviewer understands it, the original term was Allan variance, which was extended to include Peter Werle’s name after his contribution of suggesting its use in analysis of tunable diode laser spectroscopy performance. After his death, it was suggested that the term be changed to Allan-Werle variance. Suggest this term be used here.

The term “Allan-Werle deviation plots” was changed to “plots of the square root of the Allan-Werle variance”, as suggested by the referee. Therefore, the following lines were changed to the text shown below:

- line 28, page 12: “... using plots of the square root of the Allan-Werle variance (Werle et al., 1993; Onel et al., 2017a)...”
- lines 2-3, page 13: “The square root of the Allan-Werle variance, $\sigma_A(n)$, gives an estimate of the error...”
- line 9, page 13 (in the caption of Fig. 5): “...An example of the square root of the Allan-Werle variance of the absorption coefficient at 7488 cm⁻¹, $\sigma_A(n)$ as a function of the number of ring-down events averaged, n obtained in the absence of CH₃O₂ and in the presence of a typical acetone concentration of 8.8×10^{14} molecule cm⁻³ at 1000 mbar.” Now the fig. 5 label reads “ $\sigma_A(n)/\text{cm}^{-1}$ ” instead of “Allan-Werle deviation $\sigma_A(n)/\text{cm}^{-1}$ ”.
- line 18, page 13 was changed to: “...Therefore, separate plots of $\sigma_A(n)$ were constructed...”
- line 2, page 14 (Table 2 title) was changed to: “...from the plots of $\sigma_A(n)$ (Fig. 5 shows an example), ...”

Page 13, line 7. Suggest adding some explanation why the acquisition rate was only 6.5 Hz. Is it not possible to have 1000 or more ring-down events per second? Perhaps give typical ring-down times. This is mentioned on page 14, line 20. Perhaps indicate how much the frequency could be increased.

The suggested explanation was added to the text. Lines 20-21 on page 14, so the original text: “The CRDS sensitivity could be further improved by increasing the frequency of the ring-down events and using a cavity length above the current 1.4 m length.”

were replaced with:

“The relatively long ring-down times achieved here require the lasers to be blocked for several ms during which the full exponential ring-down is measured. This imposes an upper limit to the ring-down rate. The achieved rate is significantly smaller (6.5 Hz on average) for the following reasons. The width of the resonances of the optical cavity is of the order of 1 kHz, much narrower than the laser linewidth. This makes the injection of light into the cavity inefficient. Reducing the laser linewidth, e.g. with optical feedback techniques, could significantly increase the injection efficiency and the ring-down rate. Moreover, the resonance frequencies jitter and drift due to the unavoidable vibrations associated with the operation of the HIRAC chamber. The cavity length was actively modulated in order to repeatedly force coincidence of laser and resonance frequency. Due to the poor injection efficiency mentioned above, however, not every coincidence resulted in a ring-down event. Furthermore, a significant fraction of the ring-down events has to be discarded because of the passage of dust particles, moved around by the fans within the chamber, through the cavity axis.

The CRDS sensitivity could be further improved by mounting the cavity mirrors along the HIRAC length, which would result in a cavity of about 2 m length containing CH₃O₂ radicals, and, hence above the current 1.4 m length...”

Page 13, line 15. Could additional optical filters be added to minimize the impact of the 254 nm photolysis radiation?

The below sentence was added at the beginning of the paragraph above the section 3.4 (page 14):

“The use of an additional optical filter to cut-off the 254 nm light from the background of the CRDS measurements is expected to improve the CRDS sensitivity if the 254 nm lamps are used in HIRAC. The CRDS sensitivity could be further improved...”

Page 15, lines 9 and 11. While “gradient” to describe the slope of a linear fit is technically correct, usually the term “slope” is used.

As linear fits were used in the correlation plots the word “gradient” is adequate and was not changed to “slope”.

Page 15, line 25. Suggest “...and hence calibration of the CRDS...”.

“...and hence calibrate of the CRDS method...” was changed to “...hence calibrate the CRDS method...”

Page 15, line 26. Suggest “...and the intercomparison is not affect by error in the rate coefficient...”.

“...and the intercomparison is not subject to any error in the rate coefficient...” was changed to “...and the intercomparison is not affected by any error in the rate coefficient...”

Page 16, Figure 6(a). The decay of the CRDS and FAGE signals do not show the same temporal behavior. It appears there is a low pass filtering of the CRDS signals. Suggest discussing this. “Linear fit” and “orthogonal distance algorithm” are mentioned in the caption. This should be discussed in the text, with appropriate references. Also include information how the fit errors were determined. In the caption suggest “Each point is a value averaged over 3 seconds.” Same suggestion for captions of Figure 7 and 8.

Regarding the comment on Figure 6(a): “The decay of the CRDS and FAGE signals do not show the same temporal behaviour.”:

The temporal changes in the concentration of CH_3O_2 measured by CRDS and FAGE are in good agreement under all the used conditions, as described in the manuscript. There are only slight discrepancies at longer decay times, which are more evident at reduced pressure (80 mbar of He + O_2 , Figure 6(a) and 100 mbar of air, Figure 7(a)) than at 1000 mbar of air (Figure 8(a)). In Figures 6(a) and 7(a) the FAGE measurements are levelling down due to the second order kinetics going to a constant value, $[\text{CH}_3\text{O}_2] = 0$ whereas $[\text{CH}_3\text{O}_2]_{\text{CRDS}}$ 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. 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.

Regarding “It appears there is a low pass filtering of the CRDS signals”:

The reviewer is right and now the following paragraph was added in line 2, page 10:

“...to extract the ring-down time, τ . Filters were applied to process the ring-down events to exclude potential outliers caused by dust particles passing through the beam and false positives (when the acquisition is triggered by a transient noise spike), so that only legitimate ring-down events are taken into account.”

A paragraph was added in Sect. 3.4 (see the answer to the next question of the referee 1).

Regarding “Linear fit and orthogonal distance algorithm are mentioned in the caption. This should be discussed in the text, with appropriate references. Also include information how the fit errors were determined”:

A sentence was added in the line 9, page 15:

“...respectively. The data in the correlation plots of the CH_3O_2 concentrations determined by FAGE (y-axis) and CRDS (x-axis) ((Figs. 6b, 7b and 8b) were fitted using an orthogonal distance linear regression fit (Boggs et al., 1987), which accounts for errors in both the y- and x-directions. The gradient of the correlation plot at 80 mbar of He + O_2 (Fig. 6b)...”

Captions of figures 6, 7 and 8: “Each point is an averaged value over...” were changed to: “Each point is a value averaged over ...” as suggested by the referee.

Page 16-17, Figures 6, 7, and 8. The 80 mbar data are averaged for 3 seconds, while the 100 mbar and 1000 mbar data are averaged for 5 seconds. Suggest discussing the logic for selecting various averaging times in the text. For the intercomparison, would it not be better to average for 1 minute or more, and generate different radical concentrations by adjusting the concentrations of precursors and/or the lamp intensity, rather than use the decays to achieve different concentrations? Suggest discussing the logic of the experimental design in the body of the document.

As explained in lines 2–4, page 15 of the MS, the comparison data were generated: (a) by delivering various concentrations of the reagents (as suggested by the referee above, so this was already done) to achieve different $[\text{CH}_3\text{O}_2]$ that decreased slowly in time due to the reagent consumption and (b) by turning off the HIRAC lamps to get a rapid decay of $[\text{CH}_3\text{O}_2]$ in time. This way the LIF method was tested in comparison with the CRDS method by monitoring both slow and rapid changes of CH_3O_2 concentrations and a wide range of $[\text{CH}_3\text{O}_2]$ was covered (see main manuscript). Lines 2–4, page 15 clearly explain how $[\text{CH}_3\text{O}_2]$ were generated in the comparison experiments and, hence we feel that no additional text describing this procedure is needed.

The intercomparison data were averaged over several seconds to get enough points in the rapid part of the CH_3O_2 kinetic decay. In order to not alter the level of noise of the data generated with the lamps on compared to the noise level of the data where the lamps were off, the same averaging time was used for all the duration of an intercomparison measurement (both periods with the lamps on and with the lamps off as shown in Figs 6a, 7a and 8a).

The paragraph below was added after line 37, page 14 to address the referee’s comment regarding the difference in averaging times of the data: 3s (Fig.6) and 5 s (Figs 7 and 8).

“As the acquisition rate of CRDS (6.5 Hz in average) differed compared to the FAGE acquisition rate (in the range 1–10 Hz) the comparison data were averaged to enable comparison of $[\text{CH}_3\text{O}_2]$ by the two instruments at the same moments of time. The averaging interval of time was chosen in the range 3–5 s depending on the comparison measurement to average at least 10 ring-down events over each time interval as the CRDS data were filtered to exclude outliers caused by dust particles passing through the light beam trapped in the optical cavity and the number of encountered ‘dust events’ varied from one experiment to another.”

Page 17, Figure 8 caption. Suggest “The measurements by FAGE are shown in red and the measurements by CRDS are plotted in black.”

The sentence clearly refers to the comparison measurement in Fig. 8(a). As in Fig. 8(a) it is shown only one measurement there is no need to change the sentence:

“The measurement by FAGE is shown in red and the measurement by CRDS is plotted in black.”

Page 17, line 33. Suggest “...FAGE detection cell (from 3.3 to 0.9 mbar when sampling from a pressure of 1000 mbar.” It is not clear why three pressures are listed, or what the “respectively” refers back to. Suggest reworking this last sentence.

Lines 33–34, page 17 were reworded:

“...in the FAGE detection cell (from 3.3 mbar, corresponding to a total HIRAC pressure of 1000, to 0.9 mbar, corresponding to a total chamber pressure of 100 or 80 mbar).”

Page 18-19. For future reference, it is much easier for readers if the references are formatted as “hanging” paragraphs.

We thank to the referee for the suggestion for future publications. We would like to note that the present format of the list of the references followed the journal instructions. It is expected that during any typesetting of the MS that indenting of paragraphs as suggested by the referee will be implemented.