Author response to anonymous referee #3 on "A new method for atmospheric detection of the CH_3O_2 radical" by L. Onel et al.

Note: The changes in the manuscript addressing the comments of the referee #3 are highlighted in yellow below. The authors refer to the line numbers in the manuscript before revision mentioned in the comments.

The authors would like to thank anonymous referee #3 for their valuable comments to this manuscript.

Page 4 line 30 and Page 6 Figures 2 and 3*: As with detection of OH by the LIF FAGE technique, the authors must tune the laser on and off of the CH3O transition to determine the net signal due to CH3O fluorescence and the background signal due to laser scatter and other broadband fluorescence. OH LIF-FAGE instruments use a reference cell that generates high concentration of OH radicals to ensure that the laser is tuned to the correct frequency. It is unclear how the authors know that the laser is tuned to the correct CH3O excitation wavelength. Do they use a spectrometer to measure the wavelength, or do they have a reference cell that generates CH3O radicals?*

The signals were large enough that during conditions where CH_3O_2 concentrations were constant (e.g. in calibrations or during HIRAC experiments where steady-state concentrations were generated) it was established that the laser-wavelength was stable over a long period once the laser wavelength had been tuned to the CH_3O transition. Hence, the online wavelength position for CH_3O fluorescence detection was found without using a reference cell. The laser excitation scans shown in Figures 2 and 3 were performed using the flow tube method described in the sections 2.3.1 and 2.3.2.1 to generate either CH_3O (by the CH_3OH photolysis at 185 nm) or CH_3O_2 (by the H_2O photolysis at 185 nm to generate OH followed by the reaction of the produced OH with CH_4 in the presence of O_2).

In the HIRAC experiments the concentration of CH_3O_2 radicals generated in the chamber in a steady-state with the UV lamps turned on at the beginning of each experiment using the Cl_2/CH_4/air system was used to tune the laser at the correct excitation wavelength by performing similar scans to the laser scans shown in Figure 3.

In all measurements the offline wavelength position was fixed to the value obtained by adding 2.5 nm to λ(online) as described at page 5, line 14. For field measurements in the future, when the concentrations of CH_3O_2 (and hence CH_3O after conversion) will be both lower and more variable over short timescales, a reference cell will be necessary. We are in the process of developing a reference cell.

The third paragraph on page 5 (lines 10-24) was changed for clarification:

"The signals were large enough that during conditions where CH_3O_2 concentrations were constant (e.g. in calibrations or during HIRAC experiments where steady-state concentrations were generated) it was established that the laser-wavelength was stable over a long period once the laser wavelength had been tuned to the CH_3O transition. Hence, the online wavelength position for CH_3O fluorescence detection was found without using a reference cell. Figure 2 shows the laser excitation spectrum centred at ~298 nm in the υ_3 vibronic band recorded using an increment of $\Delta\lambda = 10^{-3}$ nm. The spectrum agrees well with previous work (Inoue et al., 1980;Kappert and Temps, 1989;Shannon et al., 2013). Figure 3 shows typical laser excitation scans performed over a narrower range of wavelengths in order to locate λ(online). The LIF spectra were obtained by using the CH_3O or CH_3O_2 radicals generated in a flow tube described in Sect. 2.3.1, with the flow tube output impinged close to the FAGE sampling inlet. The radicals were generated using the 184.9 nm light output of a Hg Pen-Ray lamp by either the photolysis of methanol in nitrogen to generate CH_3O or the photolysis of water vapour in synthetic air (to generate OH) in the presence of methane to form CH_3O_2. The CH_3O radicals were directly detected, while the CH_3O_2 radicals were first converted to CH_3O species by added NO prior to the fluorescence detection cell (Fig. 1). Similar laser scans to the scans shown in Fig. 3 were recorded by using the CH_3O_2 radicals produced in a steady-state concentration in HIRAC using photolytic mixtures of Cl_2/CH_4/air as described in Sect. 2.3.2.2. There were no unexpected features in the laser scans recorded when FAGE sampled CH_3O_2 radicals from HIRAC, consistent with no interference being anticipated in the FAGE measurements of CH_3O as there were no other species in HIRAC absorbing at 298 nm and fluorescing at the wavelengths transmitted by the bandpass filter (average transmission > 80 % over 320 – 430 nm).

In this work the FAGE signals were large enough that during conditions where CH_3O_2 concentrations were constant (e.g. in calibrations or during HIRAC experiments where steady-state concentrations were generated) it was established that the laser wavelength was stable over a long period once λ had been tuned to the CH_3O transition. Hence, λ(online) was found without using a reference cell. We are in the process of developing a reference cell for field measurements in the future, when the concentrations of CH_3O_2 (and hence CH_3O after conversion) will be both lower and more variable over short timescales."

***Page 8 line 25**: Equation 2 assumes that the concentration of methanol is proportional to the concentration of water vapor and that any loss of methanol in their bubbler system is equal to any loss of water in their flow tube. Can the authors justify this assumption?*

Equation 2 assumes that the concentration of methanol vapour in the photolysis flow tube is equal to the concentration of water vapour in the flow tube obtained when the bubbler contained water instead of methanol. The flow tube calibration using the water vapour photolysis represents the conventional FAGE calibration method for OH and HO_2 and previous investigations have shown that the water vapour loss in the system formed by the bubbler and the flow tube is negligible. Even less wall losses can be expected in the case of methanol, which has a significantly higher vapour pressure than water.

The following sentence was added after equation 2 (page 8, line 29):

"Equation 2 assumes that there were no losses of water vapour and methanol vapour by condensation in the tubing connecting the bubbler to the flow tube. This is as expected based on the small difference in temperature between the bubbler (*vide supra*) and the connecting tubing (typically held at ~ 20 ^{o}C) and as the gas going through the bubbler was diluted with the gas by-passing the bubbler."

***Page 12, line 25**: **(i)** The authors claim that reducing the pressure in their FAGE detection cell could increase the sensitivity of the instrument. Is this due to reduced quenching of the CH3O fluorescence by air? **(ii)** Have the authors measured the impact trace gases on the fluorescence efficiency, such as water vapor?*

(i) A potential improvement of the instrument sensitivity for CH_3O_2 by using a pressure in the detection cell lower than the present limit of 2.65 Torr is expected because of the experimental observation of an increase in the fluorescence signal when the pressure in the detection cell is reduced from 10.00–2.65 Torr. As the pressure is reduced there is a reduction in the CH_3O number density (which would decrease the LIF signal) and also a decrease in the quenching rate of the CH_3O fluorescence by air, and hence an increase in the fluorescence quantum yield (which would increase the LIF signal). These two effects are opposing, but at low pressures do not cancel, leading to the observed increase in signal with lower pressures. It is therefore expected that as the pressure is reduced further below 2.65 Torr that the signal would continue to increase. Another reason could be that the characteristics of the jet expansion and/or the ensuing flow to the LIF detection region change with pressure, leading to a more favourable transmission of radicals to the detection region, but it is difficult to test this experimentally. For clarification the text (page 12, lines 24 – 27) was modified as follows:

"The present investigations into the change of sensitivity with pressure in the range from 2.65–10.00 Torr found that 2.65 Torr is the optimum value in this pressure interval. The result suggests that, by reducing the pressure in the above range of values, the decrease in fluorescence due to the reduction in the CH_3O number density was overcome by the increase in the fluorescence quantum yield due to a lower fluorescence quenching rate. Another reason could be that the characteristics of the jet expansion and/or the ensuing flow to the LIF detection region change with pressure, leading to a more favourable transmission of radicals to the detection region, but it is difficult to test this experimentally. Hence an additional improvement in the sensitivity might be obtained by using a lower detection cell pressure than the current value of 2.65 Torr using a more powerful pump."

(ii) No measurement of the rate coefficients of the fluorescence quenching by the traces gases has been performed in this work. However, a very good agreement was obtained between the flow tube calibrations for CH_3O_2 with two different concentrations of water vapour in the flow tube: 7.5 x 10^{16} molecule cm^{-3} or 3 x 10^{17} molecule cm^{-3} (corresponding to 2.6 x 10^{14}

molecule cm^{-3} and 1.0 x 10^{15} molecule cm^{-3}, respectively in the FAGE detection cell) as shown by Figure 6 in Sect. 2.3.2.1. The result presented in Figure 6 shows that the CH_3O fluorescence quenching rate by water is minor for the above $[H_2O]$.

Methane was also present in the FAGE chamber in concentrations of several times 10^{14} molecule cm^{-3}. Calculations using the CH_3O fluorescence quenching rate coefficient of CH_4 reported by Wantuck et al. (1987), 1.05×10^{-10} s^{-1}, and a pressure in the FAGE detection cell of 2.65 Torr show only minor decreases in the fluorescence quantum yield, by few percent, when $[CH_4]$ is increased from zero to the experimental values. Assuming a quenching rate coefficient of H_2O equal to that of CH_4, similar small decreases in the fluorescence quantum yield were computed when $[H_2O]$ was increased from zero to the concentration values used in the flow tube calibration (0.3 - 1.0 x 10^{15} molecule cm^{-3}).

A paragraph which discusses the $CH_3O(A)$ quenching rates of water and methane at the concentrations used in the flow tube calibration of the FAGE instrument for CH_3O_2 has been added at the end of the section 3.1.1:

"The calibrations using the flow-tube ("wand") method have been performed under water vapour concentrations similar to the ambient $[H_2O_{vapour}]$ but few orders of magnitude higher than those present in the HIRAC chamber experiments. In contrast with $[H_2O_{vapour}]$ the methane concentrations used in the "wand" method were similar to $[CH_4]$ present in HIRAC but higher than $[CH_4]$ in the atmosphere. However, as detailed in this paragraph, the effects of methane and water on our sensitivity are minimal. Estimations using the reported fluorescence quenching rate coefficient of $CH_3O(A)$ by CH_4, $k_{quench.CH4} = 1.05 \times 10^{-10}$ s^{-1}, (Wantuck et al., 1987) and the concentrations of CH_4 in the LIF detection cell for the calibrations using the flow-tube (1.7×10^{14} molecule cm^{-3} and 3.4×10^{14} molecule cm^{-3}, corresponding to 5.0×10^{16} molecule cm^{-3} and 1.0×10^{17} molecule cm^{-3}, respectively in the flow tube) resulted in only ~ 1–2% lower fluorescence quantum yield compared to the value determined in the absence of CH_4. No literature value has been found for the fluorescence rate coefficient of $CH_3O(A)$ fluorescence by H_2O vapour. However, even if it assumed to be as large as the above reported value for CH_4 ($k_{quench.CH4}$), only a few percent decrease in the fluorescence quantum yield is computed (compared with a water concentration of zero) for the levels of H_2O vapour which are present at the CH_3O_2 FAGE detection axis when using the flow tube calibration method. These levels (1–2 % v/v) are similar to a typical water vapour concentration in the atmosphere. A very good agreement has been obtained between the calibration factors for CH_3O_2 detection with two different concentrations of water vapour in the flow tube: 7.5×10^{16} molecule cm^{-3} or 3.0×10^{17} molecule cm^{-3} (corresponding to 2.6×10^{14} molecule cm^{-3} and 1.0×10^{15} molecule cm^{-3}, respectively in the FAGE cell) as shown in Figure 6 in Sect. 2.3.2.1. This very good agreement for H_2O vapour and the above calculations for CH_4 support the use of the flow tube method for the FAGE calibration of the CH_3O_2 concentrations."

***Page 12, line 26**: How does the OH sensitivity of the HIRAC FAGE compare to the field instrument? Assuming the CH3O sensitivity scales with the differences in the OH sensitivity, can the authors be more specific regarding the potential improvement in the LOD if this technique were to be used in the field instrument?*

The HIRAC FAGE sensitivity for OH is about two times lower than the ground-based field instrument sensitivity for OH: $C_{OH\ (HIRAC)} = 8 \times 10^{-8}$ counts cm^3 molecule^{-1} s^{-1} mW^{-1}, $C_{OH\ (field)} = 1.5 \times 10^{-7}$ counts cm^3 molecule^{-1} s^{-1} mW^{-1}.

As the distance from the inlet pinhole to the laser axis in the CH_3O_2 fluorescence cell (Figure 1, 580 mm) is considerably longer than the corresponding distance in the ground–based field fluorescence cell for OH and HO_2 detection (88 mm), improvements in the CH_3O_2 sensitivity are expected for the field FAGE instrument. The decrease in the pinhole–to–laser axis from 580 mm to 88 mm would result in a reduced loss of the CH_3O_2 radicals on the instrument internal walls and would provide a greater population in the laser probed rotational level as the gas is still cooler than ambient following the pinhole expansion. However, the increase in the CH_3O sensitivity cannot be quantified simply using the difference in the OH sensitivity between the HIRAC instrument and the field instrument. A larger increase in sensitivity between the field instrument and HIRAC would be expected for OH than for CH_3O_2 based on expected heterogeneous losses, as the wall loss of OH is larger than the wall loss of CH_3O_2. However, how much the decrease in temperature at the laser axis owing to a smaller nozzle-to-laser axis distance improves the FAGE sensitivity for CH_3O compared to the sensitivity for OH needs further investigation.

We think that no modification of the text is necessary as it cannot be assumed that improvements in the CH_3O_2 sensitivity will scale with the difference in the OH sensitivity between the HIRAC instrument and the ground-field instrument.

***Page 16, line 19**: The authors suggest that based on their flow tube calibrations that the rate constant for the CH3O2 + CH3O2 reaction may be 25% too high, perhaps due to a 25% overestimation of the CH3O2 absorption cross section. What is the uncertainty associated with the recommended rate constant? Does the rate constant derived using their flow tube calibration factor agree to within the combined uncertainty of the calibration and the rate constant?*

The associated uncertainty with the IUPAC recommended value of the rate coefficient for the CH_3O_2 self-reaction, k_{CH3O2}, is ~ 12% (1σ). Our measured value, based on the flow tube calibration factor is ~25% lower than the IUPAC recommendation, with an overall error of ~20% (1σ). Therefore, the obtained k_{CH3O2} have overlapping error limits with the IUPAC preferred value at the 1σ level.

The overall uncertainties of the two calibration methods of FAGE are discussed in detail in the manuscript. Even though the kinetic method agrees well with the flow tube method, it should be noted that the use of a lower value of k than k_{CH3O2}(IUPAC) would improve the level of agreement. Therefore, the text has not been changed.

***Page 17, Figure 8**: The authors measure the concentration of CH3O in nitrogen to reduce the loss of CH3O from the CH3O2 + O2 reaction. However, it appears that they use the calibration factor determined in air to estimate the CH3O concentrations in this experiment. Does the calibration factor change in N2 compared to air due to different fluorescence quenching rates?*

The concentration of CH_3O in the HIRAC experiment shown in Figure 8 was obtained by using the calibration factor for methoxy radicals, which in turn was determined using the photolysis of methanol in N_2 method described in section 2.3.1. In this HIRAC experiment O_2 was only present in trace amounts ($[O_2]_{HIRAC}$ = 5.4 × 10^{15} molecule cm^{-3}, which corresponds to 1.8 x 10^{13} molecule cm^{-3} O_2 in the fluorescence detection cell) as described in section 3.3. This $[O_2]$ is too small to produce a faster quenching rate of the CH_3O LIF signal in the chamber experiment compared to the quenching rate when using pure N_2, as estimated using the quenching rate coefficient of O_2 reported by Wantuck et al. (1986), 2.5 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.

The following sentence was added in the first paragraph of section 3.3 for clarification:

"The concentration of CH_3O during the experiment was computed by using the FAGE calibration factor for methoxy radicals generated from the photolysis of methanol in N_2, C_{CH3O} = (5.1 ± 2.2) ×10^{-10} counts cm^3 $molecule^{-1}$ s^{-1} mW^{-1} (Sect. 3.1.1). The temporal profile of the CH_3O is shown in Fig. 8…"