Author response to anonymous referee #2 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 #2 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 #2 for their valuable comments to this manuscript.

The first two questions (1/ and 2/) address the quenching of the CH_3O fluorescence by water vapour and methane, respectively:

1/ The sensitivity of conventional FAGE instruments is known to be dependent on the ambient water concentration due to the quenching of excited OH radicals by water molecules. This matrix effect is taken into account through the calibration of the OH sensitivity at different water-vapor concentrations. Can excited CH3O radicals also be quenched by water vapor? If so, what is the implication for ambient measurements of CH3O2?

2/ For calibration purposes, CH3O2 is generated using the water-photolysis approach by adding an excess of methane in the photolysis cell. Could the authors comment on the potential quenching of excited CH3O by methane during calibration experiments?

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}). Therefore, the effects of methane and water on the FAGE sensitivity for CH_3O_2 are minimal.

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."

Minor comments

***P4 L4**: "Here we report he first …" should read "Here we report the first …"*

The suggested correction has been made.

***P4 L13**: Please report the sampling flow rate of the FAGE apparatus*

Now the sampling flow rate is given at the beginning of section 2.1 (page 4):
"The gas was sampled with a flow rate of 3.2 slm through a 1 mm diameter pinhole…"

***P5 L4-5**: Since the detection of the CH3O fluorescence is red-shifted from the excitation, why is the counting window delayed by 100 ns from the laser pulse? This time gating approach is usually used for the detection of on-resonant fluorescence.*

The off-resonance CH_3O fluorescence occurs between ~ 300 – 400 nm and, hence a relatively broad bandpass filter, with an average transmission > 80% between 320–430 nm, was used for the fluorescence collection. However, it appears that red-shifted scattered laser light (the excitation wavelength was ~ 298 nm) produced in the FAGE chamber also passed through

the interference filter, increasing the background. In order to avoid the majority of these background counts, the gate unit was opened 100 ns after the probe light pulse. As the optimum gate-width found for the CH_3O fluorescence was 2 μs (*vide infra*), no significant loss of CH_3O signal was encountered by the 100 ns delay in the fluorescence detection. Future improvements to the instrument will improve changing the cell material or coating to reduce this scattered light background.

The second paragraph on page 5 was changed as follows:

"The relatively broad bandpass filter used for the collection of the CH_3O fluorescence (average transmission > 80% between 320–430 nm) allowed some red-shifted scattered light (presumably from the walls of the chamber) generated by the probe laser to be transmitted and hence detected by the MCP-PMT. In order to ameliorate this and reduce the background signal, the gate unit was opened 100 ns after the laser pulse to detect fluorescence integrated over a gate-width of 2 μs. The optimum gate-width of 2 μs (values in the range 1-3 μs were compared) is consistent with the CH_3O fluorescence lifetimes, calculated to be in the range of 0.9 – 1.5 μs, using the reported radiative lifetimes for CH_3O of 1.5 μs (Inoue et al., 1979), 2.2 μs (Ebata et al., 1982) and (4 ± 2) μs (Wendt and Hunziker, 1979) and using the fluorescence quenching rate coefficients of N_2 and O_2 (Wantuck et al., 1987) to calculate the rate of quenching at the pressure in the FAGE detection cell ((2.65 ± 0.05) Torr). As the fluorescence lifetime of $CH_3O(A)$ in the detection cell is 0.9–1.5 μs, delaying the counting of the fluorescence by 100 ns makes very little difference (88–91%) in the fraction of fluorescence collected."

***P5 L12-15**: The authors mention that the wavelength is tuned on/off resonance with the CH3O transition line. In FAGE instruments, OH is continuously generated in a reference cell to be able to precisely tune the laser wavelength on and off resonance. How is it performed for CH3O on this instrument? Is CH3O continuously generated in a reference cell? If so, how is it done?*

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 in the third paragraph on page 5. 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 was changed to clarify how the laser is tuned to the correct CH_3O excitation wavelength:

"…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 excitation scans for CH_3O 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."

In addition, the future construction of the reference cell is mentioned in the paragraph of section 3.1.1 where all the future instrument improvements are listed:

"The further optimizations of sensitivity and the planned construction of a reference cell to find the online wavelength position could potentially enable CH_3O_2 measurements to be made in urban environments where CH_3O_2 concentrations are estimated to be considerably lower, for example a few 10^7 molecule cm^{-3} based on modeling results (Whalley et al., to be submitted)."

***P7 L15**: The authors indicate a CH3O2-to-CH3O conversion efficiency of 40% at the optimum NO concentration. However, since CH3O can also be lost through its reaction with NO (and potentially through its reaction with O2 as well), isn't the 40% representative of a lower limit of the conversion?*

The 40% value represents the optimum CH_3O_2 to CH_3O conversion efficiency as CH_3O is rapidly formed (by the CH_3O_2 + NO reaction) and removed in the system (by the CH_3O reactions with NO and O_2), as discussed in section 2.2 (page 7). The text in section 2.2 explains that this result was obtained by comparison of the FAGE signal vs. [NO] generated by numerical simulations using a chemistry system formed by the above reactions with experimental data. Therefore, no text change has been made as the value of 40% was obtained from a simulation at the relevant conditions.

***P10 L12-13**: It is indicated that the photon flux was varied between 0-1.5E14 photon/cm2/s. However, the lower bound reported for the radical generation is 1.5E10 molecule/cm3, which cannot correspond to a photon flux set at zero. Please clarify.*

The lower limit of the photon flux was corrected:

"The concentration of CH_3O_2 was varied by changing the photon flux in the range of 0.5–1.5 × 10^{14} photon cm^{-2} s^{-1} to generate [CH_3O_2] = 1.5–4.5 × 10^{10} molecule cm^{-3}."

***P12 L9-14**: The detection limits are calculated for a BKG signal of approximately 100 ct/s, which is reported as a typical value for this instrument. What are the contributions of the scattered visible and laser lights? How is the BKG signal expected to change when the solar irradiation changes during field measurements? How will it affect the detection limit during daytime?*

The contributions to be background are roughly 50% laser scattered light within the detection cell and 50% visible light which enters the pinhole. For field measurements, there will be a contribution from solar scattered light which will scale with sunlight intensity. As for measurements of OH, the detection limit depends on the standard deviation of the background signal, and for more intense solar radiation, this will increase, increasing the detection limit. The visible scattered light is recorded on its own (together with dark counts) in a separate photon collection integration gate which is delayed a long time after the laser pulse, and is subtracted from the counts from the integration gate containing the fluorescence (after scaling for any differences in the two gate widths).

The second paragraph on page 12 was modified:

"...BKG is the background signal and had a typical value of ~100 counts s^{-1}, which represents ~50 counts s^{-1} laser scattered light within the detection cell and ~50 counts s^{-1} scattered visible light which enters the pinhole from the room with a negligible contribution (1 count s^{-1} on average) of the detector dark counts, *t* is the time per data point, *m* represents the number of online data points and *n* is the number of offline data points."

***P13 L22**: caption Fig. 7. "cm-1" should read "cm-3"*

"cm^{-1}" was changed into "cm^{-3}"

***P15 L21 & L22**: Two different uncertainties are given for the on-line signal: 12% and 6%. Which one is correct?*

The paragraph on page 15 discusses the different components of the total uncertainty: 12% uncertainty represents the 2σ error in the fluorescence signal due to the uncertainty in the online wavelength position, while the 6% uncertainty is the 2σ error of the laser power measured with the power meter. A minor change was made in the last sentence of section 3.2.1:

"…of 12 % in the online FAGE signal and 6 % uncertainty in the laser power measured by the laser power meter and used to normalize the data. The uncertainty associated with the online signal, 12 % at 2σ level, was calculated as the average deviation of the signal value due to the error limits of $\pm 5 \times 10^{-4}$ nm in the online wavelength position (see the typical laser excitation scans shown in Fig. 3)."

***P16 L39**: The authors indicate that the oxygen concentration was lowered in some experiments performed on the HIRAC chamber. Could the lower oxygen concentration lead to a different sensitivity towards CH3O due to changes in quenching rates of excited CH3O?*

Line 39 of page 16 describes the methoxy radical measurement in HIRAC (section 3.3) which is shown in Figure 8. The concentration of CH_3O in these HIRAC experiments 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 the HIRAC experiment shown in Figure 8 O_2 was only present in trace amounts ($[O_2]_{HIRAC} = 5.4 \times 10^{15}$ 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, $C_{CH3O} = (5.1 \pm 2.2) \times 10^{-10}$ 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…"