Author response to anonymous referee #2 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.

Why did the authors measure absorption at 7488 cm-1 when Fittschen(2019) report σ (v) at 7489 cm-1? Given the results in figure 3, why do the authors consider the cross sections at the two wavelengths to be equal?

The methane and acetone delivery led to a decrease in the ring down time due to their absorbance in the range from ~7486 to 7491 cm^{-1} where the CH_3O_2 spectrum was measured. The measured absorption coefficient of acetone in a typical concentration of ~9 × 10^{14} molecule cm^{-3} was practically constant, ~8 × 10^{-9} cm^{-1} from ~7486 to 7491 cm^{-1}. However, CH_4 displays a more structured absorption spectrum in the probed region. Therefore, the CH_3O_2 spectrum was mapped out as a series of point measurements at fixed wavenumbers between the CH_4 absorption lines in the range from ~7486 to 7491 cm^{-1} at 80 mbar of He + O_2 and 100 mbar of synthetic air (see lines 15-18, page 10). The wavenumber of 7487.98 cm^{-1} was chosen for the FAGE – CRDS intercomparison measurements as there "the absorption feature is sufficiently strong and furthest in wavelength from interfering methane absorption lines…" (lines 17-18, page 10).

The following text was included in line 18, page 10:

"…was determined (Sect. 3.2). The absorption coefficient of CH_4 was about 7 times lower at 7487.98 cm-1 than at 7489.16 cm^{-1}, i.e. at the peak of the CH_3O_2 spectral feature where Fittschen (2019) reported σ_{CH3O2}. Therefore, 7487.98 cm^{-1} (rounded to 7488 cm^{-1} henceforth) was chosen as the measurement point instead of the value of 7489.16 cm^{-1} used by Fittschen (2019). Each data point in Fig. 3…"

We do not consider that the value of the cross section, σ_{CH3O2} at 7487.98 cm^{-1} is equal to σ_{CH3O2} at 7489.16 cm^{-1} and the text does not state this. Lines 13 – 17, page 12 clearly explains the difference:

"To enable a comparison at 7487.98 cm-1 with the very recent measurement of Fittschen (2019), who found 2.20 × 10^{-20} cm^2 molecule^{-1} at 7489.16 cm^{-1}, σ(7487.98 cm^{-1}) = 1.49 × 10^{-20} cm^2 molecule^{-1} obtained in this work was multiplied by the σ(7489.16 cm^{-1}):σ(7487.98 cm^{-1}) ratio obtained by using the high resolution spectrum reported by Faragó et al. (2013) (Fig. 3). The obtained value, σ(7489.16 cm^{-1}) = (1.9 ± 0.3) × 10^{-20} cm^2 molecule^{-1} is in reasonable agreement with the result of Fittschen (2019), σ(7489.16 cm^{-1}) = 2.2 × 10-20 cm^2 molecule^{-1}."

Finally it would be helpful to have stated that the cross-section used is not the more standard integrated cross-section used by HITRAN and other databases.

The integrated cross-section (the ‘line strength’) is useful when absorption lines are fitted (area under the fitted curved is proportional to line strength times concentration). For measurements at one wavelength, the ‘absorption cross section’ is the more appropriate, since the absorption coefficient is the concentration times the cross section. However, in case there is any confusion for those more accustomed to HITRAN, we have added in line 16, page 11:

“…, σ(7488 cm-1). Note that the cross-section used is not the more standard integrated cross-section used by HITRAN and other spectral databases. CH_3O_2 radicals…”

The quantity, L, the length also requires further explanation. It should not refer to the 1.4 M value of the mirror separation in figure 2. (Morover, the comments on p14, line20-21 that one can improve the sensitivity by increasing the mirror separation, are incorrect.) The appropriate value of L is the effective path length of the sample, taking into account the diminishing concentration of CH3O2 near to and into the extensions that support the mirrors.

As [CH_3O_2] was practically homogeneous across the entire length of the mirror separation the effective cavity length was considered equal to the mirror separation, L = 1.4 m.

The FAGE measurements of CH_3O_2 across the HIRAC diameter (1.2 m, 86% of the value of L) described in Sect.2.2.3 in the main manuscript showed that, indeed [CH_3O_2] was practically homogeneous across the chamber diameter. Each mirror was coupled to HIRAC by a 10 cm long system of flanges (14% from L) shown in Fig. 2 in the main manuscript. Our previous publication (Onel et al. 2017a in the manuscript references), reporting CRDS measurements of HO_2 performed across the HIRAC width using the same coupling system of the cavity mirrors to the chamber as in the present work, investigated the potential impact of [HO_2] = 0 over the two 10 cm distances between the mirrors and HIRAC. In this ‘worst case scenario’ the analysis found that the value for the cross section of HO_2 agrees within 84% with the value found by considering [HO_2] homogeneous along the entire L. We expect that the decrease in radical concentration in the proximity of the mirrors is less significant for CH_3O_2 than for HO_2 as the wall-loss for CH_3O_2 (upper limit of ~10^{-5} s^{-1}) is significantly lower than the wall-loss for HO_2 (0.3-0.9 s^{-1}). Therefore, the expected very small decrease in [CH_3O_2] over 14% of L in our experiments are thought to have a negligible impact on the value of the CH_3O_2 cross-section yielded by the analysis.

Following the referee’s comment:”*Morover, the comments on p14, line20-21 that one can improve the sensitivity by increasing the mirror separation, are incorrect*”, line 21, page 14 was rephrased to clarify more its meaning:

“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 CH_3O_2 radicals, and, hence above the current 1.4 m length…”