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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)

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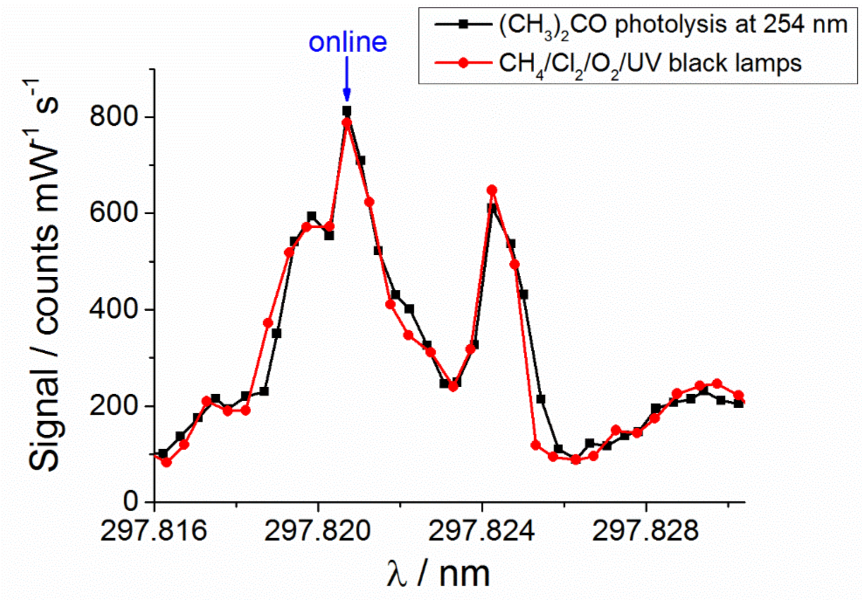

Figure S1. Typical laser excitation scans of CH$_3$O performed to find the online wavelength for the FAGE measurement, ~297.82 nm, indicated by the blue arrow. CH$_3$O radicals were generated in HIRAC using 254 nm photolysis of (CH$_3$)$_2$CO (black) and the chamber black lamps to photolyse Cl$_2$ in the presence of CH$_4$ and O$_2$ (red) at 100 mbar synthetic air to produce CH$_3$O$_2$ radicals, which were then titrated to CH$_3$O by adding NO ~25 mmm prior the CH$_3$O detection axis (see Sect. 2.2 in the main text). Fluorescence cell pressure = 0.9 Torr and the increment of the scan = 5 × 10^{-4} nm with each point corresponding to 5000 laser shots.

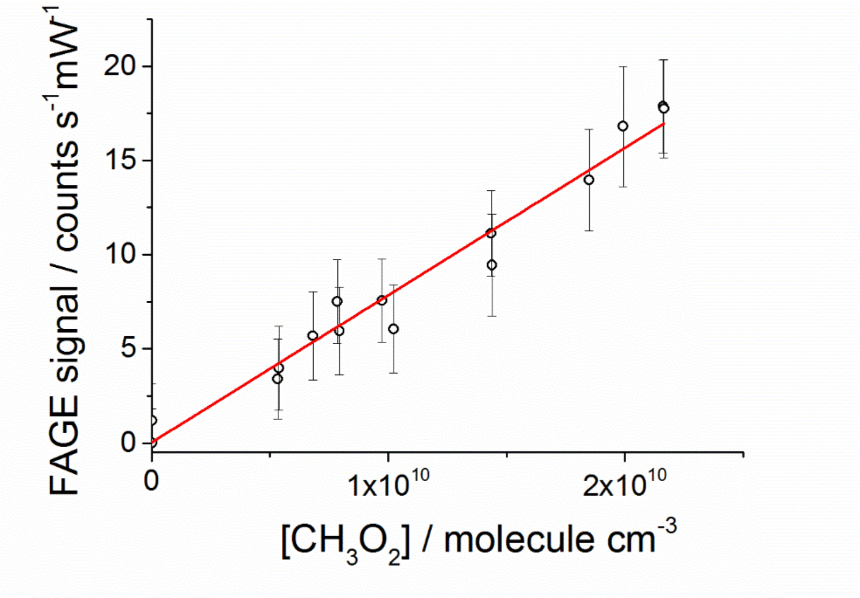

Figure S2. An example of a calibration using the indirect FAGE technique for CH_3O_2 detection using 184.9 nm photolysis of water vapour at 295 K and atmospheric pressure to generate OH radicals. CH_3O_2 radicals were generated using the reaction OH with CH_4 in the presence of O_2, in the range of ~ (0.5–2.0) × 10^{10} molecule cm^{-3} by varying the power supplied to the photolysis lamp; [CH_4] = 5.0 × 10^{16} molecule cm^{-3} and [NO] = 6.7 × 10^{13} molecule cm^{-3}. A line of best fit through these data yields a sensitivity factor C_{CH3O2} = (7.8 ± 0.4) × 10^{-10} counts cm^3 molecules^{-1} s^{-1} mW^{-1}, where the error limits are the standard error of the fit to the data. The error limits in the FAGE signal are statistical errors at the 1σ level.

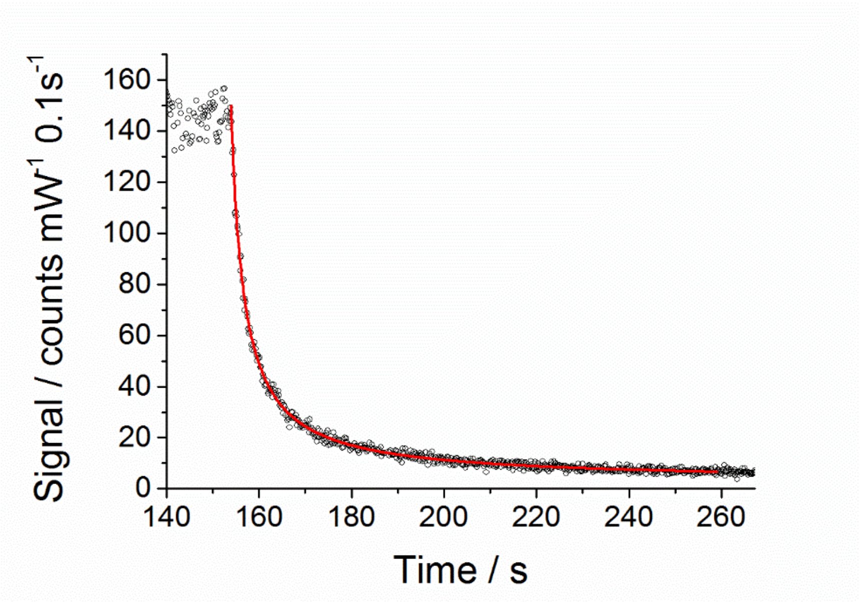

Figure S3. CH_3O_2 decay via its self-reaction measured by FAGE for the 80 mbar He:O_2 (3:1) atmosphere within HIRAC. Radicals were generated by photolysis of molecular chlorine in the presence of methane, with $[Cl_2] = 3.2 \times 10^{14}$ molecule cm^{-3} and $[CH_4] = 2.5 \times 10^{17}$ molecule cm^{-3}. The photolysis lamps were turned off at ~150 s. Fitting Eq. (5) in the main text to the data yields the sensitivity factor $C_{CH3O2} = (3.89 \pm 0.05) \times 10^{-9}$ counts cm^{3} molecules^{-1} s^{-1} mW^{-1}. The error limits are statistical errors at the 1σ level.

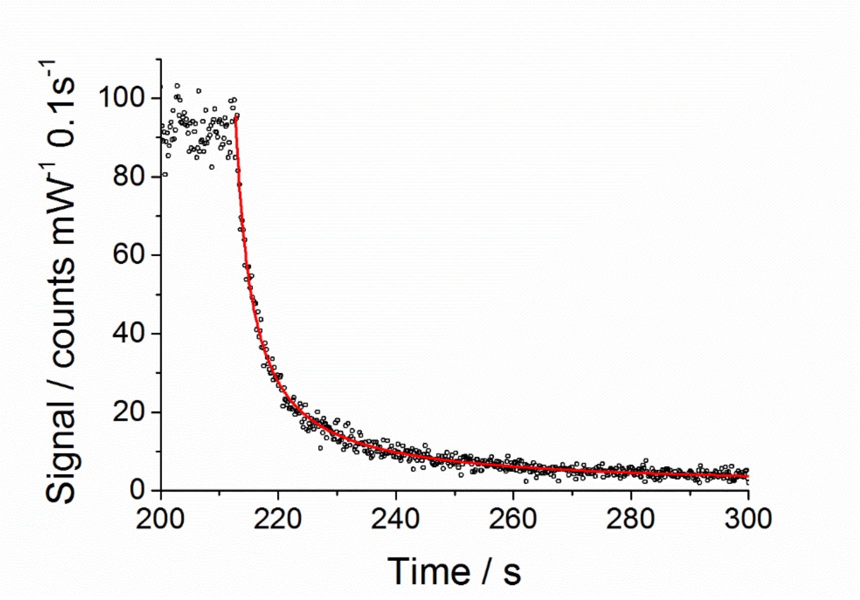

Figure S4. CH_3O_2 decay via its self-reaction measured by FAGE for the 100 mbar synthetic air atmosphere within HIRAC. Radicals were generated by photolysis of molecular chlorine in the presence of methane, with $[Cl_2] = 3.3 \times 10^{14}$ molecule cm^{-3} and $[CH_4] = 2.5 \times 10^{17}$ molecule cm^{-3}. The photolysis lamps were turned off at ~210 s. Fitting Eq. (5) in the main text to the data yields the sensitivity factor $C_{CH3O2} = (2.65 \pm 0.04) \times 10^{-9}$ counts cm^{3} molecules^{-1} s^{-1} mW^{-1}. The error limits are statistical errors at the 1σ level.

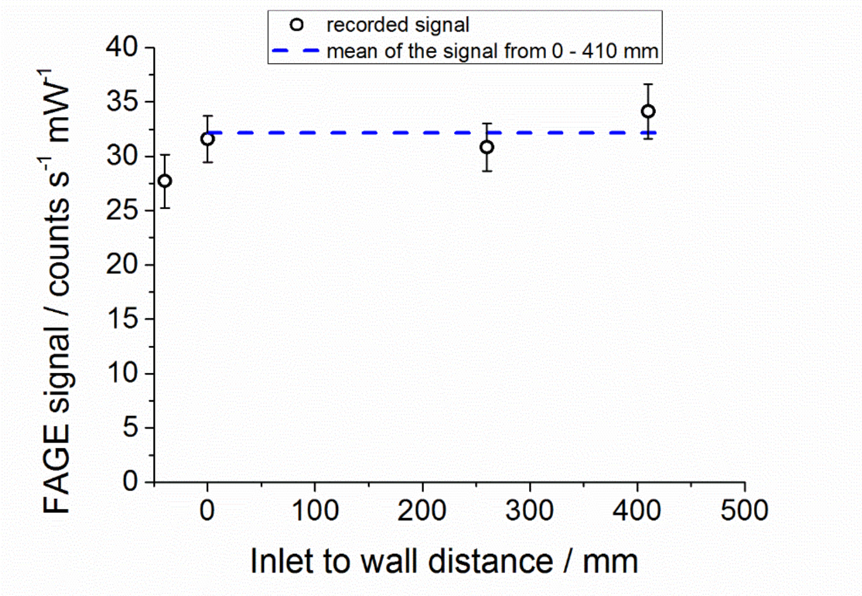

Figure S5. Measurement of the CH_3O_2 radical signal plotted against the distance the FAGE inlet protrudes from the HIRAC chamber. Each point (black circles) shows the steady-state CH_3O_2 signal averaged over 5 min for a certain position of the instrument inlet across the chamber radius. The blue line represents the mean of the signal recorded from 0 mm (inlet flush with the wall) to 410 mm inlet to internal wall distance. CH_3O_2 was generated by photolysing ozone (~2.5×10^{13} molecule cm^{-3}) in the presence of methane (2.5×10^{17} molecule cm^{-3}) at 254 nm. The FAGE instrument couples to the chamber through a flange mounted on the outside, allowing the inlet to be positioned behind the chamber walls similar to the CRDS mirrors. Here (40 mm behind the wall, so – 40 mm), a 14% signal drop was observed compared to the mean of values from 0 – 410 mm.

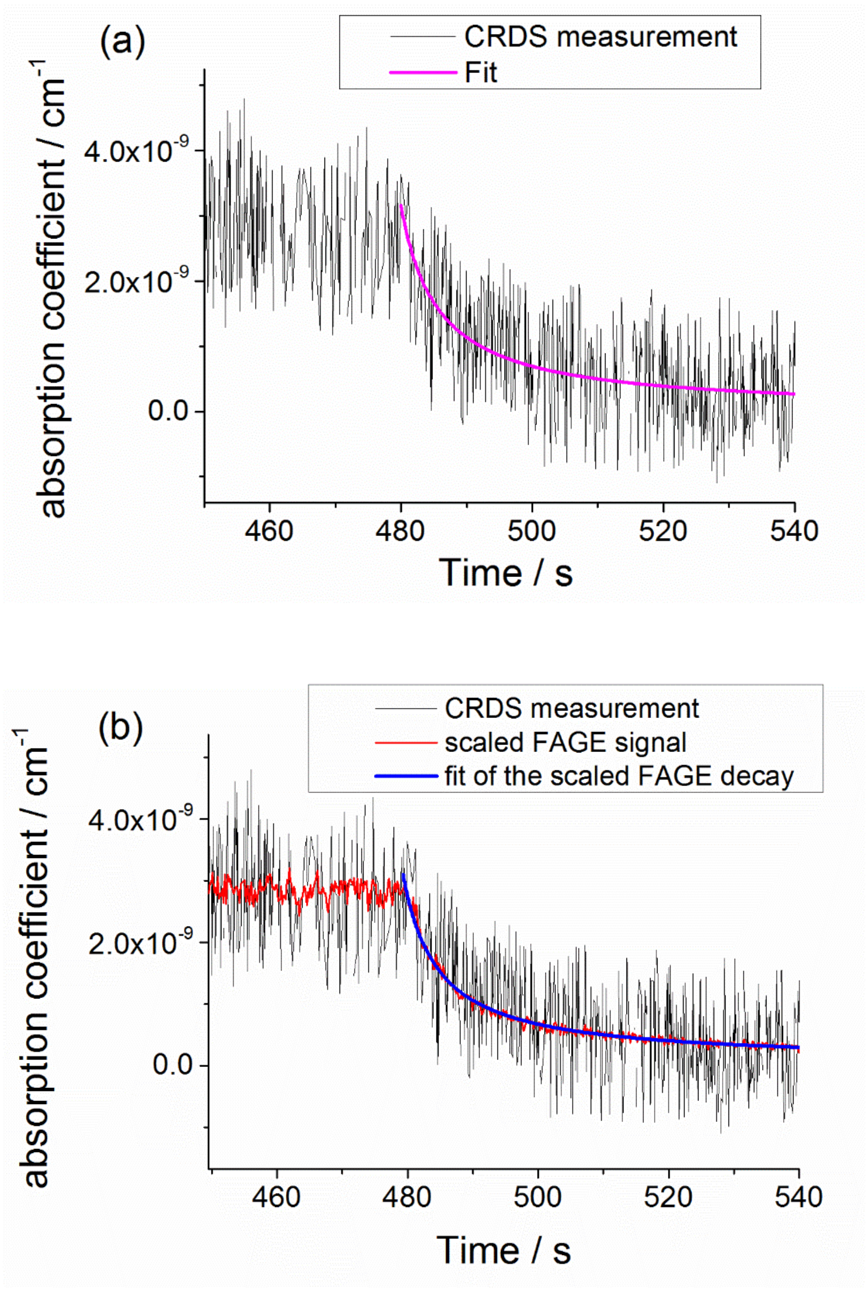

Figure S6. Second–order decay of the CH_3O_2 absorption coefficient at 7488 cm^{-1} from CRDS data (single ring-down events – black line in both panels (a) and (b)) along with the FAGE signal monitored simultaneously but scaled vertically to overlap the CRDS data (red line; panel (b)). The traces were recorded at 295 K and with a 80 mbar mixture of He:O_2 = 3:1; $[Cl_2]_0 = 1.1 \times 10^{14}$ molecule cm^{-3} and $[CH_4]_0 = 2.5 \times 10^{16}$ molecule cm^{-3}. The fit of Eq. (8) in the main text to the CRDS data (magenta line in panel (a)) resulted in $\sigma_{HO2} = (1.71 \pm 0.15) \times 10^{-20}$ cm^2 molecule^{-1} while the fit of the same equation to the scaled FAGE data (blue line; panel (b)) gave $\sigma_{HO2} = (1.55 \pm 0.02) \times 10^{-20}$ cm^2 molecule^{-1}. The error limits are statistical errors at the 1σ level.

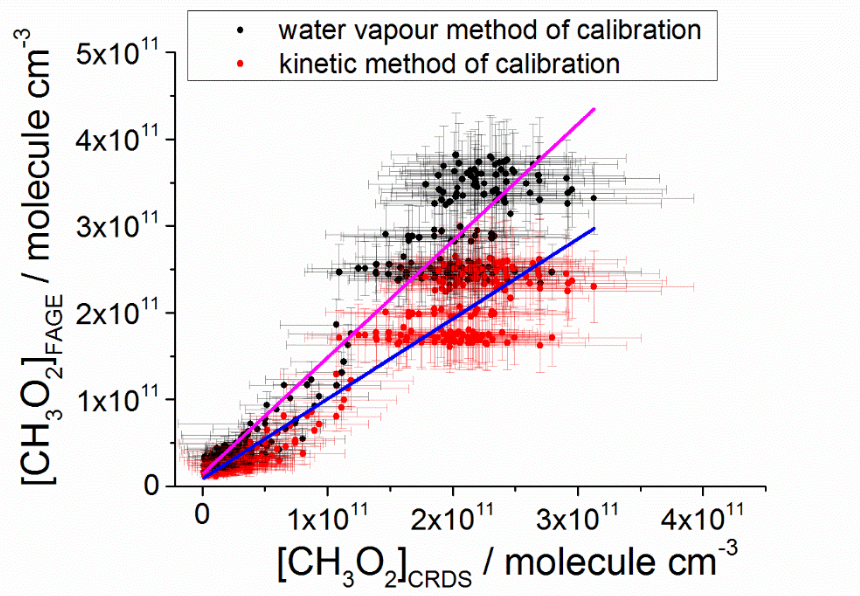

Figure S7. Correlation plots of the data generated by using FAGE and CRDS at 1000 mbar of air. [CH_3O_2] measured by FAGE is plotted against [CH_3O_2] measured by CRDS. [CH_3O_2]$_{CRDS}$ was calculated using a cross section of 1.49×10^{-20} cm^2 molecule^{-1}. FAGE was calibrated by two methods described in the main text: the 184.9 nm photolysis of water vapour in the presence of CH_4/O_2 (black circles, $C_{CH_3O_2}$ = $(8.03 \pm 1.37) \times 10^{-10}$ counts cm^3 molecules^{-1} s^{-1} mW^{-1}) and using the second order kinetics of the CH_3O_2 temporal decay (red circles, $C_{CH_3O_2}$= $(1.16 \pm 0.15) \times 10^{-9}$ counts cm^3 molecule^{-1} s^{-1} mW^{-1}). The separate linear fits to the data obtained using the two FAGE calibration methods result in a gradient of 1.35 ± 0.07 and an intercept of $(1.4 \pm 0.3) \times 10^{10}$ molecule cm^{-3} for the data using the water vapour calibration and a gradient of 0.92 ± 0.05 and an intercept of $(8.8 \pm 2.3) \times 10^{9}$ molecule cm^{-3} for the data using the kinetic method of calibration. The linear fits were generated using the orthogonal distance regression algorithm; fit errors at 2σ level. Each point is an averaged value over 5 s.