An intercomparison of methods for HO_2 and CH_3O_2 detection and kinetic study of the HO_2 + CH_3O_2 cross-reaction in the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC)

Lavinia Onel, Alexander Brennan, Freja F. Østerstrøm, Michele Gianella, Lisa Whalley, Gus Hancock,

Paul Seakins, Grant Ritchie and Dwayne Heard

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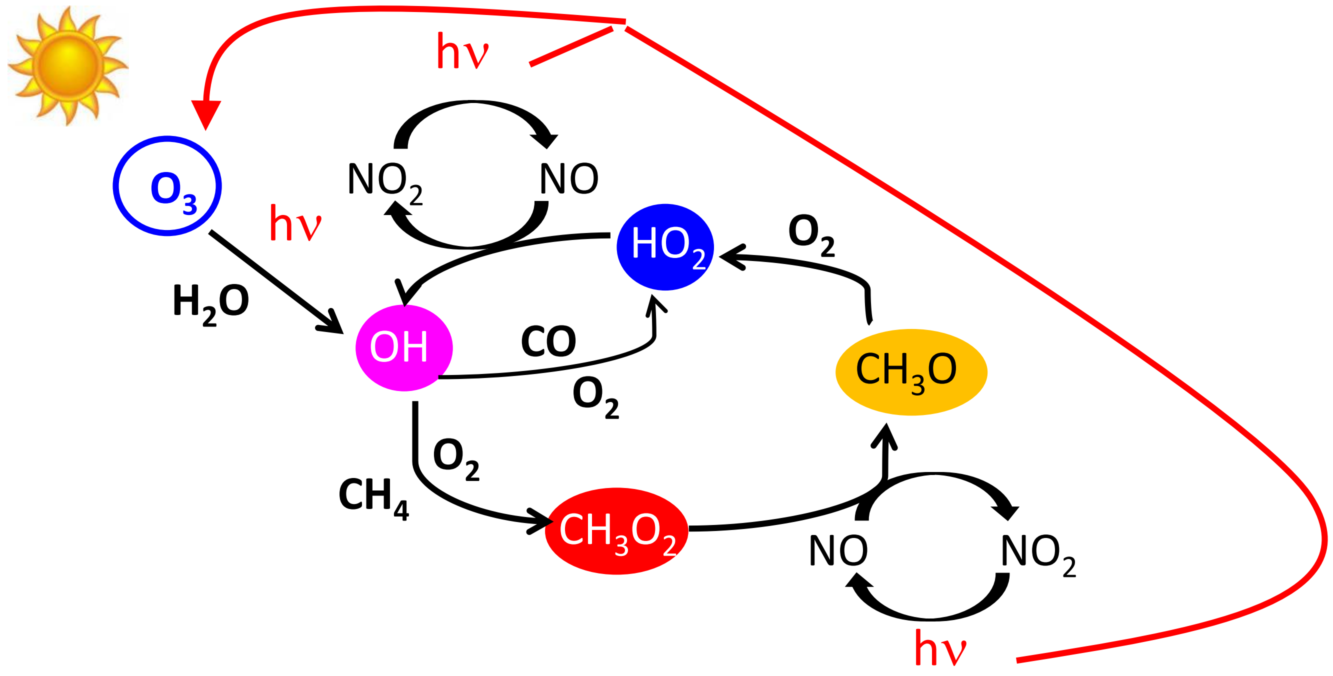
- As FAGE is an indirect method and requires calibration it has been validated performing intercomparisons of measurements of HO_2 and CH_3O_2 by FAGE and the direct and absolute Cavity Ring-Down Spectroscopy (CRDS)
- FAGE has been used in kinetic studies of the HO_2 + CH_3O_2 cross-reaction within the HIRAC chamber

HO_2 and CH_3O_2 radicals in the troposphere

- HO_2 is generated directly by the oxidation of CO and indirectly by the oxidation of VOCs
- CH_3O_2 is the most abundant RO_2 in the atmosphere
- A dominant source of CH_3O_2 is the oxidation of CH_4



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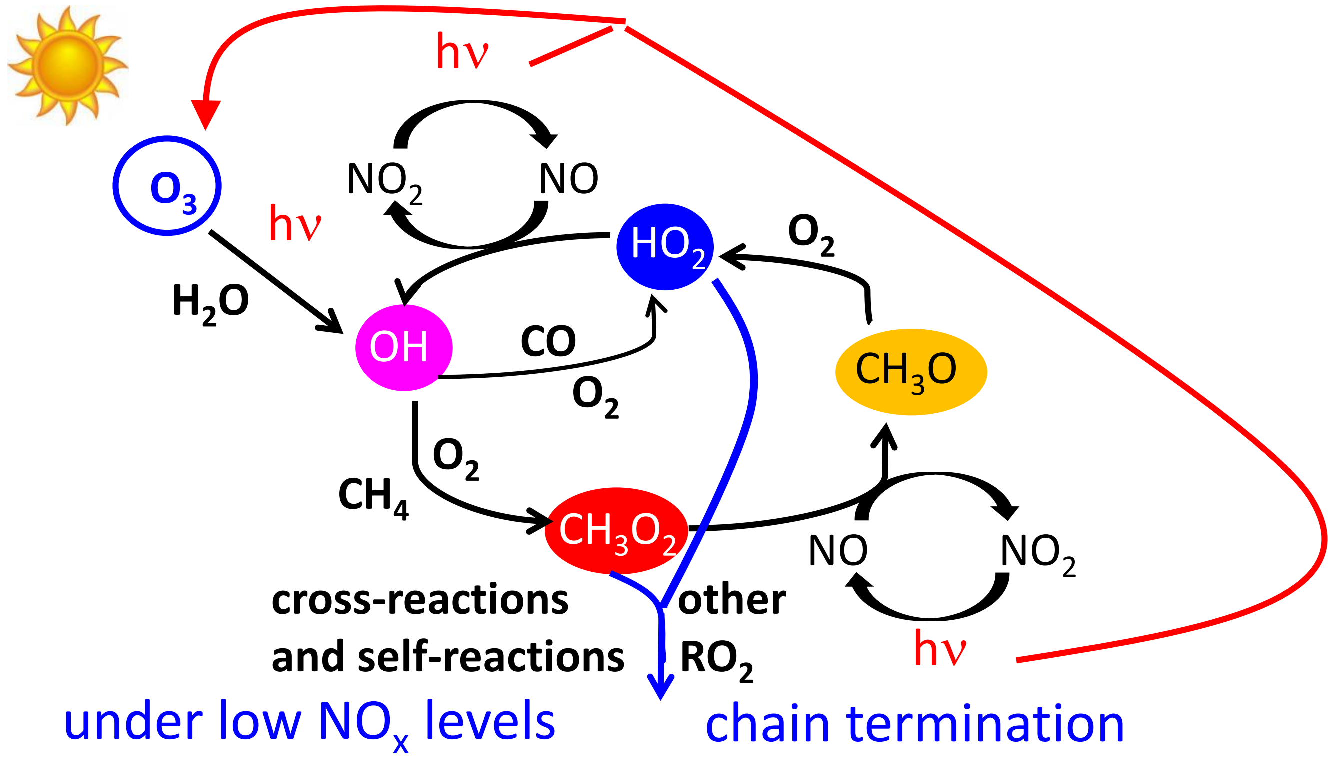

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- Box modelling using the Master Chemical Mechanism (MCM) has found that the daytime $[CH_3O_2]$ peaks in the range ~(0.5 - 6) × 10^8 cm^{-3}.*

* Whalley et al. ACP, 2010; 2011; 2018

A new method for the selective and sensitive detection of CH_3O_2 radicals

- CH_3O_2 radicals are detected by titration with known amounts of NO to generate CH_3O radicals which are then detected using FAGE.

$$\color{red}{CH_3O_2} + NO \rightarrow \color{blue}{CH_3O} + NO_2$$

LIF detection

- The $A \leftarrow X$ electronic excitation of CH_3O radicals is used to detect these radicals with high sensitivity and selectively by LIF.

A new method for the selective and sensitive detection of CH_3O_2 radicals

The method is similar to the FAGE method used for HO_2 detection:

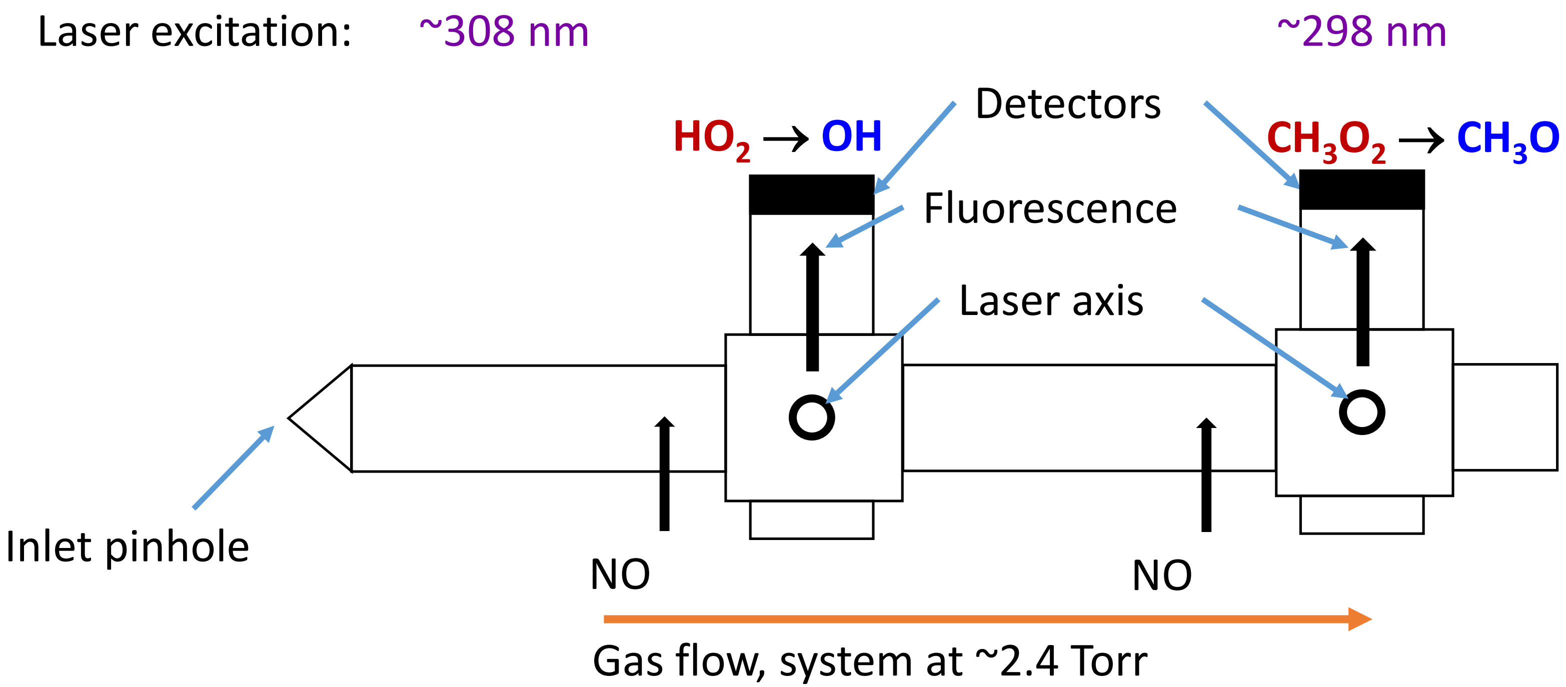
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

LIF detection

$HO_2 + NO \rightarrow OH + NO_2$

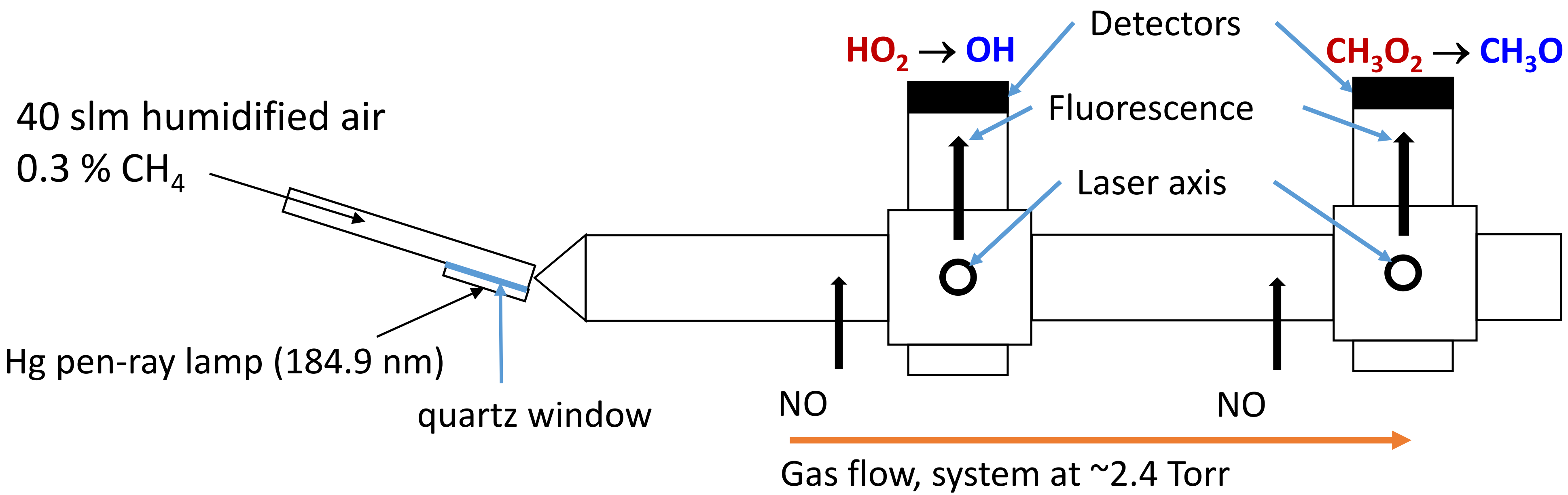
LIF detection

FAGE instrument



FAGE calibration

- Known concentrations of HO_2 and CH_3O_2 are generated in a calibration flow tube impinging outside the FAGE sample inlet



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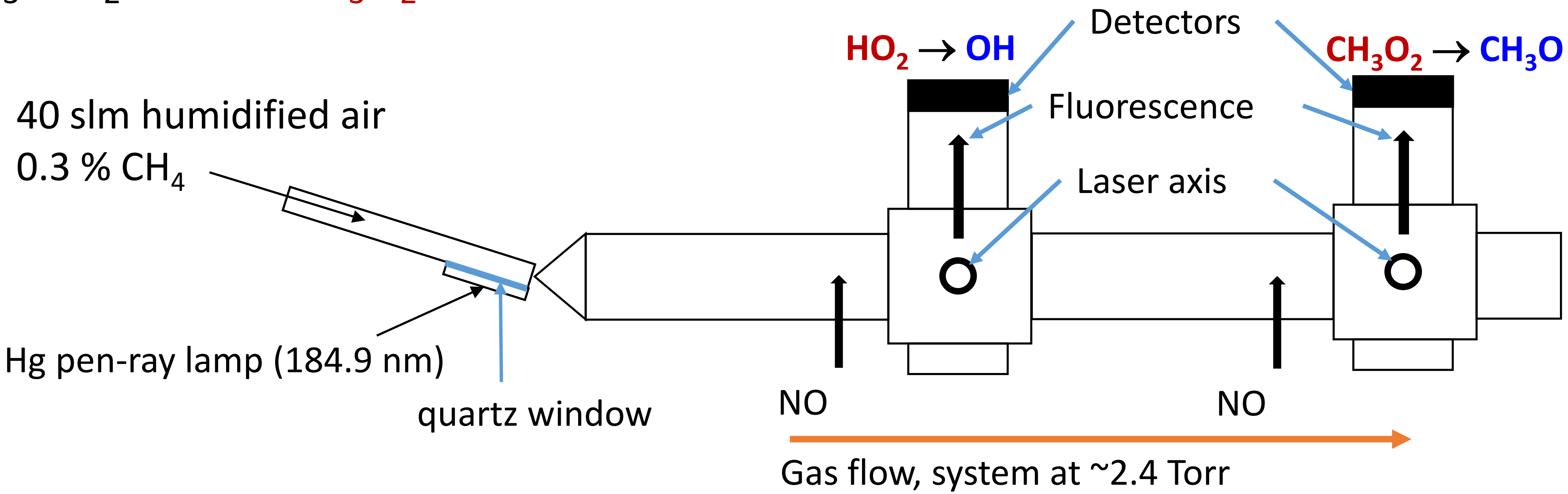
$H_2O \xrightarrow{184.9\ nm} OH + H$

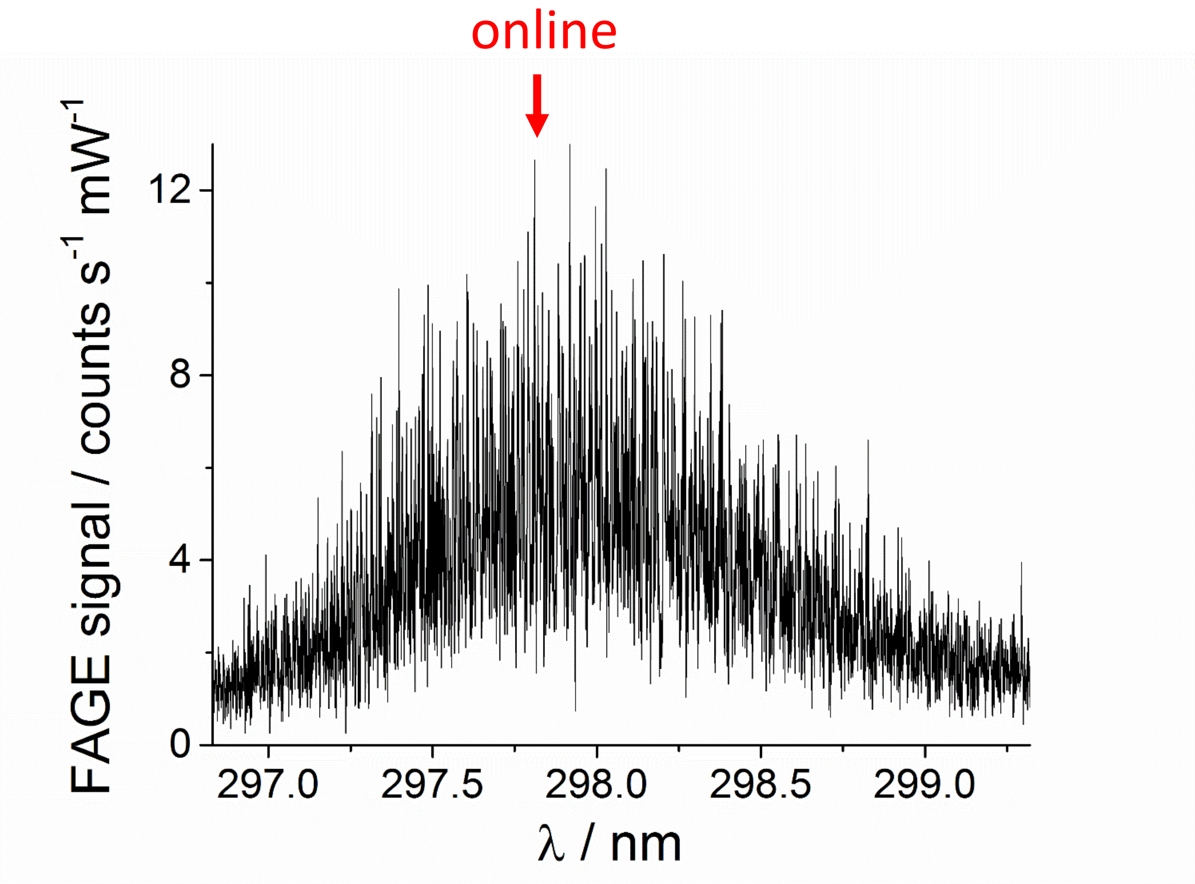
$H + O_2 \rightarrow HO_2$

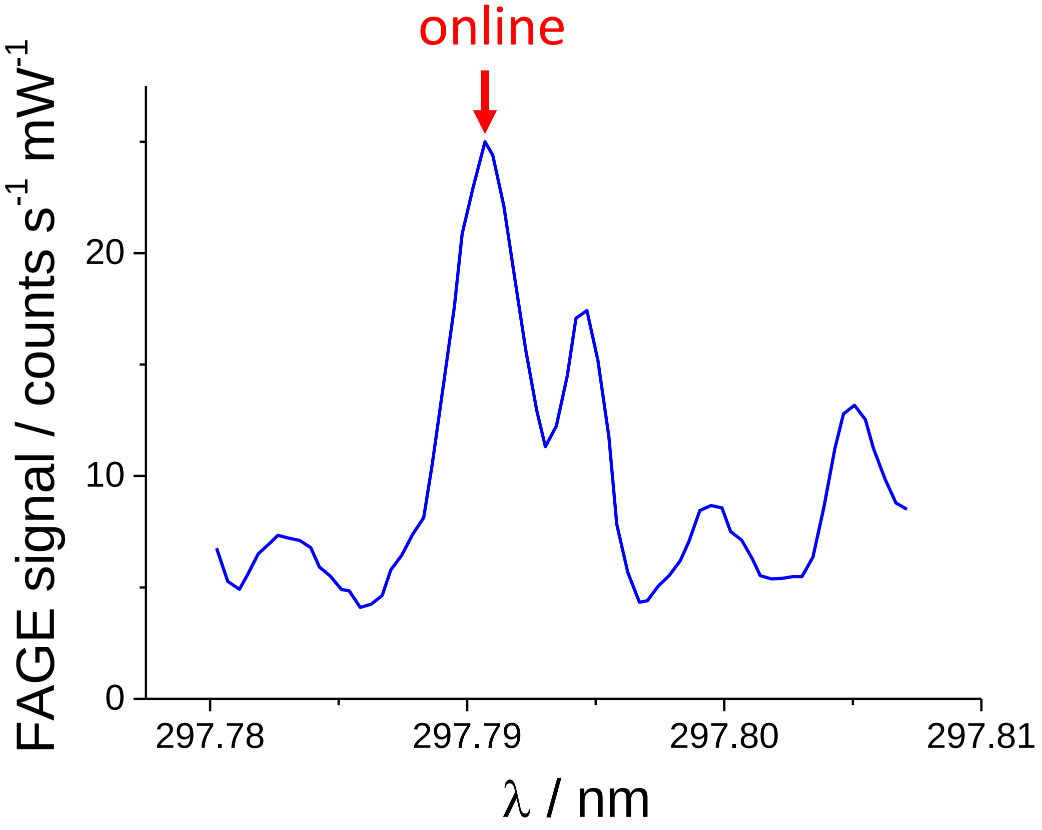
$OH + CH_4 \rightarrow H_2O + CH_3$

$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$



Methoxy (CH_3O) excitation spectrum





- λ_{online} = 297.79 nm
- $\lambda_{offline} = \lambda_{online}$ + 2.5 nm

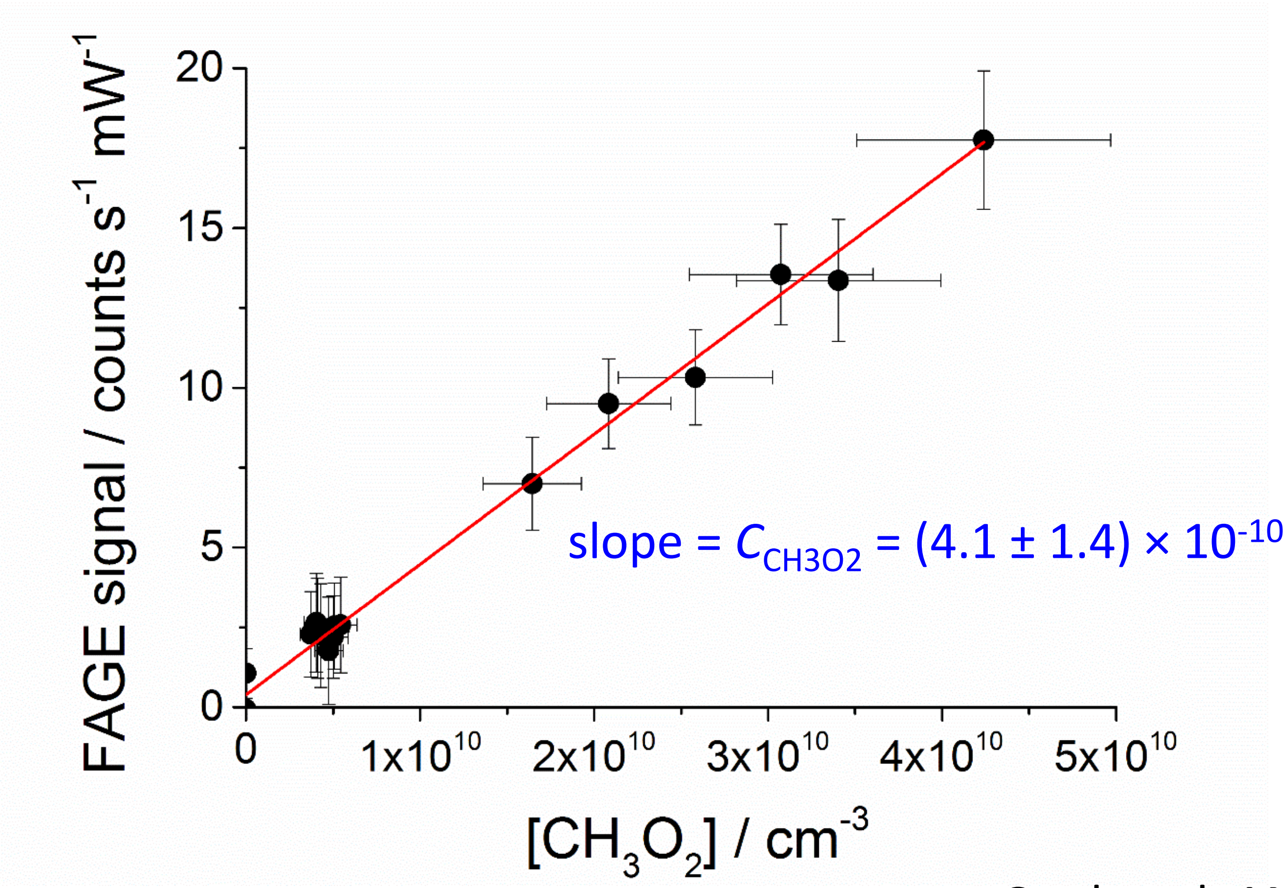
Onel et al. AMT, 10, 3985–4000, **2017**

FAGE calibration plot

S/N = 2

- $LOD(\mathbf{CH_3O_2}) = (1.2 \pm 0.1) \times 10^9\ cm^{-3}$ 30 s averaging time

  $(1.8 \pm 0.2) \times 10^8\ cm^{-3}$ 20 min averaging time



slope = $C_{CH3O2} = (4.1 \pm 1.4) \times 10^{-10}$ counts s^{-1} mW^{-1} cm^3

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- $LOD(\mathbf{CH_3O_2}) = (1.2 \pm 0.1) \times 10^{9}$ cm^{-3} 30 s averaging time $LOD(\mathbf{HO_2}) = (1.6 \pm 0.2) \times 10^{6}$ cm^{-3}

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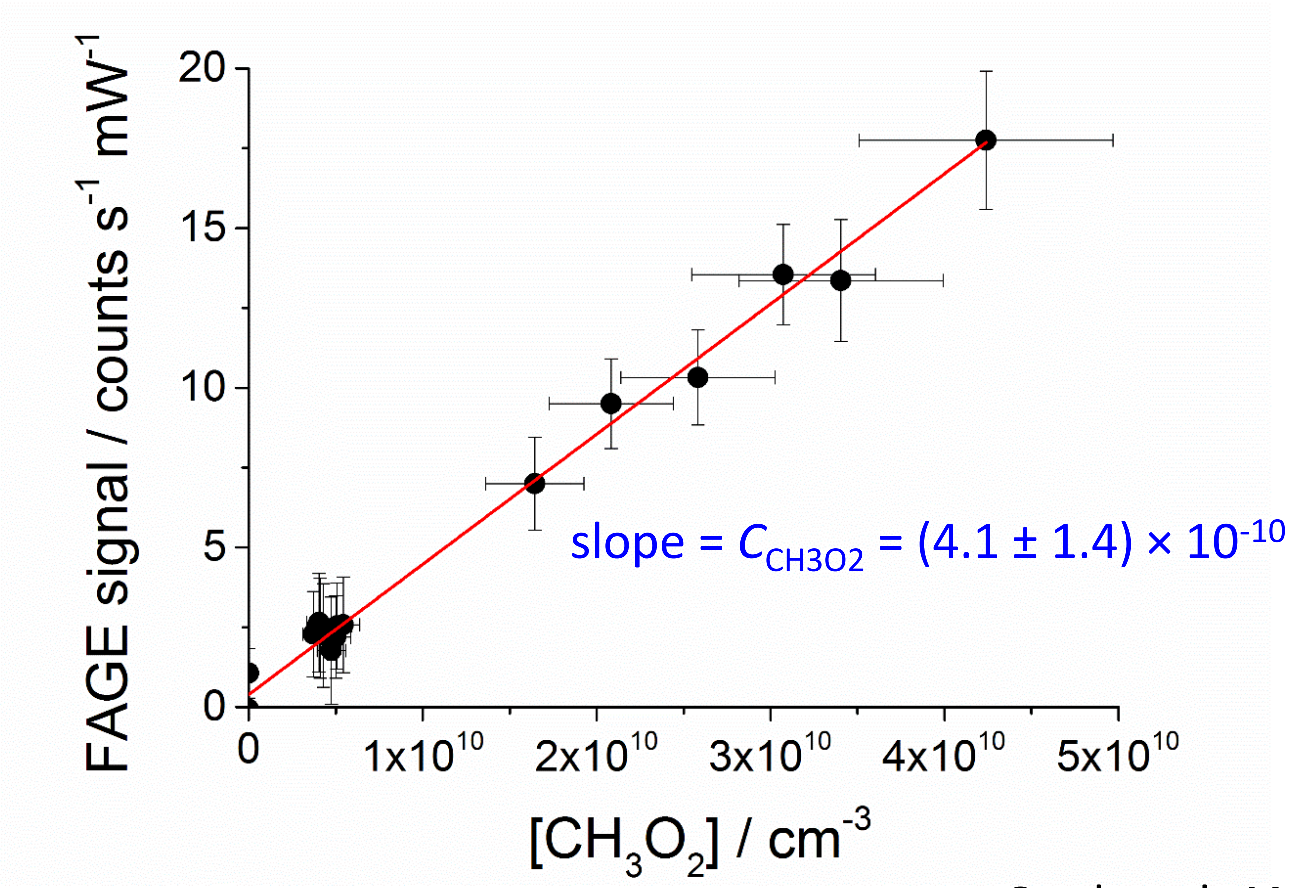

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Potential of the new method to be used in field measurements of CH_3O_2

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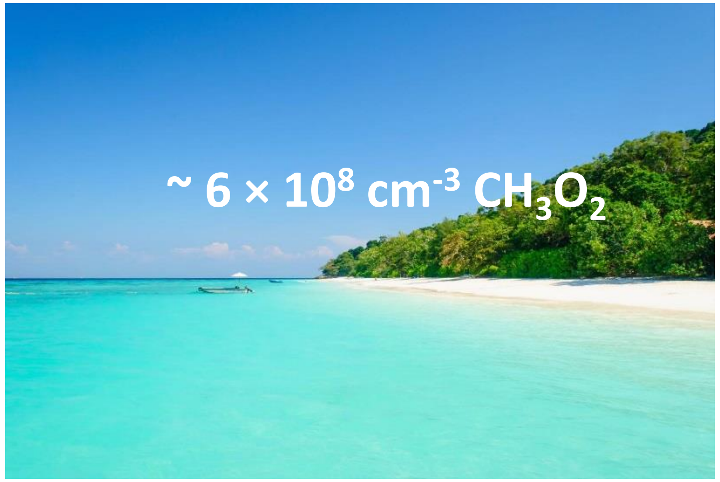

tropical Atlantic ocean*

* Whalley et al. ACP, 2010

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Further optimisations of FAGE sensitivity:

- removal of the fibre optic cables to deliver the probe laser beam directly
- lower pressure (currently 2.4 Torr)

Validation of the FAGE method for detection of HO_2 and CH_3O_2

FAGE–CRDS intercomparison

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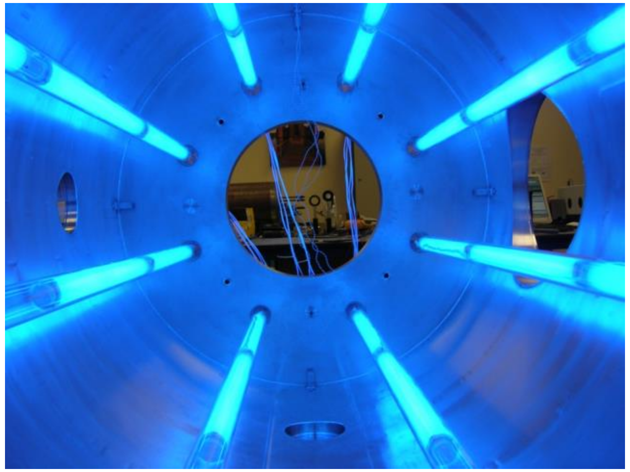
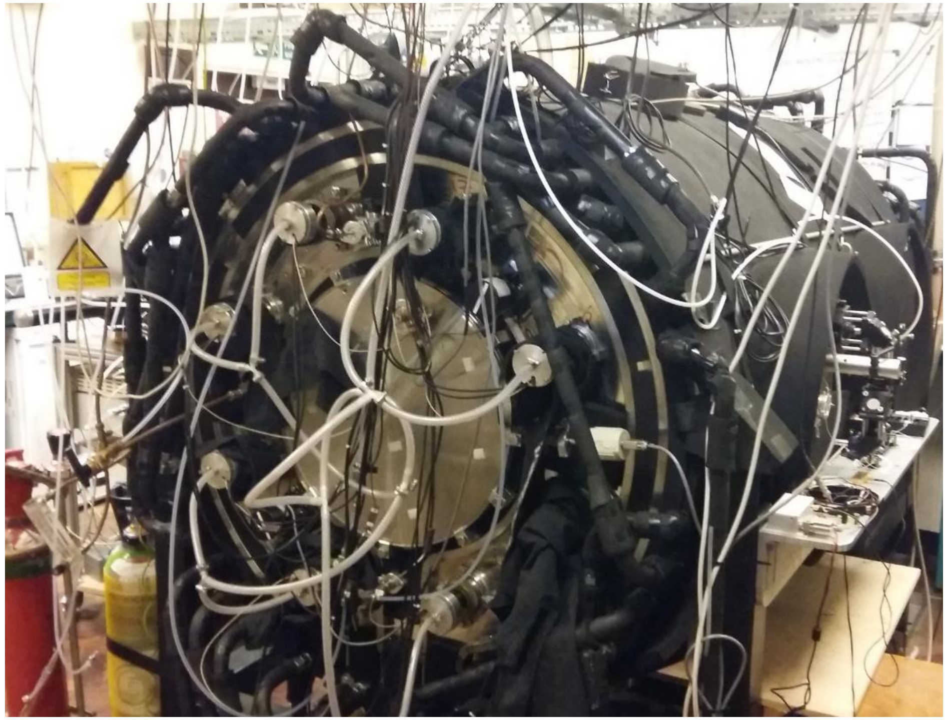
HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry)





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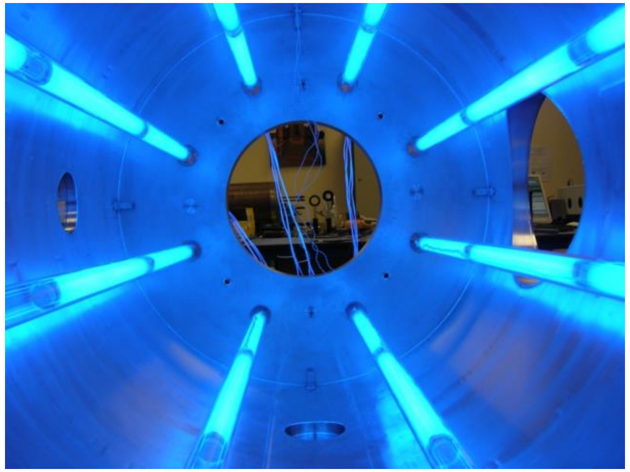
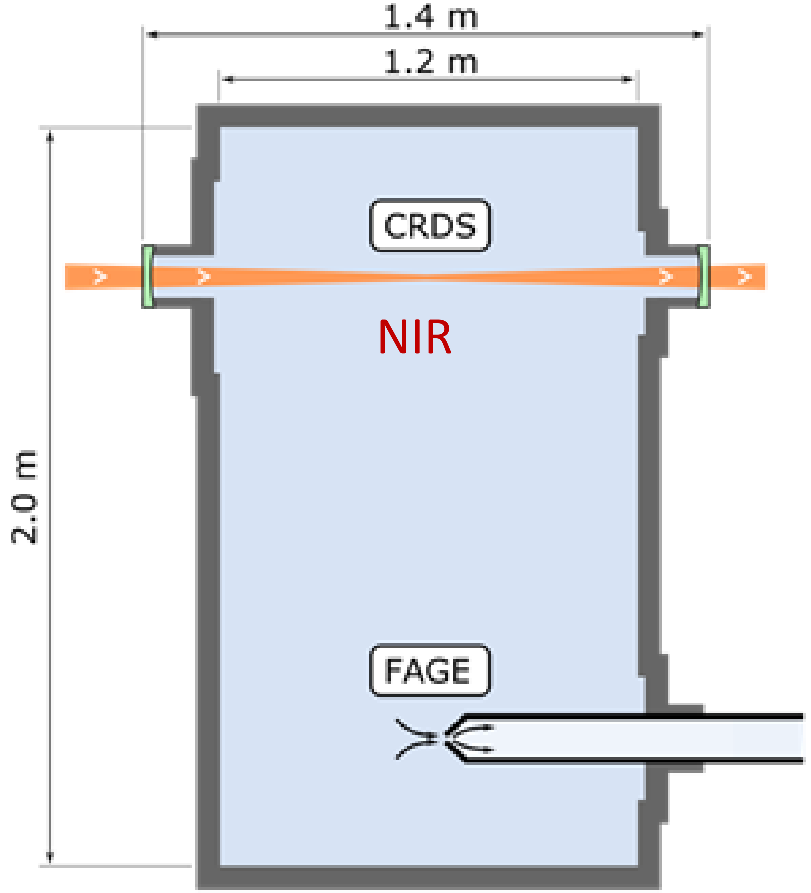


First HO_2 and CH_3O_2 CRDS measurements in an atmospheric simulation chamber



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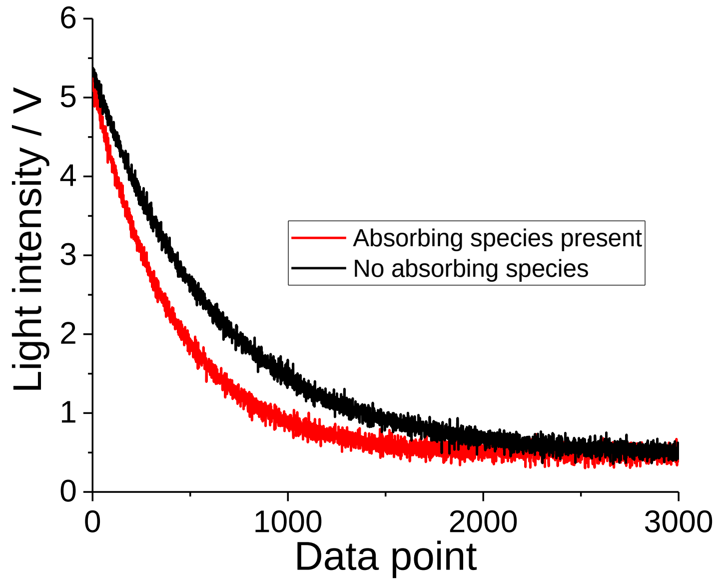

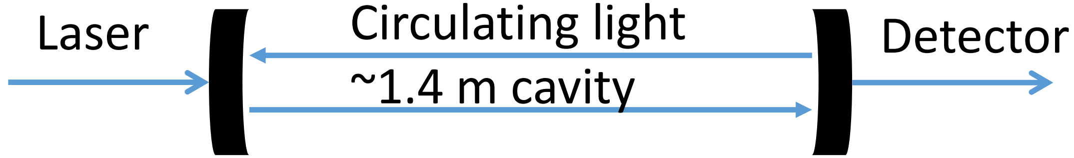

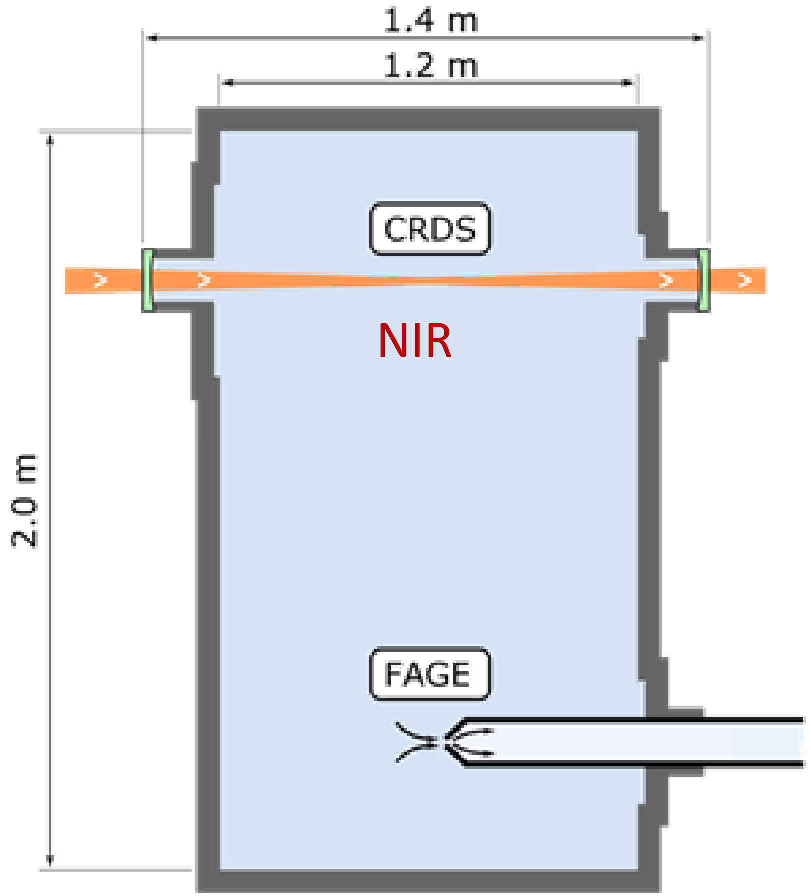

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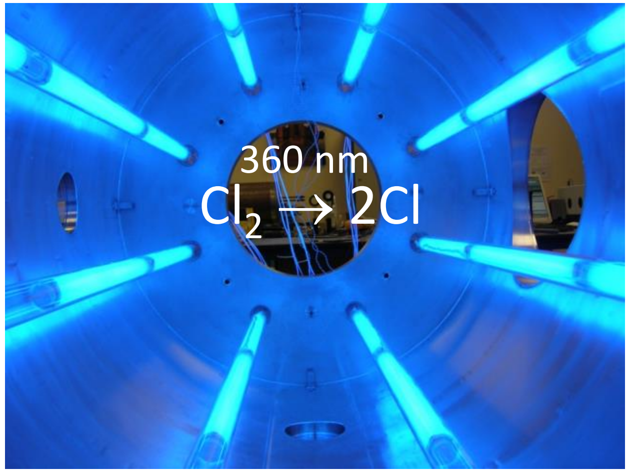
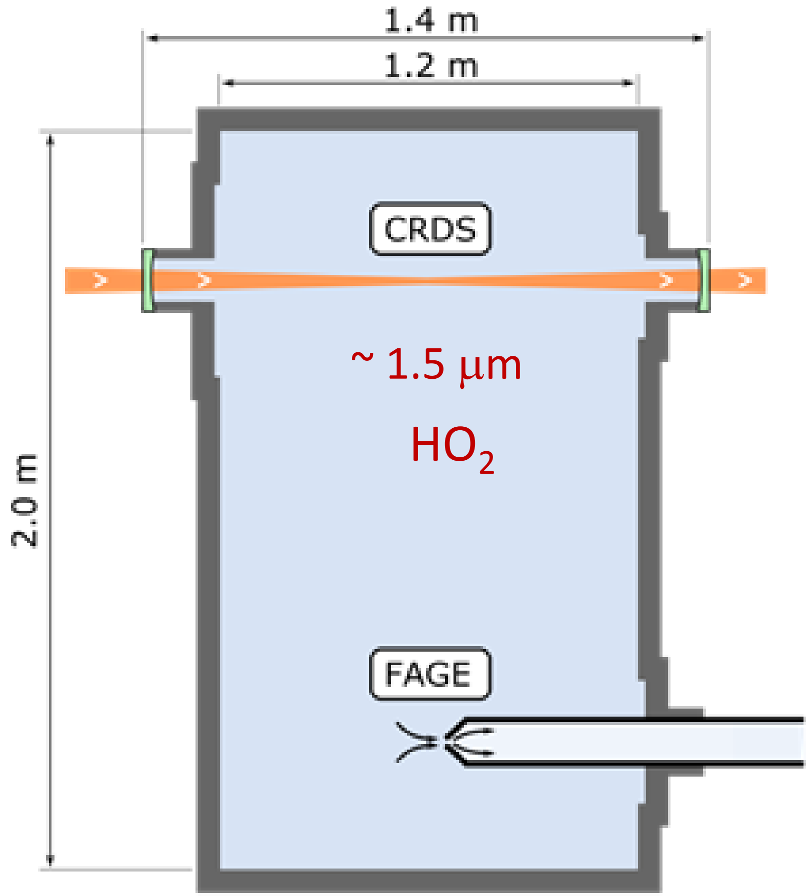


$Cl + CH_3OH \rightarrow CH_2OH + HCl$

$CH_2OH + O_2 \rightarrow HO_2 + CH_2O$



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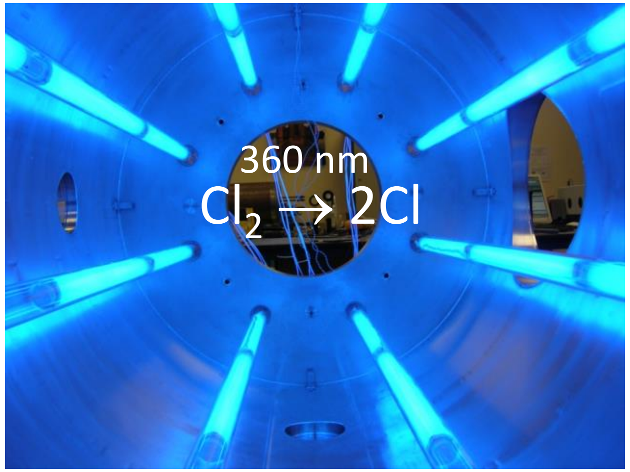
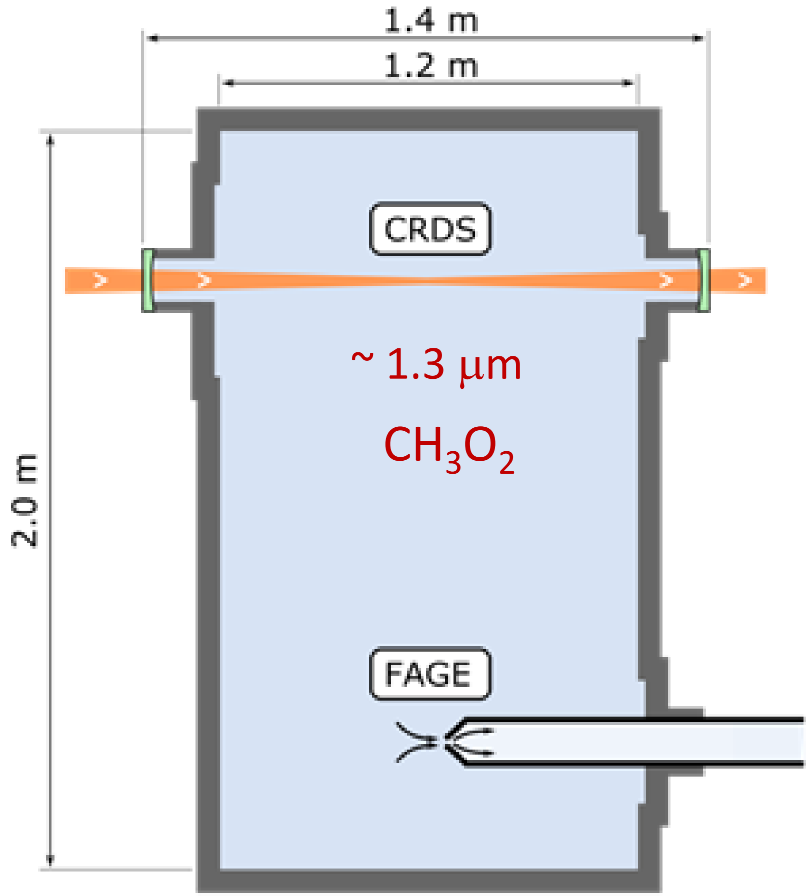


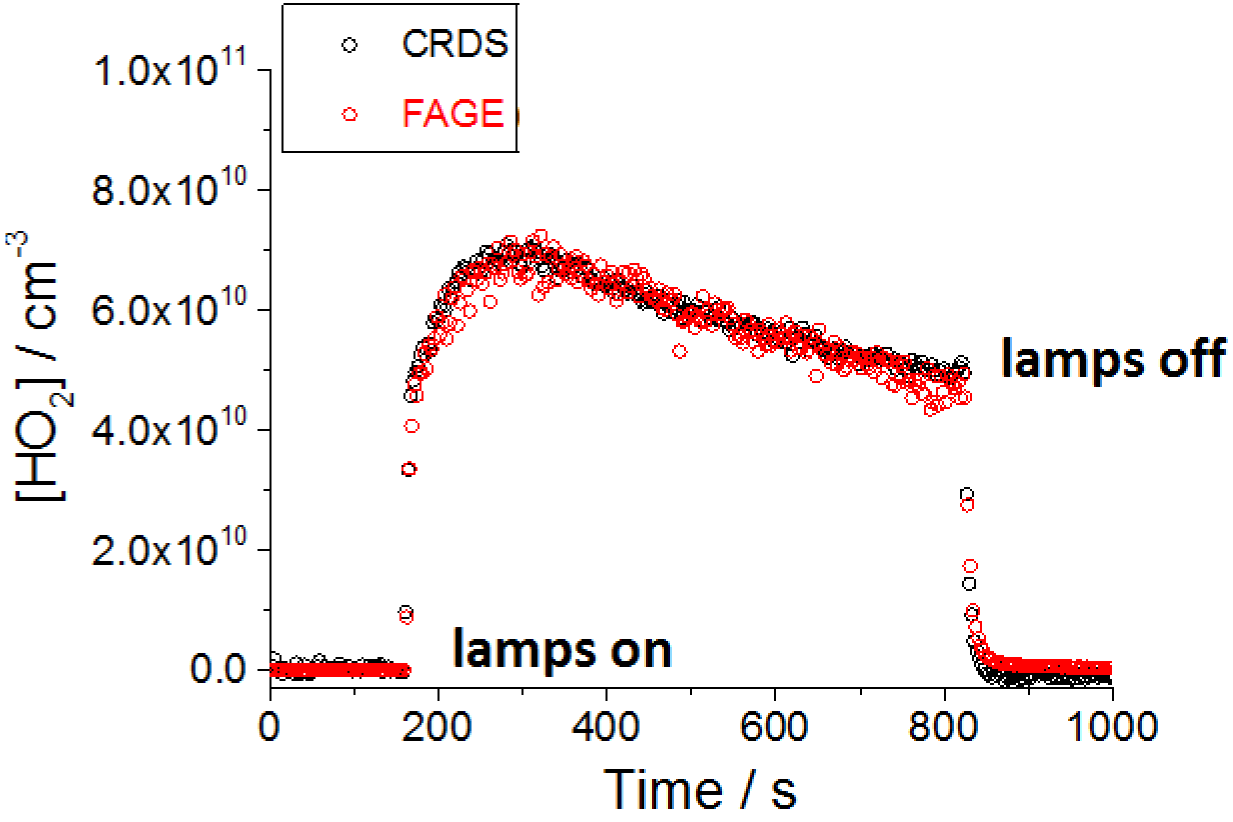


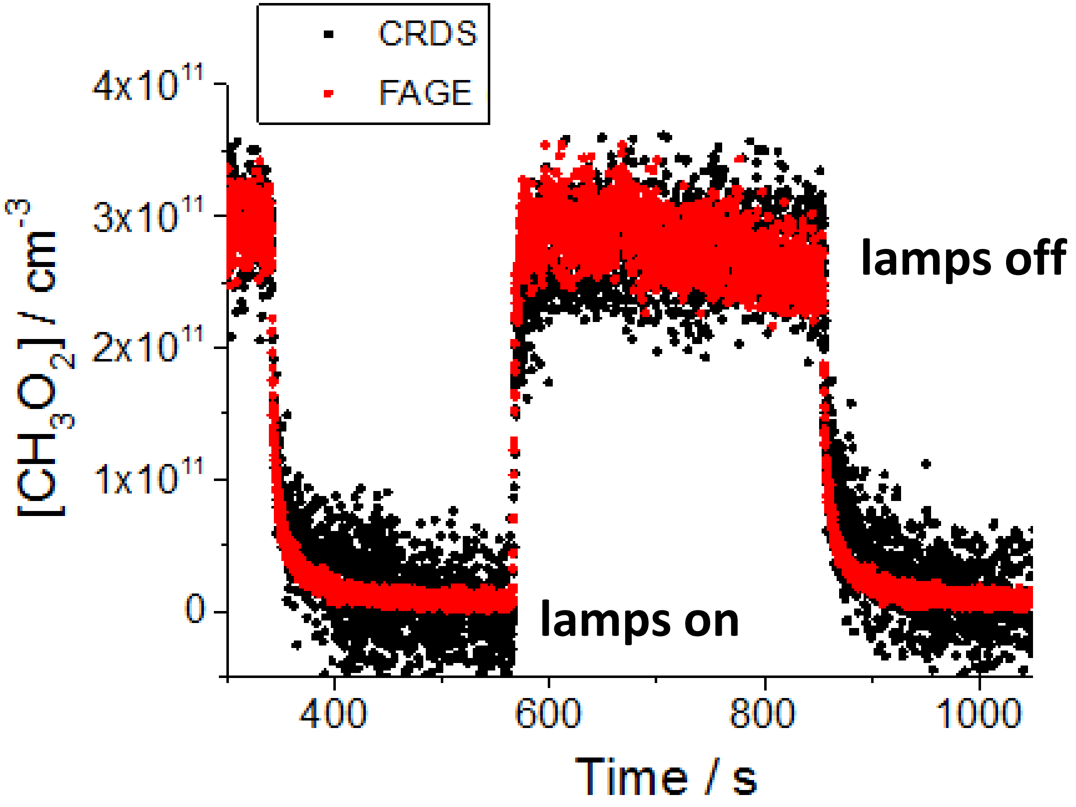
$$Cl + CH_4 \rightarrow CH_3 + HCl$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

Intercomparison of HO_2 and **CH_3O_2** by FAGE and CRDS

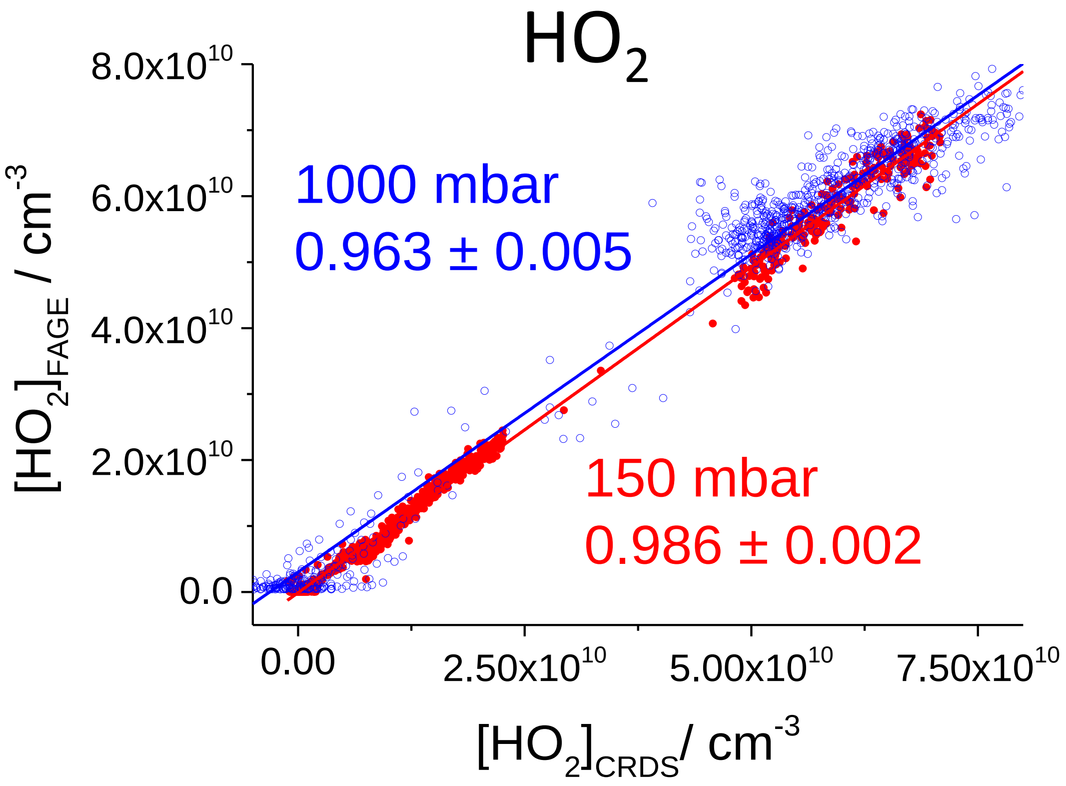
- CRDS probes HO_2 using the excitation of the first O-H overtone at 1.5 μm and CH_3O_2 using the $A \leftarrow X$ electronic excitation at 1.3 μm

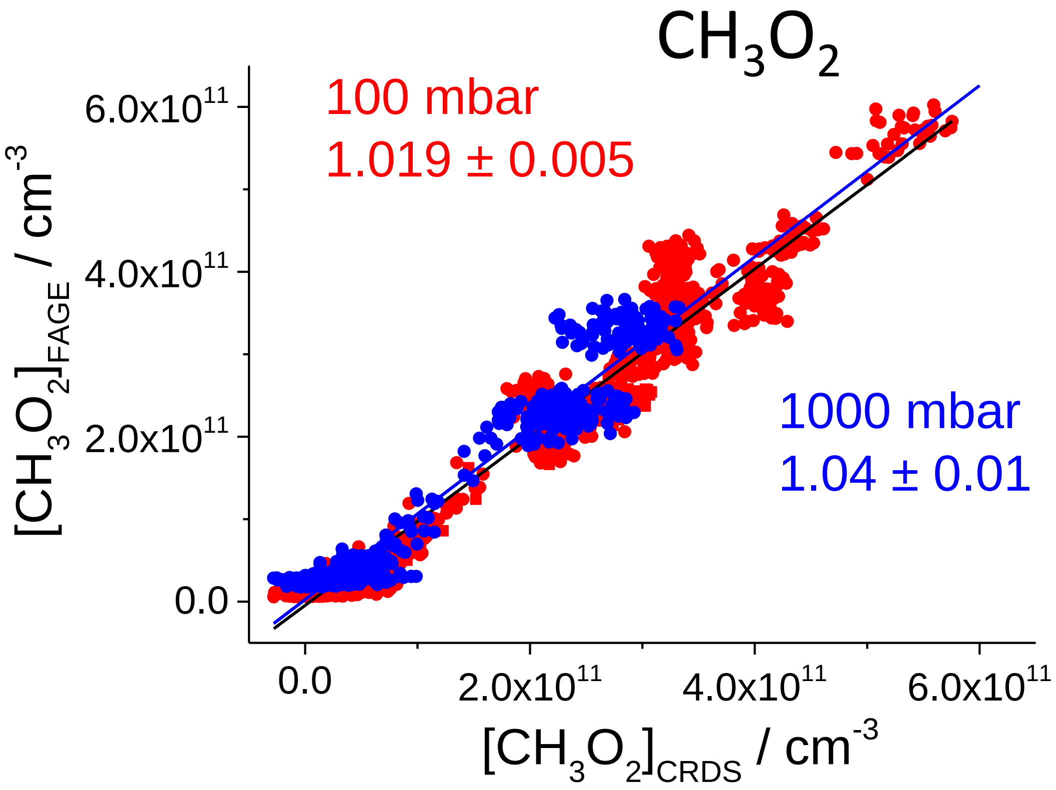




Onel et al. AMT, 10, 4877–4894, **2017**

FAGE–CRDS correlation plots





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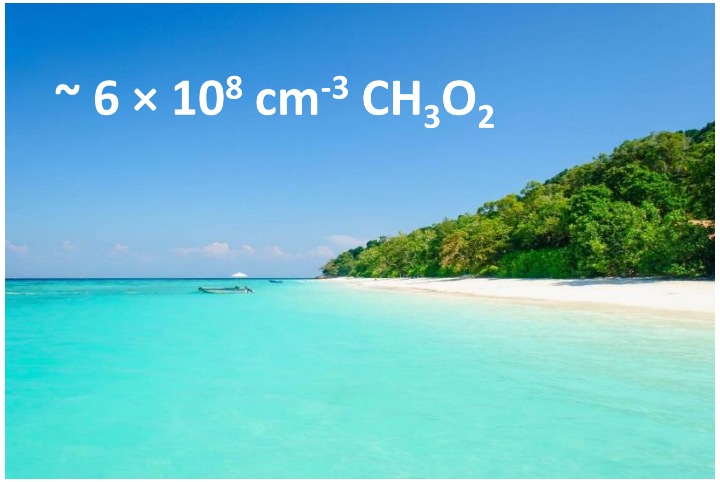
$HO_2 + CH_3O_2$ cross-reaction

$$HO_2 + CH_3O_2 \longrightarrow O_2 + CH_3COOH \qquad 0.9$$
$$\longrightarrow O_2 + HCHO + H_2O \qquad 0.1$$

- A main sink for CH_3O_2 radicals in remote areas (low NO_x)



tropical Atlantic ocean

tropical rainforest

Kinetics of the $HO_2 + CH_3O_2$ cross-reaction

$$HO_2 + CH_3O_2 \xrightarrow{k} \text{Products}$$

- 23% 1σ uncertainty in the value of the overall rate coefficient at 298 K 5.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} [1]. The majority of previous studies used UV-absorption spectroscopy, which is often an unselective technique.
- Clear need for kinetic studies of this reaction using a selective method.

[1] http://iupac.pole-ether.fr

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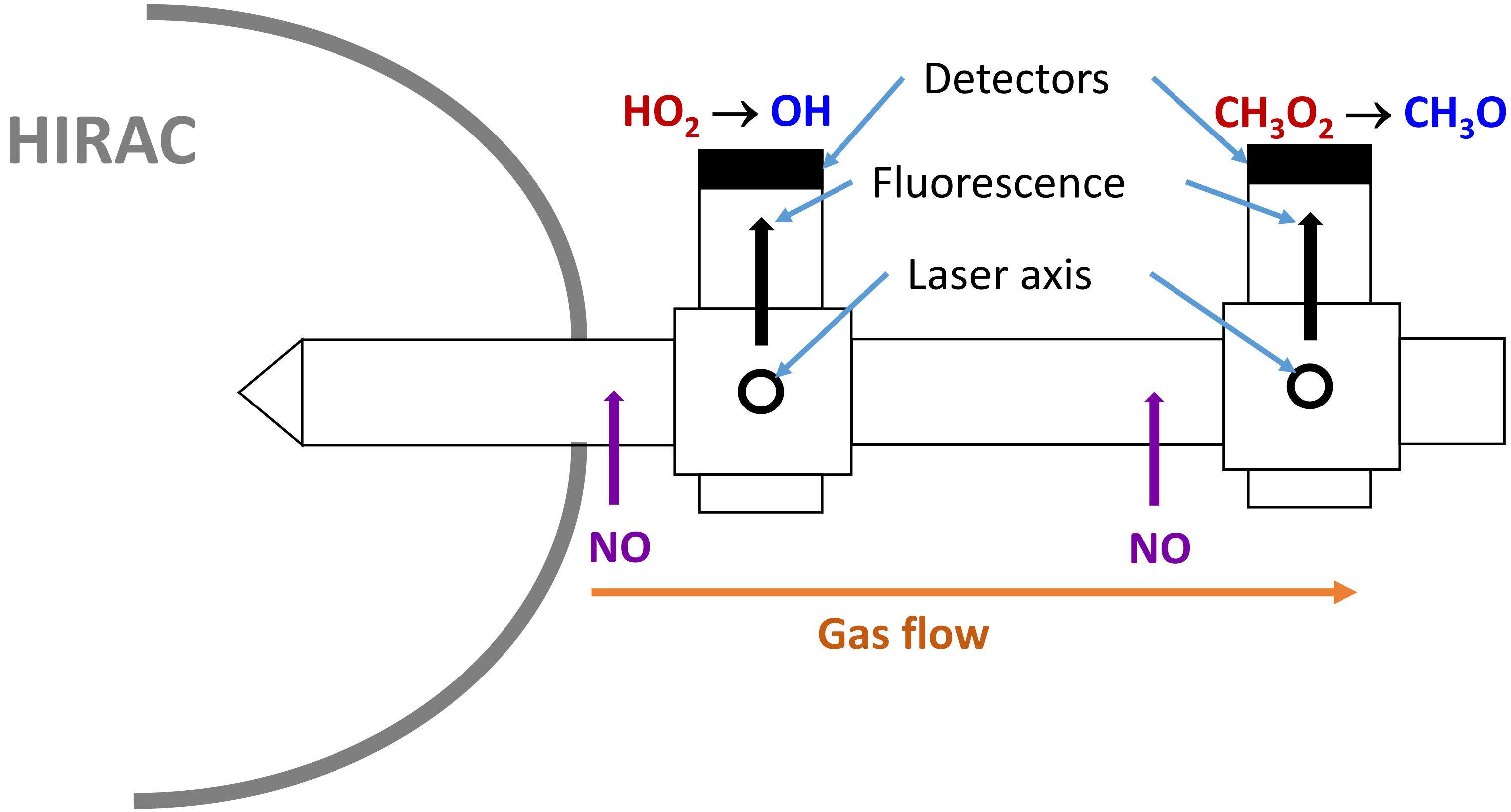

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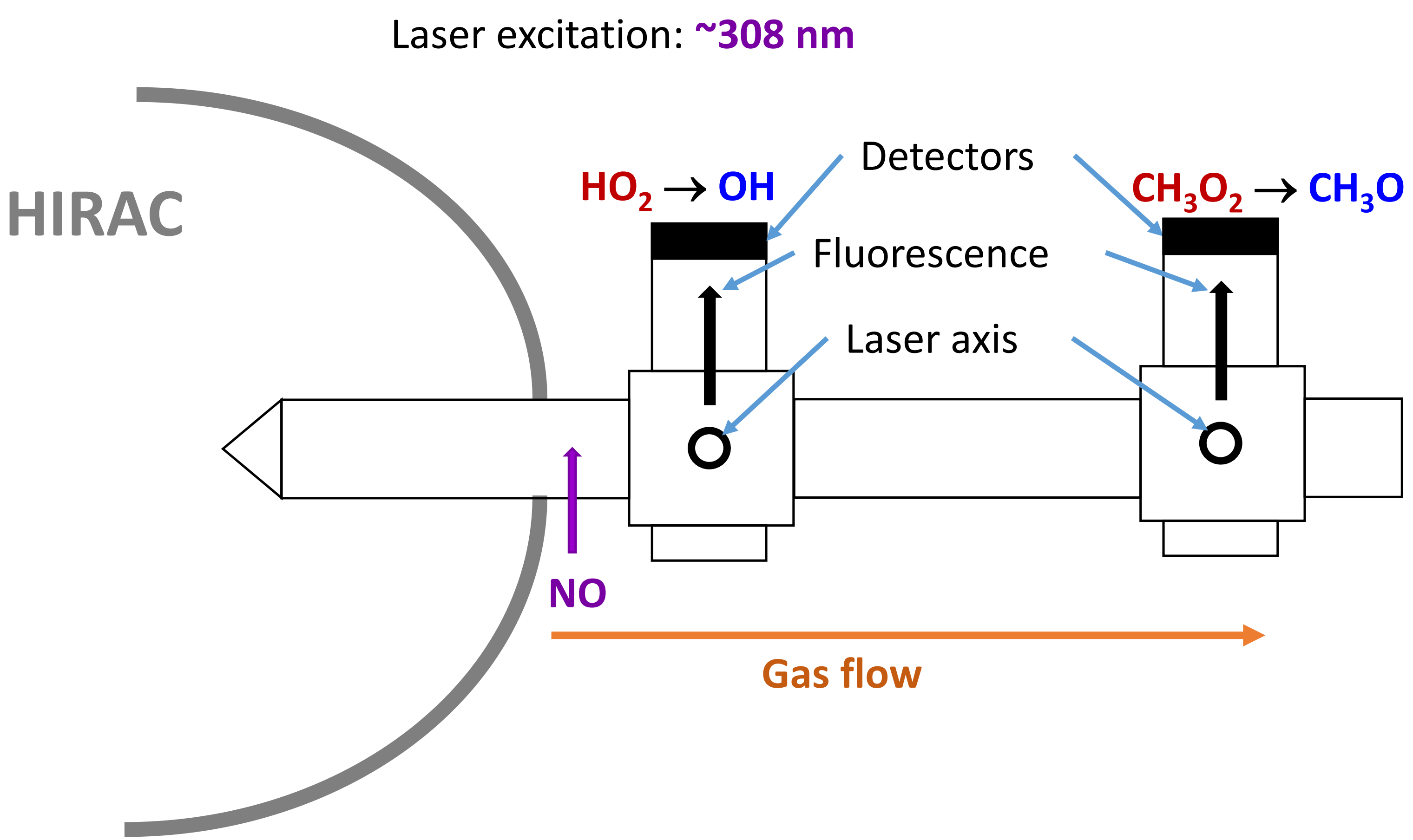

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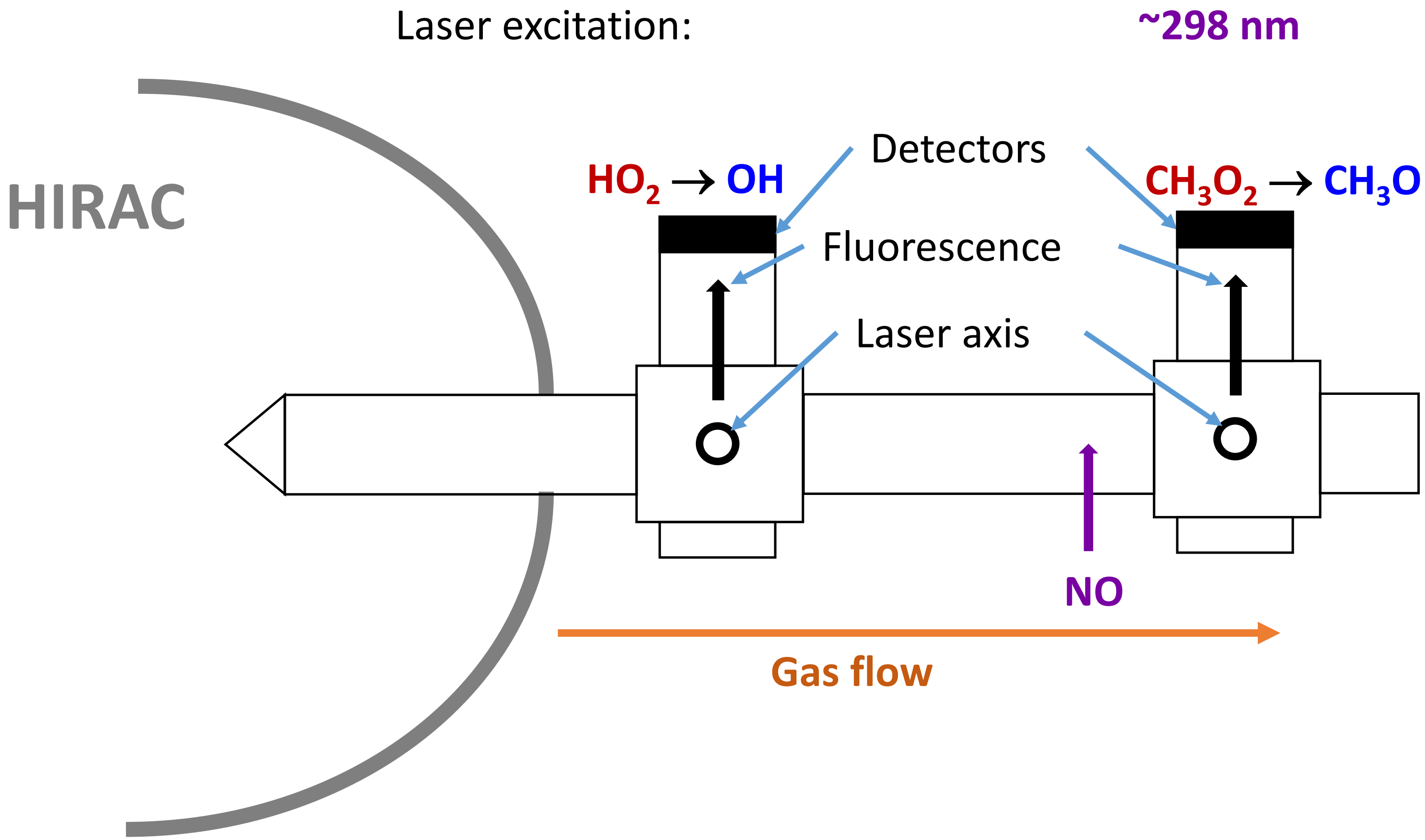

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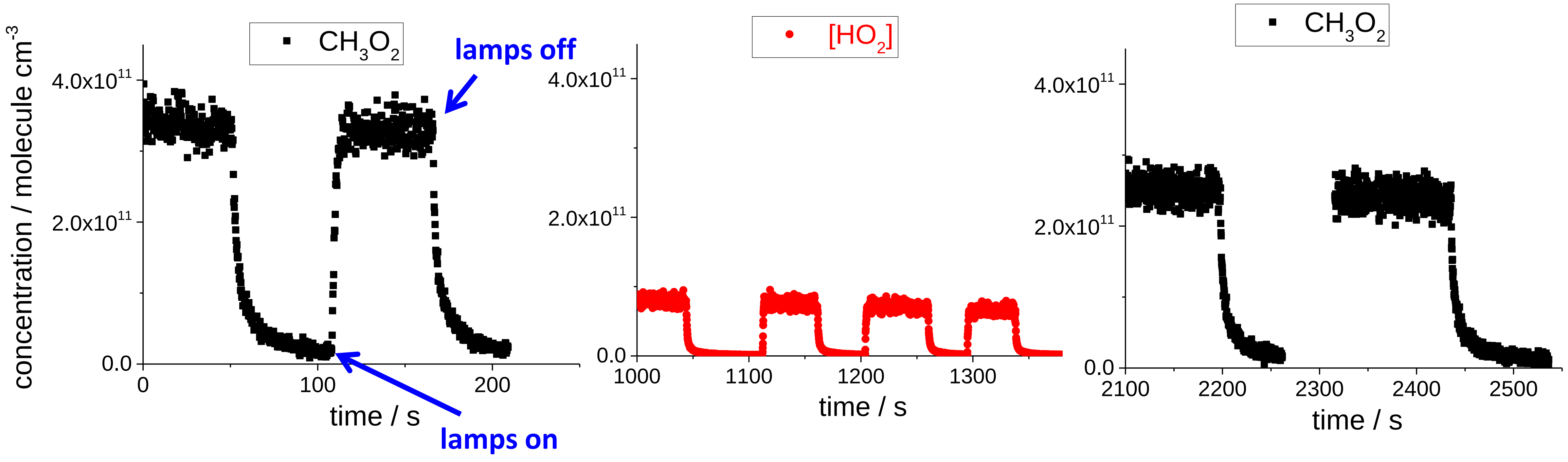
HO_2 and CH_3O_2 second–order decays

- Reaction mixtures: $CH_4/CH_3OH/Cl_2/air$
- Different $[CH_3O_2]/[HO_2]$ ratios



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Kinetic analysis

Reaction
$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2$
$CH_3O_2 + CH_3O_2 \rightarrow \mathbf{CH_3O} + \mathbf{CH_3O} + O_2$
$\mathbf{CH_3O} + O_2 \rightarrow HCHO + HO_2$
$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$ $\rightarrow HCHO + H_2O + O_2$
$HO_2 + HO_2 + (M) \rightarrow H_2O_2 + O_2 + (M)$

CH_3O_2 self-reaction

cross-reaction

HO_2 self-reaction

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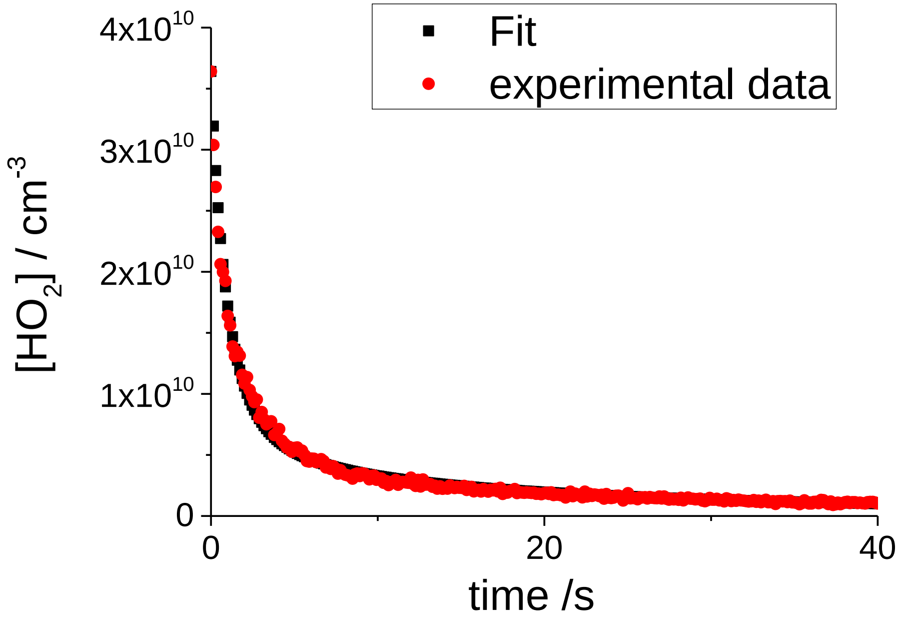
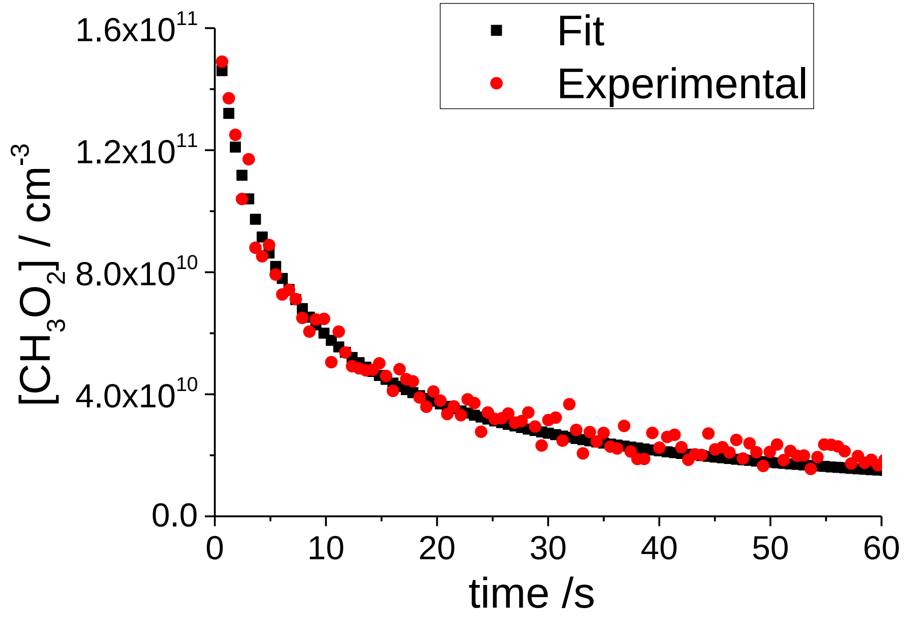
$\mathbf{CH_3O} + O_2 \rightarrow HCHO + HO_2$
$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$ $\rightarrow HCHO + H_2O + O_2$
$HO_2 + HO_2 + (M) \rightarrow H_2O_2 + O_2 + (M)$

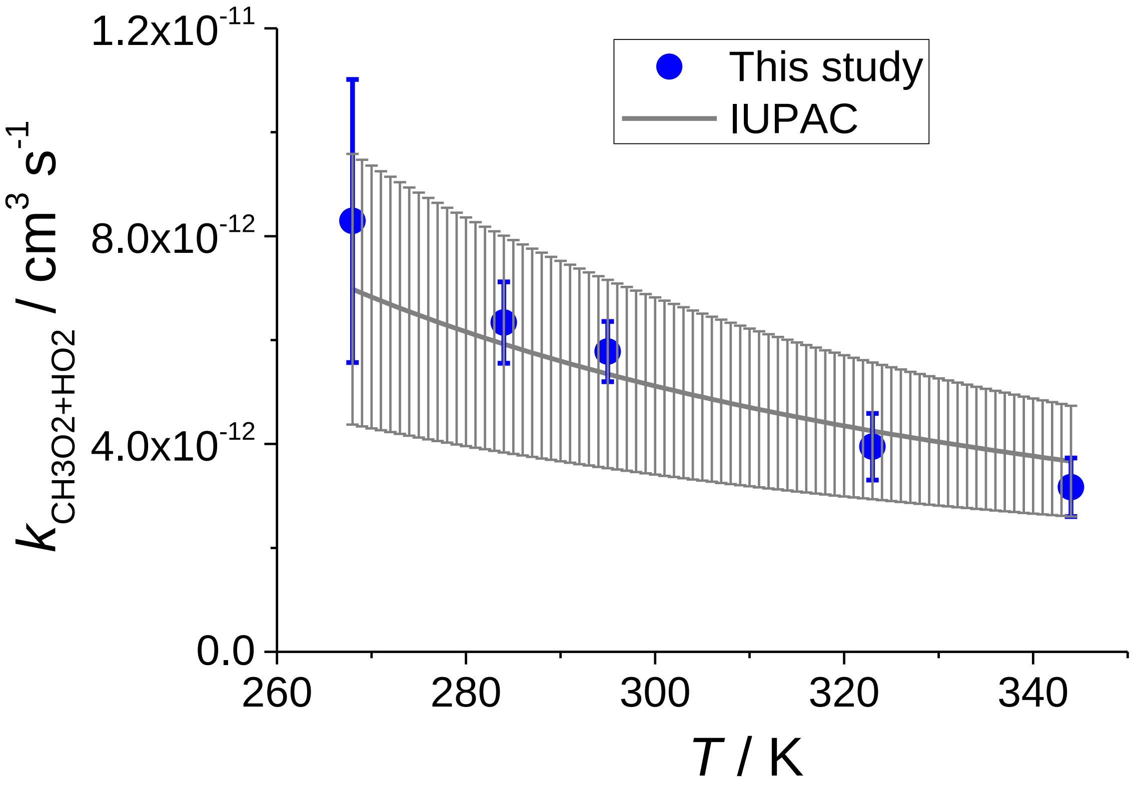
extracted: overall $k_{CH3O2+HO2}$





$HO_2 + CH_3O_2$ cross-reaction: Temperature dependence

- Experiments at 268, 284, 295, 323, and 344 K (-5 to 70 °C)



IUPAC: $k_{CH3O2 + HO2} = 3.8 \times 10^{-13} \times \exp(780/T)$ cm^3 s^{-1} (205-580 K)

$\Delta E/R = \pm$ 100 K

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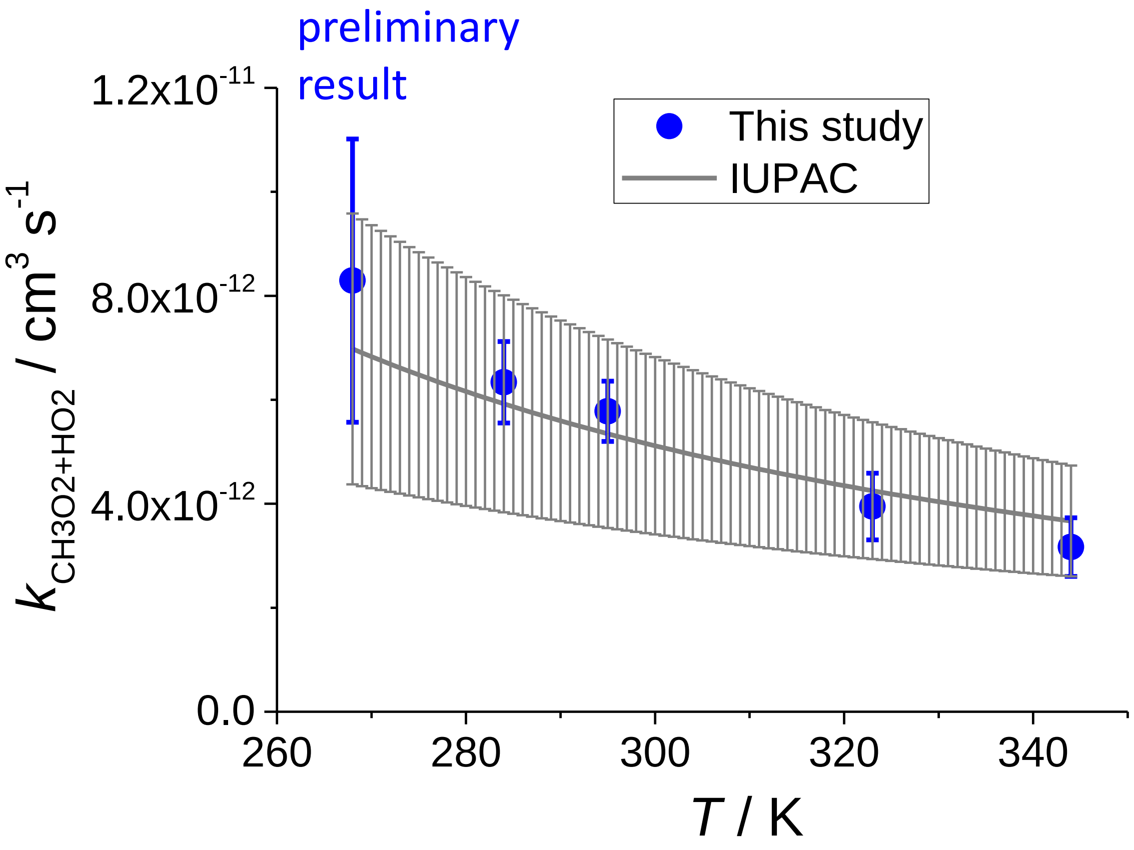

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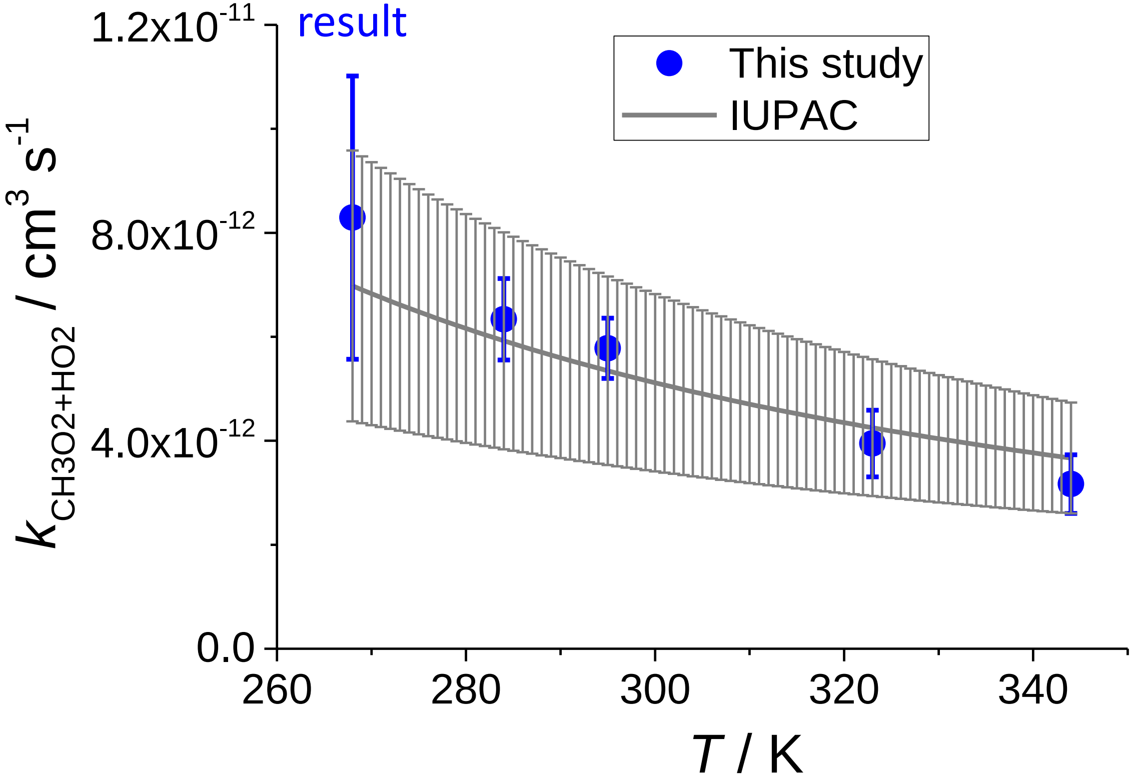
preliminary result



- Good agreement
- Smaller error margins

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Conclusions and outlook

- Speciated detection of CH_3O_2 radicals by FAGE

  New and selective method

- Potential to use the method in field measurements of CH_3O_2
- Speciated detection of $C_2H_5O_2$ radicals by FAGE

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- The FAGE method has been used to detect HO_2 and CH_3O_2 in HIRAC to reduce the uncertainty in the $k_{HO2+CH3O2}$ reported by IUPAC.

  Planned: New kinetic studies, e.g. OH + CH_3COOH (CH_3O_2: intermediate)

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- Freja F. Østerstrøm
- Joseph Parr
- Grace Ronnie
- James Hooper
- Dwayne Heard
- Paul Seakins
- Lisa Whalley

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