School of Chemistry
FACULTY OF MATHEMATICS AND PHYSICAL SCIENCES

UNIVERSITY OF LEEDS

Kinetic Study of the CH_3O_2 + HO_2 Cross-reaction in the Highly Instrumented Reactor for Atmospheric Chemistry

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Motivation: 21st Century Grand Challenges

- 7 mio. premature deaths per year due to air pollution (in 2012)*
- Understanding air pollution requires knowledge of:
  - Gas phase chemistry
  - Aerosols
  - Heterogeneous chemistry
- Radicals are central compounds in atmospheric processes
  - Kinetics
  - Products formed
  - Not all well-known

* WHO, 2014

Motivation: HO_2 and CH_3O_2 in the Troposphere

- OH and HO_2 radicals are central in atmospheric oxidation
- OH reaction > 90 % oxidation of VOCs in the atmosphere
- CH_3O_2 is the most abundant RO_2 in the atmosphere

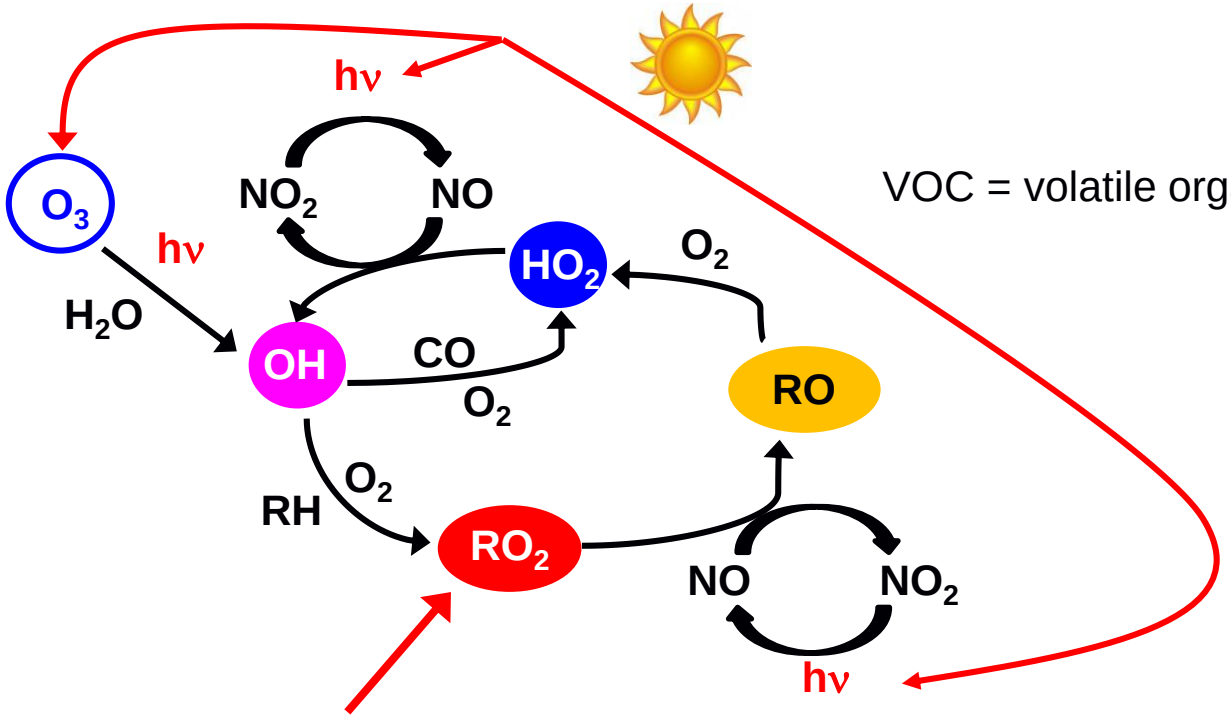
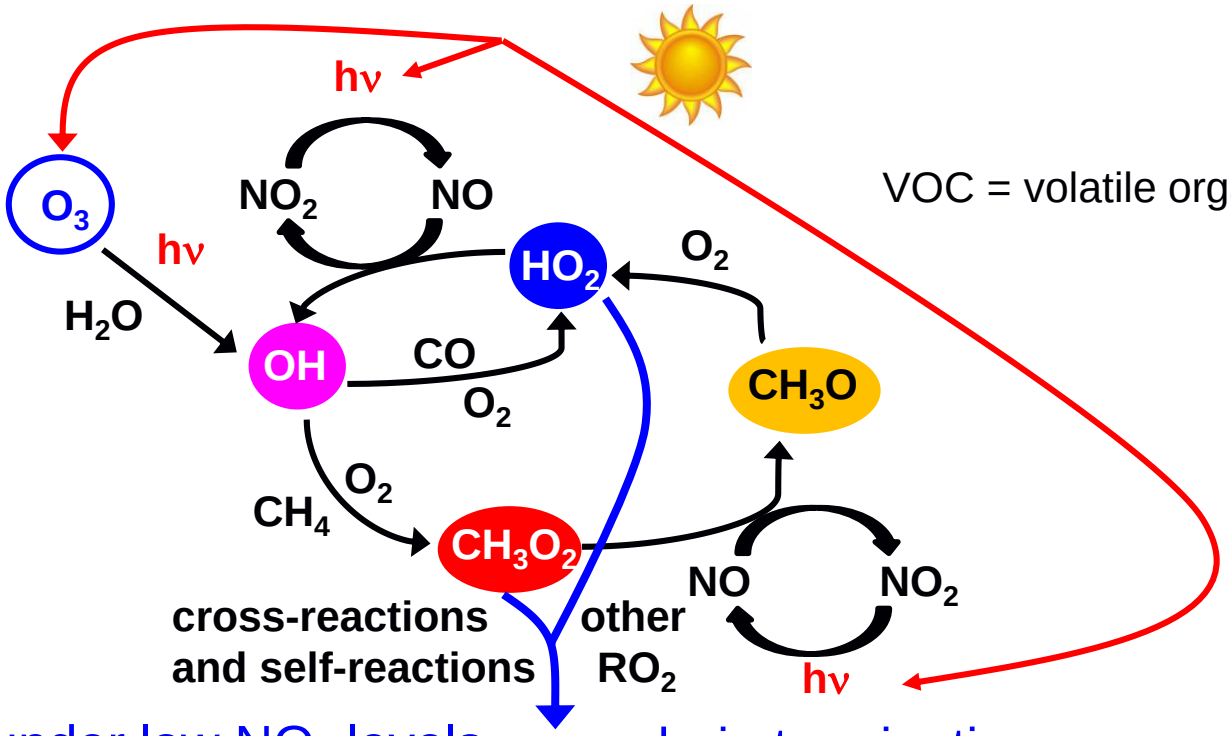


Figure: L. Onel

Motivation: HO_2 and CH_3O_2 in the Troposphere

- HO_2 and CH_3O_2 radicals formed from oxidation
  - HO_2 formed directly from CO or indirectly from VOCs
  - CH_3O_2 formed from CH_4



VOC = volatile organic compound

Figure: L. Onel

Motivation: HO_2 and CH_3O_2 in the Troposphere

- $[HO_2]$ in the atmosphere ~ 10^8 molecules cm^{-3}
- HO_2 is measured by laser induced fluorescence (LIF) in the atmosphere.
- CH_3O_2 or any other RO_2 are not specifically measured in the atmosphere
- The sum of RO_2 has been measured with different methods
  - Recently with the RO_xLIF method

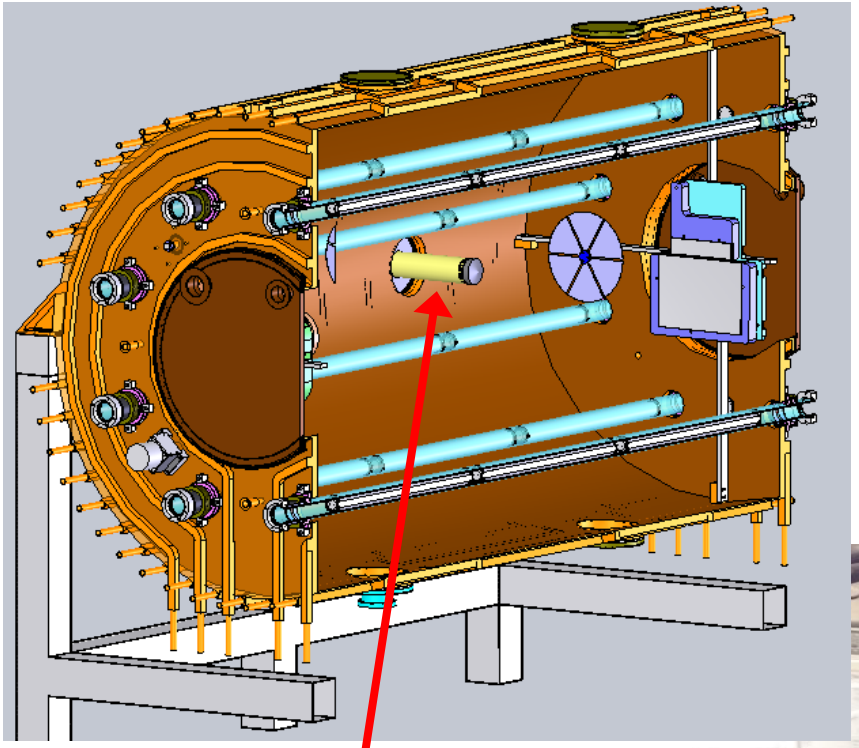
Motivation: HO_2 and CH_3O_2 in the Troposphere

- Box modelling using the Master Chemical Mechanism (MCM) finds daytime $[CH_3O_2]$ ~ (0.5 - 6) × 10^8 molecules cm^{-3} depending on the environment. *

- A new method has been developed detecting CH_3O_2 radicals in the highly instrumented reactor for atmospheric chemistry (HIRAC) using LIF. **

* Whalley et al., ACP, 2010, 2011, 2018 ** Onel et al., AMT, 2017

The Highly Instrumented Reactor for Atmospheric Chemistry - HIRAC

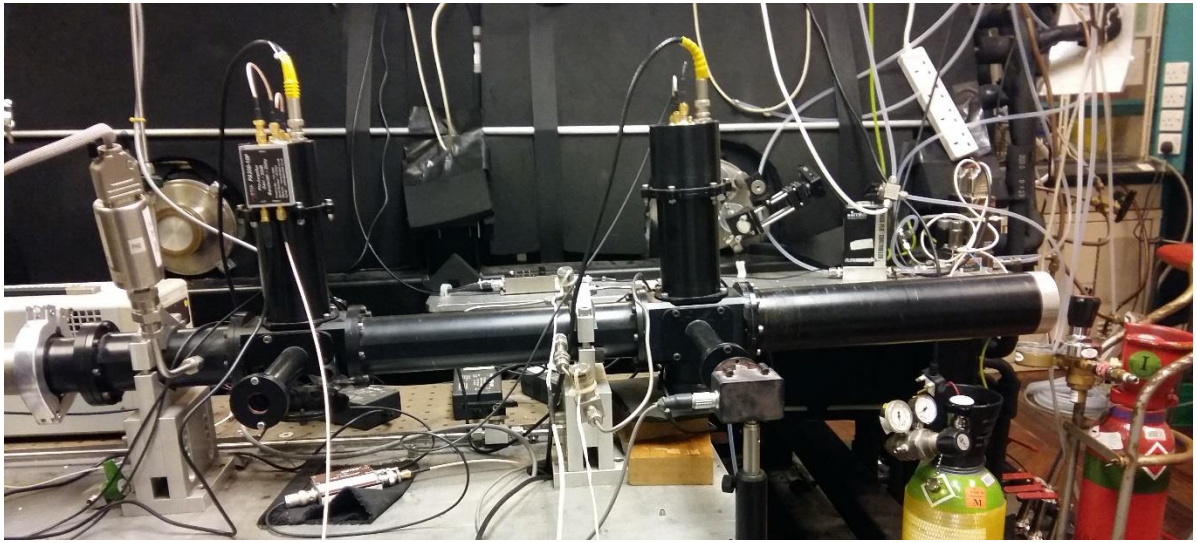


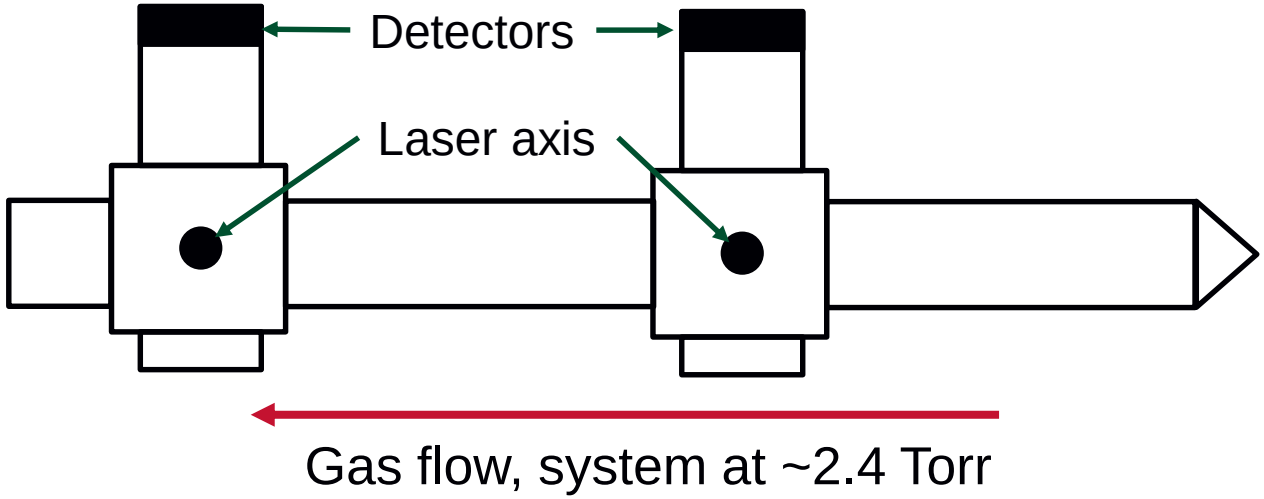
FAGE inlet

- 2250 L steel chamber
- UV lamps, Fans
- FTIR, GC-FID
- Laser induced fluorescence (LIF): Fluorescence assay by gas expansion (FAGE)

Glowacki et al., ACP, 2007

Fluorescence Assay by Gas Expansion (FAGE)



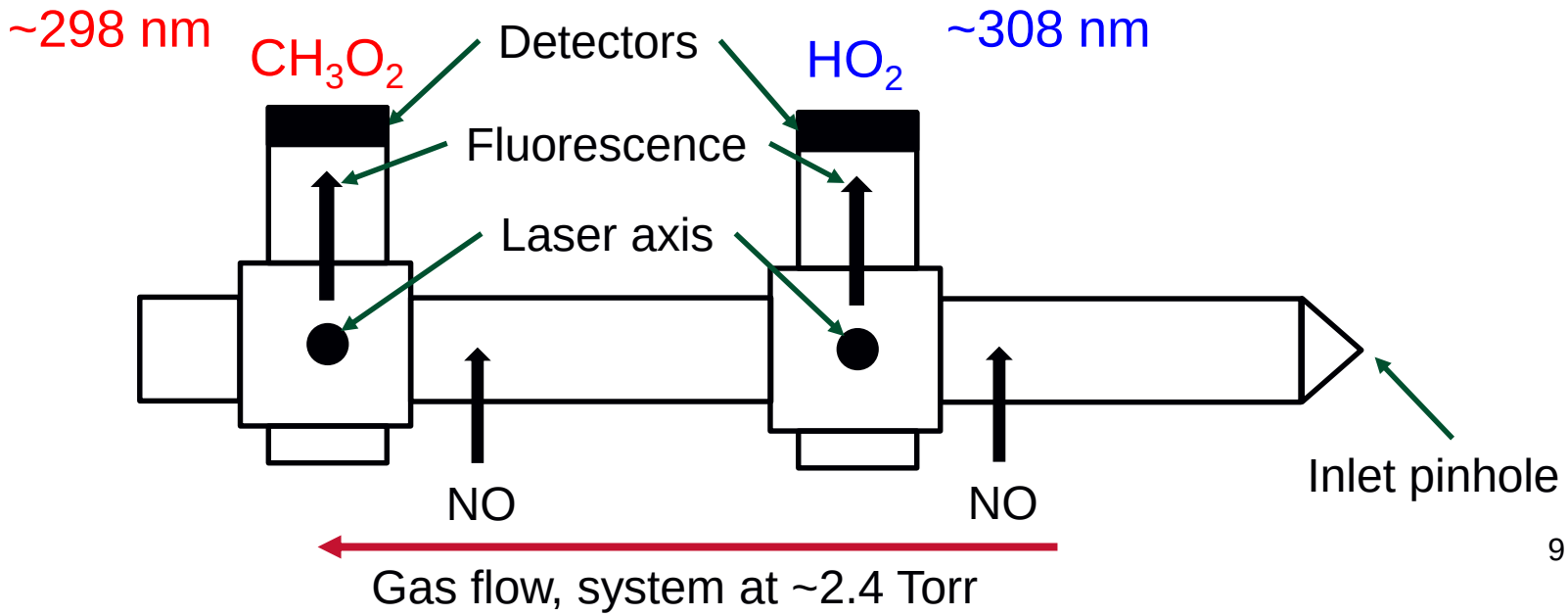


Fluorescence Assay by Gas Expansion (FAGE)

- HO_2 or CH_3O_2 radicals are detected by their reaction with NO to OH and CH_3O:

$$HO_2 + NO \rightarrow OH + NO_2$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

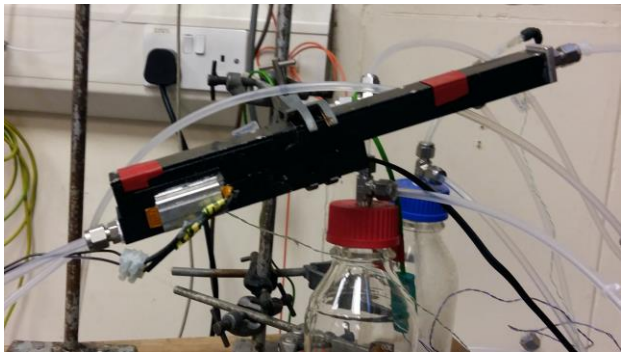


FAGE Calibration

- Photolysis of humidified air to produce OH and HO_2:

  $H_2O + h\nu\ (185\ nm) \rightarrow OH + H$

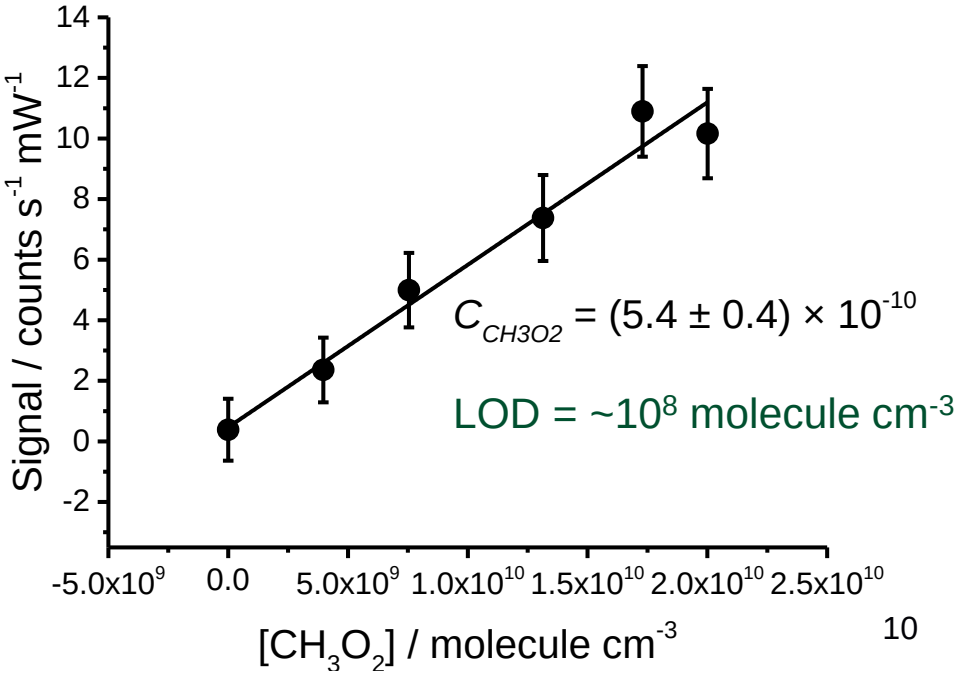
  $H + O_2 \rightarrow HO_2$



- Add CH_4 to convert all OH to CH_3O_2:

  $OH + CH_4 \rightarrow CH_3$

  $CH_3 + O_2 \rightarrow CH_3O_2$



HO_2 LOD = ~10^6 molecule cm^{-3}

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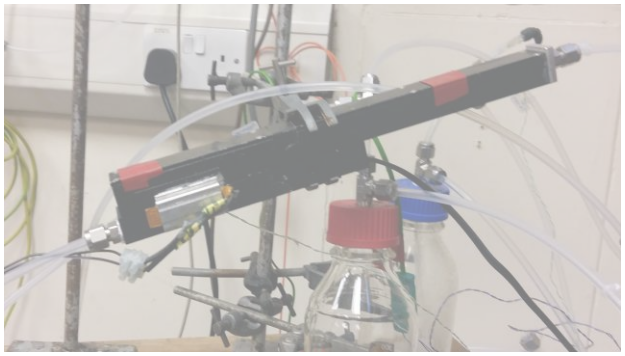
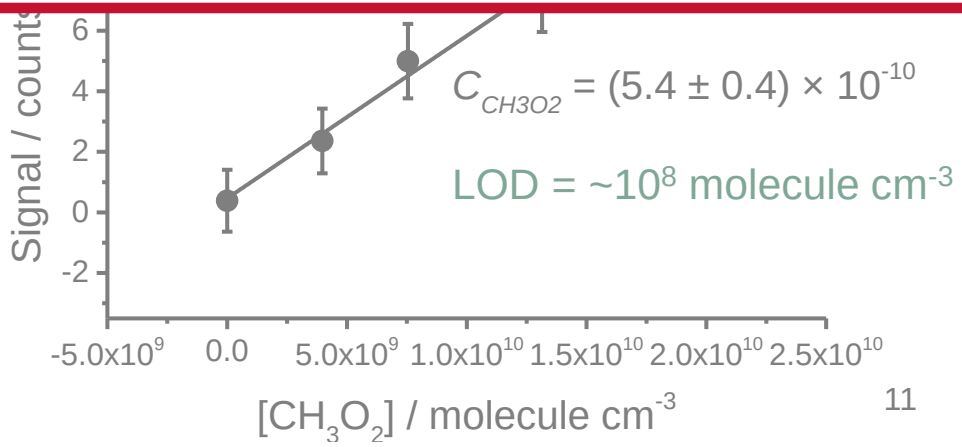


Potential for field measurements of CH_3O_2:
Tropical Atlantic ocean: $[CH_3O_2] \sim 7 \times 10^8$ molecules cm^{-3}
Tropical rainforest: $[CH_3O_2] \sim 2 \times 10^8$ molecules cm^{-3}

$OH + CH_4 \rightarrow CH_3$

$CH_3 + O_2 \rightarrow CH_3O_2$



HO_2 LOD = ~10^6 molecule cm^{-3}

$HO_2 + CH_3O_2$ Cross-reaction

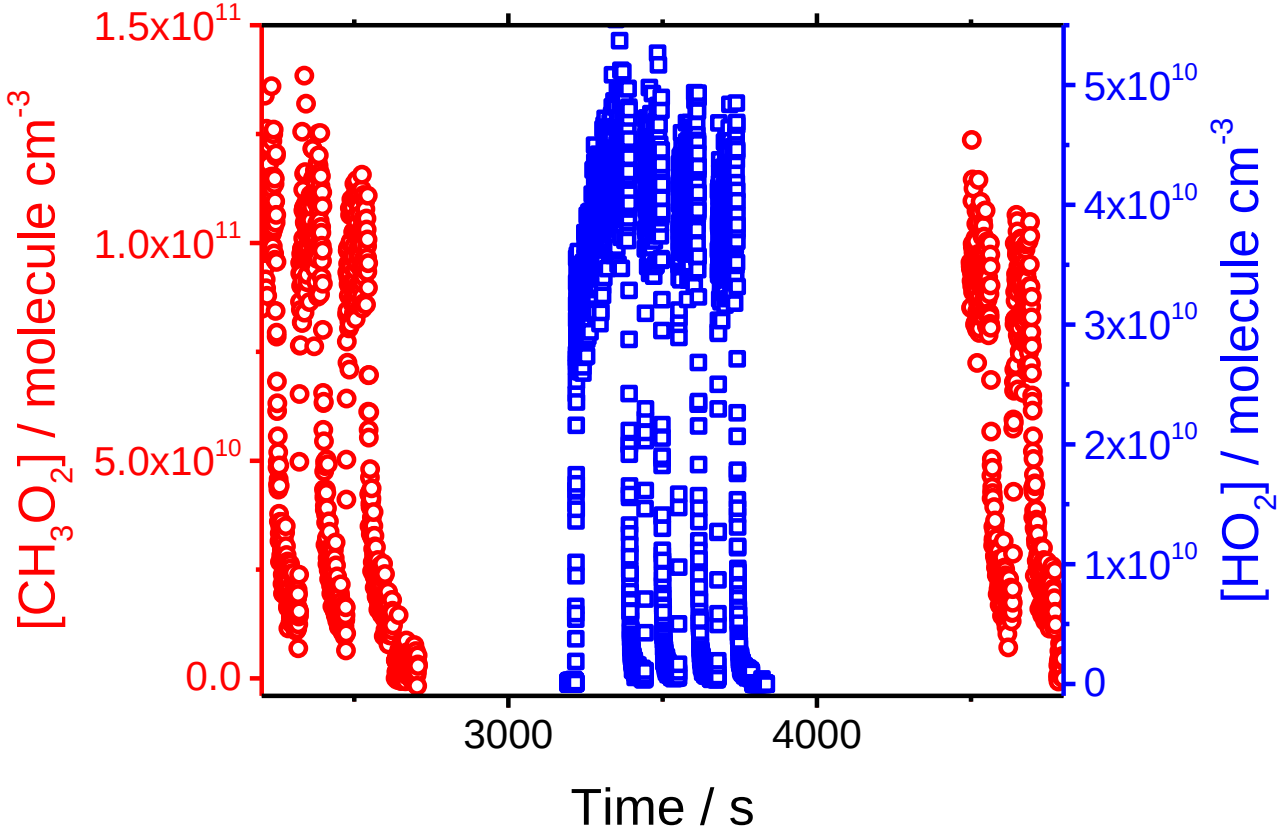
$HO_2 + CH_3O_2$	$\rightarrow O_2 + CH_3COOH$	0.9
	$\rightarrow O_2 + HCHO + H_2O$	0.1

- Current rate coefficient at 298 K *:
  - 5.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1}
- 23% 1σ uncertainty. The majority of previous studies used UV-absorption spectroscopy, which is often an unselective technique.
- Need for kinetic studies using a selective method

* http://iupac.pole-ether.fr

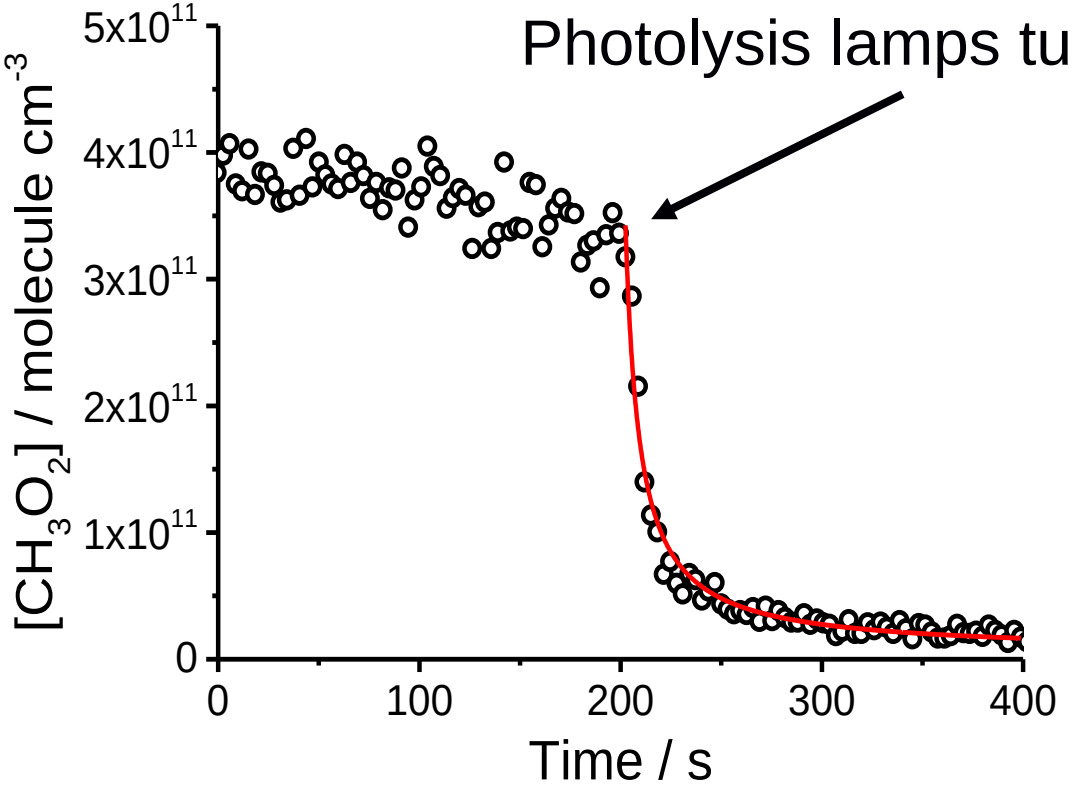
HO_2 + CH_3O_2 Cross-reaction: Results

- HO_2 and CH_3O_2 measured in HIRAC with FAGE
- Reaction mixtures of $CH_4/CH_3OH/Cl_2$



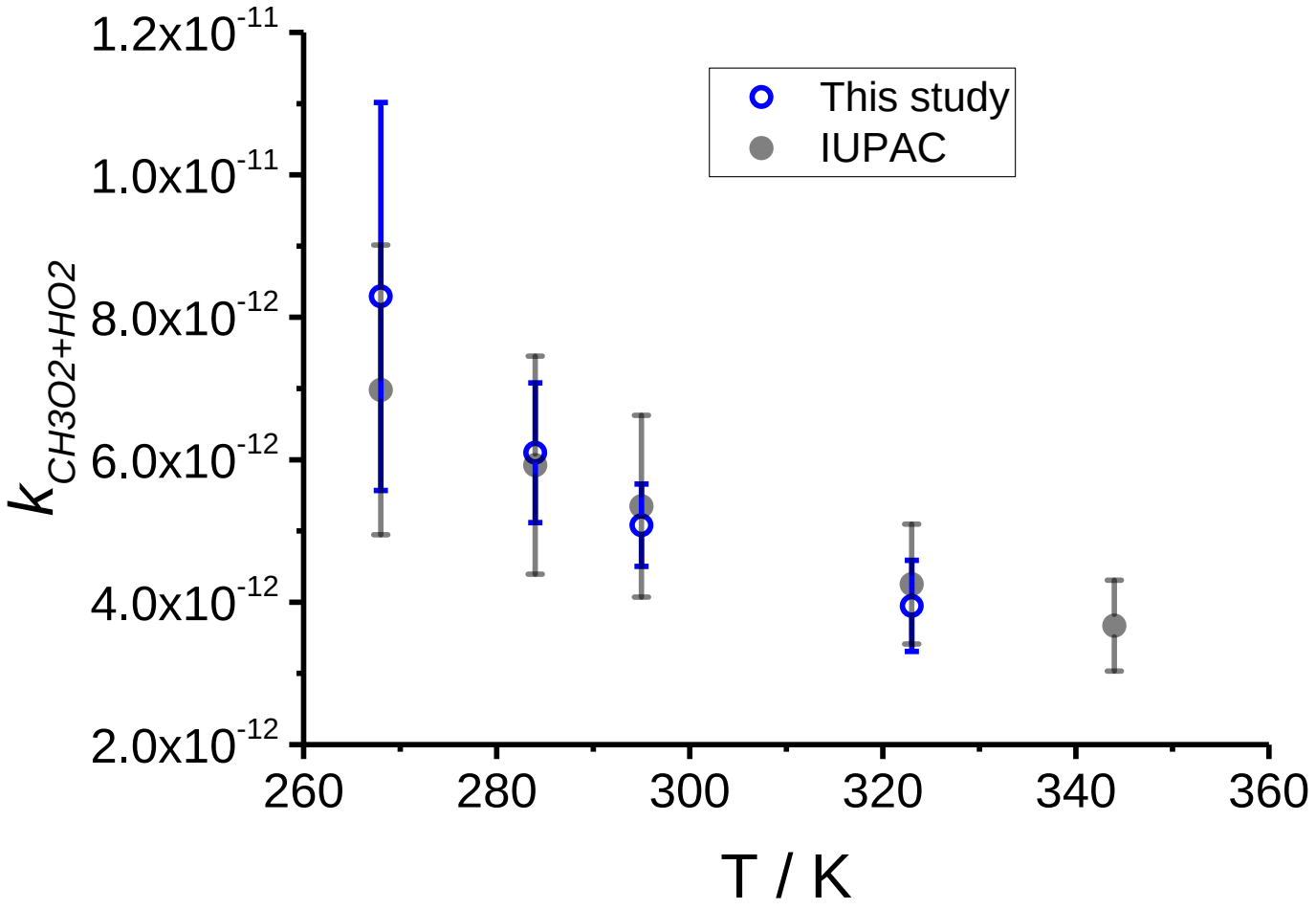
HO_2 + CH_3O_2 Cross-reaction: Fitting Data

- Second-order decays fitted to obtain the rate coefficient at different temperatures



$HO_2 + CH_3O_2$ Cross-reaction: Temperature Dependence

- Experiments at 268, 284, 295, 323, and 344 K



Conclusions

- The rate coefficient of HO_2 + CH_3O_2 measured
  - Varying temperatures
  - Detecting both radicals using a selective method
- The IUPAC recommended value confirmed
  - Improvement of the uncertainty
- Negative temperature dependence of the reaction was confirmed
- Additional experiments at 344 K are currently being performed and analysis finalised.
- Next: Experiments will be performed at varying pressures investigating a possible pressure dependency.

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