

A new method for CH₃O₂ radical detection and studies of the CH₃O₂ self-reaction in HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry)

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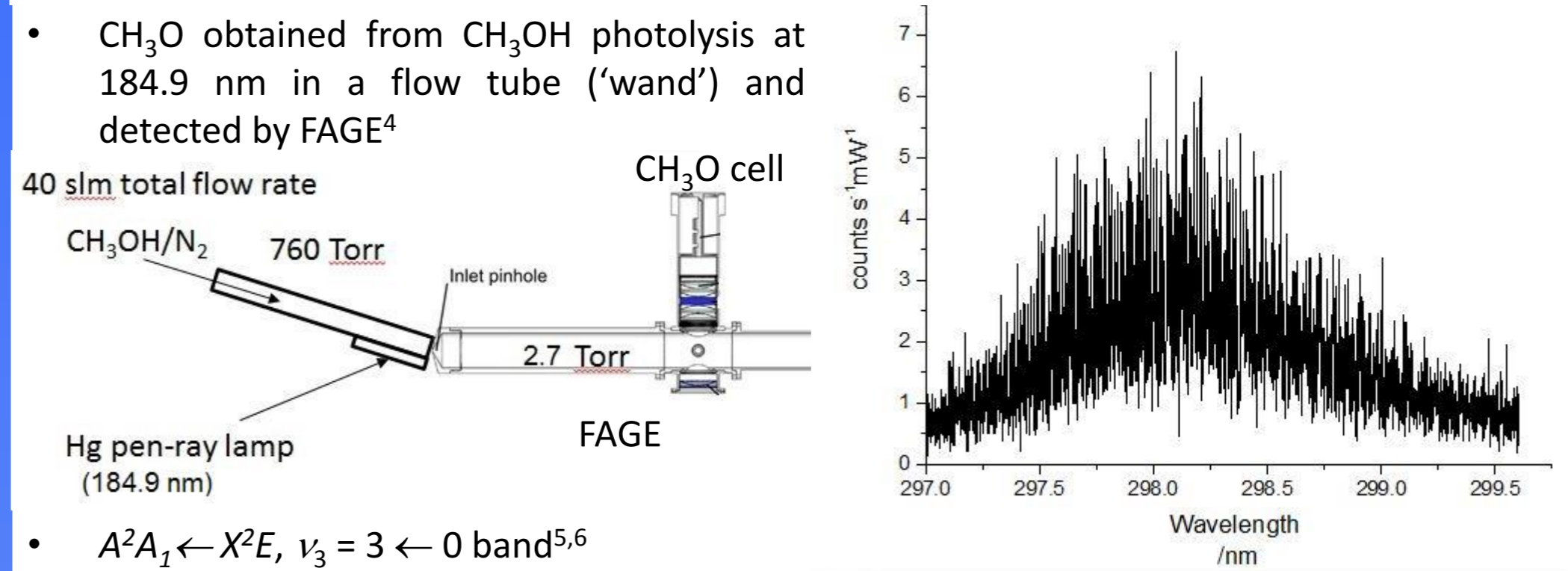


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1. Introduction

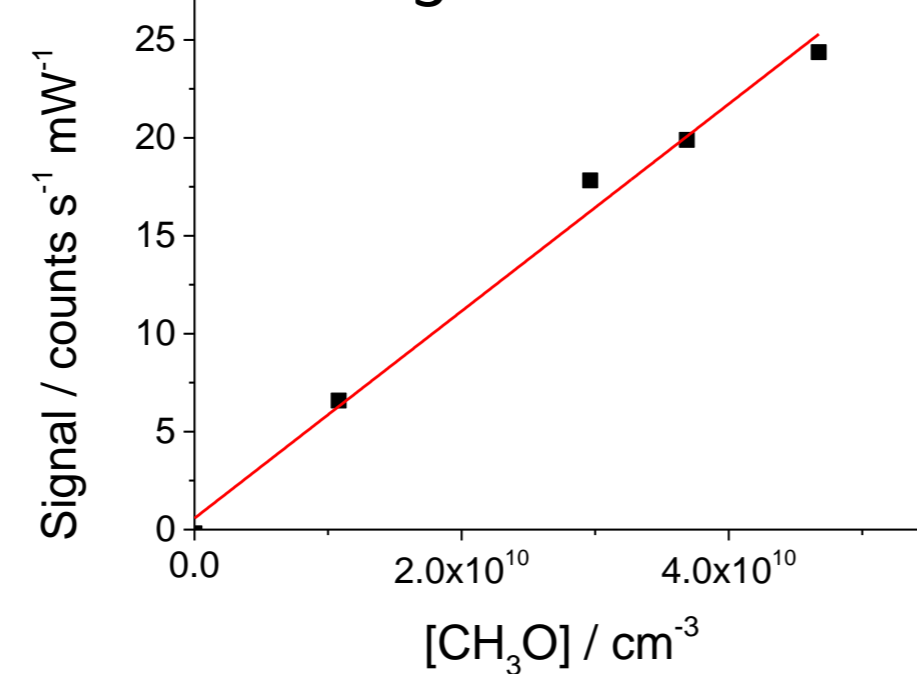
- Despite its importance, at present methylperoxy radical, CH₃O₂, is not measured in the atmosphere.
- Typically only the sum of the organic peroxy (RO₂) radicals is measured, making no distinction between different RO₂ species.¹ RO₂ are difficult species to measure in the troposphere due to their low concentrations, $\leq 10^8$ cm⁻³.
- CH₃O is at the centre of tropospheric methane oxidation. However, due to its short lifetime in air, CH₃O is in very low concentrations and not measured in the atmosphere. CH₃O in relatively high concentrations, 10^{13} cm⁻³, has been detected by laser induced fluorescence (LIF) in kinetic studies.²
- Objectives:** Detect CH₃O at low pressure by FAGE (Fluorescence Assay by Gas Expansion) to improve the limit of detection of the method.
- Develop a new method for the detection of CH₃O₂ by FAGE with the potential to directly measure atmospheric levels of CH₃O₂ and potentially other RO₂ species such as C₂H₅O₂.
- Explore the new technique in studies of key atmospheric reactions such as the CH₃O₂ self-reaction within HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry)³ to determine kinetic parameters and branching ratios.

2. Laser excitation spectrum of CH₃O



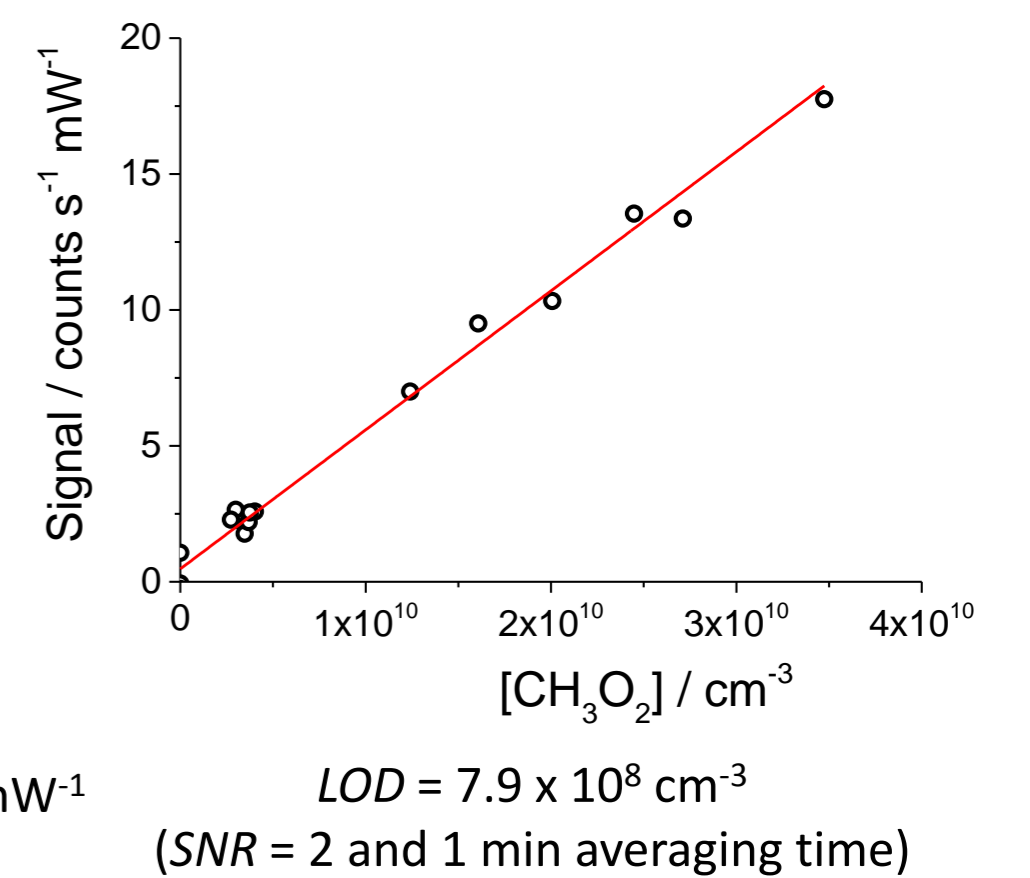
3. FAGE calibration for CH₃O

- CH₃OH $\xrightarrow{184.9 \text{ nm}}$ CH₃O + H
- CH₃O yield = 0.86, as determined at 193.3 nm.⁷
- FAGE sensitivity to CH₃O:
 $c_{\text{CH}_3\text{O}} = (5.3 \pm 0.3) \times 10^{-10}$ counts s⁻¹ cm³ mW⁻¹
- LOD = 7.0×10^8 cm⁻³ for SNR = 2 and 1 min averaging time



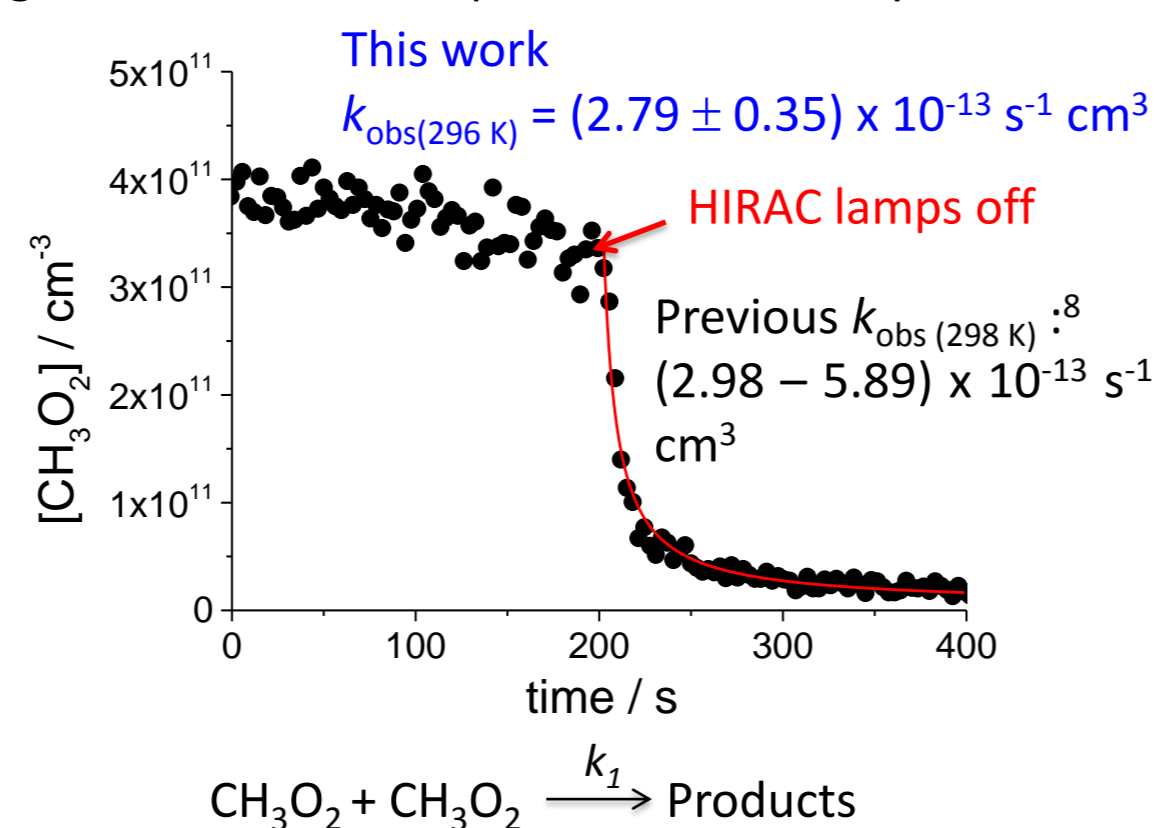
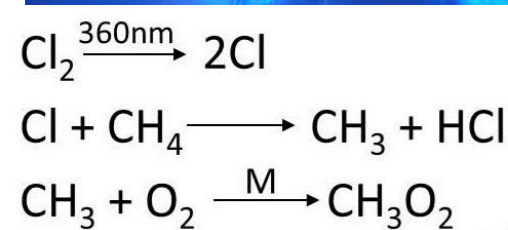
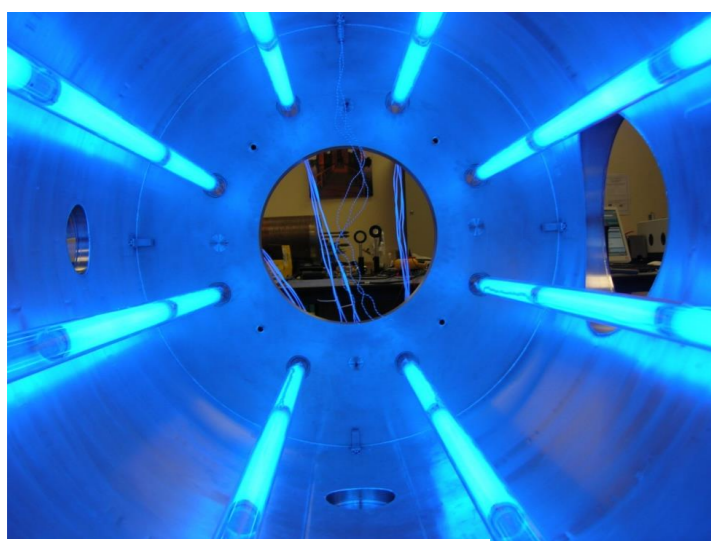
4. FAGE calibration for CH₃O₂

- Water vapour photolysis in the 'wand' through which 40 slm of humidified air and 80 sccm CH₄ are passed
- $\text{H}_2\text{O} \xrightarrow{184.9 \text{ nm}} \text{OH} + \text{H}$
 $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$
 $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$
- CH₃O₂ titrated to CH₃O and detected by FAGE at ~ 298 nm; measured fluorescence from 320 to 400 nm:
 $\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$
- $c_{\text{CH}_3\text{O}_2} = (7.2 \pm 0.8) \times 10^{-10}$ counts s⁻¹ cm³ mW⁻¹
- LOD = 7.9×10^8 cm⁻³ (SNR = 2 and 1 min averaging time)

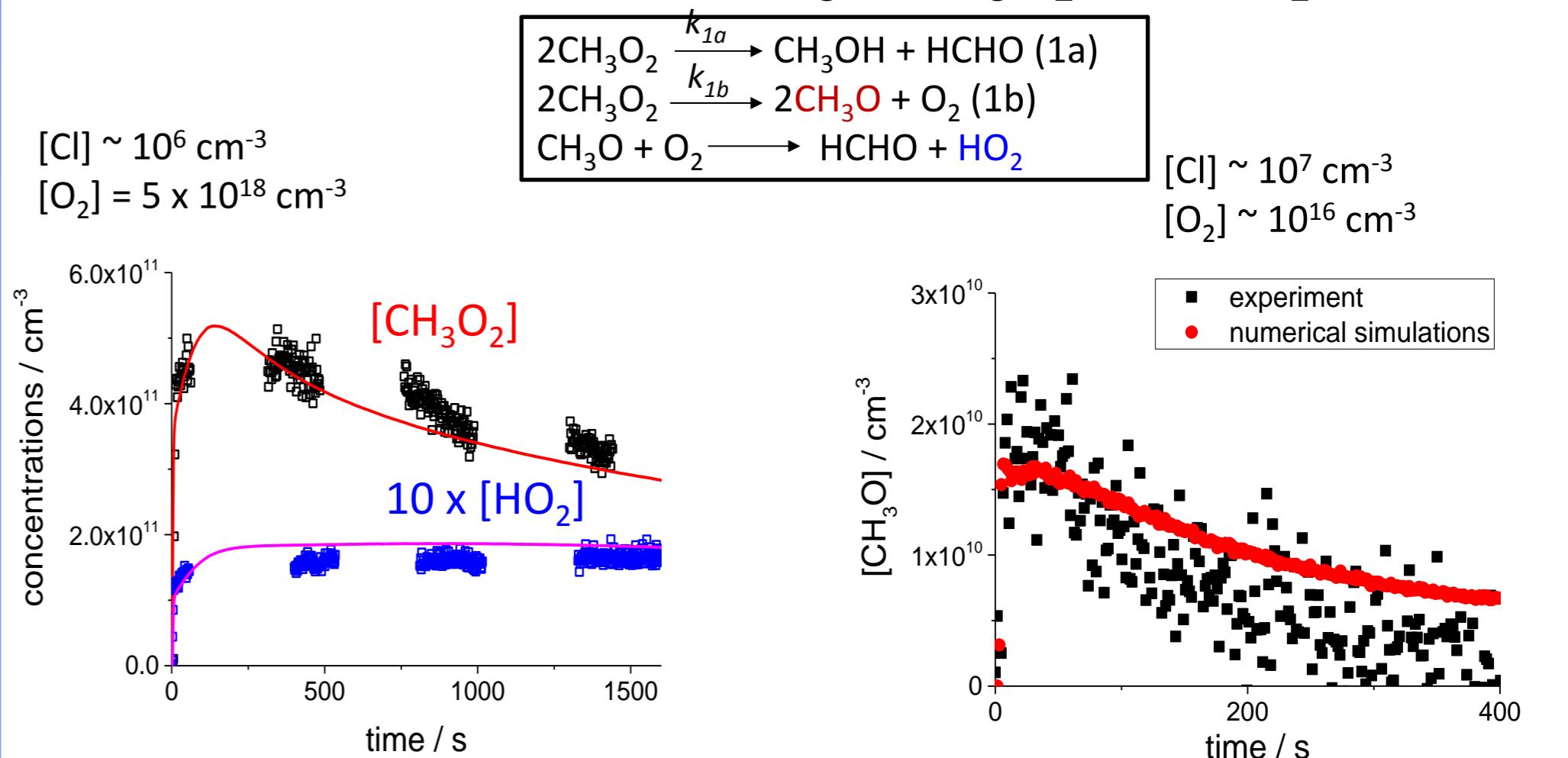


5. Kinetic study of the CH₃O₂ self-reaction using HIRAC

- HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry) is a 2.25 m³ stainless steel cylinder equipped with 4 mixing fans and 8 UV lamps mounted radially inside the chamber

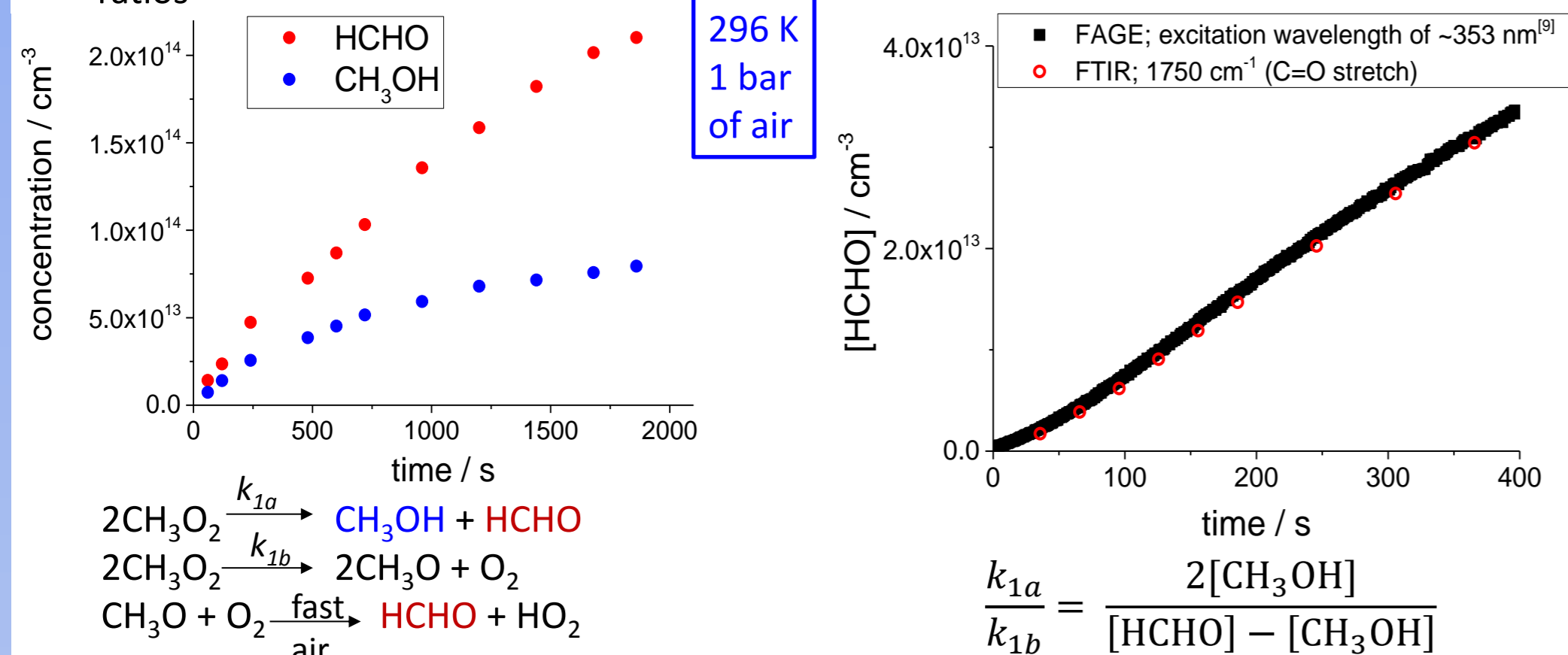


6. FAGE measurements of CH₃O, CH₃O₂ and HO₂ in HIRAC



7. Study of the branching ratios in the CH₃O₂ self-reaction

- FTIR monitoring of the formation of the stable products, CH₃OH and HCHO, to determine the branching ratios
- Good agreement between the FTIR and FAGE measurements of HCHO at 265, 296 and 320 K.



8. Branching ratio for the formation of CH₃OH and HCHO

- Temperature has little effect, within errors

Temperature / K	Branching ratio r_{1a}		$r_{1a} = \frac{k_{1a}}{k_{1a} + k_{1b}}$	$r_{1a} = 1 - r_{1b}$
	This work	Previous work		
296	0.66 ± 0.06	0.63 ± 0.06^{10}	$r_{1b} = \frac{1}{1 + [\exp(\frac{1331}{T})]/27}$	$r_{1a} = 1 - r_{1b}$
321	0.65 ± 0.06	0.56^9		
340	0.58 ± 0.06	0.51^9		

⁹Horie *et al.*'s result¹¹ modified to reproduce r_{1b} found by Orlando and Tyndall at 296 K:¹⁰

9. Conclusions

- A new method has been developed for the detection of CH₃O₂ radicals by FAGE by titrating CH₃O₂ to CH₃O by reaction with added NO and then detecting the resultant CH₃O by LIF.
- The limit of detection (LOD) of the technique is $\sim 7 \times 10^8$ cm⁻³ CH₃O₂ for a signal-to-noise ratio of 2 and 1 min averaging time and hence has potential to be used in field measurements.
- A similar LOD has been obtained by the direct generation of CH₃O followed by detection using FAGE.
- Preliminary experiments using FAGE to detect ethylperoxy (C₂H₅O₂) radicals by the titration of C₂H₅O₂ to C₂H₅O with NO followed by the LIF detection of C₂H₅O show that LOD(C₂H₅O₂) is of about one order of magnitude higher than LOD(CH₃O).
- CH₃O₂ was monitored during its self-reaction within HIRAC at 1 bar and room temperature to determine an observed rate coefficient of $(2.79 \pm 0.35) \times 10^{-13} \text{ s}^{-1} \text{ cm}^3$.
- Products of the CH₃O₂ self-reaction were also observed, namely CH₃O and HO₂ (from reaction of CH₃O + O₂) monitored by FAGE, formaldehyde (HCHO) measured by FAGE and FTIR, and methanol observed by FTIR.
- Good agreement has been obtained between the FTIR and FAGE measurements of HCHO.
- Using the concentrations of CH₃OH and HCHO, the branching ratios in the CH₃O₂ self-reaction has been determined in the range 296 – 340 K and little temperature dependence has been observed.

References

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