A new method for atmospheric detection of the CH₃O₂ radical and an intercomparison of methods for HO₂ and CH₃O₂ detection

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• CH_3O_2 titrated to CH_3O and then detection

by off-resonance LIF: $A \leftarrow X$ excitation at

~298 nm; measured fluorescence from 320

to 400 nm.¹ $CH_3O_2 + NO \longrightarrow CH_3O + NO_2$

1. Introduction

- The hydroperoxy radical, HO₂, and organic peroxy radicals, RO₂, participate in rapid chemical cycling at the heart of tropospheric oxidation.
- Laser-induced fluorescence (LIF) spectroscopy at low-pressure, known as the Fluorescence Assay by Gas Expansion (FAGE) technique, is most commonly used for the measurements of HO₂ in the atmosphere. FAGE is an indirect technique using the conversion of HO₂ to OH by reaction with added NO followed by OH on-resonance LIF at 308 nm.
- Despite their importance, at present typically only the sum of RO_2 radicals is measured in the atmosphere, making no distinction between different RO₂ species.
- We have developed a new method for the detection of CH_3O_2 by FAGE with the potential to directly measure atmospheric levels of CH_3O_2 and other RO_2 species such as $C_2H_5O_2$.¹
- In order to validate FAGE technique we have performed intercomparisons of measurements of HO₂ and CH₃O₂, respectively by the indirect FAGE and the direct Cavity Ring-Down Spectroscopy (CRDS) techniques within the Leeds HIRAC atmospheric simulation chamber.² CRDS was probing HO₂ using the excitation of the first O-H overtone at 1506.43 nm and CH_3O_2 using the $A \leftarrow X$ electronic excitation at 1335.49 nm.

3. 'Wand' calibration of FAGE at ~1000 mbar



2. 'Wand' calibration of FAGE for HO₂ and CH_3O_2

- Conventional water vapour photolysis at 184.9 HO_2 titrated to OH and then detected by nm in a flow tube ('wand') where humidified air on-resonance LIF at 308 nm $HO_2 + NO \rightarrow OH + NO_2$
 - is flowed past the lamp to generate HO_2 :³
 - $H_2O \xrightarrow{184.9nm} OH + H$ $H + O_2 \rightarrow HO_2$
- In the FAGE calibration for CH_3O_2 methane is added to the air flow prior to the wand.¹



4. FAGE calibration using a kinetic method

 HO_2 8.0x10¹⁰ ° 🥢



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8. 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.¹
- For a signal-to-noise (S/N) ratio of 2 the limit of detection of the technique is 1.2×10^9 cm⁻³ for 30 s time resolution and 1.1×10^8 cm⁻³ CH₃O₂ for 1 hour averaging time. Therefore, the method has potential to be used in field measurements.¹
- The first FAGE-CRDS intercomparisons for HO₂ and CH₃O₂, respectively, have been performed to find a very good agreement at 150 and 1000 mbar of air for $[HO_2]$ between ~ 1–80 × 10⁹ cm⁻³,¹² at 100 mbar of air for $[CH_3O_2]$ in the range from ~ 1–60 × 10¹⁰ cm⁻³ and 1000 mbar of air for $[CH_3O_2]$ between ~ 3–30 × 10¹⁰ cm⁻³.
- The limits of detection for the CRDS measurements¹² for S/N = 2 and 30 s averaging time are: 3.0×10^8 cm⁻³ at 150 mbar and 1.5×10^9 cm⁻³ at 1000 mbar for HO₂, 8.9×10^9 cm⁻³ at 100 mbar and 2.0 \times 10¹⁰ cm⁻³ at 1000 mbar for CH₃O₂.
- The very good agreement between HO₂ concentrations measured using the indirect FAGE method and the direct CRDS method provides a validation for the FAGE method, which is used widely for field measurements of HO_2 in the atmosphere.
- For both HO₂ and CH₃O₂ the CRDS sensitivity is insufficient to detect the ambient levels of these radicals (typical concentrations of $10^7 - 10^8$ cm⁻³ orders of magnitude) but is more than adequate for chamber studies where in general $[HO_2]$ and $[CH_3O_2]$ are above 10^{10} cm⁻³. Note that no chamber measurements of HO₂ and CH₃O₂ by CRDS have been performed prior to this study.