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Atmospheric Measurement Techniques Discussions

Interactive comment on "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)" *by* Lavinia Onel et al.

Anonymous Referee #3

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This manuscript reports the calibration of a laser-induced fluorescence instrument (FAGE design) dedicated to the measurement of methyl peroxy radicals using two calibration approaches: 1/ water-photolysis at 184.9 nm and ambient pressure in presence of CH4 and 2/ kinetic decays of CH3O2 from its self-reaction. The latter, performed in the Leeds HIRAC chamber, allows calibrating the LIF instrument at ambient and lower pressures (80 and 100 mbar in this study). The results showed that at atmospheric pressure the two calibration approaches agree within 30%. While this difference is

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Discussion paper

within the combined uncertainty of the 2 approaches, the authors believe that it is due to an overestimation of the CH3O2+CH3O2 rate constant recommended by IUPAC.

The LIF instrument was then compared to a CRDS by generating CH3O2 in HIRAC at low (80 and 100 mbar) and ambient (1000 mbar) pressure. The authors report a good agreement between the 2 instruments with correlation slopes close to unity (within 10%) and indicate that this study validates the use of FAGE for CH3O2 measurements.

There is currently a need for the development and the validation of new techniques capable of measuring speciated organic peroxy radicals and this study provides additional confidence in the use of the FAGE technique for the measurement of one of the most abundant organic peroxy radicals in the atmosphere. This work will be of interest for the scientific community. The manuscript is well written, clear and concise, and this reviewer recommends publication in AMT once the following minor comments have been addressed.

Minor comments:

P2-P3: Several techniques are discussed for the measurement of peroxy radicals. The authors should also briefly discuss the use of chemical ionization mass spectrometry methods such as published in Noziere and Hanson (2017), Noziere and Vereecken (2019), Hansel et al. (2018), Jokinen et al. (2014), etc.

P4 L16 & P5 L19: CH4 is used during calibration experiments as a precursor for CH3O2 and is added in the Water-photolysis calibrator and the HIRAC chamber at concentrations as high as 2.5E17 molecule/cm3. Can the authors comment on the potential impact of CH4 on the quenching of CH3O in the detection cell?

P7 Eq. 6: Please define kloss

P6 L9-13 & P12 L4-6: What were the fitted values for kloss? Are the values inferred from the two experiments consistent with each other?

P6 L22: “1E-10” should read “1E-9”

P15 L9-12 & L17-18 & L21-22: The authors show that correlation plots between FAGE and CRDS exhibit slopes that are close to unity. However, the y-intercepts of the regression lines are not discussed. Were the intercepts not statistically significant?

P16 Figures 6-7: When the lamps are turned off, (1) the CRDS measurements seem to decrease to lower values than FAGE and (2) the FAGE measurements seem to reach a plateau more rapidly than the CRDS. Could the authors comment on this?

References:

Nozière, B. and D. R Hanson (2017), Speciated Monitoring of Gas-Phase Organic Peroxy Radicals by Chemical Ionization Mass Spectrometry: Cross-Reactions between CH3O2, CH3(CO)O2, (CH3)3CO2, and câĂŚC6H11O2, J. Phys. Chem. A, 121, 8453-8464.

Noziere, B., & Vereecken, L. (2019). Direct Observation of Aliphatic Peroxy Radical Autoxidation and Water Effects: an Experimental and Theoretical Study. Angew. Chem. Int. Ed., doi: 10.1002/ange.201907981.

Hansel, A., Scholz, W., Mentler, B., Fischer, L., & Berndt, T. (2018). Detection of RO2 radicals and other products from cyclohexene ozonolysis with NH4+ and acetate chemical ionization mass spectrometry. Atmos. Environ., 186, 248-255.

Jokinen T, Sipilä M, Richters S, et al. Rapid autoxidation forms highly oxidized RO2 radicals in the atmosphere. Angewandte Chemie (International ed. in English). 2014 Dec;53(52):14596-14600. DOI: 10.1002/anie.201408566.

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