

Interactive comment on “A new method for atmospheric detection of the CH₃O₂ radical” by Lavinia Onel et al.

Anonymous Referee #2

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This manuscript reports the development and the calibration of an instrument to measure ambient concentrations of methyl peroxy radicals. This instrument is based on the well-known FAGE technique, which is currently used by several groups around the world, including the authors, to measure ambient concentrations of OH and HO₂ radicals. The FAGE technique was recently extended for measuring total peroxy radicals. One of the current limitations to investigate atmospheric free radicals chemistry is the lack of techniques to perform speciated measurements of peroxy radicals. The work reported in this publication starts addressing this issue by extending the use of the FAGE technique to the measurement of methyl peroxy radicals, one of the most abundant organic peroxy radicals in the atmosphere. The modified FAGE apparatus is well described and its calibration is investigated using two different approaches, the con-

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ventional water photolysis approach used to calibrate OH and HO₂ on conventional FAGE instruments - with the addition of methane in the calibration cell to convert OH into CH₃O₂ - and an approach based on monitoring CH₃O₂ in an atmospheric chamber when it decays due to its self-reaction. The two approaches are shown to be in agreement within uncertainties.

This manuscript is well structured, clear and concise, and the proposed approach for measuring methyl peroxy radicals seems promising for both field measurements and laboratory studies. I therefore recommend publication in AMT after the authors address the following comments:

1/ The sensitivity of conventional FAGE instruments is known to be dependent on the ambient water concentration due to the quenching of excited OH radicals by water molecules. This matrix effect is taken into account through the calibration of the OH sensitivity at different water-vapor concentrations. Can excited CH₃O radicals also be quenched by water vapor? If so, what is the implication for ambient measurements of CH₃O₂?

2/ For calibration purposes, CH₃O₂ is generated using the water-photolysis approach by adding an excess of methane in the photolysis cell. Could the authors comment on the potential quenching of excited CH₃O by methane during calibration experiments?

Minor comments:

P4 L4: "Here we report he first . . ." should read "Here we report the first . . ."

P4 L13: Please report the sampling flow rate of the FAGE apparatus

P5 L4-5: Since the detection of the CH₃O fluorescence is red-shifted from the excitation, why is the counting window delayed by 100 ns from the laser pulse? This time gating approach is usually used for the detection of on-resonant fluorescence.

P5 L12-15: the authors mention that the wavelength is tuned on/off resonance with the CH₃O transition line. In FAGE instruments, OH is continuously generated in a

reference cell to be able to precisely tune the laser wavelength on and off resonance. How is it performed for CH₃O on this instrument? Is CH₃O continuously generated in a reference cell? If so, how is it done?

P7 L15: The authors indicate a CH₃O₂-to-CH₃O conversion efficiency of 40% at the optimum NO concentration. However, since CH₃O can also be lost through its reaction with NO (and potentially through its reaction with O₂ as well), isn't the 40% representative of a lower limit of the conversion?

P10 L12-13: It is indicated that the photon flux was varied between 0-1.5E14 photon/cm²/s. However, the lower bound reported for the radical generation is 1.5E10 molecule/cm³, which cannot correspond to a photon flux set at zero. Please clarify.

P12 L9-14: The detection limits are calculated for a BKG signal of approximately 100 ct/s, which is reported as a typical value for this instrument. What are the contributions of the scattered visible and laser lights? How is the BKG signal expected to change when the solar irradiation changes during field measurements? How will it affect the detection limit during daytime?

P13 L22: caption Fig. 7. "cm-1" should read "cm-3"

P15 L21 & L22: Two different uncertainties are given for the on-line signal: 12% and 6%. Which one is correct?

P16 L39: The authors indicate that the oxygen concentration was lowered in some experiments performed on the HIRAC chamber. Could the lower oxygen concentration lead to a different sensitivity towards CH₃O due to changes in quenching rates of excited CH₃O?

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