Interactive comment on "A new method for atmospheric detection of the CH$_3$O$_2$ radical" *by* Lavinia Onel et al.

Anonymous Referee #3

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This paper presents details on the development of a new method to detect the CH$_3$O$_2$ radical in the atmosphere using laser-induced fluorescence techniques. Current methods for the detection of peroxy radicals in the atmosphere are unable to distinguish between CH$_3$O$_2$ and other organic peroxy radicals. Given the importance of CH$_3$O$_2$ radical chemistry in the atmosphere, a selective and sensitive method to detect these radicals both in the atmosphere and in chamber studies would provide an important tool for improving our understanding of atmospheric chemistry.

The method utilizes the Laser-Induced Fluorescence-Fluorescence Assay by Gas Expansion (LIF-FAGE) technique that is currently used for the sensitive detection of the OH and HO$_2$ radicals in the atmosphere. Similar to the detection of HO$_2$ radicals by this technique, the authors convert CH$_3$O$_2$ radicals to CH$_3$O radicals inside the FAGE

detection cell using the CH$_3$O$_2$ + NO reaction, and then detect the CH$_3$O radicals using laser-induced fluorescence. The paper describes several methods used to calibrate the instrument – production of CH$_3$O$_2$ radicals from the OH + CH$_4$ reaction in a flow tube (with OH radicals produced from the photolysis of water vapor), production of CH$_3$O$_2$ from the photolysis of CH$_3$OH in a flow tube, and monitoring the decay of CH$_3$O$_2$ radicals from the CH$_3$O$_2$ +CH$_3$O$_2$ reaction in the HIRAC chamber. The paper is well written and suitable for publication in AMT after the authors consider the following comments.

Page 4 line 30 and Page 6 Figures 2 and 3: As with detection of OH by the LIF-FAGE technique, the authors must tune the laser on and off of the CH$_3$O transition to determine the net signal due to CH$_3$O fluorescence and the background signal due to laser scatter and other broadband fluorescence. OH LIF-FAGE instruments use a reference cell that generates high concentration of OH radicals to ensure that the laser is tuned to the correct frequency. It is unclear how the authors know that the laser is tuned to the correct CH$_3$O excitation wavelength. Do they use a spectrometer to measure the wavelength, or do they have a reference cell that generates CH$_3$O radicals?

Page 8 line 25: Equation 2 assumes that the concentration of methanol is proportional to the concentration of water vapor and that any loss of methanol in their bubbler system is equal to any loss of water in their flow tube. Can the authors justify this assumption?

Page 12, line 25: The authors claim that reducing the pressure in their FAGE detection cell could increase the sensitivity of the instrument. Is this due to reduced quenching of the CH$_3$O fluorescence by air? Have the authors measured the impact trace gases on the fluorescence efficiency, such as water vapor?

Page 12, line 26: How does the OH sensitivity of the HIRAC FAGE compare to the field instrument? Assuming the CH$_3$O sensitivity scales with the differences in the OH sensitivity, can the authors be more specific regarding the potential improvement in the

LOD if this technique were to be used in the field instrument?

Page 16, line 19: The authors suggest that based on their flow tube calibrations that the rate constant for the $CH_3O_2 + CH_3O_2$ reaction may be 25% too high, perhaps due to a 25% overestimation of the CH_3O_2 absorption cross section. What is the uncertainty associated with the recommended rate constant? Does the rate constant derived using their flow tube calibration factor agree to within the combined uncertainty of the calibration and the rate constant?

Figure 8: The authors measure the concentration of CH_3O in nitrogen to reduce the loss of CH_3O from the $CH_3O_2 + O_2$ reaction. However, it appears that they use the calibration factor determined in air to estimate the CH_3O concentrations in this experiment. Does the calibration factor change in N_2 compared to air due to different fluorescence quenching rates?

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