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Atmospheric Measurement Techniques Discussions



# *Interactive comment on* "Technical Note: Can ozone be used to calibrate aerosol photoacoustic spectrometers?" *by* Donald A. Fischer and Geoffrey D. Smith

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1) I suspect that experiments in the absence of O2 are motivated by the reaction to reform O3 (O(3P) + O2 -> O3, JPL Publication 15-10, Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies), however, this reaction is not discussed explicitly nor are the results compared with the known rate of this reaction. The authors should discuss this reaction, and it would be helpful if the authors attempted a simple box model of O3 photochemistry in the PAS cell.

The reviewer is correct, and the O(3P) + O2 -> O3 reaction is discussed on p. 7 line 6. We thank the reviewer for referring a citation for this reaction and have cited it in



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the text. We performed a simple photodissociation calculation to assess the extent to which O3 would be lost in our experiments (see point #2, below).

2) In the discussion of photodissociation of O3 by 532 nm light, could the authors estimate the expected loss of O3 based on the residence time in the sample cell, O3 cross section, and assuming 100% yield to the photodisociation [sic] channel.

We thank the reviewer for this suggestion. We have carried out such a photodissociation calculation and estimate that most (much greater than 99.9%) of the O3 should be dissociated. We surmise that the reason that only 5% of the O3 was lost (Figure 3a) might result from rapid recombination to form O3. We estimate that it would take only 4 ppm O2 for recombination to compete with photodissociation. We have included this analysis in the discussion of Figure 3a.

3) Page 2 line 26 – My understanding is that Bluvshtein et al. measured the RI only of the nigrosine independently. For other materials, the RI was retrieved from broadband extinction measurements.

This is correct. Thank you for pointing out our error. The manuscript has been adjusted to reflect that only the RI of nigrosin was measured independently.

4) Does an absorber need to be present to determine the resonant frequency? Or is a background signal used?

Although an absorber can be used to determine the resonant frequency, it is not necessary and we conduct the frequency sweep in the bath gas without an absorber. Thank you for pointing out that we did not specify this; the manuscript has been updated to include this.

5) Figure 3 – Drifts in the PAS signal are not explained. Do the authors know the source of these drifts?

The drift in Figure 3B is likely due to drift in the O3 concentration as the trap becomes depleted of O3; we have included mention of this in the figure caption. The source

of drift in Figure 3A is not known, but it may reflect a drift in resonance frequency or temperature, but we point out that it does not affect the overall message of the figure: The effect of O3 photodissociation on the PAS signal is small and not enough to explain the factor of two discrepancy with and without O2 present. This analysis is now included in the body of the manuscript.

6) Figure 4a: The peach/orange color trace is mislabeled. I understand it to be 780 nm?

Thank you for pointing out our mistake. The legend has been updated to indicate the salmon-colored trace represents 780 nm.

7) Figure 4b: In this figure it seems that the PAS sensitivity in the absence of O2 for 662 and 532 differ by 10-20%, but in figure 2 the calibration slope is nearly the same for 532 nm and 662 nm in N2. Why are they different?

Figure 2 represents a single multi-point calibration, while Figure 4B represents multiple single-point calibrations. The latter case is especially susceptible to error as it represents a single measurement. Nonetheless, we do point out that the differences between the sensitivities for the three wavelengths is smaller with 100% O2 (7%) than with 100% N2 (17%), perhaps indicating that there is a real difference in the absence of O2. We do mention this possibility in the manuscript stating: “The differences in these values may reflect differences in the densities of states of the bath gas and the ozone when excited by the different wavelengths of light”.

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