

## ***Interactive comment on “Fast response cavity enhanced ozone monitor” by A. L. Gomez and E. P. Rosen***

### **Anonymous Referee #1**

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#### General comments:

##### Strengths:

Ozone is such an important atmospheric gas that additional instrumentation, capable of accurately and rapidly quantifying ozone's ambient concentration, is always welcome. The paper describes the design and initial laboratory testing of an ozone monitor based on cavity enhanced absorption spectroscopy (CEAS) – this work has been done well. The instrument has such an elegant simplicity that I'm surprised nobody else thought to do this before. Comparisons of the instrument's CEAS channel against its own single-pass absorption cell clearly demonstrate the sensitivity improvements accessible via the CEAS approach. I enjoyed reading the paper.

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##### Weaknesses:

(i) If this new instrument is to become a viable alternative, its performance needs to be benchmarked against other existing methods for quantifying ozone. Although comparison of the measurement capabilities of the instrument's CEAS and single-pass channels was informative, it was nevertheless an “internal comparison” of two ways of operating the same instrument. I was left wondering how much (and in what ways) this instrument's performance is better than its competitors. I would like to have seen a back-to-back comparison between the new instrument and one of the “best” commercially available ozone monitors, with both instruments sampling from a common inlet/gas supply. [I recognise that the final paragraph of the Discussions section attempts to compare the new instrument against the specifications of two widely-used commercial ozone monitors. But that is a paper exercise – as an instrument developer myself, I would like to have seen “real” co-sampled measurement data].

ii) The instrument's performance was tested under ideal laboratory conditions – ozone was generated in air that was, presumably, dry and particle-free. I would like to have seen examples of the instrument measuring ozone in “real” ambient air, e.g. drawn through a short inlet line from outside the authors' laboratory window. There are several potential interferences that need to be addressed when measuring an absorbance in ambient air. For example: does the instrument need an aerosol filter on its inlet line to prevent scattering/absorption of light by aerosol particles in its CEAS cell? Are there any other trace gases that absorb 250 nm light and that may be present in sufficient concentrations (especially in urban pollution) to make a measurable contribution to the absorbance? [The only extra in-sample loss considered in the Discussions section was Rayleigh scattering].

##### Specific comments:

Abstract, page 7224, line 6: “moderately high reflectivity mirrors ( $R = 99.3\%$ )”. In an absolute sense, 99.3% mirrors are very reflective. But compared to some CEAS

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systems that use  $R = 99.99\%$  mirrors, the mirrors used here are rather inefficient. Personally I would avoid comparative statements: the key point is that the current mirrors have the appropriate reflectivity to generate the cavity enhancements required for this application.

Introduction: I found some parts of the introduction to ozone's atmospheric importance to be confusing. Maybe the authors tried to cover too much ground too quickly. For example, page 7225, lines 14-16: "In addition to its influence on public health, tropospheric ozone also impacts climate. OH radicals formed by tropospheric ozone..." First point: explain how tropospheric ozone impacts climate (cf line 28). Second point: The juxtaposition of "climate" and "OH radicals" suggests a link, whereas OH radicals only indirectly affect climate by e.g. controlling the atmospheric lifetime of methane. I suggest the OH text fits better in the following paragraph about tropospheric oxidation chemistry.

In general, the Introduction was under-referenced. Some references were rather old – e.g. please reference modern reviews of ozone chemistry together with Molina & Rowland's seminal paper from 1974. Several key points went unreferenced, e.g. page 7225 line 28 "ozone is one of the most important greenhouse gases after carbon dioxide" – IPCC? Next line "To improve radiative models, [the] temporal resolution of data needs to be substantially improved" – says who?

Introduction & Discussion: There is an important distinction to be made when considering how rapidly ozone concentrations change in the atmosphere itself versus how rapid an instrument's response needs to be to capture these changes. The atmospheric chemistry might only be changing on timescales of several minutes; however if the instrument is travelling rapidly through the atmosphere on a moving aircraft, it would sample different air masses in quick succession e.g. at the edge of pollution plumes [Jones et al, 2005; Brown et al, 2012], and thus would need a sub-second rapid response.

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Page 7224, line 21: Lyman-alpha radiation is at 121.6 nm (not 210nm). Photolysis of O<sub>2</sub> can occur out to 240nm.

Page 7225, line 7: It's not helpful to use the comparator "low" to describe tropospheric ozone concentrations. Yes, mixing ratios are lower than in the stratosphere; but air pollution containing 100 ppb of ozone (i.e. much less than the ~10 ppm stratospheric mixing ratios) is hazardous to health and, as the authors note, 500 ppb is "extreme".

Line 22: More confusion. "When transported into the stratosphere, these SOAs serve as cloud condensation nuclei..." I'm not sure that SOA has a sufficiently long atmospheric lifetime to be efficiently transported into the stratosphere; also particles with a high organic content tend not to be efficient CCN. The text needs to mention SOA's detrimental effects – urban air pollution, health (uptake into lungs) and reduced visibility – all tropospheric phenomena. Needs references.

Page 7226, line 13: "The intensity of light through an optically transparent cell is compared to the transmitted intensity when the ozone has been neutralized..." How can the cell be "optically transparent" when it contains an absorbing ozone sample? Also what do you mean by ozone being "neutralized"? – chemical removal of ozone?

Line 25: I didn't understand the phrase "decay of the cell current"

Page 7227, line 3: It is worth noting that Washenfelder et al developed their cavity ring-down ozone instrument, in part, because ozone produces a small interference when measuring NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> by cavity ring-down at 662nm. High quality ozone measurements are thus beneficial for measuring other atmospheric species too.

Line 14-15: For balance, please add a reference to one of the papers from the S M Ball/J M Langridge/R L Jones collaboration. These authors published the first example of using LEDs for CEAS in 2004, and have published a number of instrument papers since on measuring atmospheric gases by broadband CEAS.

Page 7228, line 1: I didn't understand the phrase "load loss" of the cavity.

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Line 10: It's also worth noting that the cavity's enhancement factor is also given by  $1/(1-R)$ , as  $L$  tends to zero. The enhancement of 142 quoted in the opening lines of the Discussion is readily calculated inputting  $R = 99.3\%$  in this expression.

Page 7230, line 3: I didn't understand how/why ozone concentrations could be "controlled by modulating the sample time from the ozone reaction cell". The Teflon construction of instrument's internal surfaces is specifically designed to minimise ozone wall losses (7229, line 16); thus ozone concentrations ought not to depend on the transit time of the gas from the source. Moreover, if there are ozone losses inside the instrument, that has implications for the CEAS and single-pass cells being plumbed in series "such that both cells measure the same sample gas" (7299, line 22).

Page 7230, line 23: The transmission loss in the single-pass cell is calculated from the Beer-Lambert Law. What value do you use for ozone's absorption cross section? The UV filter selects a 252-268nm range from the LED's emission spectrum. Ozone's cross sections vary by about 25% over this range ( $1.15 \text{ e-}17 \text{ cm}^2 \text{ molecule-}1$  at the 254nm peak of ozone's absorption band, down to around  $0.9 \text{ e-}17 \text{ cm}^2 \text{ molecule-}1$  at 268nm [Sander 2011]). This suggests it is necessary to use an effective absorption cross section in the Beer-Lambert equation, calculated from a weighted average of ozone's cross sections over 252-268nm, where the weighting function depends on the spectrum of light intensity reaching the detector – is that done? And for the purposes of calculating an enhancement factor, is the spectrum of light intensity reaching the CEAS cavity's detector the same as for the single-pass cell's detector? – the cavity mirrors and the AR coated silica windows will have different wavelength dependent transmissions and thus the effective absorption cross section of ozone could be different in the two cells.

Page 7231, line 12 and the lower trace in the main panel of Fig 5: I didn't understand how an ozone standard deviation (in ppb units) can be measured for just the amplifier, with the LED turned off. No light = no signal?

Line 17: "drift of  $\pm 0.2\%$  over 100 min". The inset to Fig 5 shows that this drift is

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essentially in one direction. Better to state a "+0.4% upwards drift over 100 min" [still a nicely stable instrument!]. Did you simultaneously monitor the light intensity through the single-pass cell? – if it increases in the same way, it would suggest that e.g. the LED output is gradually getting brighter, and would allow you to discount changes in the cavity coupling efficiency.

Page 7232, line 5: Out-of-band light falling on the detector is an entirely plausible explanation for why the measured cavity enhancement factor (50) is less than expected from the  $R = 99.3\%$  mirror reflectivity (142). I read "out-of-band light" to be light outside the 252-268nm range passed by the UV filter and supported by the CEAS mirrors. Yet it's also possible that the mirror reflectivity varies significantly within the range 252-268nm. Thus rather like calculating an effective ozone absorption cross section, the measured enhancement is some kind of average over the light spectrum reaching the detector weighted by variable wavelength dependent enhancements dictated by the wavelength dependence of the mirror reflectivity. In this calculation, wavelengths at the edge of the detection bandwidth (where the mirror reflectivity is lower) are transmitted more efficiently through the cavity, biasing the measured enhancement to smaller values.

Page 7232, line 27: "keeping the limit of detection to a few hundred ppt [for an averaging time of approx 30 s, inferred from the minimum in the Allan plot in Fig 5]"

Page 7234, line 3: I agree that tightening the bandwidth of detected light to reduce out-of-band light should help the sensitivity. But be careful not to reduce the bandwidth too far: narrow bandwidth = few detected photons = decreased measurement sensitivity.

Page 7239, Fig 3: Point 1. State the slope, intercept and uncertainty of these parameters in a figure legend, since these are key for determining the cavity enhancement. Point 2. The highest transmission loss data come from the largest  $\sim 300$  ppb ozone introduction in the time series in Fig 2. Around a dozen of these data points lie significantly below the best fit line, and presumably come from the fast decaying edge of the 300 ppb introduction. Does these points' departure from the best fit line indicate a

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small time-lag in the gas movement between the single-pass and CEAS cells? What implication does a time-lag have for operating the instrument at 10 Hz? What is the gas residence time inside the instrument, and when does this become the limiting factor for high frequency ozone measurements?

Technical corrections:

Page 7224, line 17: "location" implies geographical location; instead I think the authors are making an altitude distinction (stratosphere versus troposphere).

Page 7226, line 15: leading to [a] large instrument sample volume.

Page 7229, line 2: fused silica asphere [aspheric lens?] and aperatured. . . 3 mm [diameter] beam of light

Page 7232, line 19: benefit

Page 7233, line 9 "600 ppm" versus line 19 "660 ppm".

Page 7240: inconsistent: Figure caption has "0.001 s integration [time]" whereas p 7231 line 8 states "100 Hz"

References for this comment:

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Jones, R. L., S. M. Ball, and D. E. Shallcross, Small scale structure in the atmosphere: Implications for chemical composition and observational methods, *Faraday Discuss.*, 130, 165–179, doi:10.1039/b502633b, 2005.

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