Authors' General Comments

Both Referees expressed important and valid concerns about the original scope and lack of detail in the Introduction and Experimental section. To address these concerns, the Introduction was completely re-worked to focus on the instrument and technology, and remove discussion on ozone chemistry that is better left to atmospheric chemistry reviews. Additionally, this section has been more thoroughly referenced to better reflect the state of the art. The Experimental section now includes substantially more important details regarding how the work was conducted. The re-worked Introduction and Experimental sections are appended to the end of the Author Response to Referees.

General Comments:

R#1: 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 recognize 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].

> **A:** While we would have liked to have done head-to-head comparison with "one of the 'best' commercially available ozone monitors," it was outside the scope of the project. This research was funded under a NASA Phase I SBIR contract which had limited development time and resources, with the specific goal of establishing feasibility of critical components of an instrument/technique. To this end, we focused our efforts on maximizing resonant enhancement vs. single pass instrumentation. We recognize that it is important to do head-to-head comparisons and field demonstrations and have specifically planned and budgeted for this with our proposal for follow-on funding with NASA, which will have more appropriate time and funding. We felt that it was more beneficial to the atmospheric measurement community to publish this enhancement method in its current state for measuring ozone, then to delay an additional year or more to accommodate head-to-head measurements, on the chance that we are able to secure further funding. Limitations of the study design are now noted in the Results

section where language has been added to make clear that "side by side comparisons were outside the scope of the project:

"The performance capability for measuring ozone with the IBB-CEAS technique was evaluated through direct comparison with a matching single-pass absorption measurement. Side by side comparisons with other instruments were beyond the scope of the project.

R#1: 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 measureable contribution to the absorbance? [The only extra in-sample loss considered in the Discussions section was Rayleigh scattering].

> **A:** Laboratory air was used for generating ozone, and for ozone-free measurements. No effort was made to remove particulates or to dry the air. Continuous measurements of optical throughput while slowly evacuating the CEAS measurement cell, showed no change indicating no significant loss in resonance due to scattering loss. A field instrument would require a particulate filter such as a teflon filter, physical impactor, or aerodynamic impactor. Other gases such as aldehydes do absorb at 250 nm, which is why periodic I_o correction using an ozone neutralizer is important. MnO_2 as suggested by Referee #2 might be preferential to carbon, which would uptake organics and compromise I_o. The presented resonant technique offers the same level of discrimination as the traditional optical method, but with the benefit of being able to make rapid sensitive measurements without substantial equipment costs/requirements. Please see section 2.8 Ozone Generation and Scrubber for text clarifying this (appended to end of response).

R#2: More details. The manuscript is short and basically only deals with the demonstration of the high sensitivity compared to a single-path approach. The reader can thus expect much more technical details. The technical description of the new device is only a good page long : : : this is very little for the description of a "new instrument/technique". Examples for more details are: - Well describe (with a picture) the light path, optics, lenses etc. - Assess the performance of your device theoretically. What is the power of the LED and how much of it is guided through the cells and reaches the detectors? How far away you are from shot noise?

>**A:** The technical design section has been expanded by including more detail, theoretical calculations of performance, and schematic representation to better illustrate the system setup. Please see the revised Experimental section appended at the end of the response.

R#2: Accuracy. The short-term precision of your device is high. But this statement holds for almost all CEAS instruments. Often however, they are not more accurate than multi-pass or even single-path approaches, as finally other factors and shortcomings start to play a role. The enhanced accuracy or long-term stability you haven't demonstrated, yet. You write 1 ppbv at 10 Hz. But will this hold for usual field applications? What is then the accuracy/total uncertainty? The UV-TOP LEDs from SET you use (which exact type, at all) show a typical tempera-ture drift of 1.5-2.0%/K (right?), which is 50 ppbv/K for your device (at 1 bar), right? Fig. 5 indicates that the LED was (during this test) well thermalizedt? But what is during field operation with strong temperature variations? Which other drifts you have? Here, the Allan plot (Fig. 5) helps little and it is also somewhat strange. What is the reason for the maximum at ~0.3s? I would assign this non-white-noise behaviour to 1f-noise of the UV LEDs. We created similar Allan plots based on data from our (home-made) UV photometer, see figure. We have a dual-beam single-pass system with beam splitter. In the both cells (C1, C2) we see a (compared to Fig.5) very similar Allan plot with similar values (10^{-5} corresponds to 0.5 ppbv). In the ratio C1/C2 (red), where lamp noise vanishes, we get a lower noise of only 0.1 ppbv at 10 Hz which is a factor of 5-10 lower than your numbers. To reach high accuracy, do you also need such a beam-splitter approach or can you also apply the technique of e.g. the Environnement O342M instrument where the (additionally measured) LED light emission is used to get rid of light fluctuations?

>**A:** Long term stability is most affected by temperature drifts. The LED in particular, has high drift as pointed out by Referee #2. We addressed this with thermal mass and instrument insulation as is now noted in the Experimental section 2.4 . We have also noted that a field instrument would need to directly address this concern. As the LED is isolated from air flow, its thermal stability is easier to maintain. The frequency of re-measuring I_o is assessed with Allan variance/deviation measurements and the re-calibration time is set by the desired level of accuracy. For our in-lab demonstration, 1 ppb levels would require re-zeroing with ozone scrubber every 2-300 seconds. In the Allan plot, the hump at 0.3 sec which appears in both LED on and LED off experiments, appears to be related to the 30 Hz low pass filter of the amplifier starting to roll off (data average) the highest frequency measurements.

R#2: Comparison of performance with other techniques. You have to compare the performance, advantages and disadvantages of your technique with other instruments (UV photometers, CI techniques). For instance the NOAA single-path instrument (Gao et al., 2012) appears to be more accurate than yours. Due to the strong absorption signal you get in comparison with single-path approaches you should easily reach uncertainties around 0.1 ppbv. The noise of our single-path UV photometer (absorption length 38 cm) is e.g. below 0.06 ppbv at 4s.

A: This is a good suggestion and we have added the following table comparing the performance, advantages and disadvantages of other ozone instruments:

Table 1: Performance comparison of ozone instruments

Instrument	Method	Physical length (cm)	Sensitivity (ppb)	Response Rate (Hz)	Special Considerations
This work	IBB-CEAS	14.5	<1	10	UV LED temperature dependece
2B Technologies Model 205	UV absorption	15	3	0.1	Long averaging for high sensitivity
Kalnajs, 2009.	UV absorption	50	1	1	UV LED temperature dependece
Gao, 2012	UV absorption	30	0.4	2	High power usage
Washenfelder, 2011.	CRDS UV absorption	93	0.026	1	Consumables
Zahn, 2012	Chemiluminescence	n/a	10	50	Consumables, rapid dye degradation

Abstract Comments:

R#1: 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 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.

A: Text will be changed to read: "...and 99.3% reflectivity mirrors."

Introduction Comments:

R#2: Too laxly written and too little references. The instrument is particularly suitable for the deployment for eddy flux applications, on balloons, or on aircraft. In this respect, the entire introduction up to p.7226 l.9 is not well written, i.e. as it would come from a non-expert in atmospheric sciences. Either let check this passage by an "expert" or concentrate only on the technique. But also here you have to give much more citations; there are many technical papers on UV photometers (e.g. Proffitt and

McLaughlin, Rev.Sci.Instr.,1983; Zucco et al., Meas.Sci.Techn. 2003; Hintsa et al., J.Atmos.Ocean.Tech., 2004; Viallon et al., Metrologia, 2006; Kalnais and Avallone, J.Atmos.Ocean.Tech., 2010; Gao et al., AMT, 2012;…) in which Kalnais and Avallone even seem to use the same UV LEDs. Also for the rest of the paper you need much more references.

> **A:** Points well taken. Added all of the suggested references in the Introduction overhaul with the exception of Hintsa et al which is a modification of the 2B Tech. instrument compared in Table 1. Please see commentary above regarding complete re-working of introduction in response to concerns from Referee #1 and 2.

R#1: 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.

> **A:** This entire discussion has been removed. Please see commentary above regarding complete re-working of introduction in response to concerns from Referee #1 and 2.

R#1: 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?

> **A:** Please see commentary above regarding complete re-working of introduction in response to concerns from Referee #1 and 2. In doing the re-work, we have included additional references.

R#1: 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.

> **A:** This has been addressed in the re-worked introduction. The suggested references have been added.

R#1: Page 7224, line 21: Lyman-alpha radiation is at 121.6 nm (not 210nm). Photolysis of O2 can occur out to 240nm.

      A: This was removed. Please see revised intro appended to end of response.

R#1: 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".

      A: This was removed. Please see revised intro appended to end of response.

R#1: 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.

      A: This was removed. Please see revised intro appended to end of response.

R#1: 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?

      A: This was removed. Please see revised intro appended to end of response.

R#1: Line 25: I didn't understand the phrase "decay of the cell current"

      A: This was removed. Please see revised intro appended to end of response.

R#1: 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 NO3 and N2O5 by cavity ring-down at 662nm. High quality ozone measurements are thus beneficial for measuring other atmospheric species too.

      A: This is a good point. It has been specifically noted and referenced in the revised introduction

R#1: 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.

      A: Both of these references are now included.

R#1: Page 7224, line 17: "location" implies geographical location; instead I think the authors are making an altitude distinction (stratosphere versus troposphere).

      A: This was removed. Please see revised intro appended to end of response.

R#1: Page 7226, line15: leading to [a] large instrument sample volume.

      A: This was removed. Please see revised intro appended to end of response.

R#2: p.7224, l.19 …strong impact on health, atmospheric chemistry, and …

      A: This was removed. Please see revised intro appended to end of response.

R#2: p.7724, l.20 … stratosphere (0.1 to …

      A: This was removed. Please see revised intro appended to end of response.

R#2: p.7225, l.22ff SOAs can only serve as cloud condensation nuclei in the troposphere. The stratosphere is completely free of clouds (besides very rare occurrences of polar stratospheric clouds, PSCs, in the wintertime polar vortices).

      A: This was removed. Please see revised intro appended to end of response.

R#2: p.7226, l.1ff "To improve radiative …". The entire paragraph is wrong. ALL in-situ O3 instruments available are sufficiently fast for all these studies and comparisons. However, required are fast, accurate, and light-weight instruments, e.g. for eddy-covariance measurements or the deployment on moving platforms.

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> **A:** This is a good point and the discussion has been revised and included in the introduction

R#2: p.7226, l.13 Most in-situ ozone instruments use MgO2 scrubber.

> **A:** The following text has been added to address this comment.

"For demonstration purposes, the selection of activated carbon was entirely sufficient to completely neutralize all ozone present. We anticipate that a field instrument would employ MnO_2 for this purpose in order to ensure that any potential UV absorbing organic interferents were not removed from the process stream causing measurement bias (Zucco et al., 2003; Viallon et al., 2006)."

Experimental Comments:

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

> **A:** This is phasing used from another CEAS paper. To limit confusion, text is changed to

"Transmission losses arise from the mirrors *(1-R)* and a*bsorption loss*, where *L* is the single pass loss."

R#1: 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.
R#2: p.7228, eq.4 I have never seen this equation and do not believe it. At very low ozone concentrations, E would tend to infinity. Correct is E=I/Io/(1-R).

> **A:** Equation 4 has been re-written to conform to text wording. It is simply the expression to relate single pass measurements to cavity enhanced measurements to yield an experimentally achieved enhancement. E=I/Io/(1-R) is also included now as the maximum theoretical enhancement. The text now reads:
>
> "The measured cavity enhancement gained from using a resonant cell versus a single pass cell can be expressed as the ratio of the resonant transmission loss to the single pass loss

$$E = \frac{1 - I/I_o}{L}$$

(4)

and the maximum theoretical enhancement is given by

$$E = \frac{1}{(1 - R)} .$$

(5)"

R#1: 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).

> **A:** This was poor wording on our part and has been corrected in the revised Experimental section to reflect the combination of lamp current control and secondary dilution post ozone generation. In earlier work, we were also adjusting flow rates to change ozone concentration at the generation source by allowing a longer air-lamp interaction time.

R#1: 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 e-17 cm2 molecule-1 at the 254nm peak of ozone's absorption band, down to around 0.9 e-17 cm2 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.

> **A:** We originally used a constant 1.15e-17, but your suggestion is better. We calculated a new effective cross section by taking the O3 cross section weighted it against the bandpass filter transmission function and LED output function to arrive at an effective cross section of 1.04 e-17 cm^{-2} across. Bandwidth of critical components is now illustrated in Fig 2. The transmission

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function on the AR coating, mirror coating and detector responsivity are minor in comparison. This new and improved effective cross section has been applied to all calculations in the paper and is now indicated in text as:

"For this calculation, we use an effective cross section of 1.04×10^{-17} cm^2/molec which is the ozone cross section weighted by the emission of the LED and bandpass of the filter (Fig. 2)."

R#1: 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?

   A: We agree, this does sound odd at first. The following text is added and should clear up confusion:

   "Effective concentration for the amplifier+detector noise (LED off) was calculated by scaling the signal by I_O (LED on), offsetting such that the mean of $I_{DC}=1$, and then performing Allan calculations."

R#1: Line 17: "drift of 0.2% over 100 min". The inset to Fig 5 shows that this drift is 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.

   A: The drift in that particular data set was upward. Sometimes it would go down, but remained similar in absolute magnitude. Unfortunately, at this point of the work, one of the amplifiers was out of commission, so we had to run one channel at a time. As pointed out by R#2, this could also be temperature effects (both the LED and photodiode do have small, but non-negligible temperature effects) in addition to cavity coupling. This is one of the downfalls of a DC type measurement. Allan Variance measurements are particularly useful for evaluating how often re-establishing I_o should be done to account for this drift.

R#1: 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.

> **A:** This was something we also considered early on. However, measurements of the mirror shows that the reflectivity does not go lower than ~99.2% over the bandpass of the filter.

R#1: 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]"

> **A:** added suggested text for clarity.

R#1: Page 7229, line 2: fused silica asphere [aspheric lens?] and aperatured: : : 3 mm [diameter] beam of light

> **A:** corrected to indicate aspheric lens and diameter beam.

R#2: p.7229 You use moderately reflective mirrors. Explain why. Are you already limited by dark noise?

> **A:** Correct. We initially used off-the-shelf high reflectors. There wasn't sufficiently light to measure even at maximum gain on current amplifiers. Using 99.3% mirrors we measure ~100 pA of current. This is now indicated the experimental setup section in an effort to be more complete. Dark Noise is specifically addressed later in the response.

Results

R#2: Section 3 You have neither explained the measurement procedure nor the procedure how you calculate ozone. What are the measurement times and flushing times? What you use as Io? Give an equation. Do you measure a certain time (e.g. 1 min) with high frequency (e.g. 10 Hz) and only then flushes the cell with O3-free air?

> **A:** New text added
>
> > The observed transmission loss in the single-pass and IBB-CEAS cell can be directly converted to an ozone concentration by applying Eq. 6

$$c = \frac{-\ln\left(\dfrac{I}{I_o}\right)}{E * \alpha * L * X * \dfrac{P_o}{P}} . \tag{6}$$

where E is the enhancement factor (E=1 for single pass), α is the absorption cross section, X is the molecular density of air at 760 torr and P is the measurement pressure relative to 760 torr (P_o). For this calculation, we use an effective cross section of 1.04×10^{-17} cm^2/molec which is the ozone cross section weighted by the emission of the LED and bandpass of the filter. A constant value of I_o is used and was obtained before each experiment by either not generating ozone or passing ozone laden air through a neutralizer (continuous measurements of I with neutralizer in line for ozone off and ozone generation at maximum show no change, indicating complete neutralization).

Discussion comments

R#1: Page 7232, line 19: benefit

A: benefit is the correct spelling.

R#1: Page 7233, line 9 "600 ppm" versus line 19 "660 ppm".

A: corrected for consistency (660) and updated to 730 to reflect effective cross section in calculation.

Conclusion Comments

R#1: 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.

A: Agreed. We only had about 100 pA of photocurrent to work with. I wouldn't want to go any lower than half that value.

R#2: p.7233, l.27 The typical uncertainty of commercial UV photometers is 0.5-1.0 ppbv at 6-20 s. The very compact device by 2B-Technologies should not be a benchmark for your device. (if the detection

speed is set to 10 Hz). Moreover, what sample flow you need to guarantee real 10 Hz measurements? How often you have to measure Io to guarantee also high accuracy? To my understanding you have reached the short-term precision of the best photometers existing worldwide, but you didn't get ahead yet. p.7234, l.8 That your device "allows for one to two orders of magnitude improvement …" is not shown. The NOAA device (Gao et al., 2012) is similarly accurate and fast

> **A:** Per Referee #2 suggestion, we have added a comparative table for various instruments. Please see above.


Figure Comments

R#1: 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 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 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?

> **A:** Slope, intercept and uncertainty now included in graph: slope = 49.51 ± 0.07, intercept = 1.3e-4 ± 2.12e-5
>
> Below is a detail view of the high concentration portion of the graph. Overall, they track very well. The dozen or so points that fall below the best fit from the enhancement plot, appear to mainly be at t=235 and t=246. Tracking at higher rate of change areas at 242 and 261 appear spot on, so I don't think we are seeing a lag effect. We are not sure what the exact nature of the anomaly is.
>
> We don't know exactly what the residence time is, but we can say a few things about it. The lamp pulse experiments show that the time from no ozone, to peak, is 0.4 seconds. However, there is mixing involved in the volume of the lap where ozone is generated causing a gradient in the sample. We were operating at a flow of ~500 cc/seconds and the measurement cells have a volume of 29 cc. At 10 Hz, the turnover is ~1.7x. We were limited by available pumps on hand and would like to use a more powerful pump @ ≥5x turnover/10 Hz in future work. Originally, we were operating with a ½" bore in the Teflon tube and enlarged to 5/8" to test for enhancement-reducing clipping. There was no significant change in enhancement, so reverting back to ½" will sizably drop the volume down to 18 cc.
>
> Flow information is now included in the experimental section.
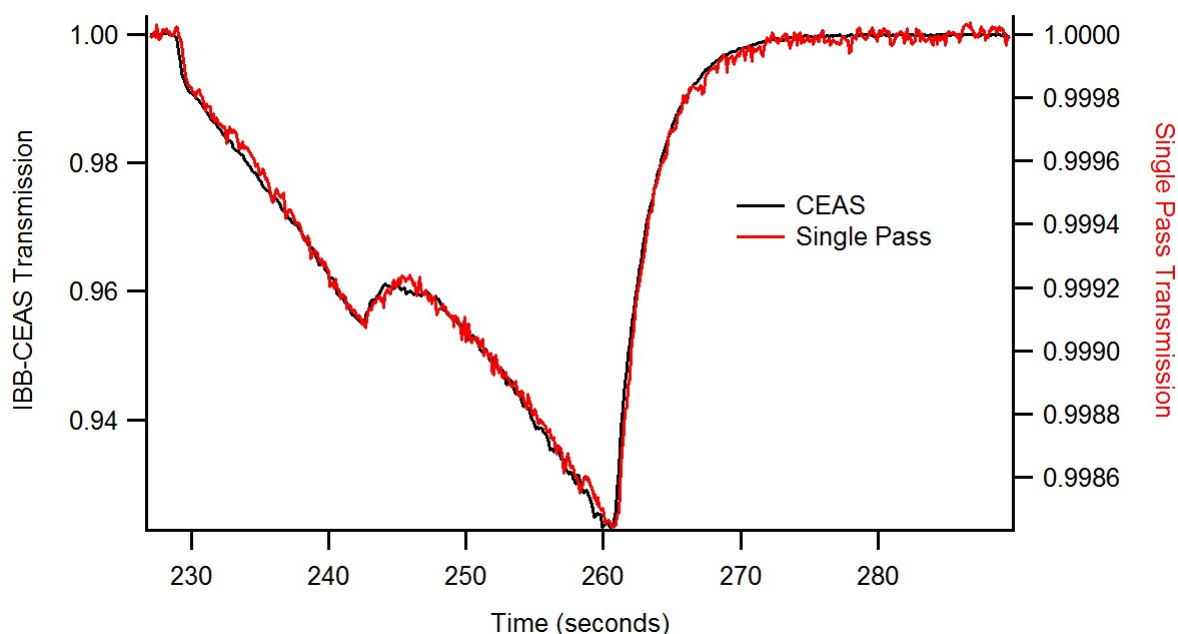
R#1: Page 7240: inconsistent: Figure caption has "0.001 s integration [time]" whereas p7231 line 8 states "100 Hz"

> **A:** corrected to 0.01 s

R#2: p.7232, l.16ff Allan plot. As written by reviewer 1, you should create such test with real ozone data. Which drifts you have, see also my comment above with the T drift of the LED? Try to find explanations for the strange Al-lan plot, see e.g. Werle et al., Spectrochim. Acta, 60, 1685–1705, 2004. A dark noise measurement and measurement of a noise-free stable voltage (e.g. from a battery) fed in the detection system allows to characterize most noise sources. The rest is due to LED noise.

> **A:** Unfortunately, the system at this stage isn't very portable. As we mention at the beginning, we have outstanding funding proposals which will allow us to further advance the instrument, do field testing and direct instrument comparison. It was just outside the scope of the feasibility study that we were funded for. This is also now mentioned in the paper.
>
> All experiments were performed under battery power (on the amplifier). We have also done measurements of battery voltage directly into the data acquisition system and the noise floor is far lower. The *dark* noise (det+amplifier+DAQ) was measured to be ~300 microvolts (RMS @ 10 Hz acquisition) on the 100 pA/V gain setting, or 30 fA. The amplifier has specification noise of 16 fA under the operating conditions and the shot noise of the detector is 6 fA. I believe what we are seeing is shot noise + thermal stability of the amplifier. At such high gain, thermal stability of the feedback resistor in the gain stage is important. This (along with the aforementioned

temperature dependence of the diodes) points to the need to have good thermal control and the desire to improve on the optical throughput of the system for higher S/N (future work).

Revised Introduction, Experimental and Figures

1   Introduction

Environmental monitoring of ozone is vital due to the profound impact ozone has throughout the atmosphere. In the stratosphere, ozone strongly absorbs solar UV radiation that would otherwise be harmful to life on Earth (Cullen and Neale, 1994). Its presence in the troposphere influences radiative forcing (Gauss et al., 2003), gas phase photochemistry (Sillman, 1999;Finlayson-Pitts and Pitts, 1997), and can detrimentally impact the health of flora (Fuhrer and Booker, 2003), fauna, and humans (Gauderman et al., 2002).

Ozone's widely varying ambient mixing ratios, which range from parts per billion to parts per million, and its reactivity impose constraints on the sensitivity, dynamic range, and response rate necessary for an instrument making in situ measurements. These constraints are compounded for instruments aboard airborne platforms, where additional limitations on instrument sampling rate, weight, power, and size exist. At typical research aircraft speeds of 100 – 200 m/s such as NASA's P3, for example, sampling rates are ideally greater than 1 Hz to achieve spatial resolution at the scale of mixing. High resolution in situ measurements of ozone made from airborne platforms are essential for capturing eddy fluxes (Matross et al., 2006), characterizing plume dynamics (Brown et al., 2012;Jones et al., 2005), refining regional and global chemical models (Taghavi et al., 2005;Monks et al., 2009), and validating satellite retrievals (Liu and Tian, 2010). Additionally, such measurements can be beneficial for accurately quantifying other atmospheric species (Washenfelder et al., 2011).

In this paper we describe the development of a new instrument for monitoring ambient ozone that is specifically designed for compatibility with airborne research platforms. The instrument is based on ultraviolet absorption, which has been routinely applied for airborne ozone detection (Proffitt and McLaughlin, 1983; Gao et al., 2012; Kalnajs and Avallone, 2009) given ozone's large absorption cross-section of 1.15×10^{-17} cm^2/molec at 254 nm (Molina and Molina, 1986). This technique has key advantages for long duration, remote measurement of ozone over common alternatives such as electrochemistry (Komhyr, 1969) or chemiluminescence (Ridley et al., 1992;Zahn et al., 2012). Namely, it offers an absolute measurement of ozone without requiring consumables for calibration and operation.

One shortcoming with traditional UV absorption methods that we have sought to overcome is the tradeoff between instrument sensitivity and form factor. Absorption sensitivity is proportional to optical path length, as defined by the Beer-Lambert Law. UV photometers relying on direct absorption (Kalnajs and Avallone, 2009) or a singly-folded path (Proffitt and McLaughlin, 1983;Gao et al., 2012) have physical lengths on the order of the total optical path length, which can limit sampling rate due to the time required to completely exchange the volume of the sample cell. Resonant optical cavities can

overcome limitations of direct absorbance measurements, reducing the physical size of an instrument while maintaining the long optical paths requisite for high sensitivity measurements. Here, we apply incoherent broadband cavity enhancement absorption spectroscopy (IBB-CEAS) to sensitively and rapidly detect ozone.

First developed by Fiedler et al., IBB-CEAS takes advantage of spectrally broad light to overlap hundreds to thousands of resonant cavity modes and generate a continuous transmission signal having an enhanced absorption response characteristic of a much longer physical pathlength (Fiedler et al., 2003). The approach has been used to make sensitive measurements on a variety of trace atmospheric gases (Venables et al., 2005;Gherman et al., 2008;Wu et al., 2008). A variant of cavity ring-down spectroscopy, which itself has been implemented recently for detection of ozone (Washenfelder et al., 2011), IBB-CEAS is less alignment-sensitive and can be implemented with simple electronics. As a continuous-wave technique, it also has far less stringent requirements than cavity ring-down regarding the light source used. Low-cost light emitting diodes have been demonstrated with IBB-CEAS (Ball et al., 2004;Langridge et al., 2006). With the emergence of solid state technology to produce LEDs operating at UV wavelengths relevant to ozone detection, LED-based UV photometers (Kalnajs and Avallone, 2009) are emerging as a useful alternative to instruments based on much more power-hungry mercury lamps (Proffitt and McLaughlin, 1983;Gao et al., 2012).

We present results from an LED-based IBB-CEAS UV photometer, which we believe to be the first application of the approach to ozone. As detailed in the following sections, its compact 14.5 cm optical measurement cell is capable of yielding IBB-CEAS ozone measurements of ~ 1 ppb sensitivity at 0.1 seconds, which compares very favorably to recent CEAS measurements of ozone (~8 ppb at 10 seconds with a 25 cm cavity) obtained using an atomic line source (Darby et al., 2012).

2 Experimental

2.1 Principle of Operation

The transmission intensity (I) of light through an optical cavity, consisting of mirrors with reflectivity R, can be described (Fiedler et al., 2003) as the superposition of the sum of discrete transmitted light per pass. Transmission losses arise from the mirrors *(1-R)* and from absorption loss, where L is the single-pass loss. The observed transmission intensity is related to the intensity of light into the cavity, I_{in}, according to:

$$I = I_{in} \frac{(1-R)^2(1-L)}{1-R^2(1-L)^2}$$

(1)

For an unloaded cavity ($L = 0$), this reduces to:

$$I_o = I_{in} \frac{(1-R)}{(1+R)}$$

(2)

Hence, the cavity transmission (T) is:

$$T = \frac{I}{I_o} = \frac{1-R^2}{1-R^2(1-L)^2}$$

(3)

The measured cavity enhancement gained from using a resonant cell versus a single-pass cell can be expressed as the ratio of the resonant transmission loss to the single-pass loss

$$E = \frac{1 - I/I_o}{L} \quad (4)$$

and the maximum theoretical enhancement is given by

$$E = \frac{1}{(1-R)} . \quad (5)$$

Conveniently, the enhancement gains are greatest when the loss is the smallest. This low loss enhancement is what allows exceptional sensitivity in a compact absorption cavity.

2.2   Technical Design

The IBB-CEAS system consists of: (1) UV source/detection; (2) measurement cells (resonant and single-pass reference); (3) flow handling; (4) ozone generation/neutralization; and (5) data acquisition. The instrument was built upon the ThorLabs 30 mm cagemount system to facilitate breadboard design and provide ruggedness. The measurement portion of the system (except current driver and amplifier) were housed in a polystyrene foam enclosure for thermal stability. A rendering and optical layout of the system can be seen in Figure 1. As a proof-of-principle benchtop system, using off-the-shelf optomechanics, the optical measurement system had dimensions of 17" x 4.75" x 2.5". A ruggedized, field ready instrument based on this technology, could be expected to have a foot print of 13.5" x 3" x 2" for the optical system, and a total instrument size on the order of 15" x 6" x 4".

2.3   Optical Design

Light from a UV LED was imaged with an f=35 mm fused silica aspheric lens and apertured with a pair of irises separated by ~5 cm to generate a nearly collimated ~3 mm diameter beam of light. A UV bandpass filter (Semrock: 252-268 nm, Fig. 2) removed most unwanted emission from the LED, and the resulting filtered light was split with a 70T/30R thin plate dielectric beam splitter (NewFocus). The 70% transmitted portion of the UV light passed through the IBB-CEAS measurement cell and was imaged onto a detector with an f=25 mm fused silica spherical lens. The IBB-CEAS cell was formed with a pair of ¼" thick fused silica concave mirrors (f= -150 mm) having a 99.3% dielectric coating on the concave surface and anti-reflection coating on the plano surface. The mirrors were separated by 14.5 cm to form a stable ($0 \leq g_1 * g_2 = 0.87 \leq 1$) resonator (Busch Kenneth et al., 1999).

The 30% reflected portion was directed by a UV turning mirror (CVI: Maxbrite 245-390 nm) through a single-pass measurement cell and imaged onto a silicon carbide detector with an f= 25 mm fused silica spherical lens. The single-pass cell had a path length of 14.5 cm matching the physical length of the IVV-CEAS cell, and used UV-AR coated fused silica windows. This dual cell design allow for simultaneous calibration and quantification of cavity enhancement, and extending the dynamic range of ozone measurements made by the instrument.

2.4   UV Source

UV light was generated by a UV-Top LED (peak = 254.5 nm, FWHM=11.1 nm) mounted into a cagemount LED adaptor. The LED was driven by an ILX current driver at 20 mA producing ~300 microwatts of available optical power. This LED has a temperature dependent drift of ~ 1.5%/K at 20 mA which necessitates temperature stability measures. High thermal mass holder coupled with insulation is sufficient for laboratory work. A field instrument may require an additional monitoring photodiode to maintain performance.

2.5   Detection and Data Acquisition

Silicon carbide photodiodes (Electro Optical Components: JEC 1.6RC with integrated UV-C filter, 1.6 mm^2) were used for both single-pass and IBB-CEAS measurement channels. Photodiodes were mounted into 1" OD machined aluminum cylinders and soldered to 12" lengths of BNC terminated, shielded coax cables. The detectors were amplified by Stanford Research Systems SRS-570 low noise current amplifiers. IBB-CEAS and single-pass channels were set to 100 pA/V and 50 nA/V gain respectively, low pass filtered at 100 Hz, and operated in low drift mode. The resulting signal ranged from 1 to 1.6 V, such that even through most of the LED emission is rejected by the aperture pair and input cavity mirror, sufficient light reaches the detector to make sensitive measurements at high signal-to-noise.
The amplified detetor signals were acquired using a National Instruments DAQ multi-function I/O card (NI USB-6251 BNC) and recorded using a custom Labview VI. Data was acquired at 10,000 points/sample at ±2 V full scale at 16-bit.

2.6   Sample Cell

To minimize ozone loss within the instrument, the sample cells were made out of virgin PTFE Teflon. 1" OD rods were machined to 14.5 cm in length and bored out to 5/8" inner diameter. Both ends were machined to accept recessed Viton fluorpolymer o-rings for compression seals with optics. NPT ports were machined into the ends and were fitted with NPT-Swagelok teflon fittings for gas flow.

2.7   Flow Handling

The IBB-CEAS cell and the single-pass cell were plumbed in series with Teflon tubing such that both cells measured the same sample gases, which were drawn through the system using a diaphragm pump. Flow was regulated with a Swagelok ball valve and monitored on a Matheson flow gauge to be ~500 cc/sec. All fittings and tubing were pure Teflon up to the exit of the final measurement cell.

2.8   Ozone Generation and Scrubber

Ozone was generated by flowing unfiltered laboratory air through a lab-built aluminum reaction cell containing a nearly continuous (fast pulse) mercury vapor lamp (Oriel). The photolysis of O_2 in air by lamp generated 183 nm light from the lamp produced sufficient quantities of ozone to evaluate instrument performance. Concentrations of ozone within the reaction cell could be varied by altering the discharge current to the lamp, and ratios could be further adjusted by mixing ozone laden air with lab air. This was necessary for generating low ozone concentrations, as at low currents, the Hg lamp pulse became resolvable (Fig. 3). When applicable, ozone was neutralized with an inline canister containing ~130 cm^3 of high surface area granular carbon to evaluate I_o. For demonstration purposes,

the selection of activated carbon was entirely sufficient to completely neutralize all ozone present. We anticipate that a field instrument would employ MnO_2 for this purpose in order to ensure that any potential UV absorbing organic interferents were not removed from the process stream causing measurement bias (Zucco et al., 2003; Viallon et al., 2006). Additionally, it is expected that a field – deployed device would also require a Teflon particulate filter.
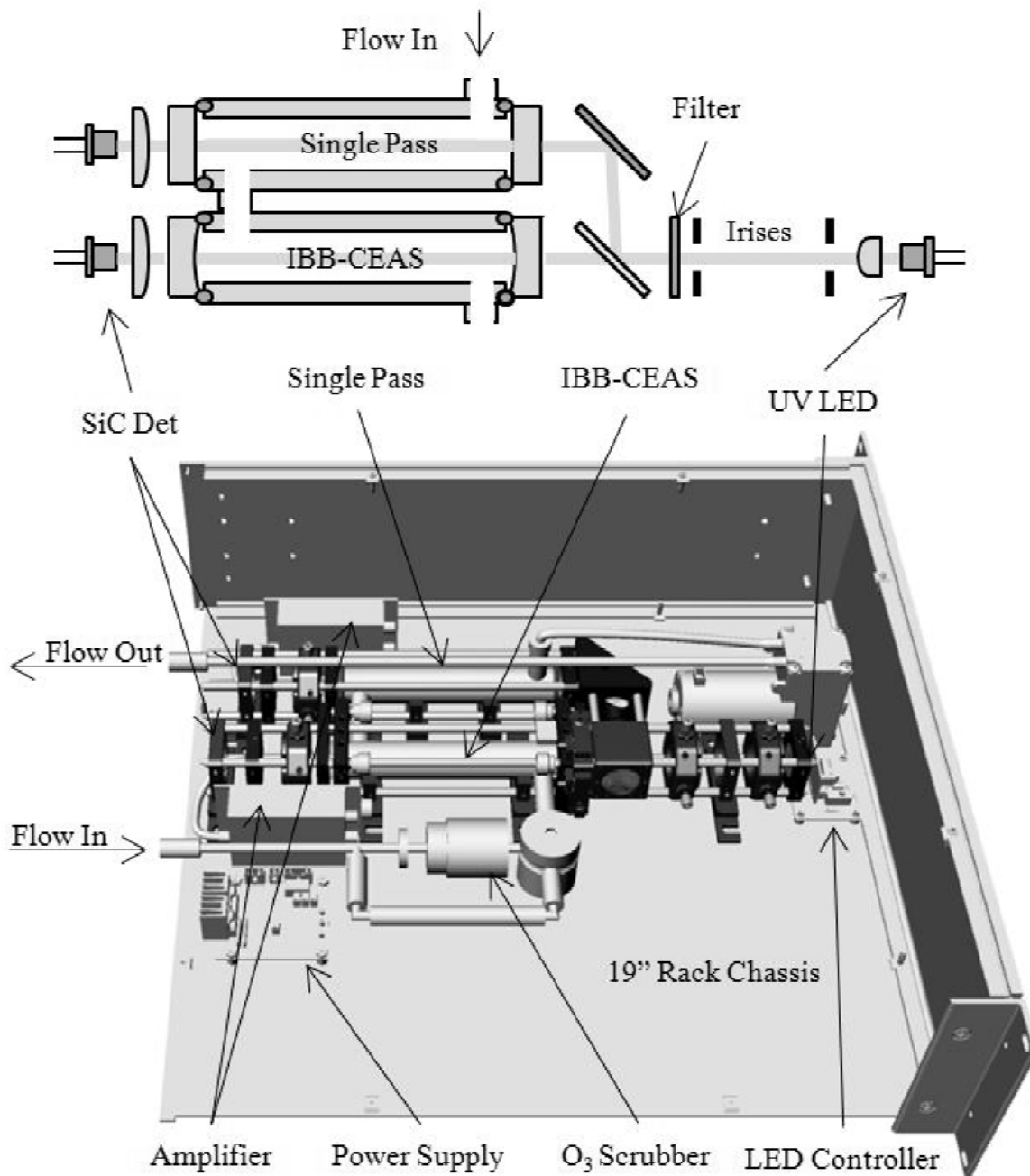
Figure 1. Optical layout (Top) and rendering (bottom) of simultaneous IBB-CEAS and single-pass ozone measurement system in a standard 19" rack-mount chassis.
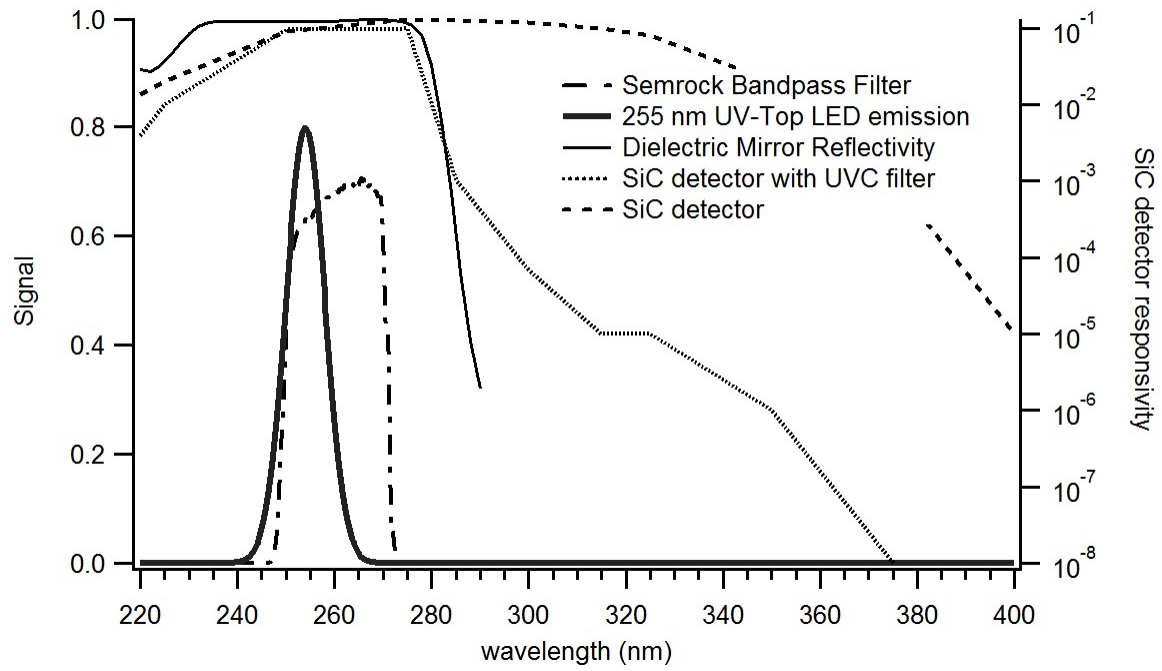
Figure 2. Wavelength dependence of elements in the system.

slope = 49.51 ± 0.07
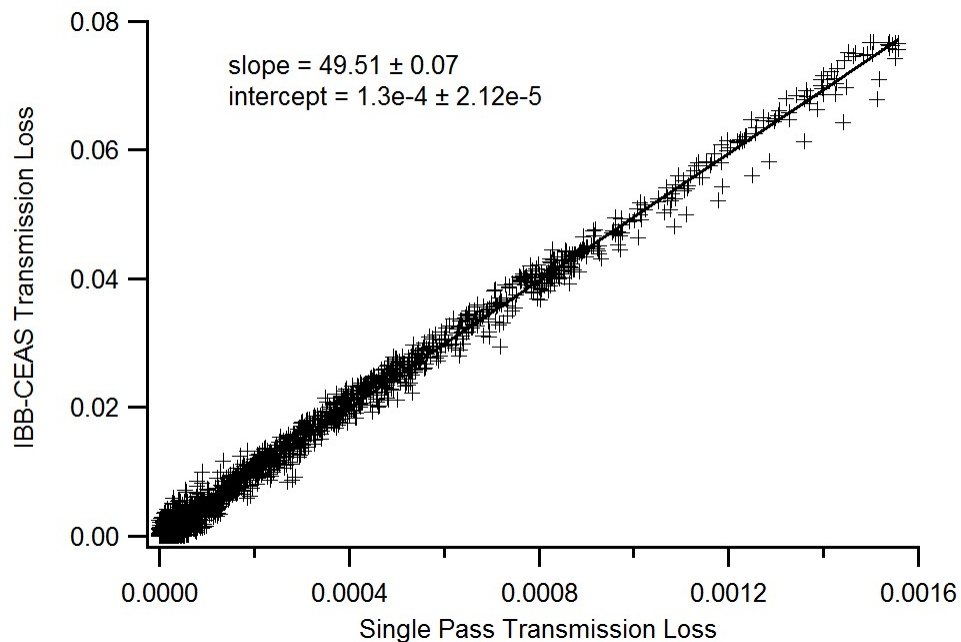intercept = 1.3e-4 ± 2.12e-5

Figure 5. Measured transmission losses for IBB-CEAS vs. single-pass sample cells with matching ozone concentrations, indicating an enhancement value of 50x. Scatter is due to noise in the single-pass measurements used in the calculation (see fig. 4).