Response to Reviewers
Manuscript Number: AMT-2015-249
Manuscript Title: Broadband cavity enhanced spectroscopy in the ultraviolet spectral region for measurements of nitrogen dioxide and formaldehyde

The discussion below includes the complete text from the reviewer, along with our responses to the specific comments and the corresponding changes made to the revised manuscript.

All of the line numbers refer to the original manuscript.

Response to Reviewer #2 Comments:

In this paper, Washenfelder and co-workers describe a broadband cavity enhanced spectroscopy instrument for use at the lower end of the short ultraviolet. The sensitivity and performance of the instrument is evaluated with respect to NO2 and formaldehyde, CH2O, and shown to be suitable for laboratory and field measurements of these important atmospheric species. The work is a valuable instrumental development in several respects: (1) it extends the broadband technique to shorter near-UV wavelengths, which is a technically difficult region as the authors correctly point out. (2) It is the first specific application (as opposed to the general demonstration of Islam et al, 2013) that uses a laser-driven light source for BBCES. (3) It is the first application of the technique to the atmospherically important species CH2O and thereby brings a new, and highly selective tool to the study of this species. It should be noted that the spectral range that Washenfelder demonstrate in their instrument has broader applicability than just to CH2O, as other organic species (most notably other carbonyls) and some carbonaceous atmospheric particles start to absorb appreciably at shorter wavelengths. Indeed, this and similar instruments may prove most valuable when applied to particle optical properties.

We thank the reviewer for the positive review and thoughtful comments. Listed below are our responses to the comments and the corresponding changes made to the revised manuscript.

Specific comments: 1. p.9941: The association/equating of the 1 standard deviation for a series of measurements with the precision and detection limit is incorrect. The detection limit is usually defined in terms of 2 or 3 times the standard deviation (as on p.9942). This should be clarified.

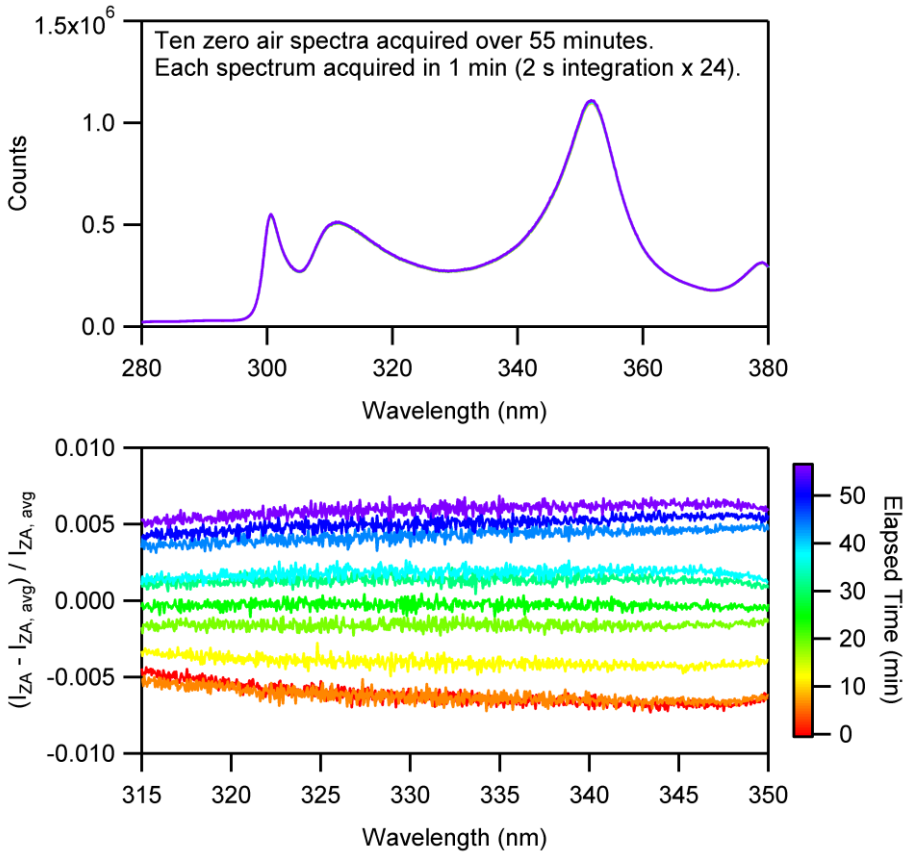
We agree with the reviewer that 2σ or 3σ is a more conservative way to report the precision and detection limit. However, we are clear about our definition and readers can easily interconvert between 1σ, 2σ, and 3σ. We have edited the text to correct any sentences that could be ambiguous:

Page 9941, lines 23-24: "Based on the acquired counts of 1.0×10^8 in 1 min, the calculated 1σ α_{min} at 330 nm would be 7.4×10^{-10} cm^{-1} in the shot noise limit."

Page 9943, lines 24-27: "The 1σ precision … is appropriate for aerosol extinction measurements even in clean environments."

2. The authors implicitly ignore any spectral dependence to the changing output of the LDLS. Have the authors studied the time dependence of the spectrum to determine that this is really the case? Although the polynomial in the DOASIS fit may remove the effect of small changes for retrieving the concentrations of gases like NO2 and CH2O with structured absorption spectra, possible spectral changes in the lamp output would compromise spectral measurements of particles or gases with unstructured absorption bands.

The reviewer has raised an interesting issue that we had not considered. The plots below show the zero air spectra from Figs. 3 and 4. The measured intensity through the cavity varied by approximately 1%, but the relative intensity across the 315–350 nm region varied by less than 0.3%.

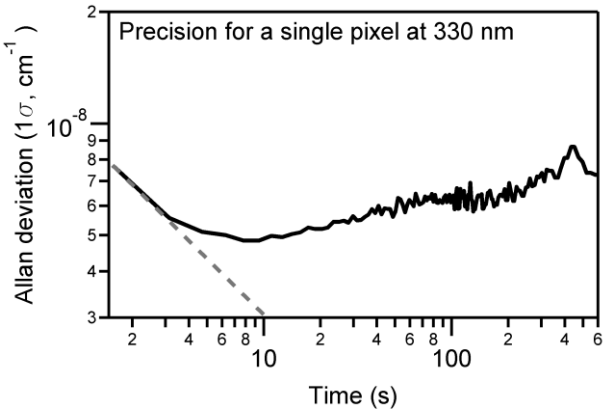


We have added a statement to the paper:

Page 9933, lines 13-15: "To eliminate this drift, we constructed custom temperature-control using water circulation through an attached aluminum plate. *Change in lamp intensity as a function of wavelength is an additional consideration, and we measured the relative intensity change over 315–350 nm to be less than 0.3% in 1 h.*"

3. An Allan variance study seems to me to be the one obvious omission from the paper. The authors have selected an acquisition time (30 s or 1 min) that seems to provide a good quality spectrum in a reasonable time; however, the assumption based on previous experience that the S/N will improve for up to 10 minutes (p.9941) may not be justified for this novel light source. For readers considering adopting such a light source, explicit quantitative information on stability of the combined LDLS-optical cavity spectrometer system would be valuable.

We have added an Allan deviation plot to the paper as Figure 8 and edited the text:



"*Figure 8. Allan deviation plot for zero air measurements acquired by the BBCEAS instrument, showing the relationship between averaging time and 1σ precision for a single pixel at 330 nm. The dashed line shows the relationship expected for statistically random noise.*"

Page 9941, lines 23 – Page 9942, line 3: "Based on the acquired counts of 1.0 × 10^8 in 1 min, the calculated $1\sigma\ \alpha_{min}$ at 330 nm would be 7.4 × 10^{-10} cm^{-1} in the shot noise limit. However, achieving this theoretical value requires a strict cavity stability, with δI_{min} = 1.0 × 10^{-4}. ~~After temperature-controlling and purging the laser-driven arc lamp to reduce intensity drift, the measured precision approaches the shot noise limit, with a value of 2 × 10^{-9} cm^{-1} in 1 min for single pixels (0.05 nm) near 330 nm.~~ *Figure 8 shows an Allan deviation plot (Allan, 1966) calculated for a 3 h series of spectra, with a minimum of 5 × 10^{-9} cm^{-1} for 9 s and 6 × 10^{-9} cm^{-1} for 1 min. Temperature-controlling and purging the laser driven arc lamp have reduced the intensity drift, but Fig. 8 shows that frequent zeroing will be useful to improve measurement precision.*

We have updated the conclusions to include the values from the Allan deviation plot:

Page 9943 line 24 – Page 9944 line 4: "The 1σ precision of ~~5 × 10^{-9}~~ *1.8 × 10^{-8}* cm^{-1} and *6 × 10^{-9}* ~~2 × 10^{-9}~~ cm^{-1} (~~0.5~~*1.8* Mm^{-1} and ~~0.2~~*0.6* Mm^{-1}) per min for single pixels (0.05 nm) at 315 and 330 nm *determined from the Allan deviation* is appropriate for aerosol extinction measurements even in clean environments. These values would be further improved by averaging multiple pixels. Field measurements of dry aerosol extinction and angstrom exponent at 360–420 nm measured in the rural southeastern U.S. (Washenfelder et al., 2015) indicate that the extinction at 315 nm would be 1× 10^{-7} – 2 × 10^{-6} cm^{-1} (10 – 200 Mm^{-1}). These values are easily measurable with the current detection limit, with signal-to-noise of ~~20–400~~ *6–110* (~~50–1000~~ *17–300*) at 315 nm (330 nm) for 1-min ground measurements, and ~~3–50~~ *6–110* (~~7–130~~ *12–250*) for 1s aircraft measurements.

We have updated a statement about measurement precision to clarify that zeroing is required:

Page 9941, lines 8-11: "Experience from prior ground-based field measurements of glyoxal and nitrous acid showed that their measurement precision scaled linearly with the square root of averaging time over 10 – 60 min periods*, when zeros were acquired at more frequent intervals* (Washenfelder et al., 2011; Young et al., 2012)."

4. The spectral acquisition procedure includes frequent measurement of dark spectra, to the point of appreciably shortening the duty cycle of the instrument and thereby, possibly, reducing the performance of the instrument. Why is this frequency of dark current measurement warranted?

For these experiments, the entire CCD array was read out and the two spectral regions were summed in software, which allowed us to use longer integration times and protected the shutter electronics from over-use. The reduced duty cycle is due to the CCD readout time and shutter

compensation time, and not due to dark background measurements. We have clarified this in the text:

Page 9934, lines 18-20: "Instead, the signal for the entire CCD was read out and the two regions were summed in software, which allowed for greater integration times *and protected the shutter assembly from over-heating by reducing its operation frequency*."

Page 9936, lines 9-11: "The total acquisition time for each sample spectrum was 1 min, which included the shutter compensation and CCD readout time, allowing 35 spectra with 1.2 s integration time to be acquired in 1 min (equivalent to a duty cycle of 70%). *This duty cycle does not include the intermittent measurement of dark spectra.*"

5. Unless I have misread the argument, the reference to δI in Eq. (3) and Sect. 4.5 should really read ($\delta I/I$). That is, an absorption/extinction measurement aims to measure a fractional change in intensity.

We agree with the reviewer that the important quantity is the fractional change in *I*. We have added an explicit definition of δI to the text:

Page 9941, lines 13-14: "An examination of Eq. (1) shows that the precision for extinction, $\alpha(\lambda)_{min}$, depends on the smallest measurable difference in light through the cavity, $\delta I_{min}(\lambda)$, *which is equal to* $((I_{ZA}(\lambda) - I(\lambda)) / I(\lambda))_{min}$."

p.9940, Sect. 4.2: It would be helpful to state the combined uncertainty of the calibration and cross-section.

We have changed this sentence:

Page 9940, lines 2-6: "Despite the weaker differential absorption features, the ultraviolet ~~BBCES~~*BBCEAS* instrument accurately quantifies the NO_2 concentrations relative to the more precise CRDS instrument and is ~~well~~ within the combined uncertainty of the Rayleigh scattering mirror reflectivity calibration ~~(± 2%)~~ and the NO_2 absorption cross section ~~(± 3%)~~ *(±3.7%; see Sect. 4.5)*."

p.9943: For readers comparing the LDLS to other light sources, it would be helpful to state the electrical and approximate optical power.

We have added this information to the text:

Page 9933, lines 9-11: "We use a broadband light source (EQ-99FC LDLS; Energetiq, Woburn, MA, USA), consisting of a continuous wave diode laser at 974 nm that pumps a Xenon plasma (Islam et al., 2013) *with a total electrical power draw of 125 W*."

Page 9933, lines 16-17: "Inside the housing, the light is collected using an ellipsoidal reflector and a 600 μm diameter fiber*, resulting in a manufacturer-specified power output of 130 $\mu W\ nm^{-1}$ across the 315-350 nm spectral region*."

Fig. 2(b): For clarity of interpretation, the right axis labels should have the same colour as the axis title and associated curve

Corrected.

Fig. 6: Even if the slope is not meaningful information, the y-intercept would be a useful secondary figure of merit and should be provided in the caption.

We have added this:

Page 9956, Figure 6 caption: "The r^2 value is 0.9998 *and intercept is -0.6 ± 0.2 ppbv*."