

Response to Comment by Ryan Thalman

Manuscript Number: AMT-2015-249

Manuscript Title: Broadband cavity enhanced spectroscopy in the ultraviolet spectral region for measurements of nitrogen dioxide and formaldehyde

Response to Comments:

Overall, some nice work on the part of the authors to combine a new light source development with untested wavelength/reflectivity ranges of highly reflective mirrors in an effort to sample formaldehyde, a key product of atmospheric oxidation processes.

We thank Ryan Thalman for the positive summary, and we are pleased that our paper has attracted interest within the scientific community.

Some discussion or comparison of the output of the laser-driven arc lamp with respect to LEDs or a conventional Xe-arc lamp would have been useful to illustrate how much this offers as an improvement over previously available light sources. Real numbers, even just in terms of absolute power (after filtration), wavelength coverage and light source stability without coupling to the cavity, would have been highly valuable to the community.

A direct intercomparison of the laser-driven arc lamp and a conventional Xenon arc lamp is an interesting question. We do not have this data, but the manufacturer of the laser-driven arc lamp has published comparison measurements (Zhu and Blackborow, 2011). Commercially-available LEDs are weak shortward of 365 nm, and not yet competitive with arc lamps. We have edited the text:

Page 9933, lines 11-12: “The resulting plasma size is less than 100×200 μm, with spectral output from 170–2100 nm. *Further details about laser-driven arc lamps and a comparison to conventional Xenon arc lamps can be found in Zhu and Blackborow (2011).*”

Reviewer 2 made a similar comment, and we have modified the text to include the power output of the laser-driven arc lamp:

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 μW nm⁻¹ across the 315-350 nm spectral region.*”

It is recommended that the most recent NO₂ cross-sections be used (Vandaele et al., 2002) rather than the old 1998 one.

For our spectral measurements at 315–350 nm, it is not possible to use Vandaele et al. (2002), because it includes NO₂ cross section values from 384–926 nm only. We used Vandaele et al. (1998) because it reports NO₂ cross section values from 238–1000 nm.

It seems that every time anything is published using a broadband cavity enhanced instrument there is discussion about what to name the instrument and the technique. I appreciate that the authors have gone with a more generalized name (BBCES – BroadBand Cavity Enhanced Spectroscopy) as previous versions of the name were too specific to absorption (IBBCEAS or BBCEAS) when cavity enhanced instruments, due to the extremely long path lengths are measuring extinction (absorption + scattering). Techniques that exclusively use a differential fitting algorithm (DOAS), and not the classic cavity equations that depend on absolute intensity (Fiedler et al. 2003) can probably justify the DOAS tag, but by design the instruments are really extinction instruments and not pure absorption instruments (a good example of this is the various aerosol ring-down instruments which cannot measure the aerosol absorption (Pettersson et al., 2004). I suggest that the authors either keep the name as given, or add an extra E (BBCEES) for extinction if there is really a desire to specify what property is being measured using spectroscopy.

We appreciate the support for “Broadband Cavity Enhanced Spectroscopy (BBCES)” as a general name that includes aerosol extinction measurements. The instrumental technique we are using was first described by Fiedler et al. (2003) as Incoherent Broadband Cavity Enhanced Absorption Spectroscopy (IBBCEAS). Eliminating the word “absorption” allows the acronym to include measurements of aerosol extinction. Currently, we are using IBBCEAS/BBCEAS for our publications about gas-phase measurements and BBCES for our publications about aerosol measurements. In the future, we will begin using the more general BBCES to describe all of our measurements, while acknowledging that this technique is the same as IBBCEAS/BBCEAS.

P. 9935 In 25 – If mirror purges were not used for this design, what would the effect of adding mirror purges be on an actual field instrument (the stated goal of this work)? Also, there is no discussion of what the expected sampling losses might be and how to deal with them.

We have made field measurements of gas-phase species with mirror purges (Washenfelder et al., 2011) and without mirror purges (Min et al., submitted). Mirror purges are necessary to keep the cavity mirrors clean when relative humidity or pollution levels are high, but they introduce additional uncertainties. The first uncertainty is the ratio of the total cell length to the sample cell length, which we have previously estimated to be 2% (Washenfelder et al., 2013). The second uncertainty is sample dilution by the mirror purge flow, which we have previously calculated to be 0.1% (Washenfelder et al., 2013). For a field instrument operated with mirror purges, we would explicitly include these uncertainties in our error budget.

Wert et al. (2002) examined inlet artifacts for formaldehyde measurements. We have added two statements to the manuscript:

Page 9935, lines 19-22: “Prior measurements under dry conditions have reported negligible losses to Teflon and metal surfaces for NO₂ (Fuchs et al., 2009) and glyoxal (a dialdehyde with greater Henry’s Law constant than formaldehyde) (Washenfelder et al., 2008; Min et al., submitted). A study of formaldehyde sampling artifacts similarly concluded it is relatively inert to adsorption by Teflon (Wert et al., 2002).”

Page 9942, lines 25-27: “With signal-averaging, the ultraviolet BBCEAS could be competitive with these direct absorption instruments, while providing a true in situ measurement. Previous work has shown that it is possible to construct inlets for formaldehyde that have minimal sampling artifacts (Wert et al., 2002).”

p. 9937 In 15 – Here and in previous works the authors have stated empirical fit values for the Rayleigh scattering cross-sections of N₂. The work by Bodhaine et al. (1999) contains no data for N₂, only values for the scattering of air and the equations for calculating the King correction factor for N₂. The only way to get the relationships presented in this work as the calibration standard for N₂ is to fit the scattering cross-section calculated from theory (see equations in Bodhaine, Bates 1980 and Sneeps and Ubachs, 2005) using the refractive index of air and the King correction factor for N₂ (given in Bodhaine). The minimum error between the stated equation for the Rayleigh scattering given in the text and that calculated by theory (refractive index for N₂ and the King correction factor) is 4.5% in the range of interest. The values for O₂ have a minimum error of 10% over the range of interest. This has been discussed previously in the literature (Thalman et al. 2014) and the values for the calculated scattering cross-sections have been verified by measurement with cavity ring-down (N₂) and BBCES relative to N₂ (Air and O₂). Fits to the data of Shardanand and Rao (1977) also have issues because of the high uncertainty (~10%) of those measurements.

The effect of the bias of these cross-sections is as follows:

Using the values given in the paper, it is possible to calculate what the ratio of the spectra intensities for Air and He were in the calibration (at 25C and 630 Torr). The mirror reflectivity can then be recalculated

using that ratio and the theory values for air. This yields a mirror reflectivity of 0.99922 instead of 0.99926 (at 330 nm).

If we then apply this further to the calculation of the concentrations of NO₂ at 330 nm, I calculate that the values reported in the paper are ~5% lower than they should be due to the use of the incorrect Rayleigh scattering cross-sections (for both the mirror calibration and for the calculation of the extinction (equation 1). This corrects the scale factor mentioned in the comparison to the cavity ring-down instrument (Section 4.2) to a slope of ~1.02 by removing the bias introduced by the choice of Rayleigh scattering cross-sections (assuming the retrieval only at a single wavelength for the sake of calculation, the actual bias will depend on the wavelength window selected for the fit and the change in the mirror reflectivity combined with the Rayleigh scattering over that range).

In previous publications by this group of co-authors on aerosol extinction (Washenfelder et al. 2013) this bias is likely accounted for in the calibration of the sample length with NO₂ when using mirror purges.

NOTE:

Below is the set of equations for common gases used in cavity instrument calibration (fixing typos in the table in Thalman et al. 2014)

$$\sigma(\nu) = \frac{24\pi^3\nu^4}{N^2} \left(\frac{n_p^2 - 1}{n_p^2 + 2} \right)^2 F_k(\nu), \quad (1)$$

$$(n - 1) \times 10^8 = A + \frac{B}{c - \nu^2} \quad (2)$$

Table 1: Terms for use in Equation 2 for the refractive index and for the King Correction Factor.

Gas	A	B	C	King Correction Factor	Ref.
He ^{a,b}	2283	1.8102x10 ¹³	1.5342x10 ¹⁰	F _k (ν) = 1	11-13
N ₂ ^{a,c}	5677.465	318.81874x10 ¹²	14.4x10 ⁹	F _k (ν) = 1.034 + 3.17x10 ⁻¹² ν ²	5,9
N ₂ ^{a,d}	6498.2	307.4335x10 ¹²	14.4x10 ⁹	F _k (ν) = 1.034 + 3.17x10 ⁻¹² ν ²	5,9
Ar ^{a,e}	6432.135	286.06021x10 ¹²	14.4x10 ⁹	F _k (ν) = 1	5,8
O ₂ ^{f,g}	20564.8	2.480899x10 ¹³	4.09x10 ⁹	F _k (ν) = 1.09 + 1.385x10 ⁻¹¹ ν ² + 1.448x10 ⁻²⁰ ν ⁴	5

^a Use N = 2.546899 x 10¹⁹ molecules cm⁻³ in Eq. 1; ^b 14285 < ν < 33333 cm⁻¹; ^c 21360 < ν < 39370 cm⁻¹; ^d 4860 < ν < 21360 cm⁻¹; ^e 5000 < ν < 33000 cm⁻¹; ^f Use N = 2.68678 x 10¹⁹ molecules cm⁻³ in Eq. 1; ^g 18315 < ν < 34722 cm⁻¹.

Based on the discussion above, we have decided to adopt the recommendation in Thalman et al. (2014) for Rayleigh scattering cross sections of N₂ and O₂. We have used the recommended values in Table 1 of Thalman et al. (2014), taken from Snee and Ubachs (2005). The Rayleigh scattering cross section for He has little influence on the measurement accuracy, and we have not modified it. We have edited the manuscript accordingly:

Page 9937, lines 15-18: “Based on the recommendation of Thalman et al. (2014), we have used Rayleigh scattering cross sections from Snee and Ubachs (2005; See eqns. 11, 12, 23, and 24) for N₂ and O₂. The Rayleigh scattering cross sections are $\sigma_{\text{Rayleigh N}_2} = 1.2577 \times 10^{-15} \times \lambda^{-4.1814}$ (fit to Bodhaine et al., 1999); $\sigma_{\text{Rayleigh O}_2} = 1.0455 \times 10^{-15} \times \lambda^{-4.1814}$ (fit to Shardanand and Rao, 1977; Snee and Ubachs, 2005); and The Rayleigh scattering cross section for He is based on an empirical fit to measurements by Shardanand and Rao (1977), $\sigma_{\text{Rayleigh He}} = 1.336 \times 10^{-17} \times \lambda^{-4.1287}$.”

This new parameterization increases the Rayleigh scattering cross section for zero air by 4.9% (average difference from 315–350 nm), and increases the fitted NO₂ and CH₂O concentrations similarly. We have recalculated the data in the paper, and updated the values for reflectivity, cavity loss, effective path length, NO₂, and CH₂O concentrations throughout.

In the error budget, we have increased the uncertainty for the Rayleigh scattering cross section of zero air to $\pm 4\%$ to better represent the uncertainty and lack of measurements in the ultraviolet spectral region.