We thank the reviewer for taking the time to review this manuscript and the insightful comments. The reviewer comments are reproduced below in *bold, italicized font*. Our responses are shown in regular font. Changes to the text are indicated as <u>underlined</u> text for insertions or are crossed out for deletions.

Anonymous Referee #1

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This paper presented a LED based cavity enhanced absorption spectroscopy at 470-540 nm. Different with previous CEAS instruments. The CEAS moved the window to cyan region (470-540 nm) and measure Rayleigh scattering cross-sections of several pure gases. This part is fundamental and very meaningful to the dataset. The authors applied the instrument to measure NO2 and I2 simultaneously. The measurement of ambient NO2 by CEAS was compared with CRDs and presented the feasibility. With respect to the I2 measurement by CEAS, which has been reported in the neighbor or the same wavelength region (e.g., Vaughan et al., 2008; Bahrini et al., 2018). Although the detecting capacity is not well improved compared with previous works, this work provides a possible way to measurement ambient I2. The following comments should be addressed before the consideration of publishing in AMT.

Major comments:

1. Section 3.3, it's interesting that using the saturated water vapor absorption to derive the effective optical absorption path determination. Are the authors make sure the water vapor was saturated by measured the RH? The sample flow of the water vapor gas keep the same with the ambient sampling flow or not (1.5-2.5 slpm). The authors should provide more details of the d0 determination, such as the convolution of effective water vapor cross section.

We thank the reviewer for having inquired about the use of water vapor in the determination of the effective absorption path and convolution of the water vapor cross-section. In response to the concerns raised, we have re-investigated the effective absorption path.

The setup used to generate gas streams saturated with water was the same as described in section 2.3.1 of (Woodward-Massey et al., 2014). In the earlier experiments, we had monitored the relative humidity (RH) using a commercial probe (VWR) and found the gas streams to be saturated. In hindsight, we agree with the reviewer that we should have monitored the RH in the experiments described in this manuscript as well, which we had not. One concern is that evaporative cooling of the liquid water reservoir could have lowered (and led to drifts in) the RH output of the source. Further, we did not observe condensation within the connecting tubing, and, again in hindsight, conclude that gas stream was likely not saturated. Another concern is that the water absorption lines in the cyan are narrower than the spectral resolution of our CEAS, such that the convolution (which has been added to Figure 1) could potentially have introduced a bias. Finally, the RH experiment was conducted at a flow rate of 1.0 slpm; at this low flow rate, R_L differs from that at a higher flow rate (see below).



Figure 1. Absorption coefficients for atmospheric absorbers in the cyan region at typical tropospheric abundances mixing ratios (stated in brackets after each species). Absorption cross-sections were downloaded from the Max-Planck Institute for Chemistry's web site located at <u>http://</u>www.uv-vis-spectral-atlas-mainz.org and are based on the following: H₂O (Coheur et al., 2002), O₃ (Burkholder and Talukdar, 1994), NO₂ (Voigt et al., 2002), I₂ (Spietz et al., 2006), IO, OIO (Spietz et al., 2005), and OBrO (Knight et al., 2000). <u>The literature cross-sections for H₂O (shown in blue) were convolved with the resolution of the IBBCEAS (shown in red).</u> The absorption cross-section of O₄ is shown in Figure S4.

Because of the above concerns, we re-measured d_0 (i.e., R_L) for our sample cell. Since the work described in this manuscript, the IBBCEAS has been equipped with a new LED and mirrors optimal for the 350 - 390 nm wavelength region, where the O_2 - O_2 collision pair has two absorption peaks near 361 and 380 nm. With this setup, we sampled pure molecular oxygen and calculated R_L from (a) the ratio of expected O_4 (calculated from known cross-sections and O_2 number density) divided by the ratio of O_4 observed and (b) by the turning the purge flows on and off (Duan et al., 2018). We used the recently reported cross-sections by (Thalman and Volkamer, 2013) with an accuracy of $\pm 4.2\%$ (1 σ).

At a sample flow rate of ~2.0 slpm and purge flow rate of 0.1 slpm, and cell pressure of 870 hPa, we observed an R_L value (calculated using method (a)) of 1.28 ± 0.05 (1 σ precision stated) with an accuracy of $\pm5\%$. Consistent values were observed by method (b) ~20 min after the mirror purge flow had been turned off. We repeated this experiment sampling a constant concentration of NO₂ and obtained consistent results. This R_L value is smaller than calculated from the ratio of the inter-mirror distance *d* to the distance between the inlet and outlet of the sample flow (~1.39), which suggests that sampled air partially mixes into the purge volume.

Duan et al. (2018) reported a flow dependent R_L in their setup. Suspecting similar behaviour in our instrument, we measured R_L at a volumetric flow rate of up to 11 liters per minute (mass flow rate of ~4.4 slpm and a pressure of ~424 hPa), similar to conditions at which the instrument was operated during ORCA. We used method (a) to calculate R_L , since turning the purge flow of (method (b)) causes substantial pressure changes, and alternated sampling zero air and oxygen. At the larger flow rate, R_L was 1.20±0.07 (1 σ precision).

On the basis of the above, we have rewritten section 3.3 as follows:

"When sampling ambient air, kK-nowledge of the path length over which sampled air is present (d_0) and the associated correction factor R_L is essential in experiments involving resonant optical cavities especially for accurate IBBCEAS measurements when purging purge gases are used to maintain clean mirrors as in this work. If the mirror reflectivity R is known, d_0 can be determined by measuring the extinction of a known amount of a strongly absorbing, non-reactive gas with known absorption cross section, which is sampled through the inlet port. Combining Eq. (1) and Eq. (2) and rearranging gives an expression for d_0 :

$d_{0} = \frac{\delta I(\lambda)}{\sigma N} \left(1 - R(\lambda) + d\alpha_{Ray}(\lambda) \right)$

(7)

Here, $\delta I(\lambda) = [I_{\theta}(\lambda) - I(\lambda)]/I(\lambda)$. In this work, we used water vapour and the absorption cross section of H₂O from (Coheur et al., 2002) to determine $R_L = d/d_{\theta}$. A saturated gas stream of water vapour was generated by bubbling air through a water reservoir at a temperature of 298 K and pressure of 0.88 atm. Using Eq. (4), d_{θ} was found to be 73.2±0.7 cm, in agreement with the physical dimension (~73 cm) of the CEAS sample path. With d = 102.0 cm, this gives $R_L = 1.39\pm0.01$. The effective cavity length, d_{θ} , was determined by sampling pure oxygen and monitoring the O₂ dimer (Duan et al., 2018). This experiment was performed in the 350 - 390 nm wavelength region using highly reflective mirrors and an LED (Thorlabs M365LP1) suitable for this wavelength region, though in principle it could have been performed in the cyan region as well since both spectral regions contain O₄ absorption lines. Following Duan et al. (2018), d_{θ} is given by

$$d_0 = d \times \frac{[0_2]_{on}}{[0_2]_{off}}$$

(7)

where $[O_2]_{on}$ and $[O_2]_{off}$ are the $[O_2]$ retrieved using cross-sections by (Thalman and Volkamer, 2013) with or without the purge flows. Consistent results were obtained when a constant mixing ratio of NO₂ was sampled (and purge flows were turned on and off) and from the ratio of expected absorption by O₄ (calculated from the square of the number density of O₂ and the O₄ cross-section) relative to the observed O₄ absorption, though the latter may be less accurate as the absorption changes non-linearly in the region where purge and sample gases mix and requires accurate knowledge of mirror reflectivity.

At a sample flow rate of 2.0 slpm, a purge flow rate of 0.1 slpm, and a cell pressure of 870 hPa, we determined $R_L = \frac{d/d_0}{d_0} = 1.28\pm0.05$ (1 σ precision stated) with an accuracy of ±5%. This R_L value is smaller than calculated from the ratio of the inter-mirror distance *d* to the distance between the inlet and outlet of the sample flow (~1.39), which suggests that sampled air partially mixes into the purge volume. At a volumetric flow rate of 11 liters per minute as deployed during ORCA, we observed $R_L = 1.20\pm0.07$ (1 σ precision)."

The results in section 4.1 are unaffected by this change, since the entire cell was filled with sample gases.

After remeasuring R_L , we discovered that it had not been correctly applied to the IBBCEAS data shown in Figures 5-8 and the results in sections 4.2 and 4.3; this has now been corrected. The following changes were made to the text:

Section 4.2.1 line 372:

"An NO₂ mixing ratio of (11.6 ± 0.4) ppbv was retrieved." was changed to "An NO₂ mixing ratio of (11.6 ± 0.4) ppbv was retrieved, corresponding to an ambient air mixing ratio of (13.9 ± 1.0) ppbv when R_L is factored in."

Line 383: "Shown in Figure 7a is a scatter plot of all of the NO_x calibration data. This plot shows a linear relationship with a slope of 0.923 ± 0.009 , an intercept of 0.18 ± 0.09 ppbv, and $r^2 = 0.975$. The slope of the line in Figure 7a reveals 7.7% difference in measurement of the calibration standard." was changed to

"Shown in Figure 7a is a scatter plot of all of the NO_x calibration data. This plot shows a linear relationship with a

<u>slope of 1.11±0.01</u>, an intercept of 0.2±0.1 ppbv, and $r^2 = 0.975$. The slope of the line in Figure 7a reveals an 11% systematic difference in the measurement of the calibration standard."

Line 388: "The scatter plot of CEAS and CRDS NO₂ data (Figures 7b and 7c) suggest that the CRDS data were systematically higher than the CEAS data, by 15% when sampling ambient air (Figure 7c). When data are filtered by removing all CEAS points below a factor of three times the standard deviation of a blank measurement for 60 s (~1 ppbv; see Sect. 4.3), the slope of the scatter plot, when forced through an intercept of zero, is 0.98 ± 0.01 (r² = 0.70)." was changed to

"For ambient air data collected on 18-19 Jul 2015, the scatter plot of IBBCEAS and CRDS NO₂ data (Figure 7b) has the same slope (1.12 ± 0.02) as that shown in Figure 7a, while the scatter plot of the entire campaign has a slope of 1.02 ± 0.01 (Figure 7C). When data are filtered by removing all IBBCEAS points below a factor of three times the standard deviation of a blank measurement for 60 s (~1 ppbv; see Sect. 4.3), the slope of the scatter plot, when forced through an intercept of zero, is 1.18 ± 0.01 ($r^2 = 0.70$), suggesting that the IBBCEAS instrument is biased high."

We modified section 4.3 (Accuracy and limits of detection) as follows:

"The accuracy of the <u>IBB</u>CEAS NO₂ measurement is influenced by uncertainties in the absorption cross-section of NO₂ (\pm 3%) (Voigt et al., 2002), fit errors \pm (3 – 5%), which can be reduced to \pm (2 – 4)% by smoothing), scattering cross-sections, i.e., mirror reflectivity (\pm 2.5%) (see Sect. 3.2 and 4.1), <u>R_L (\pm 5%; Sect. 3.3)</u>, and <u>calibration</u> errors in the mass flow controller reading (\pm 1%), sample cell pressure readout (\pm 0.5%), and temperature measurement (\pm 0.7%). The total uncertainty, expressed as the square root of the individual errors summed in quadrature, is \pm (5.5—7.67–9)%. Not included in this estimate are errors arising from interpolation of infrequent mirror reflectivity and R_L determinations in the field."

In the subsequent text starting with "The limits of detection..." on line 414 and in the S.I. we have multiplied all values by the appropriate factor of R_L . This section now reads:

For I₂ in laboratory-generated samples-<u>under optimal conditions</u>, typical 1 σ fit errors (when integrated over<u>for</u> 60 s) averaged data were \pm 5.87 pptv for 21 when 21 pptv I₂ were sampled and \pm 7-9 pptv for when 350-544 pptv I₂ were sampled (Figure S6). The accuracy for of I₂ data is, in principle, of similar magnitude to that of the NO₂ data, except that it also depends on knowledge of inlet transmission efficiency, which was not assessed in this workwas (5.4-6.4)%, with main contribution from error in the high resolution absorption cross section of I₂ (Spietz et al., 2006). The Allan deviation plot in Figure 8b demonstrates 1 σ measurement precisions for I₂ of \pm 38.49 pptv for 60 s and \pm 16 22 pptv for 5 min averaged data. During ORCA, the 1 σ precisions were \pm 100-120 pptv for 60 s and \pm 50-60 pptv for 5 min data, respectively.

For OIO, the Allan deviation analysis gives 1σ measurement precisions of $\pm 4.65.7$ pptv for 60 s and $\pm 1.82.3$ pptv for 5 min averaged data (Figure S9) in the laboratory. "

Finally, the following was inserted in the discussion section:

"An important parameter in any IBBCEAS measurement is the effective cavity length. Duan et al. recently summarized past practices in its determination and found that these practices vary considerably between groups (Duan et al., 2018). In this work, the necessary correction ($R_L = 1.28$ at 2.0 slpm sample flow rate) differed substantially from the physical dimension of the cell (1.39), underlining its importance for accurate measurements. However, it is unclear to what extent R_L varies between molecules which will need to be investigated. To improve the accuracy of future measurements, we will deploy more frequent zeroing (than during ORCA) and verify R_L periodically, for example by periodic sampling of molecular oxygen and measuring O_4 concentration."

2. The scatting cross section of N2 (Peck and Khanna, (1966)) was used in the calculation of reflectivity, but not included in the following intercomparison in figure 4(b), the author should clarify it. Our apologies - the cross-section of Peck and Khanna (1966) had been mislabeled, which has been corrected.

3. Noticed that the cyan region was affected by the strong narrow absorption of water vapor (Bahrini et al., 2018). Here the author used a "new" zero that include the same water vapor concentration to avoid the interference (mentioned that in line 231). I think it's a good way to avoid the water vapor absorption problem, but the zero spectrum should be carried out more frequently in ambient condition and the reason why dynamic zero carried out should be addressed clearly in the text.

We agree that the zero determination should have been carried out more frequently when acquiring ambient air data. We added the following in section 3.8 on line 273: "Zero air was generated using a custom-built zero air generation system (Odame-Ankrah, 2015), which delivered air at ambient relative humidity that was free of trace gases such as NO₂, NO, I₂, or O₃. This approach minimized absorption by H_2O from the extinction spectra which can create artifacts (Bahrini et al., 2018)."

We also added the following to the discussion:

"An important parameter in any IBBCEAS measurement is the effective cavity length. Duan et al. recently summarized past practices in its determination and found that these practices vary considerably between groups (Duan et al., 2018). In this work, the necessary correction ($R_L = 1.28$ at 2.0 slpm sample flow rate) differed substantially from the physical dimension of the cell (1.39), underlining its importance for accurate measurements. However, it is unclear to what extent R_L varies between molecules (it is possibly larger for molecules with short lifetimes such as the IO radical) which will need to be investigated. To improve measurement accuracy in future measurements, we will deploy more frequent zeroing and verify R_L periodically, for example by periodic sampling of molecular oxygen."

4. Line 407, it's hard to make sure the wall loss of 12 in the inlet tube by just taking a look at the time series. The statement should be more conserve or just simply deleted as the author did not carry out more lab experiments to quantify the loss.

We agree with the reviewer that the inlet transmission of iodine species will need to be investigated more thoroughly in the future. On the other hand, the fast rise and fall times (which are shorter than the time resolution of our measurement) suggest the absence of inlet issues; our opinion is based experience with other reactive gases (e.g., the nitrate radical, and molecular chlorine), and is worthwhile stating.

We have modified the sentence in question from "The square-wave response and quick rise and fall times suggest the absence of inlet transmission losses." to "While the transmission of iodine through inlets was not systematically investigated in this work, tThe square-wave response and quick rise and fall times suggest the absence of inlet transmission losses."

Specific comments:

1. *Keywords are not necessary in AMT.* They have been removed.

2. Line 48, please make up the reference. (2010) as well as in line 220.

We have added the author names to the references as requested by the reviewer.

3. Line 370 and line 394, "an example" should be change to "a spectrum retrieve example" or "a spectrum fitting example"

We have changed the text in question from "An example NO₂ CEAS measurement is shown on Figure 5a." to "An example <u>of a spectral retrieval for NO₂ in ambient air CEAS measurement</u> is shown on Figure 5a." and from "Figure 5b shows an example of an I_2 measurement." to "Figure 5b shows an example <u>of an retrieval for I₂ measurement</u>."

4. *Line 392, R2 is 0.70.* This has been corrected.

5. Line 422, is "60 s and ±50 pptv for 5 minutes, respectively." Fixed.

6. The residual plots in Figure 5 and Figure S5 should be united to the style in Figure S3.

We have updated Figures 5 and S5 as requested and have taken the opportunity to update the depiction of the polynomial, which was displayed incorrectly.

7. I suggest the authors put the figure S7 in the main text though the ambient I2 below the instrument LOD. Since the ambient air mixing ratio of I_2 was below our detection limit, we prefer to leave the Figure in the S.I.

Literature cited:

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