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 underlined text for insertions or are ~~crossed out~~ for deletions.

Anonymous Referee #2

This discussion paper reports on the development of a broadband cavity-enhanced absorption spectrometer, using incoherent light from a light emitting diode (LED) in the cyan region of the spectrum; i.e. between 470 and 540 nm. The performance of the instrument has been evaluated and characterized in the laboratory as well as in the field concerning the detection of NO2 and I2. It was further utilized to measure Rayleigh scattering cross-sections of several gases for calibration and validation purposes.

This is a well written and thoroughly prepared manuscript with good attention to detail, however, the approach to trace gas detection using incoherent broadband cavity enhanced absorption spectroscopy (IBBCEAS) is not new. In fact there is a continually growing number of IBBCEAS instruments for field, chamber, and laboratory studies and the merit of this manuscript is predominantly in the discussion of the usefulness of the cyan region for NO2 and I2 detection, as well as the independent measurement and assessment of scattering cross-sections of several gases (O2, N2, air, Ar, CO2 and CH4) which are relevant for calibration purposes and remote sensing applications, and add to the overall accuracy and knowledge of data in the literature on optical losses of the corresponding gases. Publication in Atmospheric Measurement Techniques is thus warranted in my opinion,

We thank the reviewer for this kind assessment.

subject to addressing the following aspects which caught my attention during reviewing the discussion paper:

P1 In Line 12 (Abstract) the authors introduce the acronym (CEAS) as cavity-enhanced absorption spectrometer, however, in Line 27 (Introduction) CEAS stands for cavity-enhanced absorption spectroscopy. Generally the term CEAS is used in the context of spectroscopy (just like cavity-ring down spectroscopy, CRDS). In the manuscript the authors refer to their instruments as "the CEAS", or "the CRDS", but still also use the other definition synonymously. For clarity and conformity with previous literature using CEAS as a "spectroscopy acronym". I recommend using the term "CEAS instrument" or "CRDS instrument". Moreover, in order to distinguish the experimental methodology from a laser-based approach (coherent) light, the term "IBBCEAS instrument" (see above) in this context is unambiguous.

We agree with the above argument and have made the suggested changes throughout the text.

Line 35: The authors refer to retrieval techniques that are analogous to those used in differential optical absorption spectroscopy (DOAS). Standard DOAS retrieval cannot be applied to the measured spectra, as only an effective pathlength is known in CEAS if the mirror reflectivity is known; thus the mirror reflectivity is key to the spectral analysis. The authors may want to rephrase this statement.

The statement has been rephrased as follows: "The output spectrum is integrated yielding extinction spectra from which mixing ratios are retrieved using ~~techniques analogous to those used in differential optical absorption spectroscopy (DOAS) (Platt and Stutz, 2008)~~known absorption spectra and knowledge of the mirror reflectivity and effective optical absorption path (Meinen et al., 2010)."

P2 Line 3: In the context of NO3 the authors may want to cite (Venables et al., 2006; Varma et al., 2008) which are not listed among the references.

We have added citations to (Venables et al., 2006) and (Varma et al., 2009) as suggested by the reviewer.

In line 4 other papers on I2 detection (Dixneuf et al., 2009; Ball et al., (2010); Nitschke et al., (2011); Bahrini et al., (2018)) may be mentioned, one of which is already in the reference list.

We have added citations to (Ball et al., 2010; Dixneuf et al., 2009; Bahrini et al., 2018) but have chosen not cite the Nitschke paper here because the methodology is described in the earlier paper by (Dixneuf et al., 2009). We cite Nitschke et al. (2011) on line 68.

P4 The authors may want to use σ_n instead of σ (introduced in Eq. (5)) to indicate "n-based" cross-sections.

Done.

Line 107 & 110: "resonant optical cavity" -> "optical cavity"

Fixed.

Line 116: Backing pressure stated in psi with conversion to Pa given. Later on all pressures are given in torr. This should probably be uniform. Since this is a European journal probably psi and torr should be avoided and pressures should be stated in mbar or Pa.

We have replaced the pressure unit Torr with SI unit (hPa) throughout the text.

Line 124: The authors may want to state the LED's optical output power here.

We have added the information requested and removed the phrase "to achieve a manufacturer quoted optical minimum output power of ~400 mW" from line 162 as it is now redundant.

P5 Line 138: discrete

Fixed.

Line 141: yielded an approximately Gaussian profile with -> yielded approximately Gaussian profiles of the atomic Hg emission lines with

Fixed.

Line 142: degraded -> lower

Fixed.

Line 146: net instrument weight -> net weight of the instrument

Fixed.

Line 163: asymmetric Lorentzian shape? What is meant by that? Just refer to Figure 3.

We have removed word Lorentzian.

P6 Line 172: "and d is in units of cm." Either delete this (recommended) or also state that α is in units of cm⁻¹.

We have removed the phrase as recommended by the reviewer.

Line 196: an uncertainty of +/0.1 % in pressure appears rather small given the fact that this is a flow cell experiment.

On line 180, we state that "the gases were continuously injected through the purge ports until all other sample cell constituents were displaced through the open inlet port"; typical flow rates were ~100 sccm. The inner diameter of the sample cell tube is 1.59 cm and relatively large; hence, we wouldn't expect much uncertainty due to a relatively modest flow.

No changes were made.

Line 196: an uncertainty of +/0.1 % in light intensity appears somewhat optimistic when looking at Figure S10.

Since the relative standard deviation of the data shown in Figure S10 is indeed with in ±0.1%, no changes were made to the manuscript in response to this comment.

P7 Line 219: "Convolving the NO2 ... effectively degraded the high...". The spectrum is not really "degraded", it is simply corrected for a different resolution. This sentence can be deleted in my opinion.

We have changed the sentence "Convolving the NO_2 reference spectrum effectively degraded the high-resolution spectrum but was required for the least-squares analysis." to "A ~~C~~convolv~~ing the~~ed NO_2 reference spectrum ~~effectively degraded the high-resolution spectrum but~~ was ~~required~~ used for the least-squares analysis."

Line 219-221: The authors state that the literature cross-sections of I2 and OIO were not convolved as the spectrometers resolution was higher than the resolution at which the literature spectra were measured. I do not quite follow this. The reference spectra for the fit should still be adapted to the resolution of the spectrometer used since otherwise the cross-sections do not match. What was the resolution of the literature spectra used?

We inserted "at a resolution of 0.59 nm ".

Also: (2005; 2006) -> (Spietz et al. 2006; 2005)

Fixed.

Line 224: "(relatively) low resolution CEAS instrument" -> "IBBCEAS instrument"

Fixed.

Line 233 & 234: If the water concentrations were significant they should have been included in the fit in any case and not just to minimize the residuals. However, fitting water spectra is generally difficult, since water absorption lines in the visible are genuinely spectrally narrow; in other words the resolution of the spectrometer may be small in comparison to the FWHM of water absorption features. In this case the absorption behavior is not in the Lambert-Beer regime and the H2O reference spectra used in the fit must be corrected for that fact (see Bitter et al. 2005; Varma et al., 2008). I am wondering whether the H2O mixing ratios obtained in those fits were indeed

meaningful. They do not seem to be stated in the manuscript. If H2O mixing ratios from the fit are not meaningful, then including H2O simply introduces one more degree of freedom to the fit and therefore smaller residuals can be achieved, but this is physically not justified. The H2O cross-sections in the cyan region are small in any case and might be discarded depending on the humidity during the campaign? Also see Bahrini et al., (2018) where I2 was measured in the presence of water vapour – water was simply subtracted?!

We apologize for the confusion - the next sentence clearly states that water was included in the fit (we meant to say to that the contributions by water were small and often negligible). We agree with the reviewer that fitting to the high-resolution water spectrum in this wavelength region is challenging and derived mixing ratios will not be quantitative. We attempted to avoid this issue, either by using water-free gases (as was the case for the Rayleigh scattering cross-section measurements) or by attempting to have the same water concentration in both the zero and measurement spectra, such that water only minimally contributed to the optical extinction spectra.

We have changed the text on line 233 as follows:

"The "spectral shifting" setting in DOASIS was set to ±0.2 nm, and stretching was disallowed. ~~The contributions of water vapor to the optical extinction was neglected since the relative humidity of the air sampled during the background measurement was the same as during the measurement of NO_2 or I_2.~~

The same parameters were used to fit the data from the ORCA field campaign except that in an effort to minimize the fit residuals, the convoluted absorption cross-section of H_2O based on the high-resolution data by (Coheur et al., 2002) was also included in the fit. The contributions of water vapor to the optical extinction was ~~neglected~~small since the relative humidity of the air sampled during the background measurement was the same as during the measurement of NO_2 or I_2."

Line 235: What criteria determined the smoothing parameters that yielded better seemingly better results?

In general, fourth order polynomial Savitzky/Golay digital filtering routine is commonly applied in many areas of science (including chromatography and spectroscopy). In our work, we found smoothing using this readily available algorithm did improve the signal to noise ratio of our measurement. However, the digital filtering parameters (or alternate filtering algorithms) were not systemically explored, as this is outside the scope of this manuscript.

No changes were made to the manuscript.

P8 The pure gases for reflectivity and scattering cross-section measurements are not mentioned in section 3.7.

Apologies for this oversight.

In response to the reviewer's comment, we expanded a sentence in section 3.2: "To determine $R(\lambda)$ in this work, the cavity output intensity was recorded when the cell was filled with high purity N_2 (99.998%) or with He (99.998%) to atmospheric pressure (~890 hPa). In each case, the gases were delivered from a compressed gas cylinder (Praxair) and continuously injected through the purge ports until all other sample cell constituents were displaced through the open inlet port."

Further, we modified section 3.7:

"3.7 Generation and delivery of ~~calibration~~ gases
Figure 2b shows ... (i.e., wall thickness and length).
Ar, CO_2, CH_4, N_2, O_2, air and He were delivered from compressed gas cylinders (Praxair) in the same manner as described in section 3.2."

Molecular iodine is a very sticky molecule. Do the authors have any information on, or attempted to measure iodine losses in the inlet system (see also next comment).

P9 Line 270: Did the authors try to calibrate line losses concerning I2?

This was not attempted. We made the following change in section 4.2.2:

"Figure S7 shows a sample time series of I_2 mixing ratios during the ORCA campaign. Concentrations of I_2 (and of OIO, not shown) in ambient air were below the instrument's detection limits. At 22:30 UTC, I_2 from a diffusion source was added to the inlet. While the transmission of iodine through inlets was not systematically investigated in this work, ~~The~~ the square-wave response and quick rise and fall times suggest the absence of inlet transmission losses."

Line 271: in regular intervals -> at regular intervals

Fixed.

Line 286: "...coefficients)," insert comma

Fixed.

P11 Line 348 & 349:(1973) -> (Bideau-Mehu et al., 1973)(1977) -> (Shardanand and Rao, 1977) same in Line 352(2005) -> (Sneep and Ubachs, 2005)

Fixed.

P12 Line 372/373: "The residual spectrum is lacking structure, indicating ..." The residuals in Figure 5a show asymmetric residuals, which appear to have spikes that appear to "go negative", they are not balanced (log scale?). This is strange,

The residuals are as calculated by DOASIS. We note that there are both positive and negative spikes. The average $\pm$ 1 standard deviation are $(-0.02\pm5.05)\times10^{-9}$ cm^{-1} for the residual NO_2 spectrum (Fig. 5a) and $(-0.1\pm8.1)\times10^{-9}$ cm^{-1} for the residual I_2 spectrum (Fig. 5B), so they are not misbalanced. The slightly larger residual for the I_2 spectrum may have been a result of a tiny misalignment of the reference and observed spectra wavelength scales.

in particular since the same figure is shown in the supplemental material (Figure S3). Here the residuals appear more balanced. The authors may want to check this, as it seems the data are the same but the residuals differ. Moreover, part of Figure S3 appears redundant.

In Figure S3, we are comparing the results obtained when fitting spectra with a digital filter applied to the data and without. We reproduced the data in Figure 5a in Figure S3A, but on a different scale to facilitate this comparison. Since this is in the supplemental, we have chosen to not amend the manuscript in response to the reviewer's comment.

Line 375: The authors claim that there were up to 16 ppbv of NO2 in the standard gas mixture. In Figure 6a mostly 10 ppbv are observed (with one exception that is higher). Where does this information of the 16 ppbv come from?

This mixing ratio was determined by blue diode laser CRDS, as stated ("During the ORCA campaign, the inlet of the IBBCEAS instrument (and of the CRDS instrument, which sampled in parallel) was overflowed every 30 min with a standard gas mixture of ~20 ppbv NO_x containing up to 16 ppbv of NO_2 in zero air and with ~130 ppbv of NO added to ambient air."). No changes were made in response to this question.

The reason for overflowing the sample cell with two different mixtures is not clear to me.

This was done for reasons outside the scope of this paper, but since the reviewer asked: we also operated an N_2O_5 channel (heated inlet, 662 nm diode laser) of the main sample line; it is common practice to "zero" such a channel by titration with a high NO concentration. We had reasons to distrust the supplier's stated concentration of the more concentrated NO gas cylinder (for one, its certificate had expired), and opted to cross-calibrate with a more recently purchased calibration gas cylinder.

We added the following on line 278: "A PAN-GC (Tokarek et al., 2014), commercial NO/NO_y and O_3 instruments (Thermo 42i and 49i), as well as a 662 nm diode laser N_2O_5 channel (Osthoff et al., 2017) also sampled off this common inlet line, resulting in all instruments periodically sampling a variety of calibration gases."

Why did the authors chose the specific "format" (=measurement procedure) shown in Figure 6, to characterize the instument.

Please see our answer above.

The zeroing periods are not indicated in Figure 6.

This has been added.

Section 4.2.2. Only one figure on molecular iodine is shown in the main body of the text. All other figures on iodine are in the supplemental material (Figs. S5, S6, S7). This is too much information in the additional information section. At least one time series should be shown in the main paper in my opinion.

Since the ambient air mixing ratio of I_2 was below our detection limit, the time series are of marginal value to the reader. We hence prefer to leave the Figure displaying its time series in the S.I.

Line 398: How was the mixing ratio of I2, outflowing from the permeation chamber, established?

The stated iodine mixing ratios were from IBCCEAS retrievals (as no independent iodine measurement was on hand). In response to the reviewer's question, we have removed the following sentence "The smallest amount of I_2 that was produced without dilution of the permeation chamber output flow was ~21 pptv" from the manuscript.

P13 Line 423/424: The information on OIO measurements and the Allan deviation analysis for same appear very suddenly at this point in the paper (section 4.3). Measured OIO spectra are not shown or, if present in the I2 spectra, not mentioned. Formation of OIO is not discussed. OIO was insufficiently discussed prior to section 4.3 and the supplemental material also only shows Allan deviation plots, rather than measurement or evaluation procedure. The authors should say more about OIO detection in the paper.

The chemistry leading to formation of OIO is well documented in the literature (e.g., (Cox et al., 1999; Allan et al., 2001; Saiz-Lopez et al., 2006; Huang et al., 2010)) and outside the scope of this paper. In response to the reviewer's comments, we have changed the title of section 4.22 from "Molecular iodine" to "Iodine species (I_2 and OIO)" and have modified a sentence on line 405:

"Concentrations of I_2 (and of OIO, not shown) in ambient air were below the instrument's detection limits."

In the discussion, we already stated the following:

"The sensitivity for I_2 and OIO (~~16~~ 19 and ~~1.8~~2.1 pptv for 5 min averaged data under laboratory conditions) suffices for their quantification in environmental chamber studies (Dixneuf et al., 2009). Further, these LODs are below maximum I_2 and OIO abundances reported at Mace Head, Ireland, of 94 and 13 pptv (Bitter et al., 2005) and 61 and 9.2 pptv (Peters et al., 2005), respectively, but above the maximum I_2 level of 4 pptv reported in California (Finley and Saltzman, 2008). This implies that iodine species on the West coast of British Columbia, Canada, might have been detected if the instrument had been operated optimally."

We do not believe that further modifications are warranted.

P14 Line 455: refer to the last paragraph in the discussion on Page 15 rather than listing future system "upgrades" in brackets and "etc."

We have modified the paragraph in question as follows:

"The detection limit for NO_2 achieved under laboratory conditions in this work (49 pptv for 5 min data) is ~~compared~~ of similar magnitude as those by ~~to~~ instruments operated in other wavelength regions (Table 2). However, the CEAS measurement precision in this work was surpassed by the more mature blue diode CRDS, though future upgrades (~~e.g., more highly reflective mirrors, more sensitive spectrometer, etc.~~ see below) may improve the CEAS precision."

Line 465: Conclusions are drawn on OIO, but too little is said about OIO in the manuscript.

Please see answer to the comment re lines 423/424.

References

Suggested additions:

Ball et al. Atmos. Chem. Phys. 10, 6237-6254, (2010) now cited

Bahrini et al., Opt. Laser Techn. 108, 466-479, (2018) now cited

Nitschke et al. Planta 233, 737-748, (2011) now cited

Varma et al. Appl. Opt. 48, B159-B171, (2009) now cited

Venables et al. Env. Sci. Techn. 40, 6758-6763, (2006) now cited

P18 Include initials of Shardanand.

Unfortunately, we cannot since this author did not use a first name in any of his or her publications.

Figure 3: List pressures in the caption

Done.

Figure 4f: Holm -> Hohm

Done.

Figure 5a: Check data in the residual panel (see comments above, I think the data are logarithmic plotted on a linear axis)

Figure 5 was updated (partially in response to a comment by reviewer 1).

Figure 6: Please also indicate the time when zero air was flown into the cavity

Done.

Figure 7 (panel b and c). Units missing after intercept

added

P28 Include ref (King, 1923) in caption

added

Supplementary Material

Figure S5: Improve the caption, which is simply too short for what is shown in the figure. Is there an offset in the data shown in the uppermost panel? The colour code is unclear and the assignment of residuals also (coloured residuals are too congested). What is to be conveyed through the log and linear axes? Blue residuals in the middle panel are unclear. I think this figure needs attention.

We have modified Figure S5 as follows:
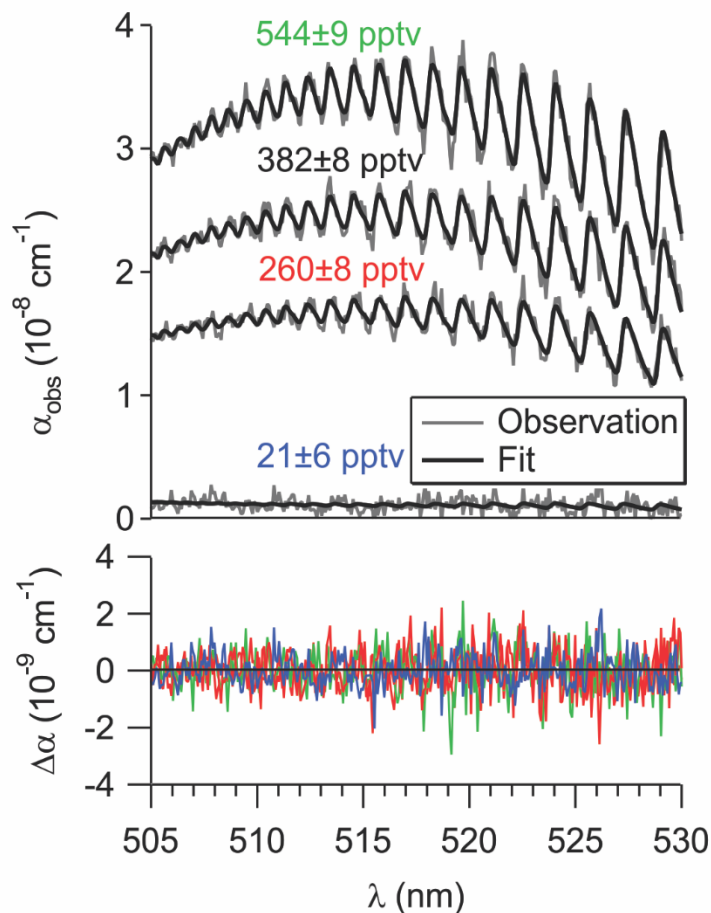
Figure S5 Examples of spectral fits of laboratory generated I_2 at different mixing ratios. The absorption cross-sections by Spietz et al. (2006) and a third-order polynomial were used. The bottom panel shows the fit residuals, colour-coded by the mixing ratio labels above.

In response to reviewer's comment, we have combined the top two panels and plotted the data on a linear scale. We thank the reviewer for noticing that the top three traces were offset; in fact, their mixing ratios were incorrectly stated, and this has now been corrected.

Figure S6: What is going on between 21:20 and 21:30? Is there zero air sampling?

We thank the reviewer for catching this error. Indeed, the instrument sampled zero air from 21:20 to 21:30. The figure now displays the zeroing periods correctly.
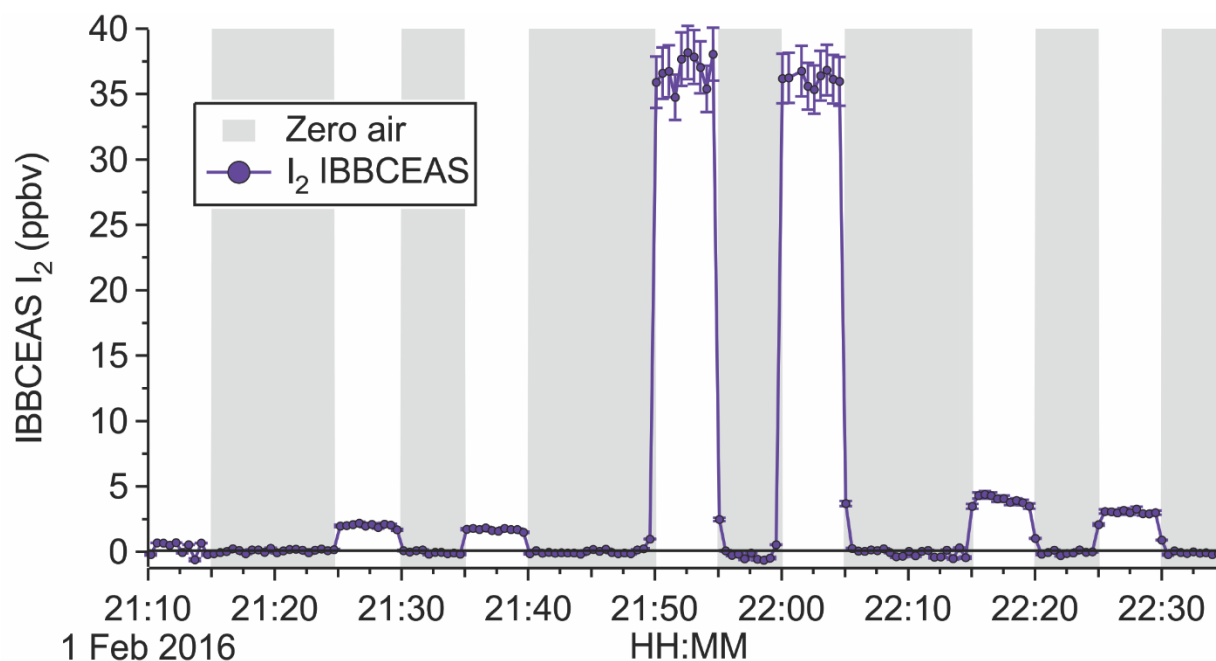
Figure S6 Time series of sample CEAS retrievals while sampling laboratory generated I_2. The grey underlay indicates times when the instrument sampled zero air. Iodine was delivered from four permeation tubes of different wall thickness, which were exchanged during the zeroing periods while the diffusion chamber output was bypassed.

Are there error bars on all data points? Are they too small to be seen except for during the two concentration maxima?

There are error bars on all data points, and there are indeed too small to be seen. No changes were made in response to this question.

Figure S8: In the left panel the minimum does not seem to have been reached. The same is true in Figure S9.

Figures S8 was combined with the top panel of Figure S9. The minimum was not reached as we are showing data for the longest zeroing period during ORCA, which lasted 15 min. The data are instructive insofar as they provide a contrast to the laboratory conditions. No changes were made in response to this comment, though the figures were modified to account for the R_L value.
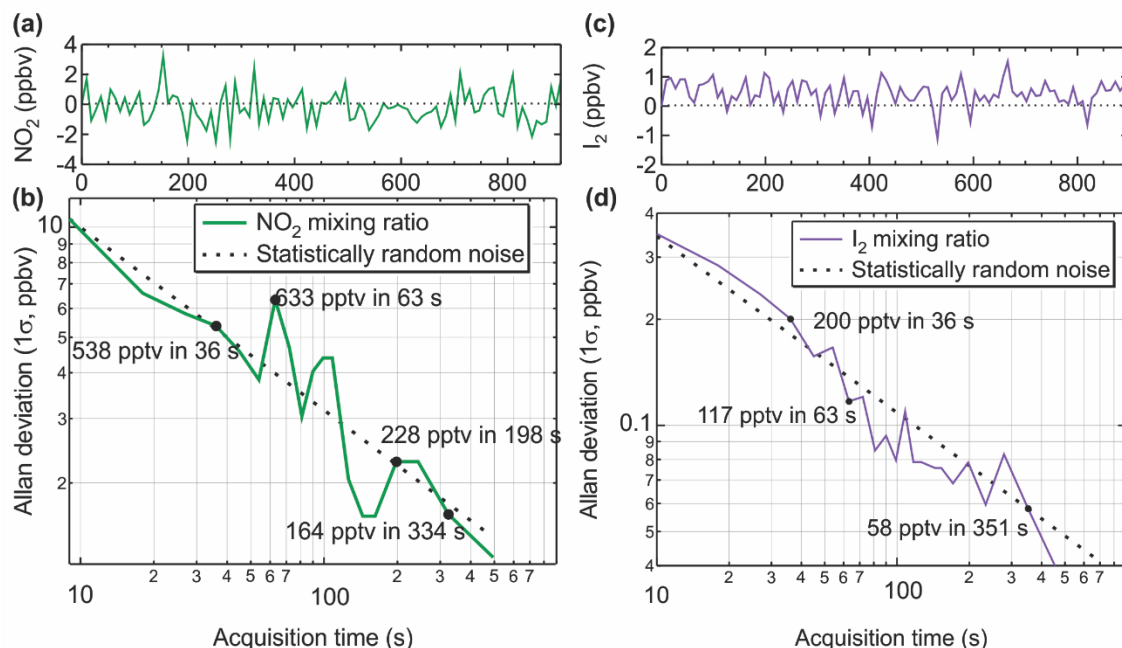
Figure S8 Data collected while the CEAS continuously sampled zero air during the ORCA campaign at a sample cell pressure of 467 hPa, flow rate of 5 slpm, and at a temperature 290 K. (**a**) Time series of NO_2 mixing ratios. (**b**) Allan deviation plot of the above data. (**c**) Time series of I_2 mixing ratios. (**d**) Allan deviation plot of the above data.
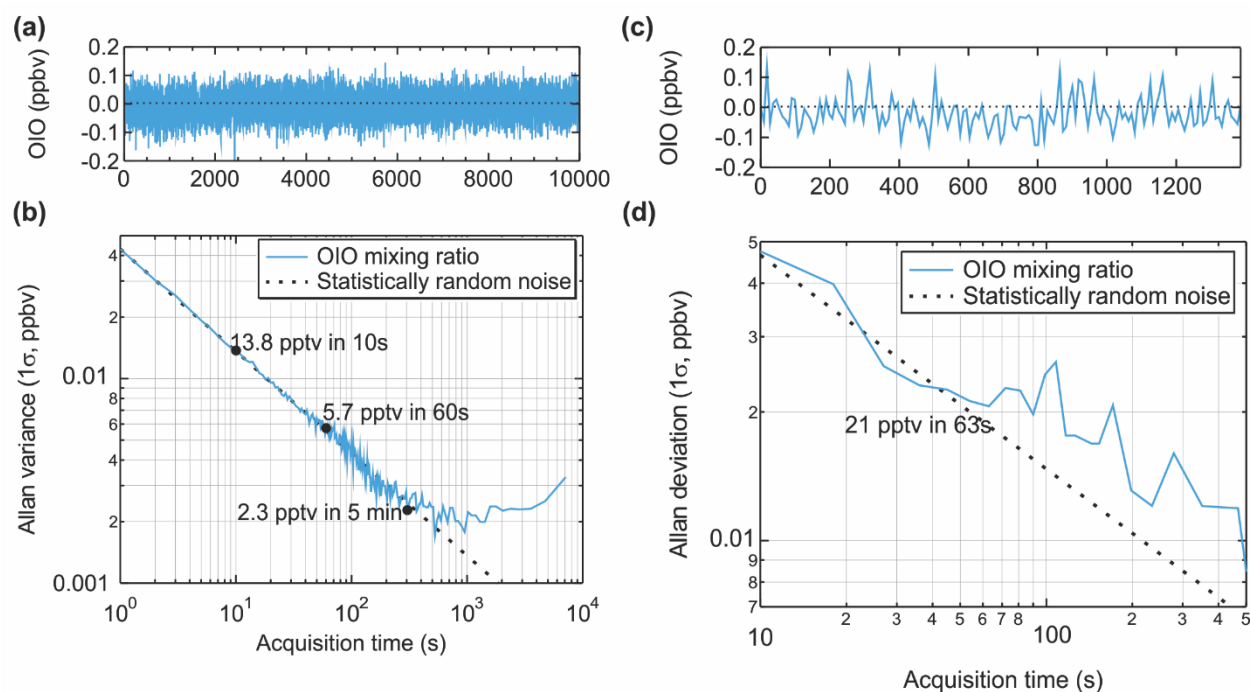
Figure S9 (left hand side) Data collected while the CEAS continuously sampled zero air in the laboratory at a sample cell pressure of 890 hPa, flow rate of 1.5 slpm, and at a temperature 298 K. (**a**) Time series of OIO mixing ratios. (**b**) Allan deviation plot of the above data. (right hand side) Data collected while the CEAS continuously sampled zero air during the ORCA campaign at a sample cell pressure of 467 hPa, flow rate of 5 slpm, and at a temperature 290 K. (**c**) Time series of OIO mixing ratios during ORCA. (**d**) Allan deviation plot of the above data.

Figure S9: More explanation on OIO is needed in my opinion.

Please see our answer for line 465 (pg 14) above.

Figure S10: CEAS emission profile for a cavity filled .... -> Intensity of light exiting a cavity filled with zero air. Three different wavelength regions within the emission spectrum of an LED (M505L3) driven at .... is shown.

We have modified the figure caption as suggested by the reviewer.

Literature cited

Allan, B. J., Plane, J. M. C., and McFiggans, G.: Observations of OIO in the remote marine boundary layer, Geophys. Res. Lett., 28, 1945-1948, 10.1029/2000GL012468, 2001.

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