Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2018-297-RC2, 2018

Atmospheric
Measurement
Techniques
Discussions

Interactive comment on “A broadband cavity-enhanced spectrometer for atmospheric trace gas measurements and Rayleigh scattering cross sections in the cyan region (470–540 nm)” *by* Nick Jordan et al.

Anonymous Referee #2

Received and published: 19 October 2018

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 en-

Printer-friendly version

Discussion paper

hanced 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, 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 spectro*meter*, however, in Line 27 (Introduction) CEAS stands for cavity-enhanced absorption spectro*scopy*. 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.

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.

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. 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.

P4

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

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

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.

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

P5

Line 138: discrete

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

Line 142: degraded -> lower

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

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

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}.

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

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

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.

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

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

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?!

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

P8

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

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?

Line 271: in regular intervals -> at regular intervals

Line 286: "…coefficients)," insert comma

P11

Line 348 & 349:

(1973) -> (Bideau-Mehu et al., 1973)

(1977) -> (Shardanand and Rao, 1977) same in Line 352

(2005) -> (Sneep and Ubachs, 2005)

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, 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.

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? The reason for overflowing the sample cell with two different mixtures is not clear to me. Why did the authors chose the specific "format" (=measurement procedure) shown in Figure 6, to characterize the instument. The zeroing periods are not indicated in Figure 6.

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.

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

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.

P14

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

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

References

Suggested additions:

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

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

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

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

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

P18

Include initials of Shardanand.

Figure 3: List pressures in the caption

Figure 4f: Holm -> Hohm

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

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

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

P28

Include ref (King, 1923) in caption

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.

Figure S6: What is going on between 21:20 and 21:30? Is there zero air sampling? Are there error bars on all data points? Are they too small to be seen except for during the two concentration maxima?

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

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

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.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2018-297, 2018.