

Interactive comment on “Measurement of glyoxal using an incoherent broadband cavity enhanced absorption spectrometer” by R. A. Washenfelder et al.

R. A. Washenfelder et al.

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We thank the reviewer for useful comments on the manuscript. Listed below are our responses to the comments and the corresponding changes made to the revised manuscript.

- p16520 line 24: "IBBCEAS is an excellent detection method for atmospheric gases with broad structured absorptions". I certainly don't disagree with that statement, but perhaps the authors could provide justification. The introduction could thus be used to establish the advantages/disadvantages of a broadband approach for the present application at the earliest stage. [Later, in section 2.2, the authors do discuss the fact that the (monochromatic) laser CRDS instruments rely on there not being any other

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unknown absorbers in the samples (e.g. aerosol extinction), whereas the broadband method can often identify whether there are spectral interferences].

We agree with the reviewer that broadband measurements offer improved specificity compared to laser CRDS instruments. The fourth paragraph of the introduction (pp. 16520 line 13 - pp. 16521 line 2) describes the IBBCEAS technique, its advantage in retrieving multiple absorbers, and gives a large number of literature citations. This includes all of the information necessary to evaluate the advantages and disadvantages of the technique.

- p16522 line 3: "This [the Xe lamp] signal can be used to normalise...". How was the normalisation performed? - a simple scaling according to the lamp's measured intensity? Was there any evidence that the lamp's emission spectrum also changed during a sequence of measurements? The authors mention residual structure in the mirror reflectivity curve due to incomplete cancellation of Xe emission lines (p16528 line 10). If there were wavelength dependent changes in the lamp's emission spectrum, to what extent were the IBBCEAS concentration measurements affected?

We have modified the text to address these questions:

Pp. 16522 line 2 - 4: "A second lens and fiber combination collects part of the light reflected by the quartz beamsplitter to monitor the signal intensity from the Xe arc lamp. [deleted: This signal] *The signal intensity at 522 nm can be used as a scaling factor to normalize the cavity spectra prior to analysis. We did not observe changes in the lamp's emission spectrum as a function of time, presumably because the water-cooled housing maintained a constant temperature for the Xe arc lamp.*"

- Section 3.1/p16526 summary/p16536. The authors choose to fit the total measured extinction saying that this "significantly improves the accuracy and precision of the retrievals for laboratory samples" [compared to the more usual DOAS method of fitting the differential spectral structure due to the molecular absorbers]. Why is this so? -

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no justification is provided in the text. In contrast, the traditional DOAS approach does have significant advantages for measurements on ambient samples, e.g. removing the unstructured (and often unknown) spectral contributions from aerosol extinction and other absorbers including, here, ozone which the authors propose would need to be quantified separately and subtracted from the IBBCEAS measurements (p 16534).

A closed-cell IBBCEAS instrument is conceptually similar to an open-path DOAS instrument. However, the closed-cell IBBCEAS instrument has an important advantage because the reference spectrum (I_0) can be measured directly. This means that the absorption can be calculated absolutely, and relative fitting retrievals are not necessary. We have compared differential and absolute fitting retrievals, and achieved greater precision with absolute fits.

The reviewer is correct that DOAS spectral fitting methods are necessary for samples containing unknown species with broad, unstructured absorptions. However, we have identified all of the extinctions in the 441 - 469 nm spectral region within our detection limit.

The reviewer specifically questions unknown extinction due to aerosols or ozone. For a field instrument, aerosol can be eliminated by sampling through a filter, as described on pp. 16535 lines 10 - 17. Measurement of ozone at typical ambient concentrations (0 - 100 ppb) is currently below the detection limit of the IBBCEAS. Unless our sensitivity improves, it will not be necessary to consider absorption due to ozone. We have clarified this particular point:

Pp. 16534 lines 16 - 21: "Additional minor absorbers in the 441 - 469 nm spectral region include ozone (O_3), iodine monoxide (IO), and methyl glyoxal (CH_3COCOH). *The optical extinction due to these three species over typical ambient concentrations is less than the detection limit of the IBBCEAS instrument (currently $4 \times 10^{-10} \text{ cm}^{-1}$). The expected extinction for ozone, with cross-section of $2.18 \times 10^{-22} \text{ cm}^2$ at 455 nm (Sander et al., 2006) and a typical concentration*

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of 50 ppb, is $2.2 \times 10^{-10} \text{ cm}^{-1}$. [deleted: Because the ozone cross-section is smoothly varying if necessary it can be independently measured and subtracted from the IBBCEAS spectra.] *If a correction is necessary, ozone concentrations can be independently measured using a standard, commercial ozone monitor and the smoothly-varying ozone cross-section can be subtracted from the IBBCEAS spectra."*

- Treatment of O_4 absorption: it is probably acceptable to account for the O_4 absorption bands as part of oxygen's Rayleigh scattering (p16528) [on the basis that the O_4 bands also make the same contribution to the $I_0(\lambda)$ zero air reference spectrum]. However, any correction made for pressure variations in samples needs to remember both the squared dependence of the O_4 bands and the linear dependence of O_2 's Rayleigh scattering. Presumably the laser CRDS results are corrected for O_4 absorption (e.g. there is an O_4 band peaking close to the 532 nm wavelength used to detect NO_2)?

This question is partially answered by Reviewer 2:

"In response to referee 4, for the spectral range used to detect NO_2 and glyoxal, the relevant O_4 band, which is centered at 446.7 nm, has a peak absorption coefficient of 10^{-9} cm^{-1} given that air is only 20% oxygen. This should be barely detectable, although typical pressure fluctuations of 2 - 3% would not be."

Both reviewers are correct in their concern that large pressure changes would require a correction for both Rayleigh scattering and O_4 absorption. However, we regularly acquire reference spectra of zero air at similar pressure to the sample spectra, and therefore no pressure correction is necessary. We have addressed this confusion with the addition of Section 2.4 describing the operation of the IBBCEAS instrument.

As Reviewer 2 observes, the O_4 absorption is barely detectable and this demonstrates the high sensitivity of our instrument. This was the intended point of the O_4 discussion, but we did not make it very clear. Because both reviewers were

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confused by this tangent, we have decided to remove the discussion of N₂, O₂, and O₄ from Section 3.2.

- p16528 "Slightly different total cavity loss curves for N₂ and zero air...". Were the mirror reflectivity curves inferred from these measurements still the same after correction the latter for the O₄ absorption features? Is the quoted 29.4 km path calculated solely from the mirror reflectivity and the cavity's length? (If so, the path achievable in a cavity containing any sample, including just zero air, will be somewhat shorter). The high resolution absorption cross section of CHOCHO (Volkamer) show considerable fine-scale structure, particularly around glyoxal's strong 455 nm feature, that will not be resolved at the 0.58 nm resolution of the present instrument. Have the authors considered whether their instrument's spectral resolution has any practical implications for retrieving the "correct" CHOCHO concentration? Previous broadband CRDS studies have investigated fitting the spectral structure due to strong, narrow, and hence under-resolved H₂O and O₂ lines at red wavelengths [Bitter et al, ACP 2005; Ball Jones, Chem Rev 2003], and found it was necessary to use effective absorption cross sections that were noticeably different from cross sections constructed from a direct convolution of high resolution cross sections with the instrument function (the method used here). I suspect the effects are probably small for the CHOCHO extinctions encountered in this work, though it would be good to be able to discount resolution effects entirely.

The quoted path length is calculated solely from the mirror reflectivity. We have added a clarification in the text and figure caption:

Pp. 16528 Line 14 - 15: "This reflectivity corresponds to an effective pathlength of 27.8 km at 455 nm. *When the cavity contains 830 hPa of zero air, the effective pathlength is 17.9 km at 455 nm.*"

Figure 2 caption: "The peak reflectivity at 455 nm is 99.9966% (34 ppm total loss), corresponding to an effective pathlength of 27.8 km, or 17.9 km when the cavity contains 830 hPa of zero air."

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The reviewer raises a useful point regarding errors in the effective absorption cross-section. We are aware of two potential artifacts, but neither of these is a problem for our retrievals. The first artifact is present in the broadband cavity ringdown studies cited by the reviewer. Broadband CRDS requires fitting an exponential ringdown that consists of the summation of exponentials with different ringdown time constants. In contrast, each of the IBBCEAS absorption terms in Eqns. (1) and (2) is linear. It is mathematically correct to convolve the reference spectra with the instrumental lineshape prior to fitting the spectra. The second artifact is present when strong, narrow absorption lines that are optically saturated are not fully resolved in spectral measurements. Based on our extinction calculations for NO_2 , CHOCHO , and H_2O , these absorptions are not optically saturated in the IBBCEAS instrument.

- The correlation between the IBBCEAS and CRDS measurements of CHOCHO (0.948 gradient, Fig 6b) and the IBBCEAS and CRDS measurements of NO_2 (0.932 gradient, Fig 4) are both about 6% below the ideal 1:1 correspondence. Whilst recognising that 6% is within the combined uncertainties of each pair of instruments, it is nevertheless seems curious that the IBBCEAS measurements should be lower for both NO_2 and CHOCHO by similar amounts. Could the IBBCEAS measurements (or fitting of their spectra) be affected by a systematic 6% error? (The CRDS measurements are more direct in the sense that the average path length through the sample is determined from the measured ringdown times).

Although we reiterate that the 6% difference is within the expected absolute uncertainty, we also recognize that there is a consistent slope difference for retrieved CHOCHO and NO_2 concentrations using the mirror reflectivity calculation presented here. We have added a statement to the text:

Pp. 16533 line 23: *"If we were to regard the NO_2 measurement as a calibration of mirror loss, following the alternative approach described in Section 3.2 (Gherman et al., 2008; Langridge et al., 2006; Venables et al., 2006), the IBBCEAS and*

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CRDS measurements of CHOCHO would be consistent within 1.5%."

- The "1 sigma standard deviations for 1 minute IBBCEAS measurements" = 20 pptv for NO₂ (p16530) and 29 pptv for CHOCHO (p16531). Please clarify. Is this the typical 1 sigma uncertainty from fitting the absorption features in a single IBBCEAS spectrum obtained with an integration time of 1 minute? Or is this the 1 sigma range in fitted absorber amounts from a sequence of n measurements (1 min each?) on a standard sample of well-defined constant composition (cf definition of the detection limit as twice the 1 sigma scatter around zero when sampling zero air, see section 4.4)?

The uncertainty in the spectral fits may underestimate the total uncertainty for the retrievals. We have instead reported the uncertainty for a series of measurements at a constant concentration. We have clarified the statement of uncertainty in both cases.

Pp. 16530 lines 15 - 16: "The 1 σ standard deviation for 1-min IBBCEAS measurements of 1.13 ppbv NO₂ is 20 pptv. *This represents the 1 σ range in retrieved NO₂ concentrations for a sequence of 1-min measurements with a sample of well-defined and constant composition.*"

Pp. 16531 lines 13 - 15: "The 1 σ standard deviation for 1-min IBBCEAS measurements of 4.5-ppbv glyoxal is 29 pptv. *This represents the 1 σ range in retrieved glyoxal concentrations for a sequence of 1-min measurements with a sample of well-defined and constant composition.*"

Technical corrections:

- p16518 line 12 (abstract): a suggestion for improved wording: "We directly compare measurements made with the incoherent... with those from cavity ringdown instruments detecting CHOCHO and NO₂ at 404 and 532 nm respectively,.."

We have incorporated this change.

- The Introduction's first paragraph lists many facts about glyoxal, but without linking

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these facts together to form a flowing introduction to the molecule's atmospheric importance.

We have modified the introduction:

Pp. 16518 line 19 - pp. 16519 line 10: "*Glyoxal (CHOCHO, IUPAC name ethandial, CAS number 107-22-2) is the simplest alpha-dicarbonyl, with structure HC(O)C(O)H, and one of the most prevalent dicarbonyls in the ambient atmosphere. Glyoxal is formed from the photooxidation of aromatic hydrocarbons (Tuazon et al., 1984; Bandow et al., 1985; Jang and Kamens, 2001) and is a minor oxidation product of isoprene (Yu et al., 1995; Carter and Atkinson, 1996) and other biogenic species (Fick et al., 2003). Satellite measurements of glyoxal in the atmosphere suggest that oxidation of biogenic volatile organic compounds in tropical regions is an important regional source of glyoxal (Wittrock et al., 2006). There is growing laboratory evidence that heterogeneous reactions of glyoxal play an important role in the formation of secondary organic aerosol (SOA) (Hastings et al., 2005; Jang et al., 2002; Kroll et al., 2005; Liggio et al., 2005). SOA is a major contributor to fine particulate matter in urban areas, and has adverse effects on air quality and human health (Seinfeld and Pankow, 2003). Reactive uptake of glyoxal on aqueous seed aerosol may lead to significant particle growth (Kroll et al., 2005). Field measurements in Mexico City show that the atmospheric budget of glyoxal can not be balanced without an aerosol loss process (Volkamer et al., 2007). In addition to its importance in SOA formation, photolysis of glyoxal is a significant source of HO_x (OH + HO₂) (Langford and Moore, 1984; Zhu et al., 1996; Chen and Zhu, 2003).*"

- p16520 line 19 "In principle, it is similar...". What is "it" (IBBCEAS)? Note that Ball Jones's broadband version of CRDS (Chem Rev 2003) is distinctly different because the ringdown event is resolved simultaneously in both wavelength and time.

"In principle, [deleted: it] IBBCEAS is similar to previous laser-based methods

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for broadband CRDS (Ball and Jones, 2003) in that the light passing through a high-finesse optical cavity is dispersed with a spectrometer and analyzed using a multichannel detector. *However, in contrast to the broadband CRDS methods described by Ball and Jones, IBBCEAS cavity output is measured continuously and the ringdown is not resolved in time.*"

- p16521 line 13: explain what "out-of-band light" is (e.g wavelengths) and why it is necessary to filter this light from the cavity's input.

"A cold mirror with 525 nm cut-off (Thorlabs FM204) and two colored glass filters (Schott Glass BG 26 and GG 420) remove [deleted: out-of-band] light *produced by the Xe arc lamp that is outside the spectral region of interest (441 - 469 nm)*. The colored glass filters are necessary to minimize photolysis of CHOCHO and NO₂ and to prevent degradation of the mirror reflectivity by exposure to UV radiation (Flad et al., 2006)."

- p16524 line 14: PMT = photomultiplier tube.

Changed "PMT" to "photomultiplier tube."

- p16527 line 10 and elsewhere: define what is meant by "cavity loss"

Described and defined cavity loss where the discussion first appears in Section 3.2:

Pp. 16527 line 12: "*Cavity loss is defined as the fractional loss in light intensity per pass. For a cavity containing zero air, it includes losses due to transmission, absorption, and scattering by the mirrors, as well as Rayleigh scattering.*"

- p16527 line 16: "...gases with different Rayleigh cross sections...". Additional reference: Keabian et al, Rev Sci Instrum 78, 063102 (2007).

The reviewer is referring to this discussion:

Pp. 16527 lines 14 - 17: "Mirror reflectivity can be determined from the intensity

change caused by the addition of a known concentration of an absorber, such as NO_2 or O_3 (e.g. Langridge et al., 2006; Venables et al., 2006; e.g. Gherman et al., 2008), or by the addition of gases with different Rayleigh cross-sections."

It is true that measurements of Rayleigh scattering have been carried out using cavity-enhanced techniques, such as cavity attenuated phase shift spectroscopy (Kebabian et al., 2007) and cavity ringdown spectroscopy (Naus and Ubachs, 2000; Sneep and Ubachs, 2005). However, we are describing methods that employ known cross-sections to calculate mirror reflectivity. The first three references (Langridge et al., 2006; Venables et al., 2006; e.g. Gherman et al., 2008) describe the use of NO_2 or O_3 to calculate mirror reflectivity. We are not aware of any previous work that uses Rayleigh scattering to calculate mirror reflectivity.

- p16527 line 24 "Helium and zero air are appropriate choices for $I_0(\lambda)$ and $I(\lambda)$...": Contradiction with p16526 line 4: previously $I_0(\lambda)$ specifically meant the reference spectrum for the cavity containing zero air.

We have clarified this:

Pp. 16527 lines 24 - 26: "Helium and zero air are [deleted: appropriate choices for $I_0(\lambda)$ and $I(\lambda)$ in] *useful for* the calculation of $R(\lambda)$, because of the large difference between their respective Rayleigh scattering cross-sections."

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 16517, 2008.

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