

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

### **Anonymous Referee #4**

Received and published: 8 September 2008

General comments:

Glyoxal is an important intermediate in the atmospheric oxidation of volatile organic compounds of both anthropogenic and biogenic origin. Glyoxal is linked to the formation and growth of secondary organic aerosol particles and glyoxal's photochemistry is an additional minor source of HOx radicals in the atmosphere. Consequently there is considerable current interest in this molecule.

This paper reports on proof-of-principle laboratory studies aimed at developing a spectroscopic field instrument for simultaneous in situ measurements of glyoxal and NO<sub>2</sub>, the two molecules absorbing at wavelengths around 450 nm. The instrument employs

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a broadband version of cavity enhanced absorption spectroscopy using light from a xenon arc lamp to measure the absorption spectrum of atmospheric samples contained inside a high finesse optical cavity. The work thus adds another molecule to the rapidly growing list of atmospherically important species that have been detected by broadband cavity methods. This research group has considerable prior experience of constructing cavity-based field instruments for quantifying atmospheric trace gases, and their multi-channel CRDS field instrument for NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> and NO<sub>2</sub> detection is world-leading. Thus one of the great merits of this work is that the authors were able to compare the performance of their new IBBCEAS instrument against other cavity ringdown instruments available in their laboratory. The work then proceeds with investigations to address some of the potential difficulties (aerosol extinction, interferences from other absorbers etc) of operating this instrument in the field, rather than under ideal laboratory conditions. Overall, these studies suggest we can look forward to this instrument being successfully deployed for CHOCHO and NO<sub>2</sub> field measurements in the near future.

The manuscript is well written; the description of the instrument is informative yet concise; the work's main results are discussed in appropriate detail in the text and are illustrated with eight clear figures. I recommend publication after appropriate consideration of the following points & suggestions.

Specific/science comments:

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

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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?

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? – 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).

Treatment of O<sub>4</sub> absorption: it is probably acceptable to account for the O<sub>4</sub> absorption bands as part of oxygen's Rayleigh scattering (p16528) [on the basis that the O<sub>4</sub> bands also make the same contribution to the I<sub>0</sub>(λ) zero air reference spectrum]. However, any correction made for pressure variations in samples needs to remember both the squared dependence of the O<sub>4</sub> bands and the linear dependence of O<sub>2</sub>'s Rayleigh scattering. Presumably the laser CRDS results are corrected for O<sub>4</sub> absorption (e.g. there is an O<sub>4</sub> band peaking close to the 532nm wavelength used to detect NO<sub>2</sub>)?

p16528 "Slightly different total cavity loss curves for N<sub>2</sub> and zero air...". Were the mirror reflectivity curves inferred from these measurements still the same after correction the latter for the O<sub>4</sub> 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).

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The high resolution absorption cross section of CHOCHO (Volkamer) show considerable fine-scale structure, particularly around glyoxal's strong 455nm feature, that will not be resolved at the 0.58nm 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 H<sub>2</sub>O and O<sub>2</sub> 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 correlation between the IBBCEAS and CRDS measurements of CHOCHO (0.948 gradient, Fig 6b) and the IBBCEAS and CRDS measurements of NO<sub>2</sub> (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<sub>2</sub> 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).

The "1 sigma standard deviations for 1 minute IBBCEAS measurements" = 20pptv for NO<sub>2</sub> (p16530) and 29pptv 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

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twice the 1 sigma scatter around zero when sampling zero air, see section 4.4)?

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 NO<sub>2</sub> at 404 and 532nm respectively.."

The Introduction's first paragraph lists many facts about glyoxal, but without linking these facts together to form a flowing introduction to the molecule's atmospheric importance.

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.

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.

p16524 line 14: PMT = photomultiplier tube.

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

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

p16527 line 24 "Helium and zero air are appropriate choices for I<sub>0</sub>(lambda) and I(lambda)...": Contradiction with p16526 line 4: previously I<sub>0</sub>(lambda) specifically meant the reference spectrum for the cavity containing zero air.

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

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