Referee #2

We thank the referee for the thorough reading, and excellent comment which we feel has helped improve our manuscript. We agree with most of the comments, and respond to all comments in detail below. We appreciate the references given, albeit some of the suggested references are not peer reviewed we have included these citations and discuss them in the revised manuscript. For ease of reading we copied the reviewer's comment first, and our reply follows. The changes to the revised manuscript are listed by giving the line number/Section at the beginning of each response.

C1) A couple of dozen research groups around the world have devised cavity-based spectrometers to quantify atmospherically important trace gases, tested their instruments under laboratory conditions and (in rather fewer cases) deployed them outside the laboratory to make field observations. A growing subset of these cavity spectrometers, like the instrument described in this paper, favour a broadband approach where the absorption spectrum of the atmospheric sample is recorded over a wide wavelength range in order to (i) identify the atmospheric absorbers by their unique absorption spectra, and (ii) quantify several absorbers in the same wavelength window. The broadband (LED or arc lamp) approach is particularly suitable for measuring absorbers that possess broad, structured absorption bands at visible wavelengths, such as the atmospheric absorbers tested in this work. Thalman and Volkamer's paper will therefore be of interest to the many practitioners of cavity-based spectroscopies, as well as the wider atmospheric science community who wish use the results obtained by deploying such instruments in field work.
For me, the two principle advances of this work are (i) the first published detection of methyl glyoxal by cavity enhanced absorption spectroscopy and (ii) a novel analysis method wherein the authors apply DOAS methods to infer absorber concentrations and aerosol optical extinction from only the spectrum of light intensity transmitted through the cavity, I(_), (i.e. without acquiring the cavity's background I_0(_) spectrum in the absence of absorbers). The former adds another compound to the growing list of atmospherically important trace gases detectable by cavity methods, and the latter analysis approach is potentially useful when operating cavities in open path mode to avoid losses of reactive species to the cavity's internal surfaces (an approach first deployed for cavity work by Bitter et al, ACP, 2005). The use of water and oxygen dimer absorptions, which are ubiquitous and usually well-defined in ambient samples, to check the effective path length of the measurement is a clever idea (if not entirely new to this work): the bandwidths of most broadband cavity spectrometers will include H2O or O4 absorption features and, whilst these features will be a familiar sight to operators who use their instruments on ambient air, few groups employ the information carried by these absorption features to the extent that is being proposed here.
Otherwise, this study builds on a substantial body of broadband cavity work stretching back nearly 10 years, some of which is referenced by Thalman & Volkamer, some of which is unfortunately not. I agree with Anonymous Referee #1's comment (3) that the authors' over-used claims to be "first" and/or "novel" distract from an otherwise good paper and are sometime unjustified. I urge the authors to revise their manuscript to address the comments of Ref 1 and Gomez Martin. The authors might also note:

R1) General response: We have narrowed our title to the ‘blue spectral range’, reduced claims of ‘first’ and ‘novel’ to an appropriate extent, and shortened the conclusion section. Following some comments by the reviewer we added a new Section 3.10 where we discuss absolute vs relative retrievals, and also compare detection sensitivity in a new Table 4.

C2) “Aerosol extinction has previously been measured at 570-590nm by Thompson and Spangler using broadband integrated cavity output spectroscopy ICOS (Applied Optics, 2465, 45/11, 2006) and at red wavelengths by Varma et al using incoherent broadband CEAS (Applied Optics B159, 48/4, 2009). The latter is referenced by Thalman & Volkamer on p2685 in the context of using the O_2 B-band at 690nm to calibrate mirror reflectivity, but they seem to have missed an obvious foretaste of the present work where Varma et al also discuss how the differential absorption of the O_2 band was diminished by a reduction in intra-cavity effective path length caused by aerosol extinction. In the present blue wavelength region, Washenfelder et al also report a time series of aerosol extinction co-measured with their glyoxal detection (fig 8).”

R2) Lines 123: The inference of aerosol extinction by Varma et al. indeed is an oversight that is now corrected in the manuscript. We thank the reviewer of pointing this out. We note though that while the approach taken in Varma et al. may appear analogue to the author’s approach (using O_2 instead of O_4 and water), nothing is demonstrated in that work in terms of verifying by independent measurements that the approach indeed works. To our knowledge ours is the only work published to date where the effect of aerosols on the effective path is verified quantitatively by demonstrating that the reduction in the SCD is indeed consistent with Mie calculations.

Indeed Dr. Volkamer had presented about the approach of using O_4 at the EGU meeting in 2008, prior to publication of Varma et al., and remembers a question from the audience after the presentation whether the approach could be applied equally to O_2 in the red. He responded affirmative at the time, and was unaware that the Varma paper contained this information. It was the considerable effort spent since EGU to demonstrate the approach by supplying known extinction that delayed, but also – we feel – greatly increased the value of our manuscript.

Line 127: We have narrowed our claim of novelty to ‘using O_4 and H_2O in the blue spectral range under atmospheric conditions’.

Line 125: With regard to the IBBCEAS inference of aerosol extinction from the ‘polynomial’ fitted by Washenfelder et al., such offsets are not unique to aerosol extinction in IBBCEAS retrievals, but for example also capture variations in the lamp intensity. A statement has been added about the inference of aerosol extinction by Washenfelder et al., which indeed is based on equivalent information content as our aerosol inferences (though less direct, as a correction for lamp drift needs to be applied).

C3) “p2682 line 12 “...first CEAS detection of methyl glyoxal, and the first CE-DOAS detection of glyoxal and IO”. Likewise p2701 line 12. As I said above, I believe the first statement is true. The second depends on nomenclature and whether one considers CE-DOAS to be its own separate spectroscopic technique. To me, CE-DOAS, BBCEAS, IBBCEAS and BB-ICOS are all variations on a common theme – certainly the apparatus/hardware is pretty similar, and the measureable produced by all these is an absorption/extinction spectrum of the sample over an extended bandwidth. Therefore I'm sceptical whether it is justifiable to claim glyoxal and IO as firsts for CE-DOAS when (as the authors acknowledge later in the introduction) these have previously been detected by other groups using other closely-related BB methods. Gomez Martin's comment about the paper's title is helpful here too: perhaps the adjective first [novel] should apply to the spectral analysis [calibration method], and not to the technique."

R3) Title, line 206, Section 3.10, Conclusion section: We agree that the hardware is similar, though not identical, but cordially disagree with the notion that the difference in CE-DOAS is purely a matter of semantics. For example, a limitation in the minimal extinction that can be measured by IBBCEAS, BBCEAS and ICOS is related to the stability of the light source (I_0). IBBCEAS hardware thus frequently spends time on measuring background spectra in absence of absorbers (reduced duty cycle), or – as is increasingly a habit with IBBCEAS (e.g., Chen and Venables, 2010, AMTD) – employs an entirely separate second spectrometer/CCD combination to measure single traverse out of band light with the single purpose to characterize lamp drifts. The CE-DOAS approach eliminates such additional hardware needs, and provides a software solution by means of retrievals that rely only on relative intensity changes. A fundamental advantage that arises from this approach is the ability to accumulate photons over extended periods of time without apparent limitation from lamp drifts (several hours or even days, see line 206, Section 3.10).

C4) "p2684 "CEAS measurements to date require separate calibration measurements to characterize the temporal variability of aerosol extinction..." and "CE-DOAS holds the promise to decouple aerosol and trace gas extinctions...". Again, this is not a unique feature of CE-DOAS and/or the present work. The sample's extinction coefficient measured by BBEAS (and related BB cavity methods) is commonly decomposed into a sum of structured molecular absorptions and unstructured continuum absorptions due to Rayleigh and Mie scattering via equations analogous to the present work's Eqn 4. The various molecular contributions are then separated from the broadband continuum by multivariate fitting of differential absorption cross sections (Langridge et al, Analyst, 2006; Washenfelder et al 2008; Varma et al, 2009 and many others). Spectral fitting process has been discussed in detail in two reviews of broadband cavity methods which the authors don't reference (Ball & Jones, Chem Rev, 2003; Ball & Jones, "Broadband Cavity Ring-Down Spectroscopy", in Cavity Ring-down Spectroscopy: Techniques & Applications, ed G Berden & R Engeln, Blackwell Publishing, 2009). Thus existing methods *are* capable of quantifying aerosol extinction. I suspect the reason why aerosol extinction isn't commonly reported in the literature is because it's not straightforward to know how to partition the continuum absorption (after subtraction of Rayleigh scattering) between aerosol extinction and the effects of instrument instability. Reductions in the cavity throughput due to degradation of the mirror reflectivity, the cavity becoming slightly misaligned, small changes in the light source intensity (cf p2687 line 17), atmospheric turbulence (cf p2693 line 13) etc... can all give rise to an apparent continuum absorption signal that, usually being unstructured too, is very difficult to separate from the aerosol extinction. Unless I've missed something, I'm not sure that the authors' novel DOAS analysis method (and the assertion in line 15-17 of p 2693) provides a solution to this problem: everything still seems to be aggregated into the "polynomial" in Eqn 5. The difficulty of separating unstructured contributions to access just the aerosol extinction is illustrated in Section 3.6 measurement of IO, where the authors have to assume that all their broadband extinction is due to I2 (whose spectrum is unstructured at blue wavelengths) and that "no aerosol was present". [One caveat:iodine oxides nucleate new aerosol particles in the atmosphere – e.g. McFiggans ACP 10, 2975, 2010 and references therein]. Are there any non-aerosol broadband contributions to Eqn 8 on p2698?"

R4) Section 3.10: We agree that drift due to changes in R or cavity alignment, and/or turbulence remain aggregated, and are not further separated from aerosol extinction by CE-DOAS. However, given the growing body of IBBCEAS literature that uses separate hardware to characterize lamp drifts, this source of drift seems to be non-negligible. We note that whether other sources of drift may dominate in a given setup is more of an engineering question (cavity stability and gas supply) than one of fundamental nature. This is mentioned now explicitly in Section 3.10.

Section 3.6, line 480: The authors appreciate the comment about Section 3.6. We have verified, and state in the revised version, that the wavelength dependence of these broadband processes is consistent with the extinction expected from I2 using an absolute BB-CEAS retrieval. Further, Mie calculations were employed to demonstrate that particle nucleation cannot explain the observed intensity loss. Neither is the wavelength dependence of the extinction loss consistent with Mie scattering of nanoparticles, nor is the extinction cross section of, e.g., 10nm particles particularly large ($\varepsilon_{aer} \approx 1\times10^{-18}$ cm2/particle). Even 10^5 particles/ccm would cause a minor broadband extinction at 450nm on the order of 1×10^{-11} cm^{-1} or an optical density of 1×10^{-5}. We have added some mentioning of why nanoparticle formation is very unlikely to contribute to extinction in the revised paper.

Line 493: The following text was added: 'Notably, in a reasonably moist atmosphere (see Table 3) the path length at the blue end of our spectral range is constrained more directly from observing water.'

C5) "p2687 line 4 "...the first well calibrated CEAS measurements [A] of trace gases [B] and aerosol extinction [C] by a single measurement [D] in open cavity mode [E] under atmospheric conditions [F]". Likewise p2701 lines 6 and 8. I hope the authors don't mean to suggest that other CEAS measurements were poorly calibrated. Consider rephrasing. Anyway, the combination of A+B+C+D+E+F has been achieved by Andy Ruth's group and others."

R5) Line 126: We have narrowed this statement to the 'blue spectral range', where we are unaware of this achievement. Our statement about 'well calibrated' now refers to the 'inherent alert' about path length, and/or its changes, from measuring O4 and water.

C6) "p2687 line 14 "LED well matched to the mirror reflectivity". p2693 line 5 "use the mirror reflectivity to balance the light intensity across the detector". This consideration isn't novel: the first demonstration of BBCEAS with LEDs (Ball et al 2004) noted the need to match the LED output spectrum to the mirror reflectivity. Ball & Jones (2009) discuss this in detail: their Fig 3.8 illustrates the same effects as the current Fig 3."

R6) Line 188: We have removed this statement, and added the references. See also our response #3 to Gomez Martin.

C7) "p2687 line 25. It'd be interesting to see a plot of the LED output as a function of time and some quantitative discussion about the long-term stability of the LED output (especially given how instrument instability can lead to continuum absorption signals that potentially compromise aerosol extinction measurements)."

R7) We have added some discussion about LED stability in the revised paper, although it is marginally related to CE-DOAS retrievals (inherently insensitive to lamp drift).

C8) "p2688 line 3 "optimum emission pattern" – do the authors mean "emission spectrum", or is there spatial inhomogeneity across the emitter's surface?"

R8) Line 197: The intended meaning was the 'emission spectra'. Language was modified.

C9) "p2689-90 Nice comparison of the performances of the two spectrometers. But I was left unsure about how much of the Acton system's better performance was due to it being an intrinsically more advanced grating spectrometer versus how much was due to its multi-core fibre distributing the cavity output light vertically onto its entrance slit. The 1mm dia fibre into the OceanOptic's 100 micron slit will necessarily lose a majority of the intensity."

R9) Line 258: The advantages of the Acton/Pixis have been clarified in the text. We have in the meantime also submitted another paper (Coburn et al., 2010) that describes this system in detail. Reference to that work, and a previous SPIE proceedings paper has been added.

C10) "p2691-92 – see also comment 2 by Ref #1. I recognise there are applications where there's an advantage to run the cavity open-path. However, even with the present CEDOAS analysis approach, it's still necessary to first characterise the mirror's reflectivity carefully as a function of wavelength using (in this case) He and N2 Rayleigh scattering; similarly for determining the fraction of the path occupied by the mirror purge gas. To do this, the present instrument has been constructed to allow a tube to be placed between the mirrors to exclude ambient air. Given that I0(_) spectra are still acquired for characterisations, I'm still unclear about the over-riding benefits of running ambient air measurements based solely on I(_) compared the usual approach of having both I(_) and background I0(_) spectra with which to calculate the ambient sample's absorption. The latter can still be performed open-path, with the cavity tube being replaced periodically to acquire I0(_) spectra. Monitoring the H2O and O4 bands would inform when new I0(_) spectra are needed."

R10) Sections 2.1.1 (line 207), Section 3.10, and Conclusion section: The inherent alert in form of available information about when lamp reference spectra are needed is no small benefit. There seems to be some confusion though about the need to measure I0. DOAS does not require measurement of I0. Only a relative intensity spectrum of the lamp is needed to measure trace gases. This greatly reduces the frequency at which the lamp needs to be characterized. For example, we can run our instrument over several days with a single lamp spectrum, without need to reduce the duty cycle to characterize mirrors and/or the lamp intensity. See Section 3.10.

C11) "p2693 line 7 et seq: a measurement bandwidth of 70 nm "... about 2-3 times wider than previous CEAS instruments". LED-BBCEAS measurements of NO2 by Hollingsworth & Ball over a 420-485nm bandwidth are discussed in Ball & Jones 2009. This text book (literally!) example needs to be included in Table 1. Ball & Jones also discuss (i) the merits of performing measurements over as wide a bandwidth as possible (this is a general axiom in long-path and max-DOAS community), and (ii) restricting the DOAS fitting window to exclude particularly noisy data at the wavelength extremes of BB spectra (see also Gomez Martin's comment about the reduced information content of the IO spectrum at long wavelengths, p2697)."

R11) Line 120: We appreciate the reference to the text book, and have added the reference in the table. The work described in the text book (fitting NO2 in evaluation wavelength ranges of variable width) is, as the reviewer notes, not entirely new and well known to the DOAS community. Ball and Jones essentially make an argument that had previously been made by Stutz and Platt (1996), i.e., that leveraging wider fit windows reduces the fit error. Notably, the intellectual motivation of the exercise described in the text book is entirely different from that pursued in this paper. Our motivation is to broaden the spectral range in order to include measurements of O4 at atmospheric conditions as a means to inherently calibrate the effective photon path length. Table 1 has been compiled under this aspect. In response to the Gomez Martin comment we have now also added a new Table 4, from which it is apparent that the cavity used by Ball and Jones (and also Langridge et al., 2006 for that matter) would not allow to accomplish similar, because the lower reflectivity mirrors can not detect O4 at atmospheric conditions with any meaningful precision, even if a detection at 477nm was attempted.

C12) "Section 3.2: I wonder whether slant column density is the best quantity to use here. Sure, it's very useful in long-path and passive DOAS where the concentration of absorbers vary along the light path. But (excepting the mirror purge regions) atmospheric samples ought to be homogeneous over the length scale of the cavity. SCD, optical depth and absorption/extinction co-efficient (cm-1) are all variously used in the figures, making the reader work hard to process their content."

R12) Section 3.2: The SCD is the 'raw' retrieval product in a DOAS fit. We view it is a good habit to show the actual raw data from a retrieval prior to its modification into other units. This logic is applied in the design of Figs. 8 and 9, which exemplifies the conversion into concentration units (molec cm-3), and aerosol extinction units (cm-1). The slant column density (SCD) is the product of concentration and path lengths; even if the concentration of absorbers is constant over the length scale of the cavity, the SCD is not, because the effective path length varies in the presence of aerosols. This is illustrated by the data shown in the Figure.

We agree that optical density and absorption/extinction coefficients are intimately related, but this relation is less straightforward in our cavity where Leff is not only determined by R. Following a suggestion from Gomez-Martin's comment, we have added a section to compare detection sensitivities which includes definitions how these quantities are interrelated.

C13) "p2695: Why have the authors chosen weight the molecular absorption cross sections by F(_), rather than the more usual convention in BBCEAS of using the cavity enhancement factor 1/(1-R) to adjust the measured absorption spectrum for the wavelength dependent effective path length? The presence of residual structure around 440nm in the uncorrected Fig 5a is unsurprising, because here the cavity mirror reflectivity drops off quickly."

R13) Section 3.2: The cavity enhancement factor as listed by the reviewer does not account for Rayleigh and Mie scattering, and hence is not appropriate to account for the wavelength dependence of our cavity. Neither do the deviations in the apparent shape of an absorption band due to self-limitation of the effective path length at the center of an absorption band (Platt et al., 2009) explain our results. We have expanded Section 3.2 to make this transparent. See also our response to comment#13 by reviewer#1.

C14) "Sections 3.7 and 3.8. The O4 and H2O bands provide information on the aerosol extinction at 477 and 443nm, but how is this enough to infer what happens at other wavelengths (to "interpolate the wavelength dependence of the aerosol extinction for the NO2 experiment" p2700 line 10)? Have I misunderstood: surely the _ˆ(-3.8) wavelength dependence of the aerosol extinction can't be retrieved from just two wavelengths? I agree that one can infer much more about the wavelength dependence of the aerosol extinction if there's a structured absorber like NO2 spanning the full measurement bandwidth. But as Gomez Martin comments, one can't rely on such helpful absorbers necessarily being present in ambient samples. Also ambient aerosol is obviously more complex than the mono-disperse aerosol used in the current tests: what can one learn about ambient aerosol from two relatively closely spaced extinction measurements? (see also comments by Ref #1)."

R14) Indeed there seems to be some confusion here. Section 3.8, Conclusion section: The wavelength dependence of aerosol extinction follows a simple power law (λ^{-n}), and it reduces the wavelength dependence of path length, as is illustrated in our Fig. 1, and also Supplementary material Figure S2. Retrieving aerosol extinction at two relatively closely spaced wavelengths, yet at opposite extremes of the mirror curve allows determination of n, and thus to account for the effect that wavelength dependent aerosol extinction has on the wavelength dependence of path length. Our approach to use O4 and water, molecules which are omnipresent in the lower atmosphere, is fully sufficient (though limited in precision by our RH sensor accuracy at the moment). Our instrument hence does not require a presence of NO2.

C15) "p2701 line 4 and Fig 10: are the quoted methyl glyoxal and glyoxal concentrations representative of ambient air in the authors' lab? [They're reasonably similar to concentrations in Fig 5 where the dicarbonyls were produced by evaporation from liquid solutions]."

R15) line 310: These are concentrations noted for the light path which is located directly above dishes of solution and are not representative of the concentrations in the lab air in general.

C16) "The Conclusions section in particular needs significant work to incorporate the above comments, analogous comments of the other referees, and to place the present study more modestly in the context of previous work."

R16) The Conclusions section has been revised, and shortened.

C17) "Figure 3: Why does the mirror reflectivity appear to increase (noisily) at short wavelengths <410nm?"

R17) Figure 3: This apparent increase is due to the lack of light available at those wavelengths. The figure has been revised to solidify the message of the plots.

C18) “Figure 7: Please indicate e.g. when the I2 photolysis & O3 generating lamps were turned on/off. Is this what causes the structure in the I2, IO and O3 time series? Panel A needs y-axis labels.”

R18) Figure 7: The figure has been updated accordingly.

TECHNICAL CORRECTIONS:
C19) “p2688: two 2.5 cm diameter mirrors; 2 inch f/1 lens.... 1 inch f/4 lens – inch measurements are diameters or focal lengths?”

R19) This has been clarified.

C20) “p2690: N = sqrt(N)/N ....is N trying to convey two different quantities here?”

R20) The text was meant to read ΔN = sqrt(N)/N; signifying the error in the signal. This has been corrected.

C21) p2690: define lpm, sccm”

R21) Done.

C22) “p 2698 line 12: For measurements in the ambient atmosphere, aerosols are likely to contribute...”

R22) line 465: The language of this sentence has been clarified.

C23) Section 3.8: polystyrene latex spheres = PLS”

R23) We refer to PSL spheres… PSL stands for PolyStyrene Latex and ‘spheres’ is always spelled out. This is consistent with acronyms used for these size standards. A reference has been included to make this transparent.

C24) “Figure 6a: should the line be green for N2 in the legend? Is it possible to put error bars on the black and red data points in panels b & c to help judge whether the retrieval error has plateaued at 4th and 5th order polynomial?”

R24) The retrieval error would not necessarily be useful as the displayed quantities are the relative fit error with respect to the calculated values in a theoretical case.