Response to the interactive Comments by J. C. Gomez Martin

Gomez Martin is very kind, and we appreciate the detailed reading and useful comments. We respond below to the individual points raised. Some of the comments, especially those regarding the figures had already been corrected by time the on-line AMTD version of the paper was published.

C1) "Thalman and Volkamer (TV) have developed a CEAS instrument for open path measurements of atmospherically relevant trace species. Spectra are analysed on the basis of differential absorption, which does not require the knowledge of the light intensity in the absence of absorption and scattering by molecules and aerosols (I0). Resembling the use of O4 retrievals in MAX-DOAS instruments, the open cavity effective path length problem is solved by the measurement of the spectral feature of O4 at 477 nm, which provides an inherent calibration of the apparatus at that wavelength. Although IBBCEAS this is not a novel technique and O4 absorption has been used previously for aerosol-free effective path length determination (see references in the text and Ball et al, 2010), the methodology presented provides a very useful practical approach to the atmospherically most interesting open cavity configuration, where empty cavity measurements of I0 are not accessible."

R1) We agree for the most part. Notably, Ball et al. 2010 utilizes O4 absorption to calibrate mirror reflectivity in a pure oxygen sample (100% O_2 gives rise to 25 times more O_4 abundance), not in an ambient air sample. We use our O4 absorption at a different wavelength with a quite different intellectual motivation of 'inherent calibration' and are to our knowledge the only paper that demonstrates this approach works for aerosols (Section 3.8).

Comments:
C2) "-title: perhaps the adjective **novel** should apply to the **calibration method**, and not to the **technique**."

R2) Title: now reads 'Inherent calibration of a blue LED-CE-DOAS instrument to measure iodine oxide, glyoxal, methyl glyoxal, nitrogen dioxide, water vapour and aerosol extinction in open cavity mode.'

C3) "-p. 2682 (abstract), and p. 2701 (conclusions): TV present the first detection of Methylglyoxal. However, measurements of Glyoxal and IO using the CEAS technique have been reported previously (Washenfelder et al., 2008; Vaughan et al., 2008). The authors should explain why the use of the DOAS retrieval method gives an extra value to their measurements. This could be reformulated in a different way, perhaps mentioning that it establishes the basis for a working open cavity system. Including in table 1 or 3 a comparison to LODs reported in the literature would be perhaps helpful."

R3) Section 3.10, Conclusion Section: We have added a new Table 4 that compares detection limits, and a new section that discusses relative and absolute retrievals. Reviewer#2 had a similar comment. We now refer to LED-CE-DOAS for the glyoxal and IO detection, to emphasize the benefits of LED light sources (for glyoxal).

Notably, there are two values of our paper: (1) the identification of a blue LED that allows us to work with mirror reflectivity curves an order of magnitude more reflective than previous techniques that employed LEDs in the blue spectral range, and (2) the retrieval based only on relative intensity changes (DOAS). The increased sensitivity that arises from (1) is the result of (1a) better photon counting statistics and lower noise (see Table 4), (1b) long path lengths, and (1c) the absence of spectral artifacts that affected past retrievals of glyoxal when using Xe-arc lamps (Washenfelder et al., 2008); variable Xe-emission lines limit DOAS retrievals in the blue spectral range. We feel that overcoming the complication with DOAS retrievals that are sensitive to residual structures caused by variable Xe-arc emission lines warrants making the use of DOAS explicit, albeit we acknowledge that the technological advances from the bright LED will benefit IBBCEAS retrievals as well. We now speak of 'LED-CE-DOAS' retrievals of CHOCHO and IO to make this clear, and added Section 3.10, and Table 4 to make benefits of DOAS retrievals, and the limitations of DOAS retrievals transparent.

C4) "p. 2684, equation 1: I have some doubts about the interpretation of this equation. The application of the DOAS high pass filter (e.g. by subtraction of a polynomial from the observed optical density) leads to the quantity ln(I0in/I) (see Meinen et al, 2010, equations8 and 9), where I0in is the intensity in the absence of differential absorption (i.e. including **all** broadband absorptions). Now, approximating ln(I0in/I) by (I0in−I)/I in the weak absorption limit and applying Whashenfelder's derivation of the CEAS expression (Washenfelder et al, 2008, appendix A), it is possible to conclude that the last term on the sum in the denominator of equation 1 in TV's paper refers to broadband absorption of trace absorbers. There seem to be some discrepancies in the recent literature about the application of the DOAS retrieval algorithm to the CEAS technique, especially regarding the dependence of the effective path length on the trace absorber concentration (see e.g. the comment by D. Venables to Meinen's paper: http://www.atmoschem-phys-discuss.net/8/S5154/2008/acpd-8-S5154-2008.pdf). My impression is that in Platt's paper (Platt et al, 2009), if DCE is really the so-called DOAS signal as they claim (eq. (26)), the intensity Iin0(n) (whose integral over n is equivalent to I0in in Meinen et al., 2010, equations (8) and (9)) should be: Iin0(n)=Iin(0)exp(-(_0+_Bd0)n) rather than only Iin0(n)= Iin(0)exp(-_0n) (eq. (25),Platt et al. 2009), where _B includes the extinction caused by the smooth part of the cross section of trace absorbers. In my view this has most likely caused the misinterpretation mentioned above (which in practice is not very important in TV's paper since the problem is solved empirically). Obviously I will be happy to see this corrected if the mentioned authors think I am wrong. Nevertheless I believe a consolidation of the differential formalism for CEAS is really needed."

R4) Section 3.1: The last term in equation 1 refers to the total extinction from trace gases- both narrow and broadband and does not separate these two quantities in this formulation for the effective path. The work by Platt and Meinen really does not apply to our results, as absorbers are optically thin (optical density < 4%), and even at the center of an absorption line the light path is not significantly different than at the wings. We have modified our Section 3.2 and added two supplementary Figures S1 and S2 to make the formalism of our CE-DOAS retrievals more transparent.

C4) “-p. 2685, Fig. 1: It would be informative to include in the figure the extinction caused by trace absorbers at realistic concentrations and their impact in the effective path to see the convenience of the correction given by equations (6) and (7).”

R4) This is made available as Figure S1 as Supplementary information.

C5) “-p. 2685: The authors should note that Ball et al., (http://www.atmos-chem-physdiscuss.net/9/26329/2009/acpd-9-26329-2009.html) use O4 at 532 nm in a similar fashion.”

R5) Line 119: This has been noted in the revised manuscript.

C6) “-p. 2686: Reference Volkamer et al., 2010 is incomplete”

R6) Corrected.

C7) “-p. 2690, line 5: Theoretical noise formula looks wrong.”

R7) Corrected to read: $\Delta N = \mathrm{sqrt}(N)/N$

C8) “-p. 2691, line 22: Reference should be Gomez Martin, et al. (2007). However, note that in that work IO was generated homogeneously inside the detection volume (White cell) by using flash lamps (cf. Vaughan et al, 2008).”

R8) Line 297: We have clarified the reference, and also that the reaction mechanism was modeled after that outlined in the reference but that the experimental setup was different.

C9) “-p. 2691, line 2692: It should be made clear here and perhaps also in the abstract that open cavity Glyoxal and Methyl-glyoxal measurements **are not gas phase measurements**, but solution measurements. For clarity, it should be mentioned how many dishes are used and how far are placed form each other.”

R9) Line 311: This is a misunderstanding. We measure gas phase glyoxal and methyl glyoxal evaporating from solutions, but these are gas phase measurements. Language has been clarified.

C10) “-p. 2694: The DOAS equations show the symbol l (lower case) for path length, but the path length is denoted as L (upper case) in equation 1.”

R10)Throughout the manuscript: We now refer to L_{eff} , as there is no single path length for any individual photon, and the path length needed to apply Lambert Beer’s law is an effective quantity.

C11) “-p. 2695, line 1, and figure 5: Which path length was used for retrievals A and B?”

R11) Figure 5 (caption): the path lengths used for retrievals A and B is now described.

C12) “-p. 2695, line 10: Question mark for _.”

R12) This type setting error has been corrected.

C13) “-p. 2695, line 14: Should say eq. 1?”

R13) Done

C14) “-p. 2695: How do equations (6) and (7) enter in equation (5)? The interpolation “between two extreme cases” is not sufficiently clear. This needs perhaps some derivation.”

R14) Section 3.2 has been restructured, and this information was added.

C15) “-p. 2697: In the retrieval of IO the authors could have easily validated their approach using an empty cavity reference and an absolute retrieval. On the other hand, the IO retrieval window looks too large. Probably not much information is gathered from 450 nm to the red given the noise level shown.”

R15) We have verified the assumption that all broadband extinction in the cavity was from I2 by an absolute retrieval. We also tested the effect of a narrower wavelength range, and it did not significantly alter the retrieved IO SCD. The wider range was meant to verify and eliminate any absorption bands of glyoxal (which was present in minor quantities in the system).

C16) “-p. 2700: The inherent calibration of the open cavity is the most interesting development of this paper. This is a simple, elegant way of determining online the effective path length, thus accounting for aerosol extinction and potential deposition of moisture and aerosol on the mirrors, which will reduce the reflectivity and has been proven to be one of the mayor challenges in open cavity field instruments, even using dry air mirror purging. It looks however, that **it is not only** O4 **what has to be measured**, but also the concentration of a molecule with substantial absorption across the two windows considered (I2 in the case of IO retrieval, NO2 in the case of Glyoxal and Methyl-Glyoxal). Such concentration is then used to retrieve the wavelength-dependent effective path length in the main retrieval window, but always based in the fact that the “bridging” **absorption cross section is significant along the full spectral range** considered. This should perhaps be regarded as an integral part of the inherent calibration. This may present practical problems in field measurements, since such bridging cross sections (NO2 seems to be the best candidate) might not be available in all environments. This also propagates uncertainty and will make the detection limit dependent on the concentration of the bridging molecule. It would be informative to see how LODs change with changing NO2 concentrations under different aerosol scenarios, what alternative bridging molecules could be used, and if the effective path could be modelled by a polynomial constrained to match the O4 Leff at 477nm. In any case, it would be of great help for the reader to see which parameters are fitted on each window, and a plot comparing calculated (e.g. using Mie theory) and O4-NO2 derived effective paths.”

R16) The authors appreciate the praise with regard to the inherent path length calibration. The comment is similar to point 14 by reviewer 2. We refer to our response to the reviewer.

C17) “-p. 2700: does the correction given by equations (6) and (7) also apply when the effective path is derived from O4-NO2?”

R17) Section 3.2: Yes. The normalization of equation (6) (formerly eq (7)) is equivalent to a choice of wavelength where pathlength is well know. This is typically O4 (477nm). There is only a single F needed for the entire cavity range. Our F values are shown as Figure S2 as part of the supplementary information.

C18) “-p. 2700: For the open cavity measurements Glyoxal and Methyl-glyoxal are in solution in a row of Petri dishes. Does this interfere in any sense with the determination of the effective path?”

R18) line 310: No, the Petri dishes are located below the light path, and do not interfere.

C19) “-p. 2701: TV have found an excellent LED to perform their measurements and have characterised it very nicely. That said, the conclusion that the use of a LED in this set up is innovative looks excessive, since LEDs have already been used in CEAS applications by several groups.”

R19) Section 3.1, Conclusion section: We are not aware that we claim to perform the first use of a LED in CEAS applications, which we agree would be presumptuous. We have synergized the conclusion section, and have made more transparent where we feel is a disconnect between the comment and the value of the LED in our particular setup.