

## ***Interactive comment on “Inherent calibration of a novel LED-CE-DOAS instrument to measure iodine oxide, glyoxal, methyl glyoxal, nitrogen dioxide, water vapour and aerosol extinction in open cavity mode” by R. Thalman and R. Volkamer***

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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 ( $I_0$ ). Resembling the use of  $O_4$  retrievals in MAX-DOAS instruments, the open cavity *effective path length* problem is solved by the measurement of the spectral feature of  $O_4$

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at 477 nm, which provides an inherent calibration of the apparatus at that wavelength. Although IBBCEAS this is not a novel technique and  $O_4$  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  $I_0$  are not accessible.

Comments:

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

-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.

-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  $\ln(I'_{in}/I)$  (see Meinen et al, 2010, equations 8 and 9), where  $I'_{in}$  is the intensity in the absence of differential absorption (i.e. including **all** broadband absorptions). Now, approximating  $\ln(I'_{in}/I)$  by  $(I'_{in} - I)/I$  in the weak absorption limit and applying Washenfelder'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 concen-

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tration (see e.g. the comment by D. Venables to Meinen's paper: <http://www.atmos-chem-phys-discuss.net/8/S5154/2008/acpd-8-S5154-2008.pdf>). My impression is that in Platt's paper (Platt et al, 2009), if  $D_{CE}$  is really the so-called DOAS signal as they claim (eq. (26)), the intensity  $I_{in0}(n)$  (whose integral over  $n$  is equivalent to  $I'_{in}$  in Meinen et al., 2010, equations (8) and (9)) should be:  $I_{in0}(n)=I_{in}(0)\exp(-(\rho_0+\epsilon_B d_0)n)$  rather than only  $I_{in0}(n)=I_{in}(0)\exp(-\rho_0 n)$  (eq. (25), Platt et al. 2009), where  $\epsilon_B$  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.

-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).

-p. 2685: The authors should note that Ball et al., (<http://www.atmos-chem-phys-discuss.net/9/26329/2009/acpd-9-26329-2009.html>) use  $O_4$  at 532 nm in a similar fashion.

-p. 2686: Reference Volkamer et al., 2010 is incomplete

-p. 2690, line 5: Theoretical noise formula looks wrong.

-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).

-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

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dishes are used and how far are placed from each other.

-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.

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

-p. 2695, line 10: Question mark for  $\sigma$ .

-p. 2695, line 14: Should say eq. 1?

-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.

-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.

-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  $O_4$  what has to be measured**, but also the concentration of a molecule with substantial absorption across the two windows considered ( $I_2$  in the case of IO retrieval,  $NO_2$  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 ( $NO_2$  seems to be the best candidate) might not be available in all environments. This

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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  $NO_2$  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  $O_4 L_{eff}$  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  $O_4-NO_2$  derived effective paths.

-p. 2700: does the correction given by equations (6) and (7) also apply when the effective path is derived from  $O_4-NO_2$ ?

-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?

-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.

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