

Interactive comment on “Using a high finesse optical resonator to provide a long light path for differential optical absorption spectroscopy: CE-DOAS” by J. Meinen et al.

Anonymous Referee #2

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Overall, this manuscript describes promising developments in combining the path-length enhancement of CEAS with the multi-wavelength DOAS method. The findings prove the principle of the technique, achieving reasonable detection limits for NO₃. However, the promise of the technique is probably more significant for other gases that cannot currently be detected effectively by single-wavelength CEAS techniques. The manuscript is generally acceptable but could be significantly improved in its presentation through some reorganization and increased explanation. We discuss more global comments first then suggest smaller changes.

*** Global comments

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1) This technique is a relatively early example of combining DOAS with CEAS, and is very positive on the strengths of this combination. However, it is important to not overplay these strengths in the context of successful existing instrumentation for NO₃. It is important in this regard to have a balanced approach assessing strengths and weaknesses of various techniques. For example, at the bottom of page 10667, the manuscript indicates that CRDS techniques of baseline determination (removal of absorbing species and multi-wavelength techniques) are "only feasible for a very limited number of species". The CE-DOAS technique essentially suffers the same limitations – a method needs to be used to determine the effective pathlength, and use of a purged cavity is employed in this publication. It is then mentioned that "a great improvement" was introduced through broadband-CRDS. While there is a great possibility of improvement with broadband-CRDS, and this and various CEAS techniques, it should be noted that the detection limits (~ 1 pptv), time resolution (~ 1 second), and ability to modify the specificity (e.g. detect N₂O₅ by heating) e.g. Dube et al., (2006) of existing techniques exceeds the demonstrated ability of any broadband technique. Unfiltered broadband techniques also suffer from aerosol presence or cloud presence (by decreasing path-length) and increased noise by variability in aerosol. They do not have "immunity to aerosol scattering", as written on page 10670, line 6. Additionally, on line 13 of page 10670, it is stated that the current instrument showed good performance as compared to more complicated and costly instruments. While some instruments were more costly and complicated, there were also cheaper and simpler instruments at the intercomparison. Overall, all CEAS/CRDS techniques are very simple, and most costs are in the engineering of the instrument. The electronics are similar, and all the optoelectronic costs continue to decline due to development of cheaper light sources and cheaper compact spectrometers. Overall, a more balanced approach would give the reader better advice with regard to which techniques are best for their application.

2) The manuscript relies extensively on a separate publication that describes the "theory" of CE-DOAS. Could this "theory paper" be integrated into this publication, published together, or be made an appendix of this paper? The current publication ex-

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presses the need to take into account pathlength reduction due to the absorber of interest, so as to account for this non-linearity in the analysis. However, a reader is not able to assess whether the calculations in the "theory paper" are correct. For this reason, it seems that the two papers need to be considered together. Another place where the lack of the theory paper is evident is on page 10673, line 4, which refers to section 3.2 regarding an optimal mirror reflectivity. This reference appears to connect to page 10679, lines 2-4. In this section, an "optimum mirror reflectivity" is mentioned, but no calculations are shown.

3) In a number of locations in the manuscript, detection limits, time resolutions, integration times, and detected concentrations are mentioned that appear inconsistent with other locations of the same manuscript. These issues are described in the section of "smaller changes" below, but in total, they constitute a significant issue with the manuscript.

*** Smaller changes

The manuscript uses the term "differential fitting". I think that "differential absorption fitting" would probably be more accurate.

p10666, line 15. NO₃ is formed by mixing NO₂ and O₃.

p10667, line 1. "witch" is a misspelling of "which".

p10667, line 2. It seems a new paragraph should start here.

p 10667, line 8. Most photons in an unfiltered cavity would be scattered or absorbed and not leave through a mirror. Mention other extinction processes here. Therefore, Eq. 2 is really only good for an evacuated cavity.

p 10667, lines 13-19. The references to Eq. 1 and Eq. 2 are not at all accurate. CRDS uses time-domain measurements, while Eq. 1 is a wavelength-dependent equation. Eq. 2 is the effective pathlength for both CRDS and CEAS. This section should be rewritten.

p 10667, line 25. This section is about CRDS, so the word "transmission" on this line should be "decay time".

p 10668, line 16 (Eq. 3). This equation is very similar to Eq 2, and could be moved closer to it to make a better flow. Effectively, the $1/d_0$ and $(1-R)$ terms are just $1/L_0$ as defined in Eq. 2. Additionally, because the variables are defined in the vicinity of Eq. 2, it was a little difficult to follow in this location.

p 10669, line 8. The text discusses R in Eq. 3 and L_0 from Eq. 2. They are really just equivalent – see the preceding comment

p 10669, lines 9-13. This sentence is unclear. Please clarify the measurement of the cavity is the effective light path, and clarify the idea of using a reference molecule that is in the cavity at known concentration.

p 10669, line 13. The length L_0 is not a "normal" pathlength like in active DOAS, but an "effective path length".

p 10671, line 4. Inexpensive diode lasers have also been used (e.g. Ayers et al., 2005).

p 10672, line 3. Do you see evidence for photolysis?

p 10672, line 15. There appears to be a new paragraph needed here.

p 10673, line 1. N_2 is mentioned as a Rayleigh scatterer, what about O_2 ? I assume the limit is similar.

p 10673, line 23. There is a comma that appears to be a decimal designator. Other parts of the paper use a period for decimals. Make consistent.

p 10673, bottom of page. The acquisition rate is specified as 0.2 min^{-1} (5 minutes). However, it later says that 60s exposure time. Please clarify how these two numbers differ from each other or correct the discrepancy.

p 10674, line 20. In this and other places, please use "effective" with optical path-

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lengths.

p 10674, line 22. How can a purged cavity be achieved in the field? In these examples, it was done by methods not compatible with field observations. What is the strategy to do this in the field implementation?

p 10675, lines 9,10. It is unclear what is meant by 1.3 seconds. Isn't this 1000 ring-down events averaged? Again, please clarify or eliminate.

p 10675, line 16. Isn't it just important here for a "strong" absorber. Inclusion of the theory paper as an appendix would help in clarifying this point.

p 10675 bottom and p 10676 top. It is unclear how the convolution involved in Eq. 4 is done. It seems like you need to assume that the mirror reflectivity gives the wavelength dependence to convert the ring down time (essentially one number) to L_0 at all wavelengths. How is this conversion done, and how is it affected by the case that at the mirror central wavelength Rayleigh scattering may also be a significant extinction mechanism? Additionally 655 nm is not the maximum NO_3 absorption (the correct maximum absorption wavelength is 662nm). The last sentence doesn't appear to make sense. The fit to the data is not mono-exponential. How does a range from 5 to 75 microseconds correspond to <3% error? What is a "wavelength-independent L_0 ". In equation 4, L_0 is explicitly a function of wavelength.

p 10676, line 14. The word "eidelbergity" is not correct.

p 10677, line 12. The word "ambiguous" does not appear correct here. Possibly "arbitrary"?

p 10678, bottom. Isn't Leff here equivalent to L_0 in the prior text. Possibly you can simplify the nomenclature. If it is different, please clarify.

p 10679, line 16 and p 10680, line 3. The ozone in the former case is 350ppmv, and the detected amount is 590ppmv (nearly twice the abundance). Can you explain this big difference? It seems like that O_3 could not reasonably be separated from aerosol,

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which will have a slowly varying absorption across the LED range.

p 10680, line 6. Doesn't your fit also include an NO₂ term ($n_{\text{NO}_2} \times \sigma_{\text{NO}_2}(\lambda)$)? NO₂ is explicitly mentioned in Fig. 3, but in Fig. 4, it is not explicitly included. Also see a later comment on the figure captions. Additionally, please explain $T(\lambda)$ in this section. How did you determine you needed to consider these "instrumental effects"?

p 10681, middle page. How does this ozone observation compare to other measurements of ozone from this study? It appears that ozone cannot be effectively measured. Please clarify the subsequent sentence about misinterpretation of the ozone data.

p 10683, line 24. This section says that the detection limit is twice the fit error, but p 10681, line 26 says that is a 1-sigma error. Please clarify this apparent conflict. Additionally, on page 10681, it says "accuracy", when it seems like "precision" is being discussed.

p 10684, line 10. The CE-DOAS method is claimed to be "insensitive" to scattering aerosol. It is clearly not insensitive because the effective pathlength decreases with increasing aerosol load. Therefore, at least its detection limit suffers. It also remains to be seen if aerosol causes other problems in actual field data.

p 10684, lines 20-22. There is again lack of clarity of exposure time, acquisition time, and 1-sigma or 2-sigma detection limits. Please clarify.

p 10690, Fig. 3 caption. Where do these NO₂ and NO₃ mixing ratios come from? The observation here or some ancillary data? What does the last sentence mean?

p 10691, Fig. 4 caption. Is the grey line a residual or a fit to NO₂? If there is NO₂ present, why not fit it? Is a polynomial used in the analysis (for aerosol scatter)? If so, it seems that the polynomial and O₃ would covary.

p 10693, Fig. 6 caption. Why is the NO₂ spectrum here apparently not convoluted to the instrumental resolution?

References:

Ayers, J. D., Apodaca, R. L., Simpson, W. R., and Baer, D. S. (2005) Off-axis cavity ringdown spectroscopy: application to atmospheric nitrate radical detection, *Appl. Optics*, 44, 7239-7242.

Dube, W. P.; Brown, S. S.; Osthoff, H. D.; Nunley, M. R.; Ciciora, S. J.; Paris, M. W.; McLaughlin, R. J.; Ravishankara, A. R., (2006), Aircraft instrument for simultaneous, in situ measurement of NO₃ and N₂O₅ via pulsed cavity ring-down spectroscopy. *Rev Sci Inst*, 2006, 77, (3).

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