

Response to
Interactive comment on "Peroxy radical detection for airborne
atmospheric measurements using cavity enhanced absorption
spectroscopy of NO₂ "
from Anonymous Referee 1
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We'd like to thank both reviewers for their contribution to help us improve this publication. Addressing their comments, both the introduction and results chapters have been partly rewritten, and new measurement results have been introduced. Below are our answers to the specific comments (in bold); text cited from the revised publication is in italics.

The authors report the development of a new instrument for the detection of atmospheric peroxy radicals. This work falls well into the scope of AMT. It reports the application of the NO₂ detection by CRDS in chemical amplifier instruments and deployment of the instrument on airborne platforms. Although the authors give many technical details about e.g. the components that are part of the instrument, the manuscript could be improved by a more detailed description of the measurement principle, which emphasizes the specific advantages of the combination of the well-known radical amplification part of the instrument and the new NO₂ detection instead of giving a partly very general description.

The description of the measurement principle has been extended.

The characterization of the specific instrument properties given in this manuscript especially with respect to its application on an airplane, which will fly at high altitudes, could be extended. The authors are very experienced in PERCA instrument and there a number of publication from this research group which report very nicely properties of earlier versions of the instrument. Nevertheless, in my opinion this manuscript would benefit from showing in detail the properties of the new instrument. I give some examples in the specific comments, but the authors may have more material about the characterization of the specific properties of this instruments, which are worth being reported here. Abstract: (1) There is some confusion in the naming of the instrument, which implies the application of cavity-enhanced spectroscopy and the description as cavity ringdown instrument.

Initially, the term "cavity-enhanced absorption spectroscopy" was meant as a general description of absorption spectroscopy methods that benefit from optical resonators. Since its main use nowadays is for a specific technique of cavity transmission measurements and to avoid misunderstandings, both the publication title and the instrument's name were changed to only retain the term "absorption spectroscopy". The set-up described in this publication is different from a typical CRDS set-up because it contains a three-mirror V-resonator and benefits from its optical feedback.

(2) In the abstract, the principle of the amplification process is not becoming clear for the reader. I would suggest to spend one more sentence, in order to explain, why radical concentrations are amplified and why the NO₂ measurement can be taken as proxy for the radical concentration.

The chemical amplification is a well established measurement technique. The work presented in this manuscript does not focus on any particular modification of the chemical amplification as such, but on the introduction of a new detection method for the product (i.e., NO₂) obtained. Therefore, a detailed explanation of the chemical amplification technique- though necessary for the general understanding - does not actually belong to the abstract but to the introduction as written in the manuscript. However, the abstract and the introduction have been reworded for clarification.

(3) The authors give the detection limit for different integration times for NO₂ and radicals. Please give comparable numbers.

The different integration times for NO₂ and radicals are provided because to calculate the radical concentration, two separate ring-down measurements (background and amplification mode) have to be analyzed. Each of these modes is analyzed for 45 s (owing to the data loss due to pressure and flow stabilization after mode switching), thus providing the NO₂ sensitivity for this time frame is appropriate. The radical concentration is then calculated by the difference of the two modes; thus two minutes are needed for a unique radical concentration. Therefore we'd rather retain these different integration times.

Introduction: Looking at the sensitivity of the instrument, it looks as if the sensitivity of the PERCA with the CRDS NO₂ detector is worse compared to an earlier version of the PERCA instrument with a Luminol detector (I would suggest to make the specs of the new PERCA comparable to the specs given for the earlier version). Is there any particular reason, why this is the case, which can be described somewhere in the manuscript? In literature very sensitive NO₂ detectors using CRDS are reported, so that one may expect that a PERCA instrument with a CRDS detector should achieve a similar good performance as with a Luminol detector.

The following statement has been added to the introduction:

The use of an optical method to detect NO₂ presents some clear advantages. Optical detection of NO₂ is chemically specific, does not require a constant addition of NO₂ to assure detector signal linearity, and is not affected by NO which is added to the sampled air. These benefits provide greater freedom in selecting measurement conditions maximizing conversion and amplification parameters (e.g. increasing NO mixing ratios in the reactor for improving the chemical conversion without

deteriorating detection sensitivity). Furthermore, the decrease of the sensitivity of the luminol detection at lower pressures limits its use for measurements in the upper layers of the troposphere.

p9658 l20: I would suggest to make clear that HO₂ detection by LIF is not making use of an amplification process.

The introduction has been changed (with respect to the initial comment) to avoid misunderstandings.

p9659 Eq 2: In principle, the difference of NO₂ between amplification and background mode would be somewhat smaller, because the background mode includes the production of one NO₂ from HO₂ and two NO₂ from RO₂. In the background mode HO₂ and RO₂ are converted to OH, so that NO₂ is produced from HO₂ and RO₂. I understand that this is negligible for a high amplification factor, but the authors may want to mention this.

The text has been changed to reflect these contributions.

Eq. 1 and p9663 l4-11: The chain length CL is mentioned in Equation 1 the first time. A clear description of its meaning is not given. By just reading the text, the reader gets the impression that the chain lengths is only the amplification factor of peroxy radicals. Later in the text, however, the author mention that the value of CL also depends on the inlet losses of peroxy radicals. I would suggest to explain the meaning of CL right after Eq. 1.

The introduction has been extended and re-structured to emphasise the difference between the chain length and the effective chain length.

p9660: The authors nicely explain, how they derive the absorption from the cavity ring-down measurement. However, the connection between Eq. 3 and Eq. 4 is not becoming clear. Eq. 3 assumes that NO₂ concentrations are measured in the amplification and background mode, whereas Eq. 4 assumes the measurement of τ_α and τ_0 . Since the authors do not mention any zero mode without the presence of any NO₂, which would allow to determine absolute NO₂ concentrations, I assume that τ_0 is the background NO₂ measurement in Eq. 3, so that the concentration n in Eq. 4 is ΔNO_2 in Eq. 3. This relationship is briefly mentioned later in the text on p9665, but I would suggest to modify Eq. 4 and add some description, so that the readers easily recognize the connection between Eq. 3 and 4.

The following sentence has been added at the end of this chapter (p. 9660):

To determine the peroxy radical concentration the NO₂ concentration difference between background and amplification mode is required. Thus, ring-down measurements taken during the background yield τ_0 and those taken during the amplification mode yield τ_α in Eq. 4.

p9660 l21: An approximate value of the NO₂ cross section is given here. It is not becoming clear, if this value refers to the specific wavelength of the laser. The authors may also want to mention, if the spectral width of the laser requires a convolution of the absorption cross section with the spectral width. The actual wavelength of the laser in a single ring-down event in this instrument depends on the mode that is coupled into the cavity. Does this have an influence on the absorption cross section that needs to be applied regarding the highly structured NO₂ absorption spectrum?

The value refers to the specific laser wavelength. The mode coupled into the resonator is always a TEM00 mode. Convolution is not necessary as both laser linewidth and scanning range are small compared to the cross section profile structures. A paragraph has been added to chapter 3.1 to clarify this:

The measurement yields a value of the absorption cross section of $\sigma_{\text{NO}_2}^{408.9\text{nm}} \sim 6.5 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ with a relative error of $\pm 2\%$ at the laser wavelength of 408.9 nm, a temperature of 296 K and a pressure of 300 hPa, in very good agreement with measurements of Vandaele et al., 2002, and Nizkorodov et al., 2004. The cited profiles may be used without requiring a convolution with the laser linewidth of 1 MHz $\sim 6 \times 10^{-4} \text{ pm}$ or the laser wavelength scanning range of 10 GHz $\sim 5 \text{ pm}$ as both values are small compared to the cross section profile structures.

p9661 l17: Why is an NO₂ gas standard needed? I would expect that one of the advantages of applying CRDS for NO₂ detection is that absorption spectroscopy does not require a calibration. Also no NO₂ calibration is further mentioned in the manuscript.

The latter issue has been changed with our answer to the preceding question; we do conduct reference measurements to check on the NO₂ cross section, which also confirms that the extended cavity diode lasers are still in optimum working condition. The gas cylinder makes in-flight reference measurements (with NO₂-seeded outside air) feasible, which would be performed if the measurement data indicates unusual operation (such as a degraded background ring-down time).

This sentence has been added to the instruments' description:

The NO₂ is to be used to seed outside air for a reference measurement if the measurement data indicates unusual instrument operation, e.g. strongly degraded background ring-down times.

p9661 127: The purpose of the stainless steel volume is not clear from this sentence. Is this only a gas distribution or is there any other need for the volume?

The pre-reactor chamber acts both as a gas distribution system and as a gas volume used for the pressure stabilization.

This sentence has been inserted into the description:

Two transparent 1/2" outer diameter PFA connections on both sides of the pre-reactor chamber allow for the removal of the surplus air by the pressure regulator.

p9662 17-8: I am not sure, if I understand this sentence correctly. Every reactor and NO₂ cavity has a flow controller downstream of the cavity (Fig. 6). In this case I would assume that a flow of 1 L/min could be achieved independent of the inlet pressure.

Unfortunately not. The flow resistance from both the flow controller and the NO_x/CO scrubbers downstream restrict the inlet pressure to > 150 hPa for a flow of 1 sLpm.

Isn't the point here that a constant reaction time in the reactor is required, which is not possible at varying ambient pressure without a bypass flow? I would suggest to make the statements more clear.

Since the *eCL* depends on the reaction time keeping the latter constant is beneficial e.g. for vertical flight profiles. A sentence has been added to clarify this:

*Inlet pressure stabilization maintains a constant peroxy radical conversion time and thus eliminates the *eCL* dependence on the ambient pressure. In the lower troposphere it also significantly reduces the relative humidity and thus the humidity-dependent *eCL* variation.*

p9662 16-13: A pressure of 300 mbar in the inlet is chosen for this instruments. Since this instrument is explicitly built for its deployment on the research aircraft HALO, a statement about the altitude range, for which this pressure is applicable, should be added. For altitudes above approximately 10km the ambient pressure will drop below the inlet pressure.

A paragraph and a graph were added to clarify the instrument operation during flights with HALO. The paragraph states:

*The optimum inlet pressure seeks to enable the measurement at high altitudes with suitable stability and sensitivity. Very low pressures at the inlet imply however a deterioration in the *eCL* and the overall measurement stability. Therefore, an approach as shown in Fig. 4 is proposed. For altitudes below 8km the gas flow and pressure controlling is robust at an inlet set pressure of 300hPa, leading to *eCL* values of around 100 (see chapter 3.2 for a complete discussion) with a moderate time response of 15s. For altitudes between 8 and 10km an inlet pressure of 200hPa yields a lower *eCL* of around 55 with a faster time response of 10s, whereas at higher altitudes the set inlet pressure of 100hPa retains these 10s as only half of the sample flow can be achieved by the actual set-up under these conditions.*

section 2.1: (1) Although all numbers are in principle given, I would suggest to give the residence time of the sampled gas in the reactor and the cavity for the chosen pressure of 300 mbar.

Done. See comment before.

(2) The authors mention that more than 1s is needed for a complete conversion of peroxy radicals. Then it is hard to understand how an amplification factor larger 120 can be achieved. I would suggest to give some more details about the amplification process, so that the reader gets more insight about the amplification process and can understand, how the amplification factor is achieved for conditions of this instrument.

This seems to be a misunderstanding. By "complete conversion" we mean the conversion and amplification of the peroxy radicals (until all radicals have left the amplification cycle).

(3) Also a brief discussion, whether differences of the amplification for HO₂ and RO₂ are expected, would help to better understand the capabilities of this instrument.

A full in-depth analysis of the expected differences (affected by the RO₂ chemical structure, (wall) loss reactions and the conversion efficiency) would be beyond the scope of this publication. Therefore, only a (very) brief mention of these differences were added to both the introduction and the results:

Note that the efficiency for RO₂ conversion is affected by additional terminating reactions depending on their chemical complexity.

p9663 117-20: What is the advantage of the V-shape of the resonator for the CRDS instrument here? At first, I

would assume that a third mirror adds light loss, which lowers the sensitivity of the instrument. Other NO₂ CRDS instruments with only two mirrors reported in literature do not suffer from stability problems, if this was the reason here. The large volume of the resonator that is required for the V-shape cavity increases the time needed to exchange the sampled air, so that the response time of the instrument to fast changes in peroxy radical concentrations may become large. This may become even larger, because inlet and outlets for the sampled air are placed on one side of the cube containing the cavity, so that I can imagine that it takes some time to homogeneously fill the cavity with an absorber. Please comment.

The third mirror does not add light loss; the overall reflectivity and losses are the same as for a two-mirror resonator. It is true that the V-cavity incorporates a higher gas volume than a two-mirror cavity. However, for our set-up a V-cavity is necessary to only receive optical feedback from the inside of the cavity, thus stabilizing the extended cavity diode laser and generating high resonator transmission. Furthermore, no optical isolator is needed, as is often the case when using a two-mirror resonator (at least with extended cavity diode lasers).

The time to homogeneously fill the cavity at 300 hPa is about 5 s, as mentioned in chapter 2.2. This is consistent with the values for the volume and the gas flow. Here it may help that the air is fed into the middle of the cavity and then splits to both its ends. The reviewer is of course correct in stating the lower gas volumes and thus shorter response times are highly desirable.

p9665 19: A ring-down time of 20 μ s is mentioned at 285 mbar. I assume that this is achieved for clean synthetic air without aerosols, so that the reduction is due to Rayleigh scatter. Is the reduction of the ring-down time consistent with this assumption?

Yes, the ring-down time measurements yield a value of $\sigma = 1.5 \times 10^{-26} \text{ cm}^2/\text{molecule}$ at 409 nm for Rayleigh scattering (Sneep, Ubachs, Journal of Quantitative Spectroscopy & Radiative Transfer, 92, 293–310, 2005).

Aerosol extinction can significantly reduce the ring-down time at the same pressure. Did the authors check, what the influence of aerosol in ambient air measurements is on the noise of the instrument? I can imagine that the extinction due to aerosol may be highly variable and make the background signal fluctuating on a much shorter timescale as the time between two background measurements. Why is there no aerosol filter downstream of the reactor, when radical losses do not play a role any longer?

The use of a filter would of course increase the minimum inlet pressure required to allow for reactor gas flows of 1 sLpm, further curtailing measurements at high altitudes. Also, no mirror degradation was seen even when measuring outside ambient air for days, which led us to the decision not to add such a filter. It could also be expected that if aerosols in general are an issue then a typical filter with diameters of a few μm may not be sufficient, as small particles with sizes $\leq 1 \mu\text{m}$ expected from anthropogenic activity (e.g. soot) will not be filtered.

p9665 124-27: The authors mention that a 1 s-averaged ring-down value is provided. I miss specifications of the number of ring-down events that are typically averaged and/or of the repetition rate of the laser scan. What is the time, over which the ringdown event is sampled?

These values are indeed missing. The value is ~ 50 ring-down events per second, and they are sampled for 300 μs . The laser scan rate is 10 Hz. These values have been added to the text.

p9666 11: This statement is somewhat contradicting the earlier statement that no absolute NO₂ concentrations is measured, but only the NO₂ difference due to the radical amplification (see also comment above). I would suggest to rephrase this sentence.

We have changed the first sentence to:

Accurate calculation of peroxy radical mixing ratios demands the knowledge of both the eCL and the NO₂ mixing ratio difference Δx_{NO_2} introduced by the peroxy radical conversion.

section 3.2: The procedure to characterize the chain length is well described, but I miss some details regarding the sensitivity of the chain length of this instrument.

(1) It is stated on p9662 that there is no significant effect of humidity on the CL of the instrument. I see the argument of that RH is going down with pressure. Nevertheless, I would suggest to add a figure proving the statement.

We have reworded this statement to avoid misunderstandings. The effect of relative humidity on the chain length has been thoroughly investigated by Reichert et al., 2003, and we would deem this sufficient. The relative humidity reduction is however only valid if the ambient pressure differs significantly from the inlet pressure. Therefore, the text now reads:

In the lower troposphere it also significantly reduces the relative humidity and thus the humidity-dependent eCL variation.

(2) When the instrument will be deployed on HALO, ambient pressure will vary over a wide range. The authors mention the dependence of radical losses in the inlet with varying pressure and therefore keep this pressure constant. Is it possible that radical losses at the orifice are different, when the pressure gap between ambient and inlet pressure changes with altitude?

Since the orifice retention time is quite small, the potential differences in the losses at the orifice for different velocities are considered to be negligible.

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(3) Is there an estimate of the radical loss in the inlet for this instrument?

A chemical box-model simulation at 300 hPa, 1.8 s retention time and a wall loss rate of $k_w = 1.92 \text{ s}^{-1}$ (extrapolated from previous experimental studies of Kartal, 2009) yields a chain length of 153. Comparing that to the mean experimental value of ~ 100 results in an estimated relative radical loss of 33% in the inlet.

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p9669 l3-10: The comparison of the chain length with results from the Ph.D. thesis is not very helpful here, because the conclusion is that the experiments reported in the Ph.D. thesis had problems. I do not think that this publication is an appropriate place to correct the results in the Ph.D. thesis.

This part of the manuscript has been modified. The data have been revised and a comparison of more statistical relevance has been included in the text.

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Interactive comment on Atmos. Meas. Tech. Discuss., 6, 9655, 2013.