

Interactive comment on “Peroxy radical detection for airborne atmospheric measurements using cavity enhanced absorption spectroscopy of NO₂” by M. Horstjann et al.

Anonymous Referee #1

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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 characterization of the specific instrument properties given in this

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

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.

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

p9659 Eq 2: In principle, the difference of NO₂ between amplification and background mode would be somewhat smaller, because the background mode includes the pro-

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duction of one NO_2 from HO_2 and two NO_2 from RO_2 . In the background mode HO_2 and RO_2 are converted to OH , so that NO_2 is produced from HO_2 and RO_2 . I understand that this is negligible for a high amplification factor, but the authors may want to mention this.

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.

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 NO_2 concentrations are measured in the amplification and background mode, whereas Eq. 4 assumes the measurement of τ_a and τ_0 . Since the authors do not mention any zero mode without the presence of any NO_2 , which would allow to determine absolute NO_2 concentrations, I assume that τ_0 is the background NO_2 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 recognizes the connection between Eq. 3 and 4.

p9660 l21: An approximate value of the NO_2 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 NO_2 absorption spectrum?

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p9661 l17: Why is an NO_2 gas standard needed? I would expect that one of the advantages of applying CRDS for NO_2 detection is that absorption spectroscopy does not require a calibration. Also no NO_2 calibration is further mentioned in the manuscript.

p9661 l27: 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?

p9662 l7-8: I am not sure, if I understand this sentence correctly. Every reactor and NO_2 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. 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.

p9662 l6-13: 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 10 km the ambient pressure will drop below the inlet pressure.

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. (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. (3) Also a brief discussion, whether differences of the amplification for HO_2 and RO_2 are expected, would help to better understand the capabilities of this instrument.

p9663 l17-20: What is the advantage of the V-shape of the resonator for the CRDS in-

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strument 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.

p9665 I9: 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? 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?

p9665 I24-27: 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 ring-down event is sampled?

p9666 I1: 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.

section 3.2: The procedure to characterize the chain length is well described, but I

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

p9669 I3-10: 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.

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