Review of "Peroxy radical detection for airborne atmospheric measurements using cavity enhanced absorption spectroscopy of NO_2" by Horstjann et al.

This paper describes a technique to measure the sum of peroxy radicals using chemical amplification with NO and CO, and detection of the NO_2 product with cavity ring-down spectroscopy. The method builds on other chemical amplifier approaches in which various NO_2 detection schemes have been used, although most have used luminol chemiluminescence. As the authors point out, luminol chemiluminescence detection, while fairly sensitive, has drawbacks. The new detection scheme is described in quite a bit of detail, which is appropriate since that is the main difference from previous instruments. The approach described thus adds a new variant for peroxy radical detection. The paper is fairly well-written with appropriate level of detail. Most of the figures are appropriate and relevant. I believe the paper should be published after the authors consider some suggestions for changes.

General comments.

When an analytical technique is presented in a scientific paper, I believe it is important to describe in detail the uncertainties in the measured quantity. This includes propagation of errors, which involves estimates of random and systematic uncertainties, and a clear description of the confidence intervals of the stated uncertainties. Within the paper, there are several uncertainties given, but rarely is it stated whether these correspond to 1σ, 95% confidence interval or other interval, and whether they correspond to total uncertainties or just random variations of observed signals. Because of the lack of propagation of errors analysis being presented, some uncertainties are not addressed. An example is the absorption cross section of NO_2, but there are other uncertainties that should be stated and included in the presentation of uncertainties.

The presentation would be more exciting if the detection limit/measurement uncertainty/time response for NO_2 was significantly better than other approaches. If I understand the factors presented, the performance appears comparable to other methods. The main advantage appears to be the lack of humidity dependence as compared to luminol chemiluminescence.

The instrument appears to be a two channel instrument (with two chemical reactors and two NO_2 detectors), but this is not clearly stated. The advantages of a two channel approach are also not discussed, even briefly, as presented in other papers in the literature (including the Bremen group). The plots of instrument signal should also then present two signals, one for each channel. It is very surprising that two chemical reactors cannot be built with the same chain length, although if they are stable and known, signals can be corrected. Perhaps more laboratory work should have been done in this area.

The production of NO_2 by ambient ozone is not mentioned. This is one of the difficulties of this chemical amplifier approach – that the radical signal is measured on top of a fairly large background due to ozone. This also means that detection limits measured with no NO_2 present are not that meaningful. The noise on a 50 ppbv signal are more indicative of that which determines the peroxy radical detection limit. I suggest some more experiments to complement the measurement uncertainty discussion on page 4.

No ambient data are presented. I think the case for the value of the method would be much stronger if some sample data were shown.

The design goals (aircraft speed, altitude, radical levels, polluted or clean atmospheres, etc.) of the instrument should also be briefly presented. While it is stated that it will be deployed on HALO (which should be defined), will the instrument be able to make measurements above the detection limit for the full altitude range of the aircraft (surface to about 50 kft) at least for some photochemical conditions? I

expect that levels above about 25 kft, even in summer, will be at or near the instrument detection limit. This is fine – it should just be stated. Suggest using some modeled levels to help with this analysis.

Specific comments.

Abstract, page 1. The detection limit of NO_2 is presented as a mixing ratio and an absolute concentration. I don't see the reason for the later, and suggest it be eliminated.

Introduction, page 1, second column, last paragraph. The acronym CIMS should stand for Chemical Ionization Mass Spectrometry.

Page 2, first column, first paragraph. Here, it states that the 3σ detection limit for peroxy radicals using luminol chemiluminescence is 3 pptv, the same as the 1σ detection limit for the present method. This leads the reader to wonder why use the new approach. There is a sentence describing the drawbacks of luminol, but I suggest a bit more discussion of why the new approach is so much better.

Several references are given for reports of ground-based and airborne measurements using a luminol-based chemical amplifier. They are very Euro-centric, and most are from the Bremen group. I suggest including a few references to other groups, including non-European groups.

Suggest changing "…Institute of Environmental Physics, and it employs…" to "…Institute of Environmental Physics, which employs…"

Page 2, first column, reaction 4. While many RO radicals react with O_2 to produce HO_2 and carbonyl compounds (not just aldehydes), there are RO radicals that either react to produce RO_2, do not react with O_2 at all, or primarily undergo isomerization or decomposition. The point is that the chemical amplifier chemistry does not measure 100% of RO_2. For most situations, the measured concentration is close to the true one, but this limitation should be briefly mentioned. This is also relevant in equation (1).

Page 2, second column, reaction 5. This is not a chemical reaction, so should probably be equation (1). Regardless, the contribution due to the reaction of NO with O_3 should also be included. Also, the meaning of $[NO_2]_{other}$ should be discussed.

Page 2, second column, reaction 6. This should be labeled as an equation.

Page 2, second column, near end of last paragraph. The term "absorption coefficient" is used without specific definition. It appears to be the equivalent of $(1\text{-}I/I_o) \times l$, which is the absorptance times the path length or equivalently, the radiation absorbed per unit length. Continuing on to the equations and discussion at the top of page 3, no mention is made of the role of mirror reflectivity in the measurement of τ and thus α. Perhaps this is obvious with definition of α, but I suggest a bit of additional discussion on this topic.

Page 3, Experimental, first paragraph. The air bypass is mentioned, but its purpose is not clear. This sentence should be changed to make it clearer.

Page 3, Inlet. Why is the pressure controlled chamber so large? Given that it is one of the main limiting factors in the switch from one reactor to the other, I would think it should be much smaller. Consideration of the flow path by minimizing dead zones could also make the switch faster.

Page 3, second column, last paragraph. Here several uncertainties are given without defining what they mean (see general comment above).

Page 4, first paragraph. It is stated that the chain lengths of the two reactors agree within their uncertainties. While there is not universal agreement what this means, I would say that it is just barely the case. I suggest pointing out that whatever the chain lengths are, they can be used to process the data.

Page 4, first column, last paragraph. I suggest changing the word "schematised" to "shown schematically" or "shown in a schematic diagram". While schematized is a perfectly valid word, in my experience it is rarely used.

Page 4, second column, end of first paragraph. Suggest changing "exposition" to "exposure".

Page 4, second column, end of second paragraph. The statement that includes "…if the change is slow…" might be changed depending on the author's response to my earlier comment about two-channel chemical amplifiers.

Page 4, second column, last paragraph. Not being a laser expert, I have trouble thinking in GHz when discussing wavelength scanning. Would it make sense to give the scan range in nm as well (I think 10 GHz is about 0.0056 nm)? What does "certain resonator transmission threshold" mean? I'm guessing it has to do with selecting the wavelength at the maximum NO_2 cross section, but there could be other explanations. Suggest making this a bit clearer. The sentence with the phrase "draws the current" needs to be reworded. It is mentioned that the data are acquired at 1 M-sample per second. If the ring-down times shown in the figures of about 20 μs are typical, would there be benefit to sampling faster. Perhaps a brief statement describing why this rate was chosen.

Page 5. NO_2 detection limit. See general comment above. Perhaps add description of uncertainties when measuring ~50 ppbv signals.

Page 5, second column, equation 4. Suggest pointing out that 2 radicals are formed per H_2O photolysed, and 2 ozone molecules are formed per O_2 photolysed.

Page 5, second column, first paragraph. Suggest justifying using Hofzumahaus et al. 1997 O_2 cross section, since it has been pointed out that the effective O_2 cross section depends on the specific photolysis cell configuration.

Page 5, second column, second paragraph. The statement that says measurement of small ozone concentrations is highly inaccurate, is not necessarily true. It depends on the analytical method and the definition of small. Suggest adding a bit more discussion. Also suggest finding someone with a state of the art reverse chemiluminescence ozone instrument. Also, the there is an implicit assumption that the detector signal is proportional the ozone produced. Has this been demonstrated?

Page 5, paragraph 4. Here is a propagation of errors analysis for the calibrator. This is good, but should include a definition of "errors".

Page 5, paragraph 5. Is "magnet valves" the same as "solenoid valves"? If so, I suggest the latter.

Page 6, paragraph 3. Suggest changing "probably" to "likely".

Page 6, Summary and Conclusions. Suggest changing "…measurements is reported." to "…measurements are reported."

Page 6, first column, last paragraph. Suggest changing "…field…" to "…ground-based…".

Page 6, second column, first paragraph. This is related to my earlier comment to specifically match the instrument capability to the design goals, which are in part based on expected concentrations in different atmospheric regions. The statement about "the upper layers of the atmosphere" is too vague to be that useful. Suggest changing "end-2014" to "end of 20414".

Figures.

Suggest combining Figures 1 and 3.

I consider the photos (Figure 2, 4 and 7) nice, but they could be left out.

Figure 4. Suggest changing “aircraft fuselage level” to “aircraft wall”.

Figure 5. Suggest adding a scale or conversion factor for GHz to nm.

Figure 6 (and discussion in the text). Suggest adding in caption and/or in text a discussion of why the V-cavity is better for this application.

Figure 9. I really like the addition of the Allan variance analysis and figure.

Figure 11. Suggest adding vertical lines separating the measurements of the various HO_2 concentrations and giving those concentrations.

Figure 12. The loss of 16 seconds of data in an aircraft campaign is unfortunate. I suggest modifications to the instrument to improve this. Perhaps a short statement saying this in text and/or in caption. Also suggest describing plans for improving the performance of the NO_2 detectors.

Figure 13. Here and in the text only HO_2 calibration is discussed. You should perform and discuss calibration of RO_2 as well. It is a simple matter to add various reactants to the water photolysis calibrator (CO, CH_4, etc..). Just make sure that you don’t add so much reactant as to influence the chemical amplifier chemistry.