

Reply to Reviewer 1 comments

We would like to thank Reviewer 1 for his/her supportive and interesting comments. We provided here detailed explanations/comments/modification. For clarity, we kept the reviewer's comments in red and our replies in Black colors.

General observations:

General comments

The paper entitled *High-precision atmospheric oxygen measurement comparisons between a newly built CRDS analyzer (Picarro G-2207) and existing measurement techniques* describes a Cavity Ring Down Spectrometer devoted to the determination of oxygen concentration in air and to the delta ^{18}O isotopic ratio measurement depending of the instrument mode. The performances of the instrument are tested in laboratory by comparing measurements of well-known samples with results obtained using other techniques (IRMS, paramagnetic technique, Licor instrument) on the same samples. In the field measurements and comparisons are also provided by the authors at the High Altitude Research Station Jungfrauoch and at the Beromünster tall tower. The paper is well-written and detailed. The paper is now much easier to read thanks to the new way the experimental description and the obtained results are presented. The performances reached by the CRDS instrument are at the state-of-the-art for optical methods. The paper is fully in the scope of AMTD and is well-suited for a publication in this journal but needs some significant corrections (see the comments below).

Main remarks:

Part of the work in Fleisher et al. 2015 to which the authors refer in lines 135-141 seems to not be published. If authors have a published reference corresponding to Fleisher et al. 2015 they can let the text as it is but if they are not able to give a published reference they have to remove the lines 135-141 as well as the lines 144-146 and the reference.

The cited work by Fleisher is not yet a published article but exist as a conference paper. For this reason, we have now excluded this citation and its associated sections.

At the end of this paragraph we added the following sentence:

“Ultimately, the usefulness of the spectral model is to be evaluated by the precision and stability of the O_2 measurements when compared with established techniques.”

The concentrations reported in Figures 8, 12, 13 have to be given in the same unit (per meg or better in ppm) to facilitate the comparison. For example in Figure 13 it will be better to plot the two layers (the paramagnetic and the CRDS measurements) on the same graph using the same units.

We used the units ppm and per meg to reflect the actual measured values by the specific analyzers as we believe it will be best to keep the reporting as closely connected as possible to what we directly measure, which is optical absorption. By reporting what we actually measure, our reported values also show most honestly whatever is missing from the picture, such as the dilution due to unmeasured

carbon dioxide. But for some sections, we have provided measurement values in the same unit for better comparison between different analyzers for example Figure 16 and Table 1.

Regarding the “specific comments”:

P2, L33: The authors have to recall the definition of *per meg* unit.

We have now added this definition at lines 35-40 as follows:

Note that the variations in atmospheric O₂ is expressed in units of per meg due to its small variations with respect to a large background and to account for dilution effects from CO₂ or any other gas of relevant amount change, which is expressed as:

$$\delta \left(\frac{O_2}{N_2} \right) (\text{per meg}) = \left(\frac{\left(\frac{O_2}{N_2} \right)_{\text{sample}}}{\left(\frac{O_2}{N_2} \right)_{\text{reference}}} - 1 \right) \cdot 10^6 \quad (1)$$

P2, L43: The authors have to recall the definition of *the oxidation ratio* and give some explanations.

Defined in lines 50-51 as:

“OR defined as the stoichiometric ratio of exchange during various process such as photosynthesis and respiration”

P4, L86: The authors have to specify the reference of the pressure gauge, the proportional valve and acquisition board allowing stabilizing the pressure at the level of 3×10^{-5} !

The pressure is stabilized such that the error signal of the pressure sensor is 3×10^{-5} . In other words, the actual pressure is (likely) not stabilized to that level, due to noise/drift in the sensor itself.

P4, L91: The authors should give the typical ring-down time they have.

We have now provided this information and added a sentence: “For this instrument the empty cavity ring-down time constant is about 39 μs .”

P5, L104: Give here the FSR value instead of p7.

We provided the numerical value 0.0206 cm^{-1} in Line 105 and remove it from p7.

P6, L125: The authors should cite the following reference: Tran et al., JQSRT (2019) 222-223, p108- 114.

This reference is added Tran et al. 2019

Tran, H., M. Turbet, S. Hanoufa, X. Landsheere, P. Chelin, Q. Ma, and J.-M. Hartmann, 2019: The CO₂-broadened H₂O continuum in the 100-1500 cm^{-1} region. Measurements, predictions and empirical model. J. Quant. Spectrosc. Radiat. Transfer, 230, 75-80, doi:10.1016/j.jqsrt.2019.03.016.

P6, L142-144: This sentence is strangely written and should be reformulated.

As the reference to Fleisher and the discussion that goes with it are excluded, this part is also removed.

P7, L146-149: The excess noise observed by the authors is probably due to the fact that shorter ring-downs have less data points available for the fit. This should give a noise level increased by a factor of $\tau^{(-3/2)}$ where τ corresponds to the RD time.

We have observed some excess noise on the ring-down time constants for the highest loss points at the peak of the Q13Q13 line that is greater than the expected $\tau^{-3/2}$ dependence, which might be caused by absorption that is not linear in optical power, but we cannot be certain of this explanation at present.

P7, L158: Put also on Figure 1 the residuals when a Voigt profile is used. Moreover, the residuals observed on this figure seem to be due to a frequency shift and not to the limitations of the Galatry model. In the description of the Galatry profile, the authors don't mention the collisional line-shift parameter. Is this parameter taken into account for the calibration procedure? What about line-mixing effect?

P7, L.158: We have now revised Figure 1 considering the reviewer comment as follows:

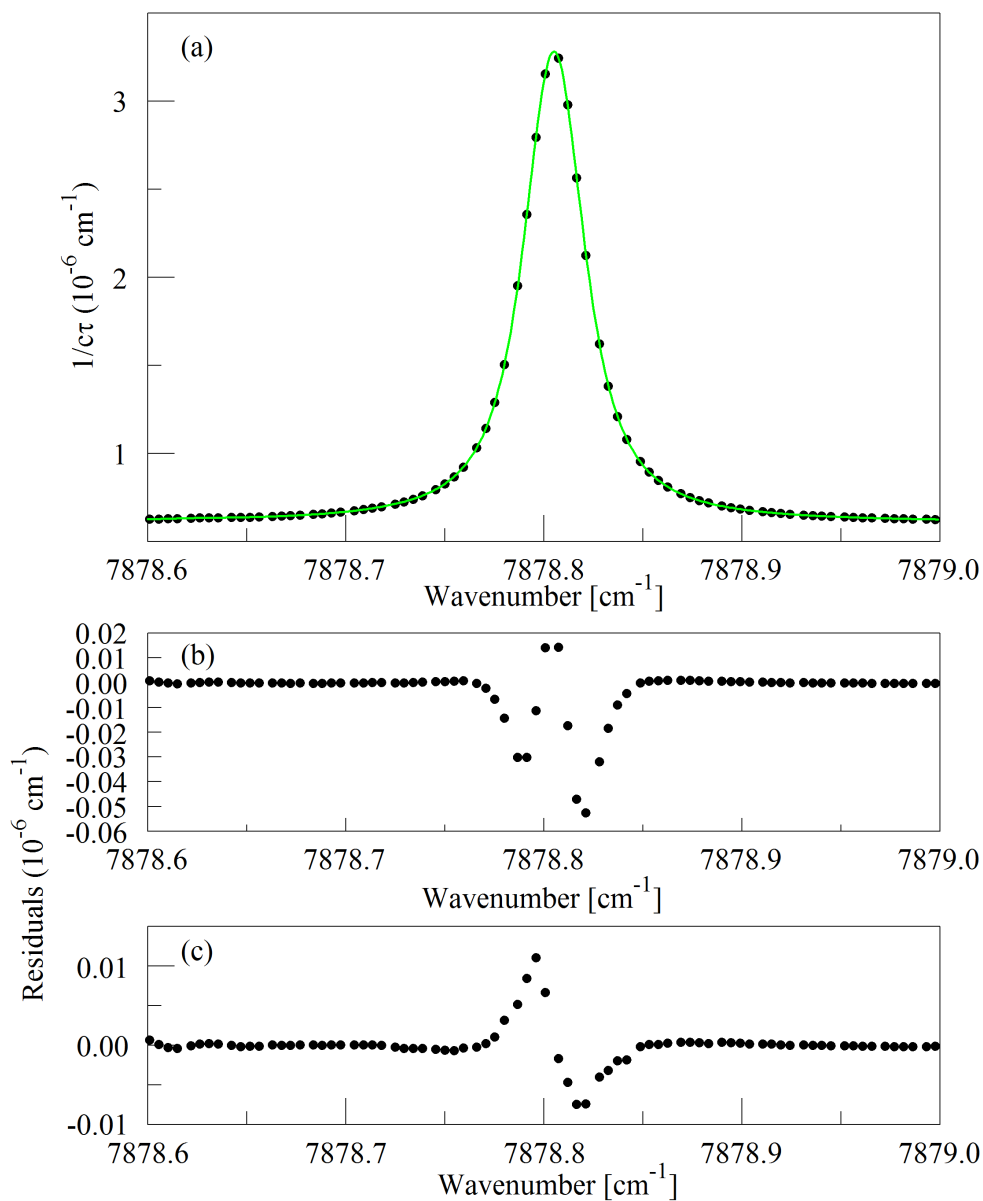


Figure 1. The top panel (a) shows the raw data (points) and the best-fit Galatry function (solid line). Residuals of the Voigt fit are shown in panel (b) and residuals of the Galatry fit are shown in panel (c).

Regarding the additional questions: (1) Yes, we take the collisional line shift into account in our calibration procedure, and (2) it is entirely possible that line mixing affects the line shape, but we are not in the position to say with confidence to what extent it does. This belongs in the class of line shape phenomena that we consider to be outside the scope of our measurement and modeling abilities, but which we also do not think are essential for the operation of the analyzer.

P7, L166: frequency of narrowing collisions should be replaced by velocity change collision rate.
This sentence is now modified accordingly

P7, L167: The authors should be more precise: ... σ_D is the $1/e$ Doppler half-width of the transition...
Corrected accordingly

P8, L169-170: The units of k_B , T , M and c have to be given.

The units of k_B , T , M and c are given as $J.K^{-1}$, K , amu and m/s , are now added to the manuscript

P8, L176: Cite HITRAN2016 instead of HITRAN2013.

We have now removed the citation of HITRAN2013 and added HITRAN2016:

I.E. Gordon et al., The HITRAN2016 molecular spectroscopic database, Journal of Quantitative Spectroscopy & Radiative Transfer (2017), <http://dx.doi.org/10.1016/j.jqsrt.2017.06.038> “

P8, L177: Give the uncertainty reported in HITRAN data base.

We have now added this information as “uncertainty code 4 for γ_{air} corresponding to 10% --20% relative uncertainty”.

P8, L178: Change the reference if required (see my comment above).

Updated to HITRAN 2016

P10, L217-219: Not true for the line near 7878.45 cm^{-1} where the water transition dominates.

We would like to thank the reviewer for pointing out this important point. Indeed, we have not used the latest HITRAN2016 version water spectrum as this statement was derived from HITRAN2012. Hence:

- We added revised Figure 5, with a “stick plot” from Hitran2016 instead of Hitran2012.

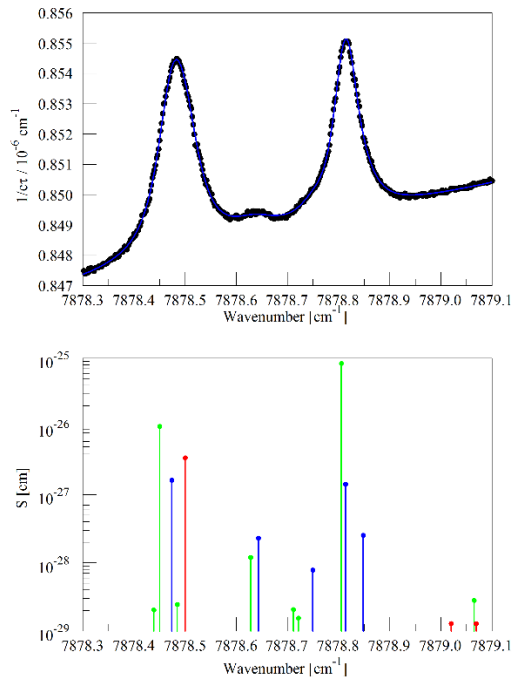


Figure 5. Upper panel: spectrum of water in nitrogen (points) and fit to Voigt model (blue curve). Lower panel: Oxygen (green), normal water (blue), and deuterated water (red) lines in the 2016 Hitran data base.”

- We also replaced the sentence that spans lines 217-219 as “The main features are the Q13Q13 line from trace contamination of oxygen in the sample and several lines that arise from normal water ($^1\text{H}_2^{16}\text{O}$, AFGL abbreviation 161) and deuterated water ($^1\text{H}^2\text{H}^{16}\text{O}$, AFGL abbreviation 162, also abbreviated HDO).”

P10, L219-220: Three lines of HDO are missing in the figure but are present in HITRAN2016.

This is now corrected in the new figure 5.

P10, L222-L224: This is not true as HDO lines are present.

This sentence is also now rewritten as: “The relative intensities of the 161 and 162 lines change with variations in the isotopic composition of the water, but fortunately the direct interference with the oxygen Q13Q13 lines comes entirely from the 161 isotopologue, with the strongest 162 line being separated by approximately 8 line widths (FWHM) from the Q13Q13 line.”

P11, L245: *the z-parameter was constrained to be proportional to y, based on earlier measurements. This is not clear for me. What are these earlier measurements and how they show that? Same remark for line 250.*

We have now changed the words “earlier measurements” on line 245 to “measurements summarized in Figure 2”. This figure shows that to a good approximation y and z are both proportional to pressure and therefore to each other when the pressure changes.

P11, L251-253: How the missing HDO lines will be treated as the HDO isotopic abundance is not determined from the 7817 cm^{-1} window.

P11, L251-253: The text describes what we did. To address this we now added a sentence between the sentence that ends on line 253 and the sentence that begins on line 254 as follows: “This procedure does not account for variations in HDO abundance, which may introduce some systematic error into the water vapor correction for samples of unusual isotopic composition, but it should accurately model the most important lines that interfere with the oxygen measurement.”

P12, L277: *sccm* instead of *scm*.

Corrected accordingly

P13, L299-308: *Maybe adding equations will make this paragraph easier to understand.*

As there are in-line equations that clearly explain that by using the ratio of amplitude to line width rather than amplitude alone we obtain better precision in the determination of O₂ concentration, we do not see the importance of adding additional equations at this section.

P14, L326-329: *What about the water lines in that spectral region (especially the H₂O line near 7881.98 cm⁻¹)?*

We are aware of these lines; they do not interfere strongly, as they are about two full-widths away from the line we measure.

P19, L436: *It is strange that only the last one minute of data was considered to determine the concentration for each standard by CRDS as each standard was flushed during 2 hours before.*

Selection of the last one-minute data done to be consistent with ambient air measurements which are usually switching from one height level to another and between standard cylinders usually within a couple of minutes.

P20, L464: *DAS has to be defined.*

We have now replaced the acronym DAS with “temperature inside the instrument chassis” as DAS seems to be too technical.

P20, L474-478: *It would be very interesting to know the origin of the problem and how the manufacturer solved it. As people from *Picarro* are co-authors of this paper it should be easy to have such information's.*

We have now included a possible hypothesis that could have led to such a drift to this line as follows:

“A possible hypothesis for the cause of the drift can be an optical amplifier in the first system and not anymore included in the design of the product which produced a significant amount of broadband light that could fill the cavity (albeit with a low coupling coefficient), and would ring down with a different (and generally much faster) time constant than the baseline loss of the cavity. However, the ringdown time on the peak of the oxygen line is just 10 microseconds, such that the broadband light might have distorted the single exponential decay of the central laser frequency, leading to the observed drift in the oxygen signal. However, we were not able to confirm this hypothesis.”

P27, L631: *An excellent agreement was observed for measurements from both instruments... Not so easy to check on Figure 18 (see the comment below).*

P27, L634: ...contains large amount of water **and** CO₂ in addition to O₂...

Corrected as mentioned above

Figure 5, lower panel: Add the missing HDO lines (see HITRAN2016). For example the transition $4_{13}-3_{12}$ of the 111-000 band near 7878.500 cm^{-1} has an intensity of $3.47 \times 10^{-27}\text{ cm/molecule}$.

We have now modified Figure 5 as explained above

Figure 14: What is the scale on the left?

It is mmol/mol but uncalibrated values and now added to the Figure as shown below

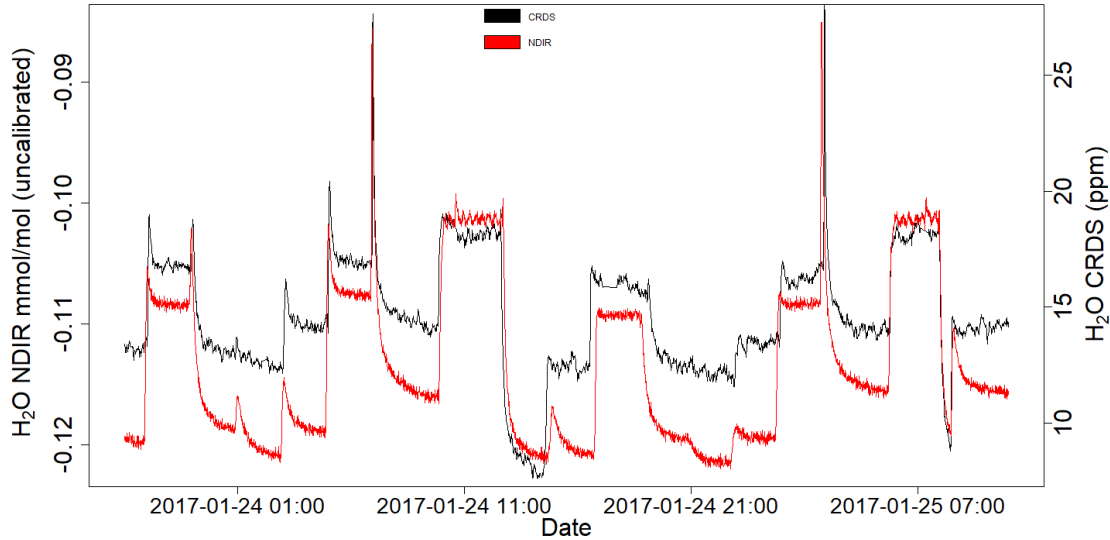


Figure 14. Parallel water vapor measurements for a dried ambient air by both the NDIR and CRDS analyzers. Note that the water values from the NDIR analyzer are not calibrated.

Figure 18: The peaks corresponding to the flasks are not observed at the same time for the CRDS and IRMS. Moreover the delay between both experiments varies from one peak to the other. What is the reason for that? It will be better for comparison purposes to plot the two layers on the same graph.

This difference is simply due to the difference in time stamps from the two analyzers and the two are not plotted in the same figure as the purpose here is to provide a quantitative view of the peak signs. We have now added the time stamps for both plots in the x-axis (figure below).

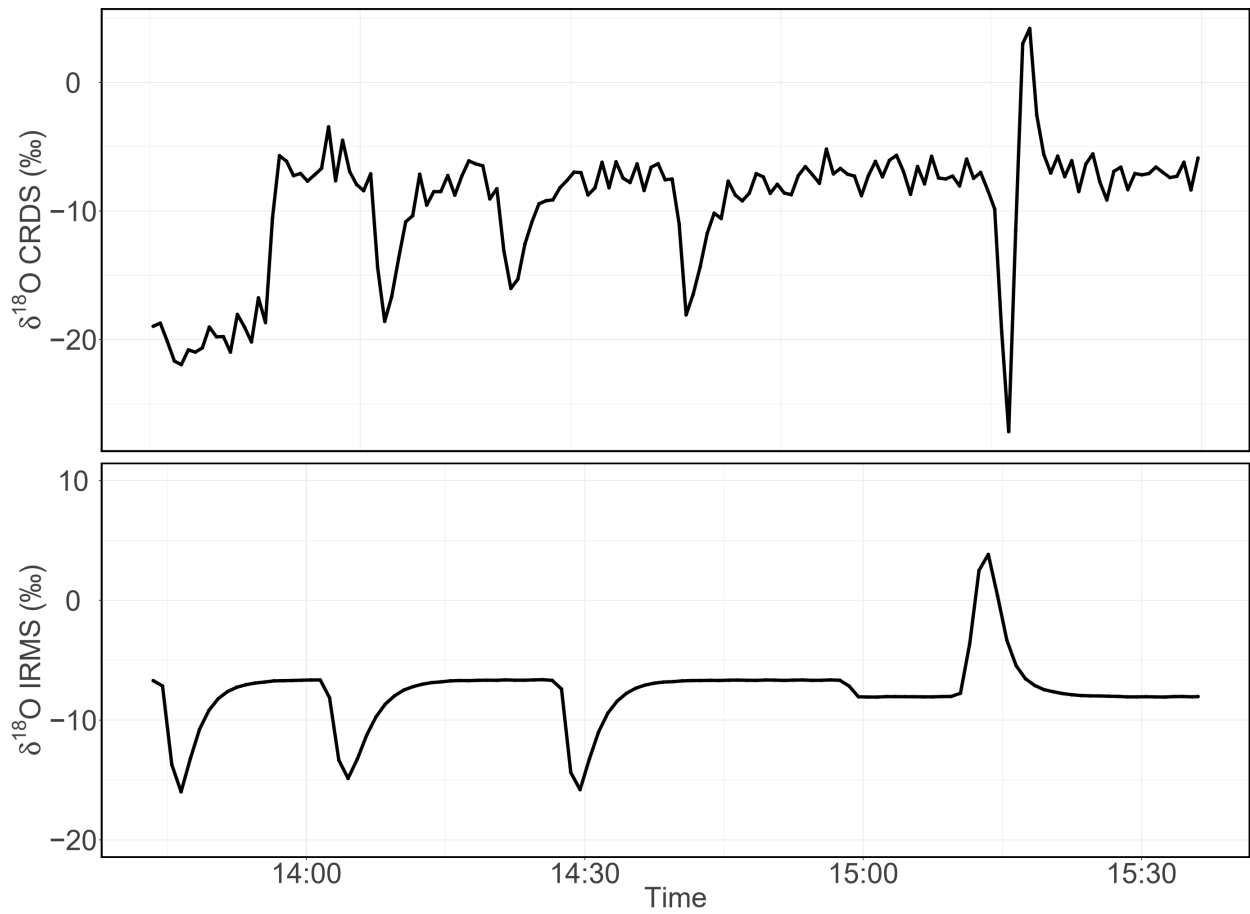


Figure 18. Consecutive $\delta^{18}\text{O}$ measurements of a standard gas (CO_2 -free air) filled into three flasks followed by measurement of breath air using the CRDS analyzer (top) and IRMS (bottom). These measurements were carried out in the middle of ambient air measurements.