Dear editor,

We would like to thank you and the reviewer 3 for their comments. We have been working toward a new version of the manuscript taking their respective comments into account. We include the comments from the reviewers in black, our responses in blue, and the modifications to the manuscript in red in this response file.

All the best,

On the behalf of all the co-authors,

Mathieu Casado

Reviewer #3:

I commend the authors on the form that their manuscript has taken.

All of my comments and concerns have been addressed with the supplied revisions.

There still exist a few grammatical inconsistencies (I will not list them here), however they do not hinder the communication of the scientific concepts and can easily be addressed in the copy editing process.

I look forward to following the future development of this new generation of stable water isotope analyzer.

We thank the reviewer for his comments that helped improve the manuscript. We'll work with the copy editing team to remove the final grammatical inconsistencies.

Reviewer #5:

The clarity of the manuscript is greatly improved, I thank the authors for their efforts.

We thank the reviewer for their comments which improved the manuscript, and we will implement the following comments.

I have a couple of minor comments:

The sensitivity on line 118 should be stated together with the corresponding measurement time.

We added the corresponding measurement time (Line 118):

> "with a sensitivity of $10^{-12}\ cm^{-1}$ after 60 s."

Line 152: the Lamb dip frequency is not a physical constant; it is affected by pressure and power shifts. Rephrase.

This is technically correct. We have modified the text as follow:

> "their frequency, which remains constant for constant conditions of pressure, can be used as a frequency reference."

The use of the lamb dip here is justified by the low values of line pressure shift, about 0.01 cm^{-1}/atm, i.e. 300 MHz/atm, or an absolute shift of 30 kHz @ 0.1 mBar. With reproducible conditions of pressure for each Lamb dip scan (better than 0.01mBar), the precision of the pressure shift is known around 2.5 kHz. We do not mention the power shift, which has not been observed (AC Stark shift). Note than again, the power is kept constant because the ring downs are triggered by a constant value of photodiode power.

Line 234 and on: I still do not understand where one can see what happens after 800 s in Fig. 4c. The longest averaging time there is 2 min, which is 120 s, not 800 s.

This was not strictly linked to Figure 4c but to Figure 4b and 4a. This has been added to the text.

The following paragraph is still incomprehensible:

Line 190: 'We separate the performances of the instrument with first, the precision and the drift of the instrument in the long term, 190 secondthe accuracy of the instrument, includingthe humidity to isotope and isotope to isotope relationships, and finally highlight the results of the frequency auto-referencing on the performances of the instrument.'

We modified the paragraph as follow:

> "We discuss the performances of the instrument with first, the precision and the long-term drift of the instrument; second, the accuracy of the instrument, including the humidity-to-isotope and isotope-to-isotope relationships; and finally by highlighting the impacts of the frequency auto-referencing on the performances of the instrument."

The language is still imprecise at places, and there are some typos:

Line 16: Technics –> techniques

Taken into account

Line 55: ‘to generate very precise absorption spectroscopy’ –> What does ‘generating spectroscopy’ mean?

Replaced by “perform”

Line 105: ‘the power injected to the cavity is amplified to 11 mW to increase the SNR on the photodiode but to ensure that saturation is not affecting the absorption profile of the gas inside the cavity’ –> is ‘but’ correctly used here? Change to ‘while ensuring’?

Taken into account

Line 109: Peltier

Taken into account

Line 120: ‘realising spectra’ –> measuring?

Taken into account

Line 131, caption of Fig 2(a): please keep the nomenclature consistent, high pace – slow pace, or high resolution?

Taken into account

Line 165: It is not clear what ‘aritificial isotopic composition measurement’ means. What is artificial?

Replaced with “biased”

Line 195: what is meant by ‘performances’?

Modified to: “To evaluate the drift in measured isotopic composition associated with the technique directly,”

Line 199: ‘generate water as stable as possible’ –> Do you mean ‘stable water concentration’? Water itself is stable.

Taken into account

Line 240: were, not where

Taken into account

Line 283: what does ‘average out the last 15 minutes’ mean? Was this data used or not?

Modified to: “and included the average value of the last 15 minutes”.

Fig. 6: a and b are missing in panels

Taken into account

Line 310: ‘distance of the spectroscopic measurement to the centre of the absorption feature’ –> detuning?

It can be explained like that, but we already used “detuning” twice before in the same paragraph to discuss when the distance was artificially increased, and so, we prefer this formulation.

Line 322 Lamb dip (also in fig. 8g)

Taken into account

Line 340: Changing the length of the CRDS cavity so the FSR aligns the frequency of the measurement at the top of all the transitions 340 align with the centre of the feature would mitigate a large part of the drift' –> 'the frequency of the measurement' should be the sampling points, and there are too many 'align'in this sentence

Taken into account

Line 435: Comparaison -> comparison

Taken into account

Wrong punctuation: line 19, 63

Taken into account

Plural/singular mixed: line 66, 125, 126, 160, 198, 251, 316, 361

Taken into account

Reviewer #4:

In the revised manuscript, most of the concerns raised by the referees were addressed and implemented leading to an overall improvement of the paper. Therefore, I can recommend this manuscript for publication after some minor corrections are made.

We thank the reviewer for their effort providing advice on our manuscript which greatly improved its quality.

General comments:

The precision of the instrument seems to be limited by the water vapor generation system, because the spectrometer is operated in flow-through (25 sccm) regime. Thus, fluctuations associated to evaporation, desorption effects, etc. contribute to the short and long-term instabilities. Despite of these issues, the authors do not consider the batch mode, i.e. enclosing the gas sample into the optical cavity and measuring the isotope ratio on such static samples. What is the reason for not doing so?

Water is an extremely sticky molecule, the current cavity was electropolished, but no further hydrophobic treatment was set up. In these conditions, the exchanges between the surface of the cavity and the atmosphere would dominate in batch mode. In principle, we could wait long enough that everything is at equilibrium. Yet, the water vapour monitoring that is required for ice core analysis or in-situ field study are always done under flow-through regimes, in part to reduce the exchange with the cavity, even in commercial instruments where hydrophobic silicosteel treatments are applied. Obtaining the performances of the set-up in static (batch mode) regime would not be representative of what could be measured in realistic conditions. Finally, the performances we are currently able to obtain are already one order of magnitude better than commercial instruments.

As the instrument is a laboratory setup, the (Antarctic) air samples have to be transferred to the instrument. A flow-through scheme would obviously means a large gas consumption. The authors should shortly discuss how they will address this issue.

There are several potential uses for this instrument. The current instrument is a proof of concept that will remain in a laboratory. In the lab, it can be used to measure ice core samples, which are routinely measured with a flow-through scheme because of how sticky water is. In this case, to generate 25sccm of air with a humidity level appropriate for measurements requires less than 0.1mL of melted ice. We currently run a dozen commercial analysers working on this principle in our institute alone. For these applications, the water and dry air consumptions are not an issue.

We are currently building the new generation of instrument that will go the field. The goal has never been to bring back canister of Antarctic air back to the institute to be measured. For these applications, we hope that very soon the instruments will be deployed in Antarctica, and as such, the gas consumption will not be an issue.

The spectral interference by CH4, especially at low humidity levels, is not addressed in a satisfactory manner. Just stating that the problem can be simply solved by adding another spectral point does not work, because the spectral separation of the transitions is not equidistant and by no means coincides with the FSR of the cavity. Therefore, the authors should either quantify the expected impact on the accuracy of the H2O isotope ratio or admit that their

reported precision and accuracy only holds for water vapor in synthetic (N2 and O2 mixture) air.

We respectfully disagree. This has already been done in (Chaillot et al., 2023) with a similar experimental setup dedicated to H2S with satisfactory performances. As we are monitoring the exact same transitions that Picarro instruments where the methane concentration is actively fitted using spectral points that are only focusing on the water transitions and not adding dedicated spectral points to aim specifically at the top of the methane transition. We believe that it is a reasonable assumption to estimate that we can do the same by adding spectral points to evaluate the methane concentration. We added a reference to Chaillot et al in the main text:

> "For instance, taking into account the impact of methane absorption features at 7199.95 cm-1 and 7200.03 cm-1 will require adding an extra spectral point for Antarctic field study as the methane absorption should be as strong as the water ones at humidity level around 1 ppmv, following a similar approach than (Chaillot et al., 2023)."

Also, the FSR of the current instrument is 297 MHz, the typical width of a methane transition at 35 mbar is several GHz, so it appears also perfectly reasonable that we would be able to aim at or near the summit of the transition while maintaining a sampling scheme based on the FSR, but the instrument is also able to actively adjust the length of the cavity as detailed in the method, even though it is slower. We could also envision scanning at a different frequency than FSR resolution if absolutely necessary. We believe that this discussion is out of the framework of this manuscript.

Specific comments:

Title: By definition, humidity is the amount of water vapour (the gaseous form of water) in the air. Saying "humidity water vapor" is exceedingly redundant. I suggest: "Reliable water vapour isotopic composition measurements at low humidity using frequency stabilised cavity ring down spectroscopy"

This is a very good point, we modified the title accordingly.

Abstract: "We produced a laboratory-bound infrared spectrometer…" change to "We present a laboratory infrared spectrometer…"

Taken into account

Abstract: "based on all these technics dedicated to measure…" change to "leveraging on these techniques to measure…"

Taken into account

Abstract: "The instrument is additionally not hindered…" change to " The instrument is not hindered… "

Taken into account

Pg1, L17: the "water stable isotope" was correct, the "stable water isotope" is not.

Taken into account

Pg2, L65: replace "in" with "at" Antarctic conditions

Taken into account

Pg3, L71: remove "for laboratory and field monitoring of"

Taken into account

Pg4, L94: the heating is only due to the heating elements, while the PT1000 is to monitor the temperature. Please check phrasing.

Taken into account

Pg5, L114: same here.

We respectfully disagree, we indicated that the cavity is “stabilised”, and the sensors are needed to actively control the temperature.

There are at least 3 different temperatures in the system: the analyser is stabilized at 28°C, the laser source setup at 26°C, while the CRDS cavity at 29°C. What is the reason of not keeping everything at the same temperature?

The CRDS cavity is heated specifically 1°C higher than the analyser to be able to regulate the temperature using only a heating element, because it is much simpler. The laser source is for now external and the temperature was suggested by Schott as good for the Zerodur to have low expansion.

Pg4, L108-110: Please rewrite, e.g.: "As mentioned above, the power injected into the cavity is amplified to 11 mW to increase the SNR on the photodiode, while making sure that no saturation is taking place that may affect the absorption profile of the gas inside the cavity."

Taken into account

Pg5, L126: replace "must be" with "are"

Taken into account

Pg5, L128: add value for the scan duration

Taken into account

Pg5, L129: quantify the far slower

Taken into account

Pg5, L131: "noise on the isotopic composition" should read "fluctuation in the isotopic composition"

Taken into account

Pg5, L133: remove "out"

Taken into account

Pg5, L134: replace "resolution" with "acquisition time"

Taken into account

Pg5, L134: delete "multiple"

Taken into account

Pg8, L176: what do you mean by "artificial isotopic composition measurement"?

Modified to “biased”

Pg8, L177: revise this sentence. If the period is one hour and the system is not measuring for 13 min then the duty-cycle is about 80 %.

Modified to: “The overall duty-cycle here was around 80%, including 13 minutes every hour during which the instrument was not able to monitor isotopic composition”

Pg8, L183: replace "stable water levels" by "stable humidity levels"

Taken into account

Pg8, L184: what is a dry air bottle? Do you mean pressurized-air or synthetic-air cylinder?

Taken into account

Pg9, L210: replace "successive water vapour stable humidity levels" with "successive stable humidity levels"

Taken into account

Pg10, L245: "Reciproquely" is not an English word.

Taken into account

Pg10, L246: replace "Hz" with "s"

Taken into account

Pg12, Fig6: the "several" is actually only two: high and low.

Taken into account

Pg13, L295: "evaluated the precision", most likely you mean accuracy.

Correct, thank you.

Pg13, L297: delete "out" or replace with "for"

Taken into account

Pg16, L355-359: remove this paragraph, because it is highly speculative and practically cannot be achieved. Also the sentence is more confusing than explaining.

We respectfully disagree. This is not speculative; we are currently building a cavity that is 25cm long. We included this so it can help other people who would want to build similar setups, to indicate that the targeted transitions (and their respective distance) should be considered when conceiving things as trivial as the exact length of the measurement cavity.

Pg17, L376: replace "here and based" with "here is based"

Taken into account

Pg17, L382: replace "Relying on relatively cheap, fibered lasers which are commonly build for telecommunication, …" with " Relying on cost effective, fibered telecom lasers"

Taken into account

Pg18, L395: replace "be needed to disentangle the variability coming from the water generation from the one coming from the measurement." with " be needed to disentangle the various contributions"

Taken into account