

Interactive comment on “High precision laser spectrometer for multiple greenhouse gas analysis in 1 mL air from ice core samples” by Bernhard Bereiter et al.

Anonymous Referee #2

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Review of AMT-2020-279 manuscript

General comments:

The work by Bereiter et al. "High precision laser spectrometer for multiple greenhouse gas analysis in 1 mL air from ice core samples", describe the development of a new optical spectrometer for multiple detection of CH₄, N₂O, CO₂ and d¹³CO₂ using a dual-QCL multipass absorption technique. The manuscript is clear and well written, the authors did a good effort on the development as well as on the instrument characterization. This sensor is unique on its kind since it is optimized for small samples size (with the aim of using it for ice core measurements) and include the high precision

C1

measurement of d¹³CO₂ which is key on the study the climate / carbon cycle coupling. I believe that the performance of the spectrometer could have been improved by improving the fit routine, therefore I suggest to the authors to explore this suggestion. This hopefully would not require them to redo the analysis, if they saved data for playing with the fit parameters at posteriori. However, I would say that this is not compulsory since the authors seems to have achieved the target precision on the measurements (although it would further improve the precision, and it would perhaps allow to remove or at least minimize the corrections on the pressure and concentration dependencies). I therefore recommend this manuscript for publication on AMT, after considering the comments below.

Specific comments:

The whole story regarding the absorption line saturation need more discussion in the paper. Authors should mention the optical power in the multipass cell as well as the beam waist. With those two parameters, the optical pathlength and two parameters available from the HITRAN database (the Einstein coefficient and the degeneracy of the excited state) they should be able to estimate the saturation parameter (s), which is the ratio between the intensity (I) used and the saturation intensity (I_{sat}) that is calculated. Then, the difficulty to find the exact saturation effect is due to the fact that it depends on the regime "homogeneous" (Lorentzian broadening dominate) or "inhomogeneous" (Gaussian broadening dominate). But authors could calculate this assuming that at 5 mbar they are in the inhomogeneous regime. Authors should therefore calculate their saturation intensity (I_{sat} in W/cm²) and $s = I/I_{\text{sat}}$, and therefore the effect of saturation on the absorption lines ($1/\sqrt{1+s}$). An s of 0.05, for instance would corresponds to a 2.5% effect on the absorption lines. Then they should check if this value can be in line with an estimation of the amplitude stability of their laser source. (A good reference for saturation spectroscopy is Giusfredi, et al.: Theory of saturated-absorption cavity ring-down: radiocarbon dioxide detection, a case study, J. Opt. Soc. Am. B, 32(10), 2223, doi:10.1364/josab.32.002223, 2015).

C2

L51-52. In the paper you mention about discrete measurements in ice-core and here you mention a continuous extraction system. Please be more consistent on this point. And if possible, please refer to a paper “in preparation” for the extraction technique.

L84-85. In the selection of the absorption lines did authors take into account the temperature dependency of the absorption lines? This should be then discussed in the manuscript.

Figure 2. This wiggled shape in the residual is very large, I think authors should consider using a different line-shape profile which would include Dicke narrowing and perhaps also speed dependence collisional broadening. The intensity of the peak absorption is only 150 times higher than the peak-to-peak on the residual, which is in with the 11 permil precision on a single spectrum. But this also shows that on the $d^{13}CO_2$ precision authors are limited to those wiggles and that they could further improve their measurements. Furthermore, looking at HITRAN2016 simulation the intensities at 5 mbar and 20°C do not seem to have the same intensity as shown here. Is there an error in the HITRAN database? If so, authors could mention it in the paper and say which line has the wrong cross-section and by how much is wrong (based on their gas standard mixtures). Last, they should mention that this is a single scan spectrum (acq. Time 75 μ s). What is the strategy then? How many spectra do the authors average before performing the fit? This should be also mentioned.

L116-119. Please provide the power injected in the MPC. Are authors not annoyed by optical fringes from the ND filter?

L121: how the accuracy on the temperature was measured? With an independent temperature probe? Is this the accuracy of the temperature stabilization or just the precision of the temperature sensor itself? Please specify. This could then be related to the temperature dependency of the absorption lines and to the achieved precision on the $d^{13}CO_2$.

L130-131. What about for the $d^{13}CO_2$? It is weird that authors fixed they required

C3

optical pathlength based on the CH_4 and N_2O required precision rather than on the $d^{13}CO_2$ measurement.

L139. Significantly longer. Could you provide a value?!

L155-156: How can authors simulate the frequency of the optical fringes produced by the multiple passages?! It is just a maximization of the distance between the neighboring spots as mentioned few lines below or is something else?

L203. Critical orifice. Can authors mention the size? Well, in flow measurement this would probably fractionate... please explain.

Table 1. When second digit precision is reported (eg. 0.01) then concentration should be reported with the same number of digits (eg. 248.8x ppm). Did authors monitor their standard mixtures over time? Do they see any drift?

Figure 7. It would be interesting to see the same AW statistical analysis for a static experiment. Can authors add this information? Since the ice core measurements will certainly be done using discrete samples and in static mode, I guess.

L281: This sequence is repeated several times: Can authors provide information about the frequency of those 50 measurements?

L293-294. “Even for discrete samples...”. What do they mean with this sentence? Because for a single discrete measurement the performances are maintained for a time given by the AW analysis, which is shown only a maximum integration time of 16 minutes. What do authors mean with this 24h of continuous operation? Can they prove it with an AW plot?

L311-312: “This two-point calibration...” This is normally not a linear relationship, but rather an exponential with discrepancy becoming larger and larger at low concentrations... It is possible that authors would be able to approximate it to a linear relation in the range of concentrations they will have in the ice cores? Why do authors not just apply different dilution factors to one of their standards to study this effect on

C4

a larger concentration range? Just to mentioned, I see an artefact of 0.94 permil on the working range of 157.7 - 345.5 ppm, which is more the 20 times larger than the claimed accuracy.

Figure 9. So, if I understand well, the difference between the measured and the reference corresponds to the difference between the measurement done by the commercial instruments used for calibrate the standard gas mixtures and your new instrument, is that correct? But you should say what is your approach for your instrument. Do you stick with the intensities provided by HITRAN database or you calibrate the spectrometer with one of the standard bottles? Because if it is the second option, then you should have at least one point which would match well the reference measurement. And what about the $\delta^{13}\text{CO}_2$? Because for that you have to rely on a reference measurement. So I do not get why there is this offset between reference and measurement for all isotopic ratios rather than a crossing point.

L343. "This indicates that. . ." You should explain your approach here. I believe that you leave the Lorentzian contribution on the absorption lines free to adjust with pressure. This should be mentioned in the text. As well as that the concentration in mixing ratio is then corrected for the total gas pressure in the cell. I believe that the artefact you see could be removed (or at least minimized) by changing the fit profile as mentioned above.

L345. Can authors estimate the dependency for $\delta^{13}\text{CO}_2$ around 5 mbar? what precision in pressure is required the 0.04 permil precision and how it compares with your accuracy on the pressure measurement?!

L356: "possibly at value ≥ 5 mbar." Here you should rather report $5 \pm xx$ mbar, with the error estimated in order to stay within the 0.04 permil (comment above).

L370-371: mention that those are 1 sigma precisions.

Technical corrections:

C5

L9. I would rather call it multi-pass absorption rather than direct absorption (or direct multi-pass absorption if authors want to keep the word direct).

L61-80. This part should go to the introduction rather than in the methods. The latter should be focus on the description of the methods.

L108. Mention the photodiode model.

L173. I suggest By applying.

L293: replace "targets" with "target performances"

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C6