

Responses to First Reviewer's Comments

The first reviewer's comments are greatly appreciated. The manuscript will be substantially revised following the reviewer's suggestions. Below are the explanations to the changes will be made in the revised version and the responses to the reviewer's comments.

The manuscript untitled "High precision measurements of nitrous oxide and methane in air with cavity ring-down spectroscopy at 7.6 μ m", AMT 2018-385, presents a Cavity Ring Down Spectrometer (CRDS) dedicated to atmospheric measurements of nitrous oxide and methane at room temperature. A particularity of this setup is that it works in the MIR (7.4-7.8 μ m). Few CRDS setups are currently operating at those wavelengths. The described CRDS setup is claimed having a detection limit of about $7 \cdot 10^{-10}$ cm⁻¹, also, standard deviation on the ring down time is of about 0.03%, which is a standard for CRDS setup. Here are some comments, first part are general comments and second part are technical questions.

General comment: Some English corrections are needed like for example: line 8-10, p 4 "the threshold trigger sends out a triggering signal to shutdown the AOM and a ring-down signal sequence is occurred and recorded by...". "is occurred is not correct.

Reply: The manuscript will be carefully checked for English mistakes.

Some other spots like this one have been detected.

Mistake line 14, p2 "fineness" is "finesse".

Reply: English words will be carefully checked and corrected when necessary.

Please add reference "Long et al, Opt Lett. 2016 Apr 1; 41(7): 1612–1615, doi: [10.1364/OL.41.001612]" line 30 p 2. This work shows the development of MIR CRDS setup.

Reply: This paper will be cited in the revised manuscript.

Specific comments:

Temperature fluctuations: line 26, p 3: why not having picked Invar as material instead of stainless steel? Since the authors are not using frequency stabilisation scheme to correct for frequency drifts due to temperature changes. The cell body thermal expansion generates absolute frequency change of the cavity mode position and small changes of the FSR. This will result in variations in the ring down time. I agree that stainless steel is the standard material for commercial tubing and therefore easier to obtain. But Invar thermal expansion is 17 times smaller than stainless steel and so would be the frequency fluctuations. Using Invar and stabilizing the tube temperature using simple PID setup could de fac to remove the help of processing correction, therefore eliminating additional sources of bias.

Reply: The reviewer's suggestion is certainly a good idea. But, in our case, as described in the second paragraph of section 3 and Fig.4, the effect of temperature fluctuation on the CRDS measurements is mainly caused by the different temperature dependences of the responses of the three PZTs for cavity length modulation as well as the sensitivity of the ring-down time to the

misalignment of the cavity mirrors. The cavity length fluctuation caused by temperature fluctuation via thermal expansion mismatch is negligible as compared to cavity alignment fluctuation. We have put a lot of effort to identify the cause of the temperature effect and are pretty sure about the cause. Therefore in our case the use of Invar is not necessary.

Line 11, p 4: what is the pressure sensor used and then, it's accuracy? Then, what is the impact of the pressure sensor accuracy on the measurement uncertainty? We know that the pressure is one of the principal sources for abundance measurement's accuracy.

Reply: The pressure sensor used in our experiment is a Keller LEX-1. The nominal absolute pressure accuracy is 0.5 mbar. Figure 1 below shows the 1311.4 cm^{-1} spectral intensity change (assume a Voigt spectral profile) of 2ppm CH_4 when the pressure changes from 1000mbar to 999.5mbar (a change of 0.5mbar) calculated from the HITRAN database. The calculation result shows that the spectral measurement error caused by a 0.5mbar pressure error is not significant.

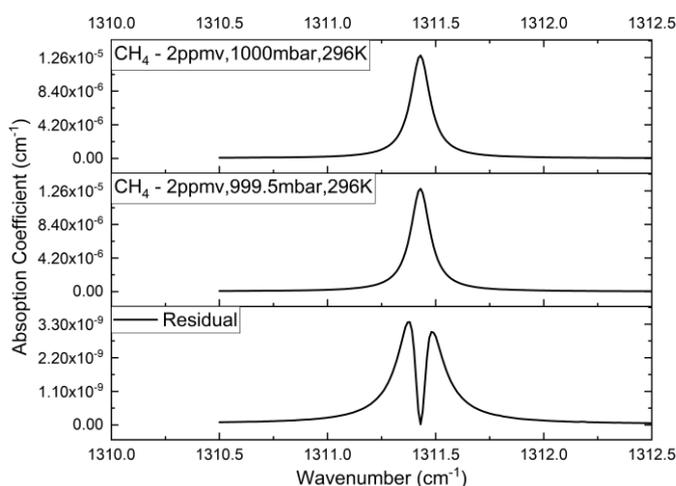


Figure 1. The 1311.4 cm^{-1} spectral line of 2ppm CH_4 at pressure 1000mbar and 999.5mbar, as well as the difference calculated from the HITRAN database.

To respond, the used pressure sensor and its nominal accuracy will be mentioned in the revised manuscript.

Line 18, p 5: The authors say that the cavity is pumped down to 6.4 mbar. Is this the lower pressure reached?

Reply: Yes, 6.4mbar is the lowest pressure reached in our experiment, which is determined by the capacity of the vacuum pump used in the experiment. This point will be mentioned in the revised manuscript.

P7: The authors show that the ring down time is linearly dependent on the offset voltage applied to each of the 3 PZTs used. The time constant change can be as high as 10%... How are the mirrors attached to the cell? Are they glued?

Reply: The mirrors are mounted to the sample cell by screws. The linear relationship between the offset voltage on each PZT and the measured ring-down time is measured when an offset voltage is applied to only one PZT while no offset voltage is applied to the other two PZTs. When CRDS

measurements are performed, the same voltage is synchronously applied to all three PZTs. In this case, the measured ring-down time is nearly independent on the drive voltage, as Fig.2 below shows. [This point will be explained in the revised manuscript.](#)

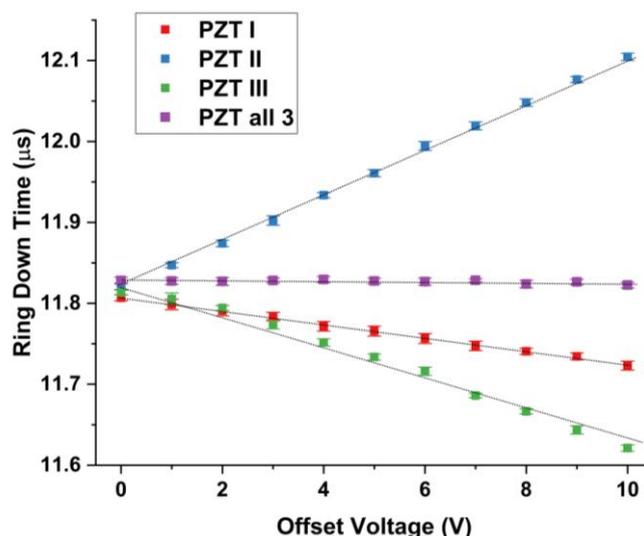


Figure 2. Linear relationship between the offset voltage on each PZTs and on all PZTs synchronously and the measured ring-down time.

Spectra acquisition: The authors do not describe how they jump for one cavity mode to another during spectra acquisition. Do they use wavelength meter for targetting the next TEM₀₀ mode? How stable is the frequency axis of the spectra?

Reply: During CRDS measurements the QCL is operated at a hop-free mode, the nominal line width is <10MHz (in 1s). The wavelength is tuned by a controller of the QCL (via synchronously controlling the tuning grating and the cavity length) with a step of 0.01cm⁻¹. At each step, the length of the ring-down cavity (RDC) is modulated via the PZTs by approximately one FSR (300MHz) so the laser spectral line is in resonance with one RDC mode. However, the wavelength at each RDC mode is not accurately controlled. In our case the maximum wavelength error is less than 0.01 cm⁻¹, determined by the QCL, though the wavelength is stable as the QCL is operated at the hop-free mode, as demonstrated by the low sensitivity limits of CH₄ and N₂O measurements, which are determined by recording the CRDS signals at their spectral line peaks. [This point will be mentioned in the revised manuscript.](#)

Spectra processing: The authors specify that the differences between CH₄ or N₂O measured VMR are due to AOM-induced small change in deflection angle. Then, is this effect systematic? repeatable? How can we identify the true value from the 3 sections? Can the authors provide fit residuals along with spectra (Fig 6)? The measurement differences can also be attributed to spectroscopic uncertainties or on the section B, due to the presence of N₂O line beneath CH₄ lines... Have these options been investigated by the authors? If so, can the author explain what are the conclusions of their investigation?

Reply: The differences between CH₄ or N₂O concentrations measured at different spectral sections are mainly due to AOM-induced change in deflection angle. This effect is systematic and repeatable. As the RDC is aligned at 1310 cm⁻¹, in principle the concentrations obtained from

section B is close to the true values. The reviewer is certainly right that the wavelength uncertainties, spectroscopic uncertainties as well as line mixing are also sources for these differences. It is well known that collisional line mixing can significantly affect absorption spectral shapes, and line mixing cannot be neglected for accurate retrievals of atmospheric CH₄ abundance (Gordon et al., 2017). The fit residuals are added to the spectral fitting and are presented in Fig.3 below.

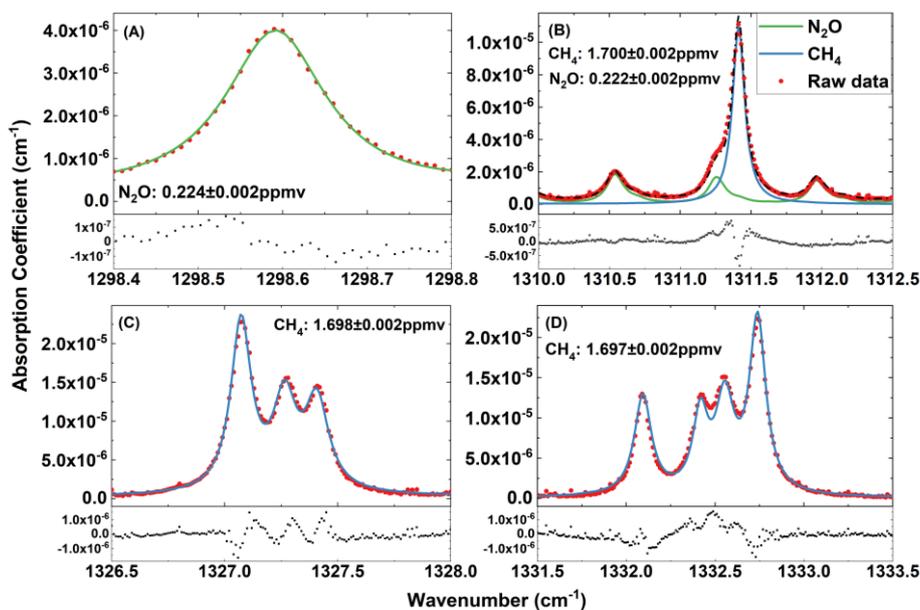


Figure 3. Measured spectra (circles), corresponding best fits (solid lines), and fit residuals (lower figures) for four selected spectral bands, respectively.

From the fit residuals the estimated uncertainties for N₂O concentration are 4.3ppbv from section A and 13.2 ppbv from section B, and for CH₄ concentration are 18.5 ppbv from section B, 18.9 ppbv from section C, and 17.9 ppbv from section D, respectively. These values are higher than 2ppbv determined from repeat measurements due to the large fit residuals appeared around the absorption peaks, which are caused by uncertainties in wavelength, HITRAN spectral line intensity, line mixing, pressure, and temperature, etc. Our calculations indicate wavelength uncertainty and HITRAN spectral line intensity error are the major sources for the large residuals around the absorption peaks. From the residuals departing from the peaks the estimated uncertainties for N₂O concentration become 1.9 ppbv from section A and 3.6 ppbv from section B, and for CH₄ concentration are 2.6 ppbv from section B, 3.8 ppbv from section C, and 3.9 ppbv from section D, respectively. These uncertainty values are comparable to the 2ppbv determined from repeat measurements. As in principle CRDS measures the absolute absorption, the concentration uncertainties obtained from the spectral fit residuals represent the absolute accuracy for the concentration determination, the uncertainties obtained from the repeat spectral measurements represent the relative accuracy, and the uncertainties obtained from Allan variances of repeat measurements at fixed wavelengths represent the measurement sensitivity. From these analyses we estimate the measurement sensitivity, relative accuracy, and absolute accuracy of our experimental setup for CH₄ and N₂O detections in air are around 10-20 pptv, 2 ppbv, and 20 ppbv, respectively. It is worth mentioning that the absolute accuracy can be improved to become

comparable to the relative accuracy by calibrating the measurement with standard “known” sample of concentration in ppb level.

In the revised manuscript, the spectral fit residuals will be added to the spectral measurement figure (Fig. 6 in the original manuscript). The influence of wavelength uncertainties, spectroscopic uncertainties and line mixing on the measurement accuracy will be discussed in details.