

Responses to Second Reviewer's Comments

The second 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 presents a QCL-based CRDS instrument developed for ambient N₂O and CH₄ analysis. A moderate sensitivity of 7E-10 cm⁻¹ was obtained. A detection limit of 18 and 14 pptv respectively for CH₄ and N₂O was claimed with an averaging time of about 20 seconds.

I have several comments on the methods and results given in the manuscript.

(1) I am not convinced on the method used to suppress the temperature fluctuation. The authors did not give a direct correction of the data according to the temperature (there is no simple quantitative relation between them), but simply cut off the low frequency components in the FFT signal of the data shown in Fig.2d, which leads to a more stable baseline in Fig.2c. The effect was "proved" to be useful as the Allan deviation (note that variance is the square of the deviation) shown in Fig.3. The new minimum in the Allan deviation appears at around n=3000 (t=400s), being consistent to the cut-off frequency of about 0.002Hz shown in Fig.2f. Is such a method applicable in a real measurement if the user does not know the exact value he/she is measuring? To any noisy spectrum, one can "remove" the low-frequency noise and "improve" the performance in respective Allan deviation. I cannot see the value of this method. At least the data presented in this manuscript is not enough to support the effectiveness of the method.

Reply: We agree with the reviewer. The original thought was that we experimentally observed a correlation between the ring-down time fluctuation and the temperature fluctuation and we wanted to eliminate the effect of temperature fluctuation on the spectroscopic measurement. Cutting off the low frequency components in the FFT spectrum is an easy to eliminate the effect of temperature fluctuation, which is within the low frequency range. But as the reviewer points out, the effects of other low frequency components are also simultaneously eliminated. After careful thinking, we believe subtracting the FFT spectrum of the temperature fluctuation in the FFT spectrum of the ring-down time should be more appropriate if the temperature fluctuation is periodical, as is in our case. The results are presented in Fig.1 below. Both FFT spectra are normalized to the frequency components with the maximum amplitudes, which appears at the main frequency of the temperature fluctuation. This is reasonable if at the frequency of the temperature fluctuation, the contributions of other factors to the fluctuation of the ring-down time are negligible as compared to that of the temperature fluctuation. From the results presented in Fig. 2 below, the improvement obtained with the subtracting method is comparable to that obtained by simply cutting off the low frequency components of the FFT spectrum as we did in our original manuscript. **In the revised manuscript, the cutting off method will be replaced by the subtracting method, and all results related to the elimination of the effect of temperature fluctuation will be re-calculated.**

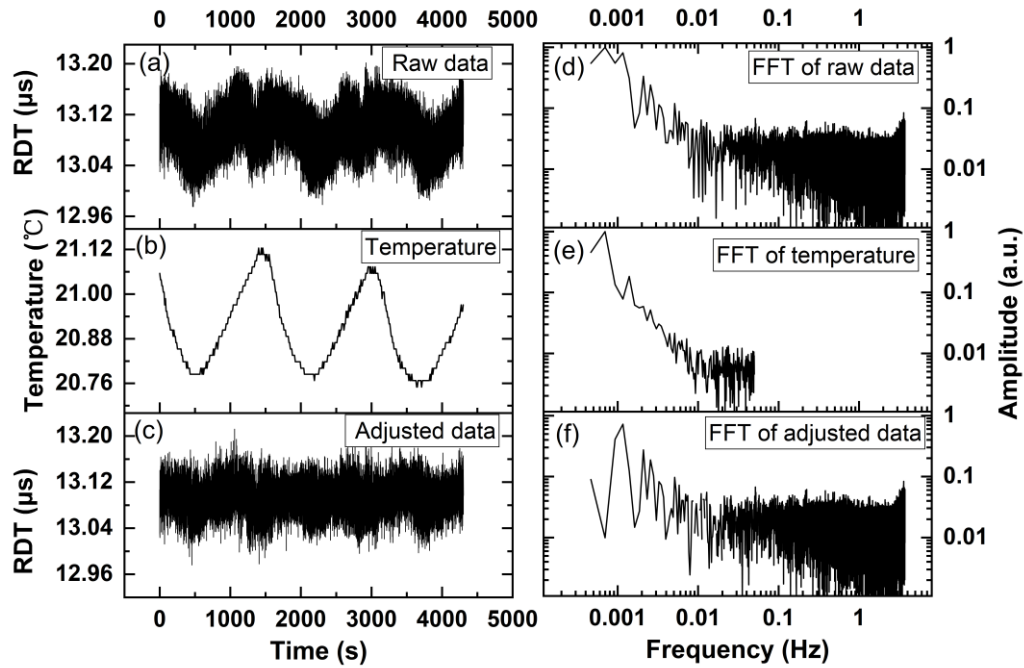


Figure 1. The “empty” ring-down time sequence recorded in a long time period (over 1 hour) and (d) corresponding FFT spectrum. (b) The synchronously recorded temperature in the laboratory room and (e) corresponding FFT spectrum. (c) The “empty” ring-down time sequence after the temperature effect is eliminated with the subtracting method and (f) corresponding FFT spectrum.

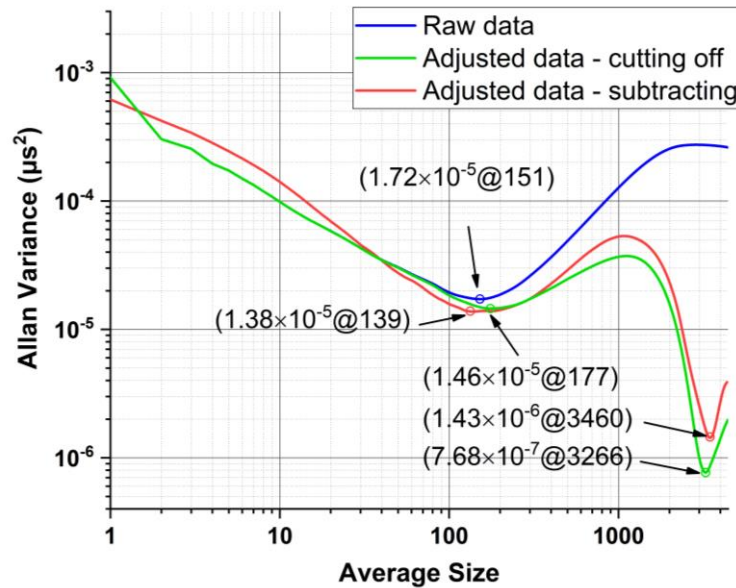


Figure 2. Allan variance plot of raw and adjusted data (temperature effect correction with the cutting off method and the subtracting method).

Worthy mentioning that even though this subtracting method may be not the most appropriate one to eliminate the effect of temperature fluctuation, it is practical in our case as only the temperature fluctuation at the detection site needs to be monitored.

In principle, the effect of temperature fluctuation can be eliminated by establishing a quantitative

relation between the temperature and the ring-down time. We also tried this method and the results are presented in Fig.3 below. Taking into account the difference of the temperature influence on the ring-down time during temperature rising and dropping periods, the data of temperature rising and dropping are fitted with third-order polynomials, respectively, and quantitative relations are established for the rising and dropping periods, respectively. Then, the ring-down time sequence is adjusted with the quantitative relations to the average temperature of 20.9 C. With this method, the absorption coefficient sensitivity limit α_{\min} is improved to $7.0 \times 10^{-11} \text{ cm}^{-1}$, with the optimal averaging number changes to 1594. It is indicated that better results are obtained with this quantitative relation method than with the subtracting method. This method is applicable if a simple quantitative relation between the temperature and ring-down time exists and is measurable. In our case, such quantitative relation is so complicated that makes this method not practical.

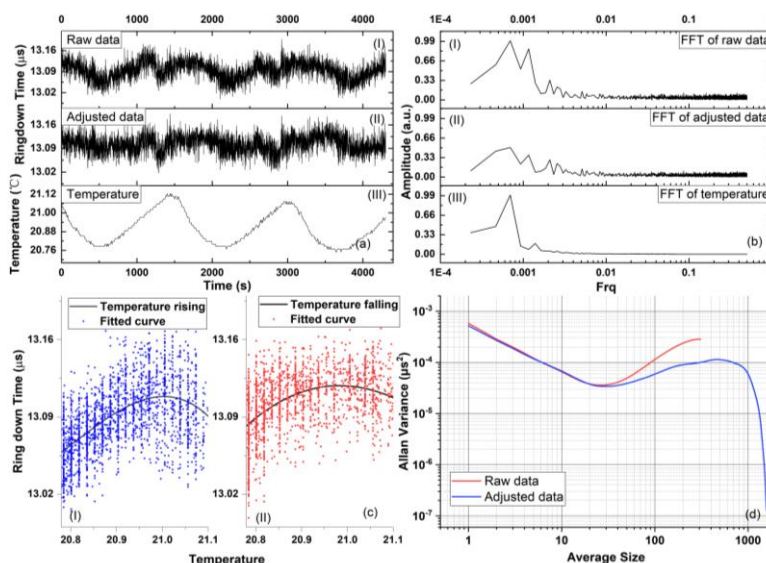


Figure 3. Temperature effect correction by establishing a relation between the measured ring-down time and the temperature. (a) The “empty” ring-down time and temperature recorded over 1 hour and (b) corresponding FFT spectrum. The temperature-corrected data and FFT spectrum are also presented. (c) The correlation between the ring-down time and the temperature. (d) Allan variances.

We would like to mention that the effect of temperature fluctuation can be eliminated only if such effect can be measured and well described mathematically in some way. In some cases the effect of temperature fluctuation is very complicated and cannot be described mathematically, therefore cannot be eliminated. [This point will be mentioned and more discussion on the methods of data processing for temperature effect correction will be presented in the revised manuscript.](#)

(2) The present manuscript is lack of quantitative analysis. A very high precision in the abundance was given, about 0.12% in the CH₄ concentration shown in Fig.6. As far as the authors have shown in this manuscript, the absolute value of the gas concentration was not calibrated using standard/known samples. Many factors need to be clarified: How accurate is the pressure gauge (company stated value is over 1mBar)? Note the line strength data in the HITRAN database also has limited accuracy (typically 1%). Has the correction due to temperature change been included? Note that the values given in HITRAN is that at 296K. Corrections (ideal gas, population on the lower state, etc) are needed since the measurements were taken at different temperatures (and drifting!). The concentration derived from the fit of the spectrum is also dependent on the line

profile used in the fitting. The profile (I guess Voigt) and the parameters used in the fitting should be explained explicitly for such a highly accurate measurement. Note the accuracy of the original parameters for these transitions.

Reply: the reviewer is certainly right. From the viewpoint of testing instrument development, the absolute accuracy should be given by calibrating the experimental setup with standard “known” samples of comparable concentrations. Unfortunately, due to the difficulty to prepare “standard” gas mixture with known concentrations in ppb level locally, the calibration is not performed (A standard “known” sample with the lowest concentration of 1 ppmv and relative uncertainty of 2% (± 20 ppbv) could be prepared by Messer Group GmbH, which is not good for our calibration purpose). Even though CRDS is in principle an absolute measurement technique therefore the CRDS-reported concentration values should represent the true values, many factors as mentioned by the reviewer affect the absolute accuracy of the measurement results. In our manuscript, the reported uncertainties of the concentration measurements are the standard deviations of multiple measurements, which represent the repeatability or the relative accuracy, not the absolute accuracy of the measurements. On the other hand, the absolute accuracy can be much improved by a calibration procedure. As the focus of our manuscript is mainly the high measurement sensitivity, not the absolute measurement accuracy, we hope it is acceptable.

To respond, in the revised manuscript, we will also present the concentration uncertainties determined from the spectral fit residuals between the measured and HITRAN spectra, which we believe represent the absolute measurement accuracy. We will discuss the sensitivity limit, relative accuracy, and absolute accuracy in details to address the accuracy issue from the Allan variances of repeat measurements at fixed wavelengths, uncertainties determined by repeat spectral measurements, and uncertainties determined from fit residuals between measured and HITRAN spectra.

(3) How the laser frequency is calibrated in this study? Is it good enough to support a quantitative analysis with 0.1% precision? Note that the typical line width is about 0.1cm^{-1} , I would say, a frequency precision better than 0.001cm^{-1} (30MHz) is the minimum requirement for a measurement with 0.1% accuracy.

Reply: The absolute frequency of the laser is not calibrated, but linearly shifted to match the spectral lines of the target gas when performing the spectral fitting. The QCL is operated at a hop-free mode with a nominal line width $<10\text{MHz}$ (in 1s). The frequency is tuned by the 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) to make the laser spectral line in resonance with one RDC mode. However, the frequency at each RDC mode is not accurately controlled. In our case the maximum frequency error should be $<0.01\text{cm}^{-1}$, determined by the QCL. Due to the influence of frequency error and spectral intensity error, the precision will be around 1%. The reported 0.1% precision is the result of repeat measurements, represents a relative precision. This point will be mentioned and the influence of frequency error on the measurement accuracy will be discussed in details in the revised manuscript.

(4) It is interesting that the PZT voltage has a considerable impact on the ring-down time: Fig.4 shows a change of about 2%. Since different PZT voltage was applied to match the cavity length with the laser frequency, the voltage (and consequently the ring-down time) would be changing during the frequency scan. How this effect was included in the determination of the $\text{N}_2\text{O}/\text{CH}_4$

concentrations?

Reply: 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 independent on the drive voltage, as Fig.4 below shows. [This point will be explained in the revised manuscript.](#)

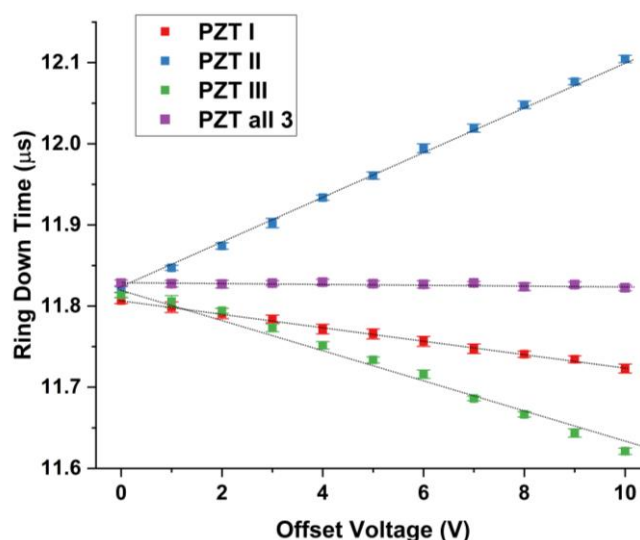


Figure 4. Linear relationship between the offset voltage on each PZTs and on all PZTs simultaneously and the measured ring-down time.

(5) The measurements shown in the study are all for samples with concentrations at the 1ppmv level, which does not support (or not enough) the 10 pptv sensitivity claimed in the manuscript. Perhaps a measurement using standard samples with much lower concentration (<10 ppbv) would be helpful.

Reply: the reviewer is certainly right. The difficulty for us is to obtain “standard” gas mixture with known concentrations in ppb level locally. The best we can get is a standard “known” sample with a concentration of 1 ppmv and relative uncertainty of 2% (± 20 ppbv) prepared by Messer Group GmbH. On the other hand, 10 pptv is the measurement sensitivity, which is mainly determined by the instrument’s response to small change in absorption of the gas under test and is usually obtained by the standard deviation of multiple measurements. [In the revised manuscript, we will discuss the sensitivity limit, relative accuracy, and absolute accuracy in details to address the accuracy issue. Our experimental setup shows a low sensitivity limit and a high relative accuracy due to the high stability of the setup, but a relatively low absolute accuracy due to the wavelength uncertainty, spectral intensity error, pressure error, etc. and lack of calibration with standard samples. The absolute accuracy can be much improved by calibration, which will normally be performed for real applications. Please also refer to our reply to comment \(2\).](#)