

Responses to Third Reviewer's Comments

The third 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 author's present a cavity ringdown spectrometer operating in the mid-infrared for measurement of CH₄ and N₂O. Applications for urban air and breath analysis were demonstrated. Detection limits presented for temperature-corrected measurements of target species are lower than values previously reported for MIR-CRDS in this wavelength region in literature or commercially available.

Specific Comments:

1) A more detailed discussion of the drying procedure and the impact of water vapor on the data is necessary. It would be beneficial to provide data before and after the drying procedure and to discuss in detail how data could be influenced by water vapor (in the various spectral regions discussed here), if it is not successfully removed. Does the data analysis approach look for interferences and flag spectra if necessary?

Reply: Due to the strong absorption of water vapor in the MIR spectral range, the water vapor has to be largely removed from the target gas. Otherwise no CRDS signals can be observed in the whole laser spectral range. Figure 1 below shows the calculated HITRAN spectra of CH₄, N₂O and H₂O at 1 atm pressure and 296K temperature. The assumed concentrations are CH₄: 2ppmv, N₂O: 0.3ppmv, and H₂O: 1.39% (no drying at 296K, 50% RH) and 10 ppmv (after drying. In our experiment <1ppmv is reached).

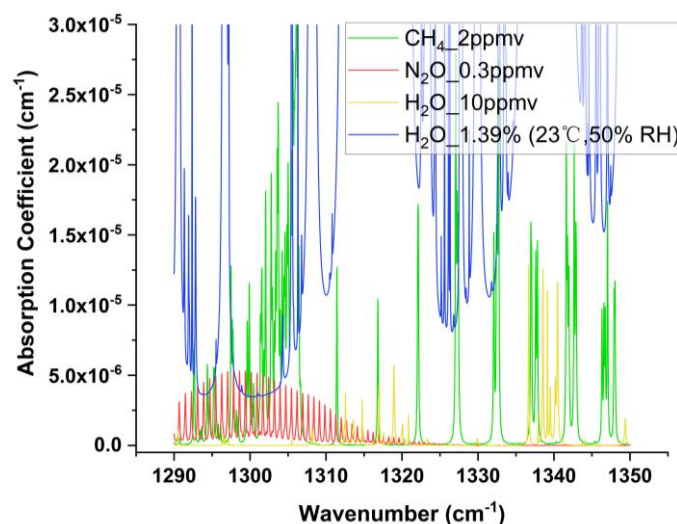


Figure 1. HITRAN spectra of 0.3ppmv N₂O, 2.0ppmv CH₄ and 1.39% and 10ppmv H₂O in the spectral range from 1290 cm⁻¹ to 1350 cm⁻¹ at 1 atm pressure and 296K temperature.

When the water vapor is largely removed from the sample cell, for example when its concentration becomes below 10 ppmv, its influence on the measurements of CH₄ and N₂O becomes negligible,

as Fig.2 below shows. In our case, the residual water vapor after drying is below 1 ppmv. The drying method we used can keep the water vapor below 1 ppmv in the sample cell for several months. On the other hand, the spectral line of 1312.5 cm^{-1} of the water vapor, as presented in section B, can be used to monitor the water vapor concentration if necessary.

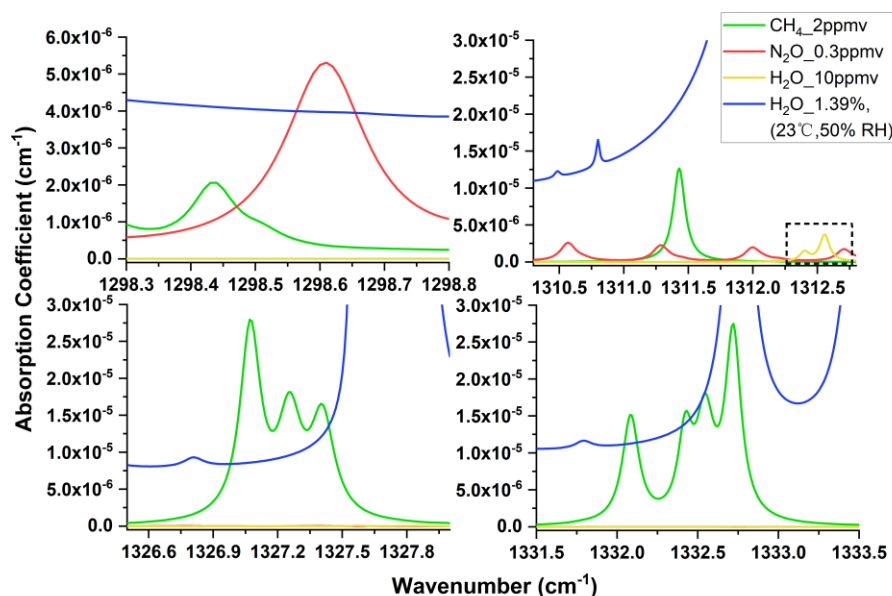


Figure 2. HITRAN spectra of N_2O , CH_4 and H_2O in the four spectral sections A, B, C, and D at 1 atm pressure and 296K temperature.

To respond, a more detailed discussion of the drying procedure and the impact of water vapor on the data will be given in the revised manuscript.

2) Additionally, providing more information regarding the protocol for human breath analysis would be beneficial. Some questions that come to mind: what volume of sample is required to fill the cavity and how long must a participant exhale to achieve this sample volume?

Reply: In our experiment, the exhaled breath air is first collected with a 3L sampling bag, which can be fully filled with only one deep breath of a participant. The filled sampling bag is then connected to the sample cell via a valve. The sample cell is first vacuumed by the vacuum pump and then filled with the exhaled air by opening the valve. This procedure is repeated two times for a complete replacement of gas in the sample cell by the exhaled air. As the volume of the sample cell is around 0.5L, the exhaled air of the 3L sampling bag is sufficient for exhaled air measurement. These details will be described in the revised manuscript.

3) Page 11, Line 13: Since you show that the temperature correction improves your overall detection limit, why wouldn't you implement the corrections for all scenarios? Although you indicate the system achieves sensitivity necessary without correcting for temperature fluctuations, it would be useful to state if there is a quantitative difference between uncorrected and corrected data under all experimental conditions.

Reply: In general, we agree with the reviewer. The purpose of presenting the temperature correction is to show in some cases the effect of temperature fluctuation on CRDS measurement

is significant and needs to be taken into consideration. We do not implement temperature correction when performing the spectral measurements to determine the concentrations of CH₄ and N₂O in air for the following reasons: (1) In our experiment the temperature fluctuation induced uncertainty of absorption measurement is below 10⁻⁸ cm⁻¹, which is well below the fitting residuals between measured and HITRAN spectra, makes the correction unnecessary, as there will be no quantitative difference between uncorrected and corrected data under our experimental conditions. (2) When spectrum measurement is performed, the effect of temperature fluctuation on the measurement becomes more complicated that makes the correction more difficult. For these reasons, we prefer not to implement the temperature corrections for the spectral concentration measurements. Hope this is acceptable.

4) When making assumptions or inferences regarding the cause related to your observations, include supporting literature. Two points stick out as needing further explanation or support: page 10, line 8 regarding the effect of rain on N₂O retrievals and page 11, line 4 pertaining to ventilation system impacts on N₂O.

Reply: The reviewer is absolutely right. Those assumptions without supporting literature will be deleted in the revised manuscript.

Technical Corrections:

There are numerous grammar errors throughout the paper that need to be addressed. A few are listed here:

- 1) Page 2, Lines 4 and 9: Remove “On the other hand”
- 2) Page 2, Line 27: Remove “in” after 16 _W
- 3) Page 3, Line 5: The word “details” should be corrected to read “detail.”
- 4) Page 3, Line 12: The word “agreements” should be corrected to read “agreement.”
- 5) Page 4, Line 9: The phrase “is occurred and recorded” should be corrected to read “occurs and is recorded.”
- 6) Page 5, Line 29: Consider rewording this sentence

Reply: These grammar errors will be corrected in the revised manuscript.

In addition to grammar, consider the following structural changes:

- 1) Adding subheadings within the results and discussion section
- 2) Page 8, Line 20 to Page 9, Line 5: Consider using a table to describe the spectral regions. It would be easier for the reader to digest.

Reply: these two suggestions will be followed in the revised manuscript.