Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2018-385-RC2, 2018

Atmospheric Measurement Techniques Discussions

Interactive comment on "High-precision measurements of nitrous oxide and methane in air with cavity ring-down spectroscopy at 7.6 µm" *by* Jing Tang et al.

Shuiming (Referee)

smhu@ustc.edu.cn

Received and published: 12 December 2018

The manuscript presents a QCL-based CRDS instrument developed for ambient N2O and CH4 analysis. A moderate sensitivity of 7E-10cm-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

Printer-friendly version

Discussion paper

(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.

(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.

(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.

(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 N2O/CH4 concentrations?

(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.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2018-385, 2018.

Printer-friendly version

Discussion paper