

In response to the Associate Editors comments from February the 14th, 2019.

Dear Authors, Thank you for your detailed and authoritative responses to the referees' comments. I have carefully reread your well-written paper that certainly merits publication in AMT. At this stage, there are some very minor and technical issues remaining, which should be addressed before publication. Please find these listed below.

5 Dear Associate Editor,

Thank you very much for your detailed corrections and the careful look over the manuscript. We greatly appreciate your help with this paper. The technical corrections have been implemented in a revised version of the manuscript.

Minor corrections:

(page and line numbers refer to the manuscript version that keeps track of revision changes)

10 1. **Some company names appear in capital letters, others do not. It seems preferable to keep a common format. I suggest capitalizing only the first letter in company names, which is an easier read, especially for long names.**

We have tried to keep everything in a common format now.

15 **In the same veins, there is excessive use of the brand name to denote the CRDS analysers, but other instruments such as the modified QCLS/ICLs instrument are not presented by insisting on the original brand each time. This poses the risk of inadvertent advertising of one particular instrument as compared to others and hinders easy understanding for people outside the field. In general, it is preferable to use brand/model names only when instruments are presented for the first time and when required for the understanding. Otherwise instruments should be referred to by their operational principle or instrument function (eg "hygrometer" instead of "Sensirion", etc.). Please modify Figures 10, 11, 12, 13 and the text accordingly.**

20 We have modified the text and the figures as suggested.

2. **The typesetting guidelines of Copernicus journals require a space between quantity and unit. This also applies to dimensionless units such as the % sign (ie 78 % instead of 78%, ...).**

We hope to have modified the text accordingly at all occurrences of values/units.

25 3. **p 7, l 17-18 : " ... CH4 (Cert.-Nr. CB11361, WMO X2004A for CH4 (Dlugokencky et al., 2005)). C2H6, CO and N2O are compared to NOAA ..." -> CO2 is missing in the list even though it is mentioned later on in chapter 5, p 17. Please complete the list.**

CO₂ has been added to the list.

30 4. **p 16, Fig 8 and discussion of frequency lock : There is a regular spike pattern in Fig 8 with a period of about 30/6 5 min. This supports the hypothesis that shifts are not only caused by mere laser drifts, but are also caused by some well-timed mechanism. It is not clear whether this is meant by "high-frequency shifts are evident, including discontinuities". The discussion of the spikes could be added to the discussion on p 16.**

We have included the missing reason for these well-timed spikes. These are due to switching over from calibration to sample gas.

35 5. **p 22, l 20-21 and p 23 Fig 13 : According to the figures, the QCLS-CRDS and the QCLS-FLASK comparison shows a good agreement in relative deviations, except for CH4, where QCLS-CRDS gives a 1-sigma of 1.4 ppb, but the flask comparison seems to give a different number (1-sigma = 3.9 ppb (n=40)). This needs to be commented.**

This could be due to different sampling times of the fast QCLS and CRDS observations compared to the slow flasks. We have added this in the main text.

40 6. **p 21, l 12+, discussion 13CO2 measurement : "We estimate the required isotopic composition that could explain a large bias of up to 17 ppm (see Supplement Section 3) in CO2 to be 98.447% primary isotopologue and 1.079% secondary isotopologue or $\delta^{13}C = -19.6\text{‰}$ which seems reasonable according to B. Coplen et al. (2002)." This**

statement seems to be in direct conflict with the Supplement, where it is derived that d13C must be -37 ‰ to have an impact of 17.2 ppm. Please correct and be more detailed about the -19.6 ‰ and your calibration procedure that should be crucial in inferring a particular isotope composition.

Thank you for pointing us towards this error. The derivation in the Supplement is correct. Here, we wanted to refer to the 10ppm bias found in this study.

The discussions in the main text and in the supplement also merit clarification. In particular, the definition of x_retrieved remains dubious, as remains the meaning of "possible influence estimate". It might help to differentiate between two effects of opposite sign : HITRAN conventions (a -5 ppm effect when measuring background air CO2) and the systematic bias that could play a role here (up to about +12 ppm). HITRAN assumes 13C isotope abundances of VPDB (d13C = 0) to derive line intensities, and, for the purpose of demonstration, one assumes that these are correct. When we then measure CO2 as 13CO2 we can use the rule of thumb that a relative change of 13C will translate into a relative change of CO2 even if the concentration of CO2 remains unchanged (less 13C leads to less CO2 measured and higher 13C leads to higher values of CO2). This means that the QCL measurement of air with d13C = -9.7 ‰ leads to CO2 that is roughly 1 ‰ (or 4 ppm at 400 ppm CO2) too low (effect of -4 ppm). A positive offset of +10 ppm can only be obtained if the instrument is calibrated with a gas of d13C = -40 ‰. This seems to be reasonable provided the tank CO2 derives from fossil fuel. Air, which has a d13C that is higher than fossil fuel CO2 by 30 ‰ will yield a $0.03 * 400 \text{ ppm} = +12 \text{ ppm}$ higher CO2 abundance. Note also that line 15 on p 3 of the Supplement wrongly refers to methane.

We tried to change the wording of x_retrieved and "possible influence estimate". To our knowledge HITRAN does not assume 13C isotope abundances of VDPB, instead the natural terrestrial abundances used in HITRAN which are available on the official website are used. Unfortunately we do not quite understand the derivation given above. We tried to give a detailed derivation in the supplement, that we think is complete as is.

To which degree has the 13C isotopic composition of CO2 to be known to reach WMO compatibility ?

The requested info has been appended to the supplement.

25 Technical corrections:

(page and line numbers refer to the manuscript version that keeps track of revision changes)

1. **p 1, title** : use subscripts in chemical formulae
Changed accordingly.
2. **p 1, abstract** : "... and central US." -> "... and central US." (note you use USA without full stops later on)
Changed accordingly.
3. **p 3, l 5** : "since the pre-industrial era, where ..." -> consider replacing "where" by "and"
Changed accordingly.
4. **p 3, l 11** : "Aircraft provide ..." -> "Aircrafts provide" (eventually "aircraft provides")
We refer to the plural of Aircraft here. We think it should be Aircraft not Aircrafts.
5. **p 4, l 25** : consider replacing "... required to operate the instrument on research aircraft." by "... required to operate the instrument on a research aircraft."
Changed accordingly.
6. **p 4, l 27** : "The spectrometer is split into an electronics compartment and an optics compartment." -> "The spectrometer is split into an electronics and an optics compartment."
Changed accordingly.
7. **p 4, l 28** : "... , etc.." -> "... , etc."

8. **p 5, l 3** : "... , etc.." -> "... , etc."
Changed accordingly.
9. **p 6, l 2** : "every half of a second." -> "twice per second."
Changed accordingly.
- 5 10. **p 6, l 17** : "... avoiding injecting large vibrations into the ..." -> "... reducing vibrations of the ..."
Changed accordingly.
11. **p 6, l 18** : "This translates to a net flow rate of 25 SLPM". Different entities use different standard conditions (IUPAC, NIST, EPA ...) SLPM is therefore not a well defined unit. It would help to recall "your" standard conditions here (just once in the text). Even better, you could (just once) give the molar flow rate in mole/s here. Note that since 1982 IUPAC defines T = 273.15 K and p = 100 kPa as standard conditions.
10 Changed accordingly.
12. **p 6, l 19** : "when operating with a cell pressure" -> "when operating at a cell pressure"
Changed accordingly.
13. **p 7, l 3** : "Polytetraflouroethylene" -> "polytetraflouroethylene"
15 Changed accordingly.
14. **p 7, l 16** : "cross-calibrated using a Picarro CRDS against NOAA standards" -> "cross-calibrated against NOAA standards using a CRDS "
Changed accordingly.
15. **p 7, l 24** : "Typical calibration distribution diagrams ..." sounds like a technical term. It could be easier to understand using "Histograms of typical calibration measurements are provided ..."
20 Changed accordingly.
16. **p 8, legend Fig 2** : A letter "H" appears in the drawing, which is not explained in the Fig legend.
Removed clipping of information on this figure
17. **p 10, legend Fig 4** : change all chemical names to small letters, add axis title to x-axis. What is the difference between quantities and units used on the y-axis in this and in the previous (Fig 3) figure ? Shouldn't they have same names and spellings ? Since "adu" does not refer to a proper name, it should be spelled using small letters.
25 Changed accordingly.
18. **p 11, legends and axis labels Fig 5** : font size is too small
Changed accordingly.
- 30 19. **p 11, Fig 5, y-axis label** : The plot does not show the optical depth but the transmittance
Changed accordingly.
20. **p 11, Fig 5, graph labels** : replace "microwindow" by "fit window"
Changed accordingly.
21. **p 11, l 6** : "... shift variables are held constant at the mean over its last 10 values." -> "... shift variables are held constant at their means over the last ten values."
35 Changed accordingly.
22. **p 13, l 6** : "Eq. (1)" instead of "Eq. 1"
Changed accordingly.
- 40 23. **p 13, Table 1** : Broadening coefficient (γ_{air})
Changed accordingly.

24. **p 15, l 2** : "Power drawn from the aircraft remained under 50 A at all times and settled at approximately 40 A." Replace "power" by "current" or "electrical current".
Changed to "Electric current ..."
- 5 25. **p 15, l 3** : "The volumetric flow rate at ... SLPM". You specify the flow of an absolute amount of gas and not a volume flow. I suggest dropping the term "volumetric".
Removed "volumetric".
26. **p 15, l 9** : "will decrease the signals standard deviation" -> "will decrease the standard deviation of most of the signals"
Changed accordingly.
- 10 27. **p 15, Fig 7 left panel** : Legend is difficult to read, please increase font size. Plot could be made more readable by excluding data for $\tau > 500$ s (does not seem significant anyway) and restrict y-scale from $1e-4$ to $1e1$.
We increased font size of the legend.
- 15 28. **p 15, Fig 7 right panel** : It appears that the confidence interval given for linear fit parameters ignores the uncertainties of the x-values. If this is so, it is better not to insist on the confidence intervals of the parameters. Give R-squared with number of digits required to see the deviation from 1.
Changed accordingly.
29. **p 16, Fig 8** : Please increase the thickness of lines in legends. Traces are difficult to identify otherwise.
Changed accordingly.
30. **p 20, l 2** : "(Gordon et al., 2017))" -> "(Gordon et al., 2017)"
Changed accordingly.
- 20 31. **p 20, l 15** : put "H2O" in upright letters
Changed accordingly.
32. **p 20, l 18** : Please add + or - sign to bias constants in order to avoid ambiguities, assuming that "+" means that the QCLS is higher than the reference.
Changed accordingly.
- 25 33. **p 21, l 22** : "(see 2.3)" -> "(see Section 2.3)"
Changed accordingly.
34. **p 21, l 23** : "Eq. (1)" instead of "Eq. 1"
Changed accordingly.
- 30 35. **p 21, l 27-28** : "... precision (uncertainty) estimates based on ambient measurements at stable conditions of 0.3 (2) ppb, 0.02 (0.1) ppm and 2.0 (5) ppb ...". This notation is non-standard and quantities in parentheses might therefore be confused with uncertainties. I suggest writing "... precision/uncertainty estimates based on ambient measurements at stable conditions of 0.3/2.0 ppb, 0.02/0.1 ppm and 2.0/5.0 ppb for ...".
Changed accordingly.
- 35 36. **p 23, Fig 13** : y-axis label "Norm occurrence" should come with units in 1/ppb or 1/ppm
Changed accordingly.
37. **p 23, Fig 13, central panel** : symmetrize y-axis (from -2.x to +2.x)
Changed accordingly.
38. **p 23, Fig 13 caption** : Please add legend for colour code of flask samples.
Changed accordingly.

39. **p 23, Fig 13 middle panel on top** : Is there a reason for the skew in the distribution ?
Changed accordingly.

40. **p 24, l 2** : "(5 to 10mins interval)" -> "(5 to 10 min interval)"
Changed accordingly.

5 41. **p 24, l 10** : "above the eastern U.S.." -> "above the eastern US."
Changed accordingly.

Adaptation and performance assessment of a Quantum / Interband Cascade Laser Spectrometer for simultaneous airborne in situ observation of CH_4 , C_2H_6 , CO_2 , CO and N_2O

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Abstract. Tunable laser direct absorption spectroscopy is a widely used technique for in situ sensing of atmospheric composition. Aircraft deployment poses a challenging operating environment for instruments measuring climatologically-relevant gases in the Earth's atmosphere. Here, we demonstrate the successful adaption of a commercially available continuous wave quantum cascade (QCL) and interband cascade laser (ICL) based spectrometer for airborne in-situ trace gas measurements with a local to regional focus. The instrument measures methane, ethane, carbon dioxide, carbon monoxide, nitrous oxide and water vapor simultaneously, with high $1\text{s}-1\sigma$ precision (740 ppt, 205 ppt, 460 ppb, 2.2 ppb, 137 ppt, 16 ppm, respectively) and high frequency (2 Hz). We estimate a total $1\text{s}-1\sigma$ uncertainty of 1.85 ppb, 1.6 ppb, 1.0 ppm, 7.0 ppb and 0.8 ppb in CH_4 , C_2H_6 , CO_2 , CO and N_2O , respectively. The instrument enables simultaneous and continuous observations for all targeted species. Frequent calibration allows for a measurement duty cycle $\geq 90\%$. A custom retrieval software has been implemented and instrument performance is reported for a first field deployment during NASA's Atmospheric Carbon and Transport America (ACT-America) campaign in fall 2017 over the eastern and central U.S. This includes an inter-instrumental comparison with a calibrated cavity ring-down greenhouse gas analyzer (operated by NASA Langley Research Center, Hampton, USA) and periodic flask samples analyzed at the National Oceanic and Atmospheric Administration (NOAA). We demonstrate good agreement of the QCL/ICL based instrument to these concurrent observations within the combined measurement uncertainty after correcting for a constant bias. We find that precise knowledge of the $\delta^{13}\text{C}$ of the working standards and the sampled air is needed to enhance CO_2 compatibility when operating on the 2227.604 cm^{-1} $^{13}\text{C}^{16}\text{O}_2$ absorption line.

1 Introduction

With steadily increasing greenhouse gas concentrations in the Earth's atmosphere an improved understanding of the anthropogenic influence on climate is of major interest for the global civilization. Globally averaged carbon dioxide (CO_2) mole fractions have increased by ~~40%~~ 40% since 1750. Methane (CH_4) mole fractions have more than doubled since the pre-industrial era, ~~where over 60% and over 60%~~ of this increase is estimated to be of anthropogenic nature (Ciais et al., 2013). Nitrous oxide (N_2O) is a strong greenhouse gas and is expected to have the most important ozone-depleting anthropogenic impact throughout the 21st century (Ravishankara et al., 2009). Ethane (C_2H_6) is a powerful tracer commonly used to discriminate between different types of methane sources (Smith et al. (2015); Barkley et al. (2017); Peischl et al. (2015)) and carbon monoxide (CO) is a marker for incomplete combustion processes and relates to the formation of tropospheric ozone (Klemm et al., 1996).

Aircraft provide a flexible platform for satisfying the fundamental need for accurate, temporally and spatially dense observations of these climatologically-relevant gases from local to regional scales. On-board meteorological data acquisition systems allow for concurrent observations of important atmospheric state variables like the local wind field, which is particularly useful to estimate emissions. Spectroscopic instruments making use of molecular ro-vibrational absorption allow for high temporal coverage through fast instrument response times (Chen et al., 2010). Some have already been used for airborne research, e.g. established IR spectrometers (O'Shea et al. (2013); Santoni et al. (2014); O. L. Cambaliza et al. (2015); Filges et al. (2015)). Significant effort led to instruments operating in the mid infrared (IR) region, e.g. liquid nitrogen cooled lead-salt diode laser based spectrometers (Fried and Richter, 2007). With the commercial availability of continuous-wave lasers emitting in the mid IR region near ambient temperature (Capasso (2010); Vurgaftman et al. (2015); Kim et al. (2015), Beck et al. (2002)) several new instrument designs have emerged (McManus et al. (2015); Zellweger et al. (2016)). QCL/ICL based systems exploit several orders of magnitude stronger molecular absorption features in the mid infrared compared to near infrared based instruments. Richter et al. (2015) reported on a custom-built difference frequency generation (DFG) absorption spectrometer for simultaneous in-situ detection of formaldehyde (CH_2O) and C_2H_6 providing high detection sensitivities of 40 ppt and 15 ppt, respectively. The custom-built airborne QCL spectrometer described by Catoire et al. (2017) allows for simultaneous observation of CO , CH_4 and nitrogen dioxide (NO_2) with in-flight precisions of 0.3 ppb, 5 ppb and 0.3 ppb for a sampling time of 1.6 s. McManus et al. (2011) reported on the development of a high-sensitivity trace gas instrument based on quantum cascade lasers and astigmatic Herriott cells with up to 240 m path length. Unlike many established instruments measuring different species sequentially (one species after the other), the described spectrometer allows for concurrent sensing of the selected species and faster response times. These instruments have already been operated on different research aircraft. Santoni et al. (2014) describe the successful deployment and evaluation of a similar airborne spectrometer (Harvard QCLS) for more than 500 flight hours. However, Pitt et al. (2016) reported a severe cabin pressure dependency of their N_2O and CH_4 measurements using a commercial instrument (Aerodyne QCLS). By implementing a pressure-differentiated calibration method they were able to correct the corresponding data set, but had to omit roughly half of the measured data. Recently, Gvakharia et al. (2018)

reported on a similar cabin pressure dependency for their N₂O, CO₂ and CO measurements (based on an Aerodyne QCLS). They suggested a fast calibration procedure to overcome these dependencies while maintaining a $\geq 90\%$ duty cycle. Here, we describe the setup and performance of our flight-proven (over 100 flight hours) airborne QCL/ICL system developed for simultaneous airborne measurements of CH₄, C₂H₆, CO₂, CO, N₂O and H₂O. The instrument is shown to provide multi-species airborne observations for assessing greenhouse gas fluxes with a local (e.g. single facilities) to regional focus (e.g. urban agglomerations). Simultaneous observations of CH₄ and C₂H₆ facilitate to pinpoint sources of CH₄ enhancements (Smith et al., 2015). At the same time, the instrument provides measurements of N₂O, the third most important greenhouse gas. This makes the instrument an ideal tool for airborne quantification and source attribution of greenhouse gas emissions using e.g. the aircraft based mass balance approach. Section 2 summarizes the refinements over the commercial system for use on aircraft. We show that frequent two-point calibration can mitigate cabin pressure dependencies. Section 3 describes our custom-built retrieval software developed for tuning the retrieval process. Sections 4 and 5 report on instrument performance in the laboratory and in the field during NASA's ACT-America fall 2017 campaign, including an inter-instrumental comparison with a calibrated cavity ring-down instrument and periodically taken flask samples. Section 6 summarizes our findings and concludes the study.

2 The airborne DLR QCL/ICL spectrometer

The spectrometer system used here builds upon the *Dual Laser Trace Gas Monitor*, a commercial tunable IR laser direct absorption spectrometer (TILDAS) available from ~~AERODYNE RESEARCH INC~~ [Aerodyne Research Inc.](#), Billerica, USA, acquired by *Deutsches Zentrum für Luft- und Raumfahrt* (DLR) in late 2016. The basic instrument has already been extensively described in McManus et al. (2011). We will therefore only briefly introduce the basic instrument setup followed by a description of the refinements required to operate the instrument on a research aircraft.

2.1 Basic instrument setup

The spectrometer is split into an electronics ~~compartment~~ and an optics compartment. The electronics compartment includes an embedded computing system, thermoelectric cooling (TEC) controllers, power supplies, etc. The optics compartment includes the lasers, the sample cell, the pressure controller, etc. Figure 1 shows a top-view photograph of the optics compartment. A combination of a continuous wave (CW) QCL and ICL measures mole fractions of CH₄, C₂H₆, CO₂, CO, N₂O and H₂O simultaneously by direct absorption spectroscopy. The sample cell is an astigmatic Herriott cell with approximate physical dimensions of 15 cm x 15 cm x 50 cm (WxHxL) made from aluminum. It provides an effective absorption path length of 204 m with a net volume of 2.1 L. Two laser light sources are tuned to a specific center wavelength by adjusting the operating temperature using Peltier elements contained in the lasers housing. Excess heat is removed through a liquid cooling/heating circuit (~~SOLID-STATE COOLING SYSTEMS~~ [Solid State Cooling Systems](#), New York, USA). Laser #1 is an Interband cascade laser manufactured by ~~nanoplus~~ [Nanoplus GmbH](#), Gerbrunn, Germany with a peak output power of 9.5 mW operated at 4.7 °C and modulated between 2988.520 cm⁻¹ and 2990.625 cm⁻¹ using a linear current ramp of up to 40 mA. Laser #2 is a quantum cascade laser manufactured by ~~ALPES~~ [Alpes Laser](#), St-Blaise, Switzerland with a peak output power of 40 mW operated at 1.5

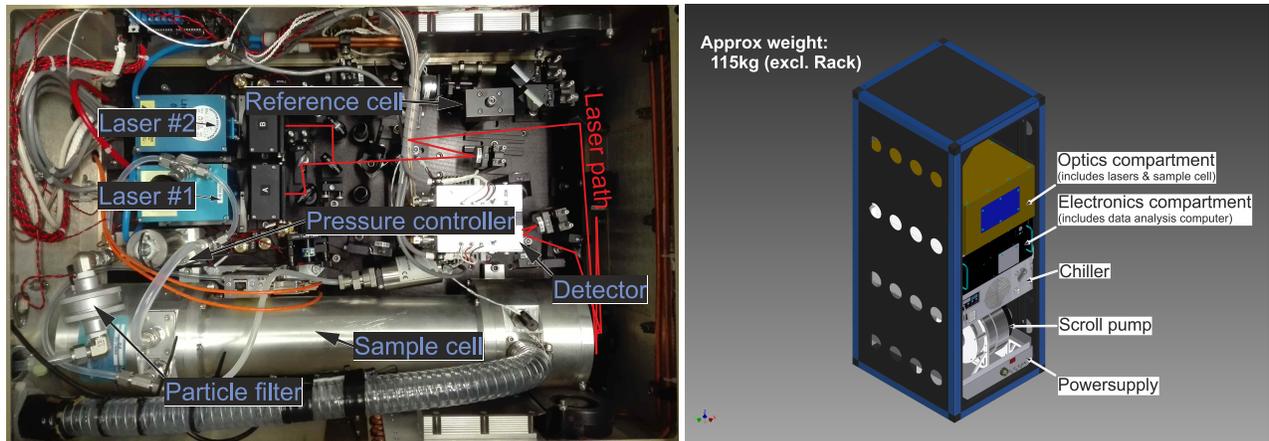


Figure 1. Top-down photograph on the optics compartment (left panel). The sample cell made from aluminum along with the pressure controller and pressure transducers can be identified in the lower half. The QCL/ICL lasers are mounted inside the blue housings to the left of the collimating Schwarzschild telescopes in the two black housings. The two detectors are mounted below the silver aluminum cases, housing the pre-amplifiers, on the right. The first detector is used for detecting both lasers after passing through the sample cell. The second detector is used for spectral referencing through an auxiliary optical path. The right panel illustrates the rack mounted instrument. The figure includes solid models from Aerodyne Inc. and Solid State Cooling Systems.

°C modulated between 2227.550 cm^{-1} and 2228.000 cm^{-1} using a linear current ramp of up to 300 mA. The lasers are modulated sequentially at a fixed frequency of 1.5 kHz. Laser #1 scans over absorption lines of CH_4 , C_2H_6 and H_2O , Laser #2 sweeps over N_2O , CO_2 and CO lines. Each laser is sampled at 450 spectral points. Acquired spectra are co-added to yield a single output spectrum every half of a twice per second. Before reaching the sample cell, the laser beam travels approximately 5 1.6 m inside the instrument under ambient conditions. This will be referred to as the open-path of the instrument, which is heavily influenced by variations in cabin pressure, temperature and humidity during airborne operation. After passing through the sample cell, the combined output from both lasers hits a single TEC-cooled detector. A second, identical detector collects radiation from two auxiliary paths. The first auxiliary path contains a small, sealed reference cell filled with CH_4 and N_2O . This allows for spectral referencing during system startup. The second path introduces an etalon into the beam, allowing for 10 experimental determination of the laser tuning rate, which relates laser supply current and emitted wavelength.

2.2 Refinements for airborne operation

The key challenges for a successful deployment on research aircraft are limited space and power, the occurrence of linear and angular accelerations and large pressure, temperature and humidity fluctuations in both cabin and sampled air. Airborne instrumentation further requires a fast system response time, owing to the rapid movement of aircraft in the atmosphere. The 15 response time is controlled by the time it takes to completely exchange the air in the sample cell which is driven by the highest achievable volumetric flow rate given a specific pump and sample cell volume.

Here, a scroll pump has been chosen to enable a constant sample flow through the sample cell. The lubricant-free scroll pump runs very smoothly, ~~avoiding injecting large vibrations into~~ reducing vibrations of the measurement system, yet providing good pumping performance with a nominal value of 500 liters per minute at standard conditions. This translates to a net flow rate of 25 SLPM ~~when operating with~~ (given IUPAC standard conditions of $T = 273.15$ K and $p = 1000$ hPa) when operating at a cell pressure of 50 hPa. Earlier experience showed that large electrical inrush currents have jeopardized nominal system startup (priv. comm. Stefan Müller, MPI Mainz). Sudden power failure, due to over-current triggering aircraft circuit breakers, may lead to failures in the data analysis equipment. The original motor has therefore been exchanged with a synchronous three-phase motor (~~BAUMUELLER-NUERNBERG-GMBH~~ Baumüller Nuernberg GmbH, Velbert, Germany). This DC motor provides a rated power of 627 W at 28 VDC. By using a digital motor controller the maximum startup current can be limited amongst various other tuning options. From previous studies the motor is known to emit a considerable amount of heat; a forced airflow provided by a standard axial fan ensures motor temperatures stay in the rated range.

Aircraft deployment requires the entire system to operate with a maximum of 50 A at 28 VDC. Power consumption of the instrument is mainly dominated by the pump and the thermoelectric cooling making up more than 3/4 of the total power requirement. Both components have been electrically converted without the need for power inverters from 230 VAC to 28 VDC to increase overall efficiency. The spectrometer and its internal computer are driven by a power inverter.

Large parts of the wiring harness have been exchanged from standard PVC cables to aviation-grade fire-resistant wiring. Mandatory electromagnetic compatibility/interference (EMC/EMI) tests have been carried out to comply with Federal Aviation Administration (FAA) regulations. The rack-mounted instrument sums up to a total mass of approximately 115 kg and has been tested to withstand linear accelerations of up to 9 g on the aircraft forward axis, 8 g on the downward axis, 6 g on the upward and 2.25 g sideways. Due to aircraft certification issues, pure water is used as process fluid for the liquid cooling/heating circuit instead of the intended propylene glycol / water mixture.

A 3/8" inner diameter hose made out of ~~Polytetrafluoroethylene~~ polytetrafluoroethylene (PTFE) has been chosen for the sample air intake as a compromise between pressure drop across the inlet and to minimize lag time between the inlet and the sample cell. Inside the instrument and upstream of the sample cell, an aerosol filter holds back particles bigger than $2 \mu\text{m}$. The inlet is rear facing, preventing large particle entrainment and protecting the instrument from liquid water and ice. Owing to the small diameter, the intake flow is inside the turbulent regime at all times ($Re \sim 4000$).

Finally, the sample cell pressure is regulated by means of a fully-configurable pressure controller (~~BRONKHORST~~ Bronkhorst High-Tech B.V., Ruurlo, Netherlands). A chip-scale temperature-compensated pressure transducer (*Measurement Specialties (Europe), Ltd.*) and a humidity sensor (*Sensirion AG, Staefa ZH, Switzerland*) have been built into the optics compartment, to allow for monitoring the open path state variables (see section 2.1).

2.3 In-flight calibration strategy

A custom-built calibration system has been implemented as illustrated in Figure 2. Using mass flow controllers (MFCs, ~~BRONKHORST~~ Bronkhorst High-Tech B.V., Ruurlo, Netherlands), two gases can be mixed at arbitrary ratios. The calibration gas mixture has been chosen to resemble "target" gas mole fractions close to atmospheric ambient values. The cylinders

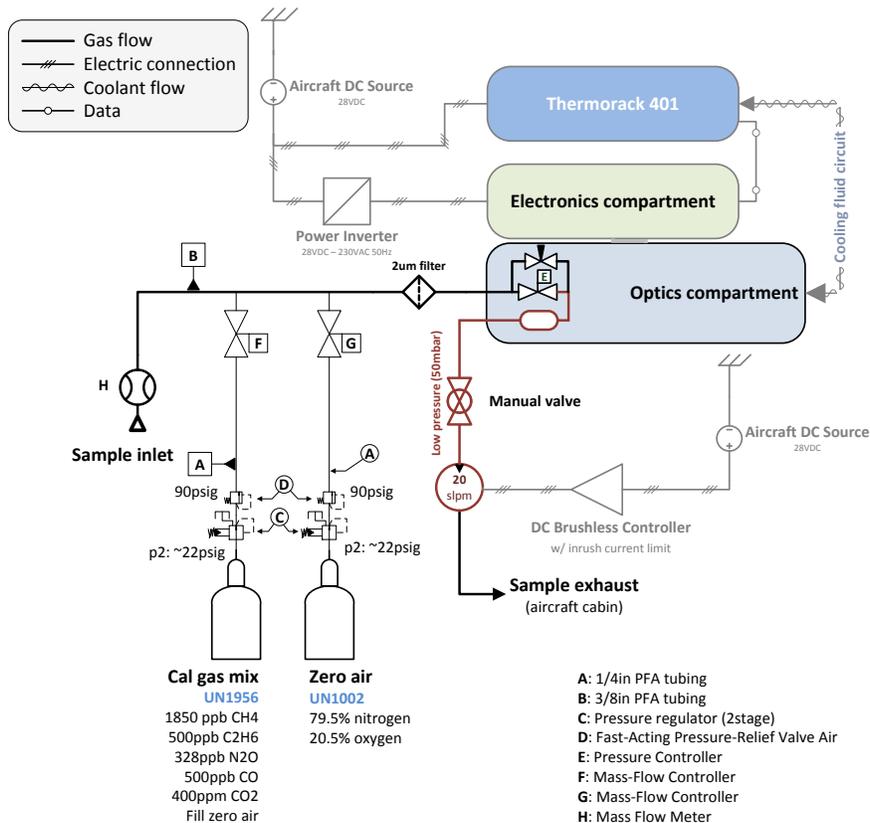


Figure 2. Schematic showing the main components with emphasis on the calibration system. A mass flow meter allows for measuring the sample flow rate. Two reference gases can be mixed at any arbitrary ratio by means of two calibrated mass flow controllers. A $2\mu\text{m}$ particle filter upstream of the sample cell avoids cell contamination.

have been cross-calibrated [using a Picarro CRDS](#) against NOAA standards [using a cavity ring-down spectrometer \(CRDS\)](#) and are thus traceable to World Meteorological Organization (WMO) standards for CH₄ (Cert.-Nr. CB11361, WMO X2004A for CH₄ (Dlugokencky et al., 2005), [WMO X2007 for CO₂ \(Zhao and Tans, 2006\)](#)). C₂H₆, CO and N₂O are compared to NOAA flask samples taken during the ACT-America field campaigns, which are also traceable to WMO standards. We use ultra-pure synthetic air as "zero" gas instead of pure nitrogen (N₂) to be in accordance with aircraft safety regulations and because the mole fraction of synthetic air (79.5 % N₂ and 20.5 % O₂) is chemically closer to sampled atmospheric air. Our calibration setup allows the net flow rate from the calibration cylinders to be slightly higher than the sample flow rate, minimizing pressure variations in the sample cell during switchover from normal to calibration sampling. To avoid contamination with cabin air, leak tests have been carried out on a regular basis during the ACT-America field campaign. [Typical calibration distribution diagrams are available](#) [Histograms of typical calibration measurements are provided](#) in the Supplement Section 4.

Owing to the high sensitivity of the retrieved mole fractions to changes in ambient conditions during flights (Gvakharia et al., 2018), calibration cycles are carried out automatically every 5 to 10 minutes. Each cycle consists of a pre-programmed sequence of flushing the sample cell with zero gas for 10 seconds followed by another 10 seconds of calibration gas. These time intervals have been found to be a good compromise between calibration gas cylinder endurance and measurement duty cycle.

5 The online mixing feature is not used for in-flight calibration. Hence, no dilution of the calibration standard with zero air is introduced during flights and the uncertainty in the flow rate measurements can be omitted. Online mixing (relevant for linearity checks) adds the uncertainty of the controlled mass flow (~~0.5~~0.5 % relative error) on top of the gas cylinder uncertainties. Measured mole fractions of all detected species settle to an approximately constant value within the first two seconds after switchover from calibration gas to sample air and vice versa. The only exception is water vapor, which is observed to settle

10 after approximately 30 seconds because of its stickiness and because the inlet tubing is made out of PTFE. The observed decay in H₂O is different from the decay in other species in that a slow, almost linear decay follows the initial exponential decay, due to remaining water vapor in the inlet tubing and the sample cell.

3 Data Retrieval & Post-processing

The standard approach to retrieve dry-air mole fractions from the Aerodyne QCLS instruments is by making use of the software

15 supplied by the manufacturer (TDLWintel). Here we utilize a custom retrieval software (JFIT) developed to double check the output of the TDLWintel software and to enhance the ability of tweaking the retrieval process. Our main goal in developing a stand-alone algorithm here, was to learn about possible error sources, mitigation possibilities of instrument dependencies and to be able to extend the instruments capabilities in the future.

The code is written in plain C++. It digests the sample cell pressure and temperature measurements to generate a synthetic spectrum based on line-by-line parameters from the HITRAN2012/HITRAN2016 (Rothman et al. (2013); Gordon et al. (2017))

20 database using a conventional Voigt profile approach. Ethane line-by-line data have been taken from high-resolution FTIR spectra due to deficiencies in the HITRAN data for this particular species/wavenumber combination (Harrison et al., 2010). The computation of the Voigt profile has been adopted from Abrarov and Quine (2015). Our retrieval code differs from the TDLWintel approach in the determination of the spectral baseline, the handling of shift parameters and open path water absorption.

25

A typical raw spectral output, as saved by the instrument in binary format is illustrated in Figure 3. The two consecutive laser scans are clearly visible. On the left side, Laser #1 sweeps between 2988.520 cm⁻¹ and 2990.625 cm⁻¹ and hence, over absorption features of CH₄, C₂H₆ and H₂O. The right side corresponds to the wavelength range of Laser #2 (2227.550 cm⁻¹ to 2228.000 cm⁻¹) and includes absorption features of N₂O, CO and CO₂. After the lasers have scanned their full range, both

30 lasers are completely turned off to allow for the determination of the detector zero-intensity offset. The abscissa corresponds to the individual sampling points, which can be converted to spectral units using the known laser tuning rate. The flat sections of the spectrum with no molecular absorption, are considered to represent the spectral baseline. The shape of this baseline is

mainly controlled by laser characteristics, the detector response function and optical properties of the installed mirrors and windows inside the instrument.

The spectrum is broken down into 3 fit windows for the retrieval process (see Figure 5). These were chosen based on the best overall performance found in retrieval tests and named after the chemical species included. A synthetic spectrum, including a polynomial representing the spectral baseline, is generated and fitted using an unbounded Levenberg-Marquardt least-squares algorithm (Marquardt, 1963). The degree of the background-fitting polynomial has been adjusted empirically for each different fit window. Species independent shift parameters have been included allowing individual absorption features to freely move on the spectral axis. Special care has been taken to group weak and strong absorption features together in a single shift parameter, to provide sufficient certainty on their spectral positions. In other words, not every absorption line has its own shift parameter, but they are grouped as schematically shown in Figure 4. As a result, only 5 shift parameters are included although the synthetic spectrum in Figure 4 is composed of more than 20 individual lines. When the absorptivity does not yield enough certainty to ensure proper determination of the shift parameters for a single spectrum, the shift variables are held constant at ~~the mean over its last 10~~ their means over the last ten values. If another species in the relevant fit window allows for a proper determination of the spectral position, remaining shift parameters are coupled to those with enough certainty. This allows to properly model absorption line center frequency changes and provides a means for observing spectral stability.

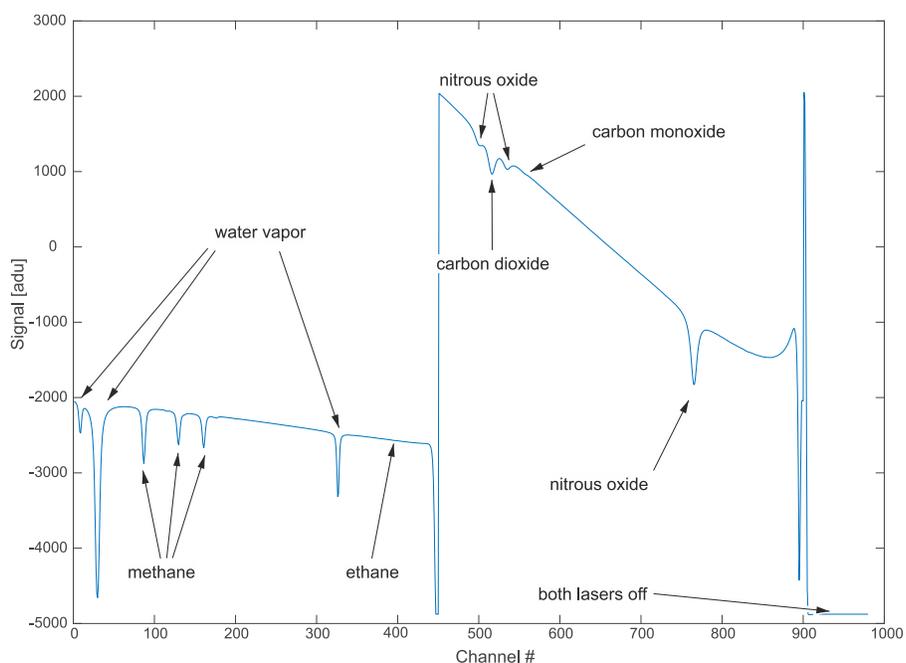


Figure 3. A typical raw spectrum as recorded in binary format by the instrument. Arrows have been added to ease identification of the observed chemical species. Channel numbers on the abscissa can be converted to spectral units using the laser tuning rate. The intensity offset can be corrected by shifting the entire spectrum to yield zero intensity when lasers are turned off.

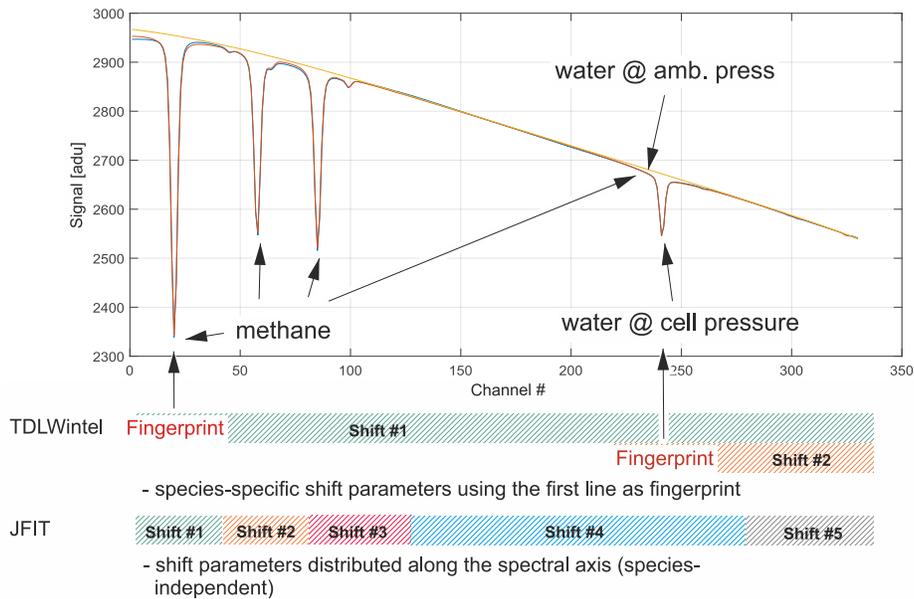


Figure 4. Schematic depicting the handling of spectral shift parameters and baseline modeling. The spectral baseline is fitted as a polynomial together with absorption features over the entire fit window. Shift parameters have been implemented in a species-independent way. Open-path water is also included in the model.

Typical shift parameters for ground-based operation are given in Figure 8 for the $\text{CH}_4\text{-H}_2\text{O}$ and $\text{CO}_2\text{-CO-N}_2\text{O}$ fit windows. Pressure, humidity and temperature data obtained from within the optics compartment are used to model H_2O absorption at cabin pressure in the open-path region.

The $\text{CH}_4\text{-H}_2\text{O}$ fit window covers almost the entire set of spectral features covered with Laser #1 except for the C_2H_6 absorption features. The spectral baseline is modeled as a third-order polynomial over the full range of the fit window. A typical spectrum including fit is depicted in Figure 5 along with typical spectra for the other two fit windows.

The C_2H_6 fit window includes absorption features of CH_4 and C_2H_6 . The main challenge of retrieving precise C_2H_6 mole fractions arises from its very low background concentration in the atmosphere (approximately 1.05 ppb in the northern hemisphere (Simpson et al., 2012)). A single adjacent CH_4 line, located at 2989.981 cm^{-1} has been included in order to obtain C_2H_6 data even under these challenging conditions. In this case, the weak CH_4 absorption is not modeled as a free parameter and is hence not used for retrieving the CH_4 mole fraction, but for localizing the spectral position / shift parameter of the C_2H_6 absorption feature in the absence of a clear C_2H_6 signal. The CH_4 mole fractions are fixed to the values determined from the previous fit window. Using this approach, we found a clear improvement in the C_2H_6 data quality including a higher precision and the absence of discontinuities. The associated spectral baseline is modeled as a second-order polynomial.

The $\text{CO}_2\text{-CO-N}_2\text{O}$ fit window covers the entire second laser and is the most complex spectral scene. It includes several overlapping absorption features making the retrieval of mole fractions of the targeted species challenging. As illustrated in Figure

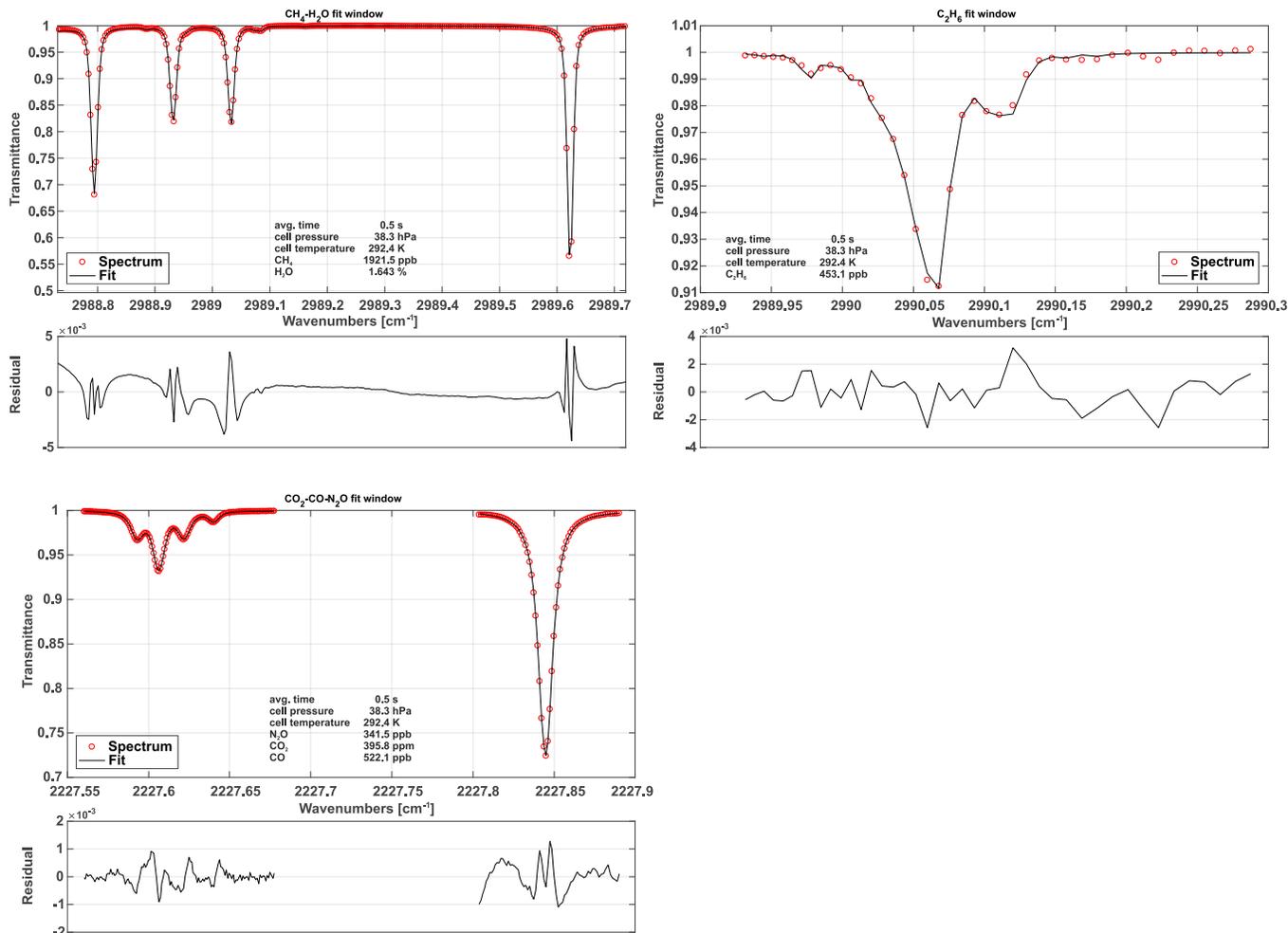


Figure 5. Typical, normalized spectra for each fit window including fits and associated residuals. The first fit window (top left) includes CH₄ and H₂O absorption features. The top right fit window depicts C₂H₆ absorption. The lower left spectrum shows CO, CO₂ and N₂O absorption.

5, a single CO₂ absorption line is surrounded by two N₂O lines. The CO line is directly adjacent to one of the N₂O lines. This results in comparatively large signal noise and increased uncertainty in the retrieved mole fractions due to crosstalk between the N₂O, CO and CO₂ absorption lines. However, the spectral range includes another N₂O line at 2227.843 cm⁻¹, which is slightly stronger than the other two (see Figure 5). Our approach is to fix the mole fractions of the first two N₂O lines to the stronger third one, in order to reduce the uncertainty in retrieved N₂O and hence the noise on the CO₂ and CO retrieval. The spectral baseline has been split into two parts, the first covering the first two N₂O, CO₂ and CO lines, and the second covering the individual N₂O line only. Both are modeled as second-order polynomials.

3.1 Water vapor correction

In the current instrument setup, water vapor is not removed from sampled air before entering the sample cell. Therefore, the influence of water vapor on the retrieved mole fractions has to be corrected in order to report dry-air mole fractions. Here, we correct for both, dilution and water broadening effects. The first describes the fact that concentrations appear smaller when analyzing moist air, although the dry air mole fraction might be constant. This effect can be remedied for if the absolute water concentration is known for each individual sample using Eq. (1)

$$c_d = \frac{c_x}{(1 - c_{H_2O})} \quad (1)$$

where c_d is the dry-air mole fraction, c_x is the raw concentration of a particular species of interest diluted in moist air and c_{H_2O} is the water vapor concentration (Harazono et al., 2015). Spectroscopic water broadening effects are approximately an order of magnitude smaller than dilution effects, yet they do have to be corrected for to obtain precise measurements. HITRAN's air broadening parameters are listed for a particular chemical composition of air excluding water vapor. H_2O , however, can be a more potent broadening agent than nitrogen or oxygen (Kooijmans et al., 2016). These coefficients have been determined using the setup depicted in Figure 6 and are summarized in Table 1. Therefore, the pressure broadening has to be modified to include this effect. Under dry air conditions it is common to split the pressure broadening into two parts: self-broadening and air-broadening. The self-broadening coefficient allows computation of the broadening induced by mutual collisions of a particular species of interest. The air-broadening coefficient can be used to approximate the broadening induced through collisions of a particular species with all the other species in a given air standard excluding the species itself. From the HITRAN definitions, the pressure-broadened half width at half maximum for a gas at pressure p and temperature T is given by

$$\gamma(p, T) = \left(\frac{T_{ref}}{T} \right)^{n_{air}} (\gamma_{air}(p - p_{self}) + \gamma_{self}p_{self}) \quad (2)$$

where T_{ref} is a fixed reference temperature ($T_{ref} = 296$ K), p_{self} is the partial pressure of a particular species of interest and n_{air} is the coefficient of the temperature dependence of the air-broadened half width. This model has been extended to include collisions with H_2O molecules yielding

$$\gamma(p, T) = \left(\frac{T_{ref}}{T} \right)^{n_{air}} (\gamma_{air}(p - p_{self} - p_{H_2O}) + \gamma_{self}p_{self} + \gamma_{H_2O}p_{H_2O}) \quad (3)$$

with the partial pressure of water vapor p_{H_2O} and the water broadening coefficient γ_{H_2O} . The former can be computed from the measured water vapor concentration. The latter can be empirically determined. Not including the self and water foreign

Table 1. Empirically determined water vapor foreign broadening coefficients

Chemical species	CH ₄	C ₂ H ₆	CO ₂	CO	N ₂ O
Broadening coefficient $\times \gamma_{air}$ (γ_{air})	1.05	1.18	2.2	2.1	2.2

broadening leads to relative errors in the range of 0-2 % for the described setup, depending on the species of interest. While small for C_2H_6 and CH_4 with $<0.03\%$ $<0.03\%$, the influence on retrieved CO is rather large with $\sim 2\%$ $\sim 2\%$. In order to obtain γ_{H_2O} two MFCs are used to modify mole fractions of water vapor in a clean and dry calibration gas. This does not involve measuring water vapor at absolute levels, instead it is only necessary to span the range of atmospheric H_2O . An additional downstream pump allows, in combination with a manually-controlled needle-valve, tuning the absolute pressure at the instrument inlet to simulate altitude changes. For these tests, the QCLS instrument has been operated at low flow rates of approximately 1 SLPM due to limitations on the two mass flow controllers. The water broadening coefficient γ_{H_2O} has been adjusted iteratively until reported dry-air mixing-ratios of the species of interest remained constant for the set of water vapor mole fractions.

10 4 Ground-based performance

Extensive ground-based instrument checks have been conducted, including tests in a pressure chamber at the Karlsruhe Institute of Technology (KIT) and laboratory tests at DLR Oberpfaffenhofen, Germany. These tests confirmed the presence of an ambient pressure dependence found in earlier studies (i.e. Pitt et al. (2016)). Here, we show in-field, ground-based instrument checks conducted in Hangar N-159 at NASA Wallops Flight Facility, Wallops Island, USA, to ensure proper instrument operation and determine instrument precision. Power-Electric current drawn from the aircraft remained under 50 A at all times and settled at approximately 40 A. The volumetric-flow rate stabilized at 23 SLPM for a sample cell pressure regulated at 50.0 ± 0.5

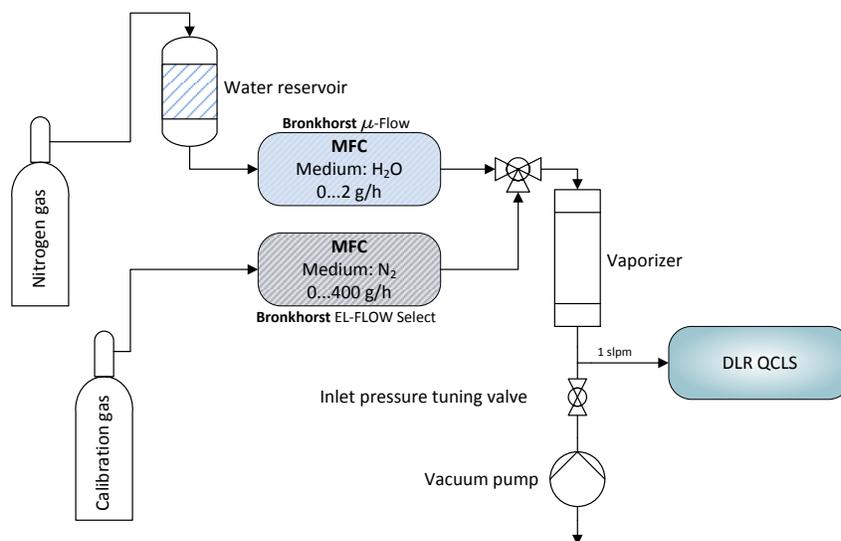


Figure 6. Schematic depicting the water correction lab setup. A reference gas can be humidified to typical atmospheric values between 0 % and 2 % absolute water using mass flow controllers and an electronically controlled vaporizer. A downstream pump allows for simulation of different flight levels.

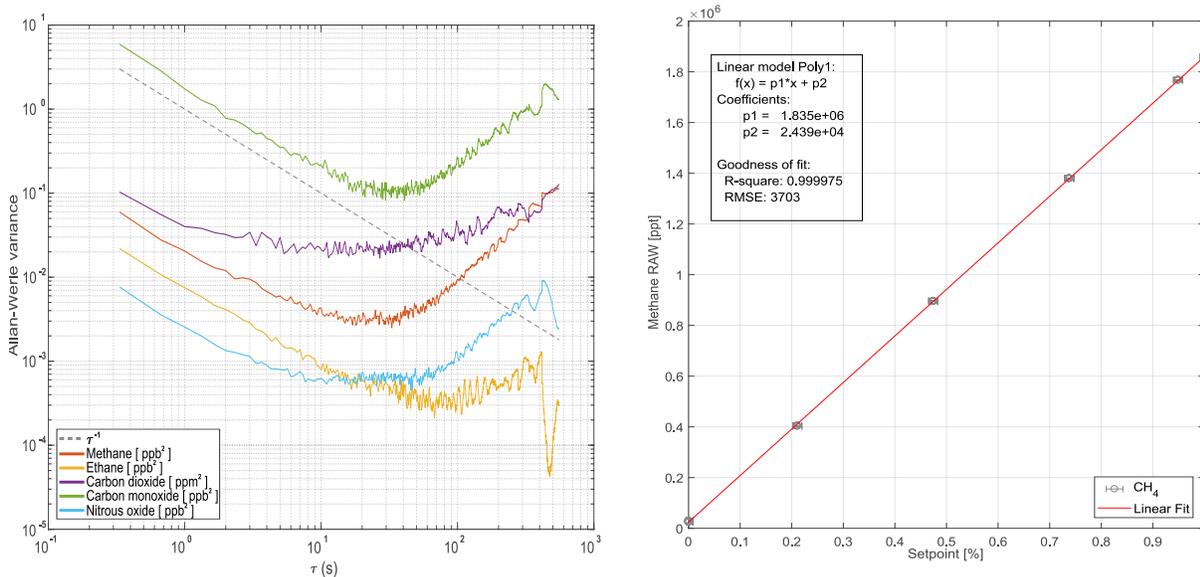


Figure 7. Allan-Werle variance for all measured chemical species during ground-based operation (left panel). The right panel demonstrates linearity for methane is within achievable error bounds during ground-based operation using the online calibration gas mixing system from Section 2.3.

hPa (0.2 hPa precision @ 5 Hz frequency). Typical precision (standard deviation for 1 s averaging) for ground-based operation is summarized in Table 2.

Figure 7 shows the Allan-Werle variance for common averaging times τ for the individual trace gases monitored. For most species averaging up to 20 s will decrease the ~~signals standard deviation~~ standard deviation of most of the signals, before deteriorating effects (i.e. drift) occur. Figure 7 also addresses retrieved mole fraction linearity. Linearity checks have been carried out for all species using the calibration system described in Section 2.3. All retrieved species are linear within the achievable controlled mass flow uncertainties from Section 2.3. CH₄ is used in Figure 7 for demonstration purposes.

Typical shift parameters (as introduced in Sect. 3) for ground-based operation are depicted in Figure 8 for the CH₄-H₂O and CO₂-CO-N₂O fit windows. These shift parameters can be considered as a tracer for instrument stability for both lasers.

10 Overall spectral stability is in the range of $\pm 10^{-3} \text{ cm}^{-1}$. ~~Apart from~~ The regular short-timed spikes with a period of ~ 5 min result from switching from sample to calibration gas and vice versa. Apart from these well-timed spikes and expected

Table 2. Typical $1s - 1\sigma$ precision during ground-based instrument checks.

Chemical species	H ₂ O	CH ₄	C ₂ H ₆	CO ₂	CO	N ₂ O
Precision $1s - 1\sigma$	2.1 ppm	142 ppt	87 ppt	169 ppb	1.3 ppb	45 ppt

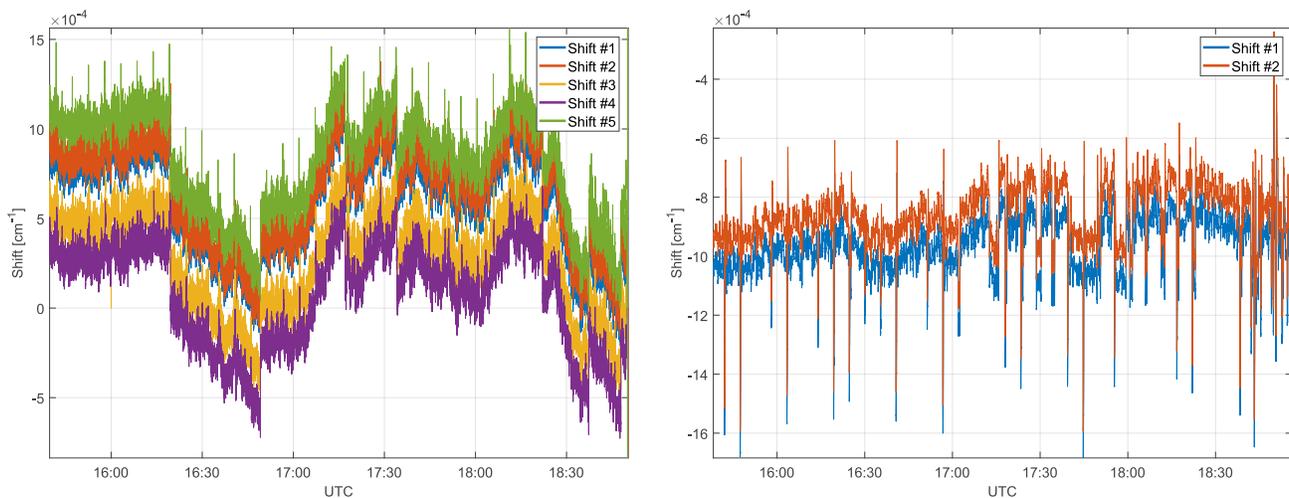


Figure 8. Spectral shifts for the CH₄-H₂O fit window (left) and the CO₂-CO-N₂O fit window (right). Spectral stability during ground-based operation is in the range of $\pm 10^{-3} \text{ cm}^{-1}$.

low-frequency instability (due to thermal changes) on the lasers spectral output, high-frequency shifts are evident, including discontinuities. The source of these discontinuities remains unclear. They could be introduced by the software based frequency lock mechanism, by instabilities of the laser itself or by timing changes in the sampling. Software based frequency lock refers to a controller regulating the laser temperature to compensate for drifts using the spectral shift as the controller input and the current to the Peltiers as controller output. The controller itself is implemented in software on the data analysis computer. The shape of the individual shifts match and so does their trend over time, which is a good indicator for a stable tuning rate during ground-based operation.

5 Airborne instrument performance aboard NASA WFFs C-130

The instrument was successfully operated during 18 research flights aboard NASA Wallops Flight Facility's C-130 within the framework of the ACT-America fall 2017 field campaign. Other instrumentation in the ACT-America payload provided an excellent opportunity for instrument inter-comparison. In situ CH₄, CO₂, and CO were measured using a [PICARRO Picarro](#) G2401-m cavity ring-down spectrometer, and in situ CO₂, CH₄, and H₂O (g) were measured using a [PICARRO Picarro](#) G2301-m cavity ring-down analyzer. Both [PICARRO cavity ring-down](#) instruments are anchored to WMO X2007 for CO₂ (Zhao and Tans, 2006), WMO X2004A for CH₄ (Dlugokencky et al., 2005) and WMO X2014A for CO (Baer et al., 2002). Precise C₂H₆ measurements were obtained by periodic flask samples by NOAA ESRL. Three onboard lidars, and in situ sensors measuring the meteorological state variables - winds, temperature, pressure and water vapor - completed the C130s instrument suite. Here we present data from a typical flight (10/03/2017) to demonstrate the airborne instrument performance through inter-

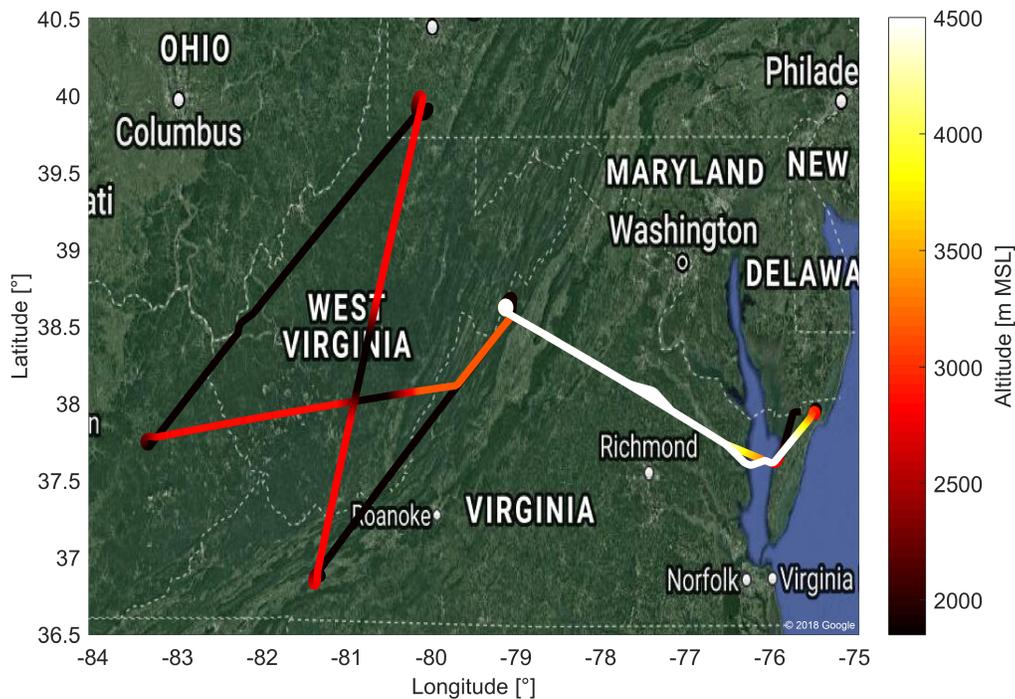


Figure 9. A typical flight during ACT-America. This figure shows the flight pattern for Oct. 3, 2017 with color coded altitude. The flight includes two low-altitude (≈ 300 m AGL) legs downwind and upwind of parts of the Marcellus shale area. High-altitude transects between the two low-altitude legs include two en route descents and ascents in West Virginia. Fair weather conditions and light southerly winds were present throughout the flight domain.

comparison with well-established measurement techniques: the cavity ring-down **PICARRO** greenhouse gas analyzers and flask samples.

As depicted in Figure 9, the flight starts off from the eastern U.S. (Wallops Flight Facility, Virginia). A high-altitude transect to West-Virginia is followed by two low-altitude legs downwind and upwind of parts of the Marcellus shale area: a large shale gas extraction region. The transects between the two low-altitude legs are flown at high altitude to facilitate nadir lidar observation, with two en route descents and ascents near the center. Figure 10 depicts dry-air mole fractions for CH_4 , C_2H_6 and H_2O measured by the different instruments during the 5-hour flight. This figure provides evidence, that the QCLS and **PICARRO CRDS** methane data agree to within 1.4 ppb (1σ) over the entire flight. QCLS and flask methane data agree to within 3.9 ppb (1σ). It should be noted, that care must be taken when interpreting the differences between slow flask samples and fast in situ measurements for high-variability flight segments. The center panel of Figure 10 depicts the QCLS-retrieved C_2H_6 data superimposed with flask measurements. Here the QCLS-retrieved ethane data matches the flask measurements (blue dots) to within 0.4 ppb (1σ). Unlike the QCLS, **PICARRO cavity ring-down** and flask data are both sampled through an upstream dryer. These were computed by interpolating QCLS data to the flask end fill times. The lowermost panel of Figure 10 provides water

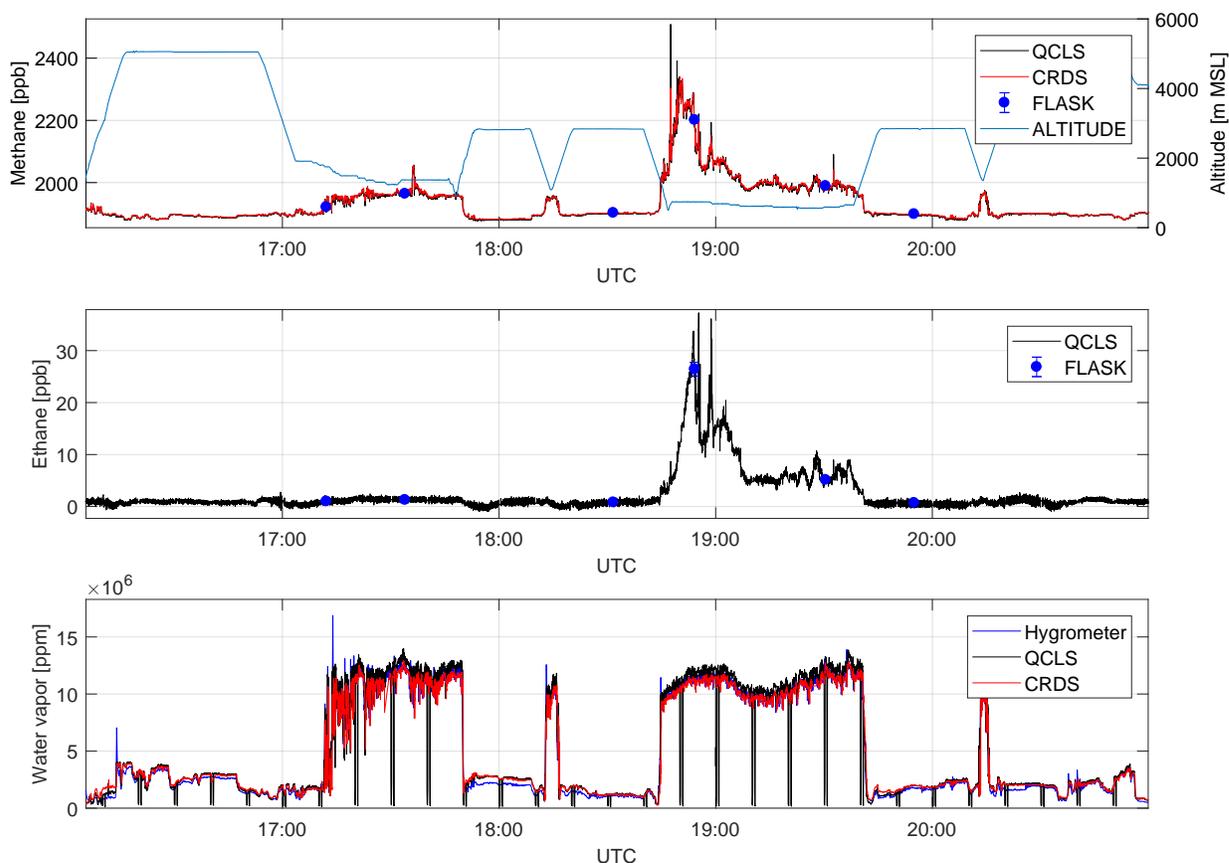


Figure 10. A direct comparison between dry-air mole fractions retrieved from different measurement techniques for a complete flight on Oct. 3, 2017. Depicted are methane (uppermost panel), ethane (center panel) and water vapor (lowermost panel) mole fractions. QCLS-retrieved methane data matches with [PICARRO-CRDS](#) and flask data to within 1.4 ppb (1σ) and 3.9 ppb (1σ), respectively, after correcting for a constant bias. QCLS-retrieved ethane data agrees with flask data to within 0.4 ppb (1σ). Water vapor sensed by an on-board dewpoint hygrometer does differ from the [PICARRO-CRDS](#) and QCLS data.

vapor mole fractions obtained from an on-board dewpoint hygrometer, from the G2301-m [PICARRO](#)-analyzer and from the QCLS. The QCLS water vapor data is used to correct for water vapor effects during the retrieval of dry-air mole fractions from the QCLS raw spectra as described in Sect. 3.1. By taking a closer look on the upper two panels, the benefit of simultaneously measuring several species can be readily identified. Figure 10 shows enhanced CH_4 without coinciding C_2H_6 enhancements for the first low-altitude leg. For the second low-altitude leg above the Marcellus area, however, concurrent CH_4 and C_2H_6 enhancements suggest that natural gas is the dominant source.

Time series for the species N_2O , CO and CO_2 are shown in Figure 11. The data obtained are comparable within instrument uncertainties. The N_2O time series matches available flask data to within ± 1.1 ppb. The CO_2 absorption is retrieved from a molecular transition of the $^{13}\text{C}^{16}\text{O}_2$ carbon dioxide isotopologue and scaled with its natural abundance of approximately

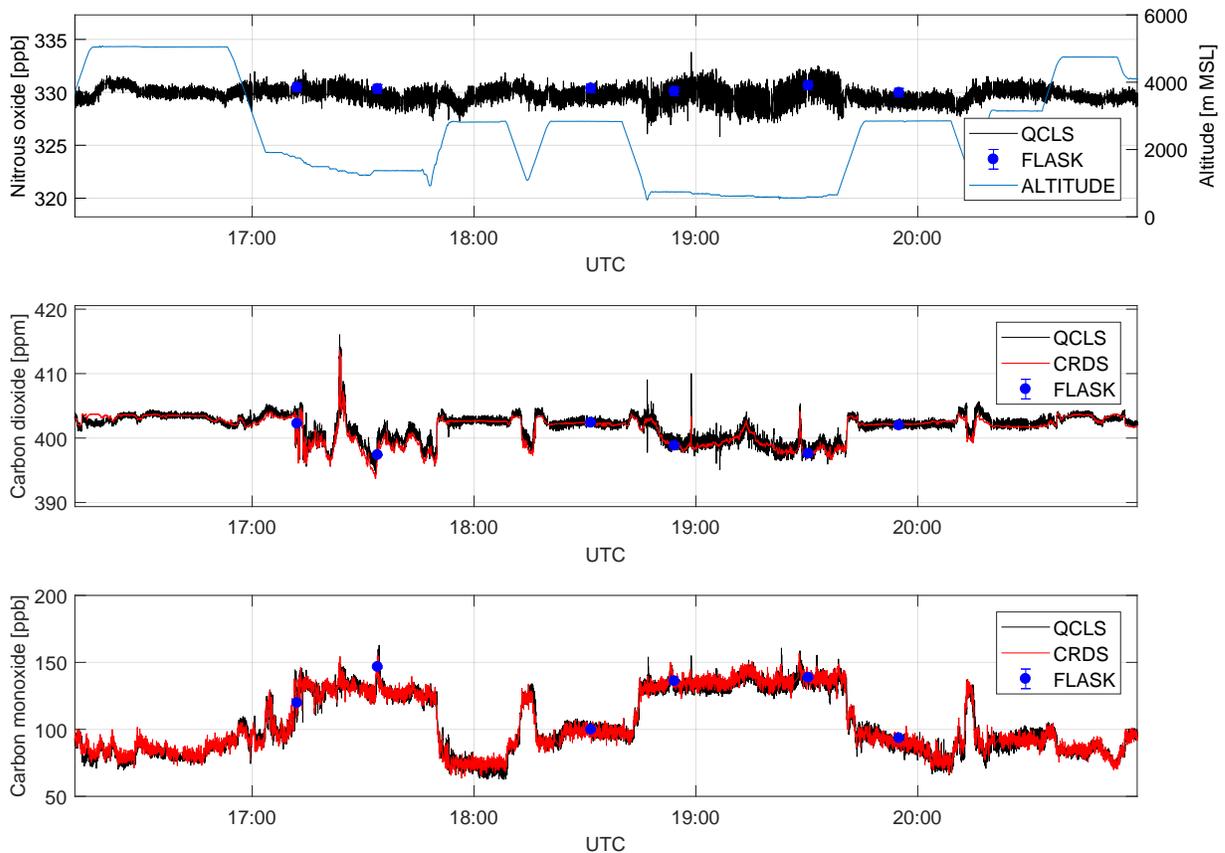


Figure 11. Dry-air mole fractions retrieved from different measurement techniques for a complete flight on Oct. 3, 2017. Depicted are nitrous oxide (uppermost panel), carbon dioxide (center panel) and carbon monoxide (lowermost panel) mole fractions.

1.1% (Gordon et al., 2017) to report total CO₂. Despite the much lower abundance compared to ¹²C¹⁶O₂ the QCLS-retrieved CO₂ data coincides with PICARRO-cavity ring-down data to within ±0.6 ppm (1σ) after correcting for a constant bias (see below). QCLS-retrieved CO mole fractions (center panel) agree with PICARRO-retrieved CRDS-retrieved data to within ±5 ppb (1σ). Figure 11 suggests that in-flight precision depends on whether flying within the planetary boundary layer or above it. This is due to aircraft vibration excited by running engines and turbulence propagating into the instrument optics inducing slight changes in optical alignment and enhanced natural variability in the planetary boundary layer. We identified temperature fluctuations within ~0.3 K, pressure changes of up to ~200 hPa and relative humidity changes of up to 35 % in the instruments optical compartment during this flight.

Typical in-flight precision figures based on ambient measurements at stable conditions for both regimes (standard deviation for 1s averaging) are summarized in Table 3. Total measurement uncertainty can be estimated from the uncertainty of the working standards, the uncertainty of calibration sequence evaluation, the uncertainty introduced by the H₂O-H₂O correction, the precision of the instrument and errors due to drift. We found a bias constant for the whole measurement series of ~-2 ~+2

Table 3. Typical in-flight performance including contributions to overall uncertainty. The total measurement uncertainty at 1 s temporal resolution is given by the quadrature sum of the individual contributors. Due to the lack of the appropriate NOAA standards during the deployment, the uncertainties in C₂H₆, CO and N₂O include combined uncertainties from concurrently measuring instruments (CRDS & Flasks). The total uncertainties stated for these species do therefore not reflect the intrinsic uncertainties of the instrument, but worst-case values, that may be better given the availability of appropriate standards. The WMO compatibility goals for Global Atmosphere Watch network compatibility among laboratories and central facilities have been added for completeness.

Chemical species	H ₂ O	CH ₄	C ₂ H ₆	CO ₂	CO	N ₂ O
Precision 1s – 1σ (within PBL)	16.2 ppm	740 ppt	205 ppt	460 ppb	2.2 ppb	439 ppt
Precision 1s – 1σ (above PBL)	2.5 ppm	300 ppt	146 ppt	182 ppb	1.4 ppb	208 ppt
Working standard reproducibility (1σ)	—	0.03 ppb	—	0.1 ppm	—	—
Compared instrument uncertainty (1σ)	—	—	1.5 ppb	—	5.0 ppb	0.4 ppb
Measurement calibration (1σ)	—	1.5 ppb	0.5 ppb	0.9 ppm	4.4 ppb	0.5 ppb
H ₂ O correction (1σ)	—	0.8 ppb	0.1 ppb	0.2 ppm	0.2 ppb	0.1 ppb
WMO compatibility goal	—	2.0 ppb	—	0.1 ppm	2.0 ppb	0.1 ppb
Total 1s-1σ uncertainty	—	1.85 ppb	1.6 ppb	1.0 ppm	7.0 ppb	0.8 ppb

ppb for CH₄ and $\sim -10 \sim +10$ ppm for CO₂ between the QCLS and ~~PICARRO~~CRDS/FLASK datasets. This constant bias has been corrected for. The origin of the biases is not yet fully understood. It was suggested that water vapor correction could have an impact on this. The reason for this assumption is that the calibration standards are always dry, whereas sampled air is not dried before entering the sample cell. Correlation plots however show no significant influence of water vapor on the residuals

5 between the dry-air-sampling ~~Picarro~~CRDS and the QCLS. It is therefore very unlikely that the water vapor correction is the source of the large bias in CO₂. Instead we identified the difference in isotopic composition of the calibration standard versus sampled atmospheric air as the most probable cause. In this study we used working standards of synthetic nature from *Air Liquide*. Usually these are produced with CO₂ from natural gas & oil combustion processes. We determined the CH₄ and CO₂ values of each working standard gas cylinder using a NOAA-anchored (Cert.-Nr. CB11361) Picarro G-1301m. This has the

10 drawback that we do not know the isotopic composition of our working standards as its impact had been considered negligible, e.g. Chen et al. (2010). We learned during development of JFIT, that the instrument is using a ¹³C¹⁶O₂ line to derive ambient CO₂. We estimate the required isotopic composition that could explain ~~a~~the large bias of ~~up to~~17-10 ppm (see Supplement Section 3) in CO₂ to be 98.447 % primary isotopologue and 1.079 % secondary isotopologue or δ¹³C = -19.6 ‰ which seems reasonable according to B. Coplen et al. (2002). Since we are reporting retrieved mole fractions relative to the WMO

15 scale, only the working standard reproducibility contributes to the total uncertainty of CH₄. Comparability of CO₂ is difficult to assess here because of the unknown isotopic composition in our working standards. Uncertainty in the other measured species is taken from the ACT-America dataset to allow for WMO traceability. Due to the lack of the appropriate NOAA standards during the deployment, the uncertainties in C₂H₆, CO and N₂O include uncertainties reported in the ACT-America dataset from

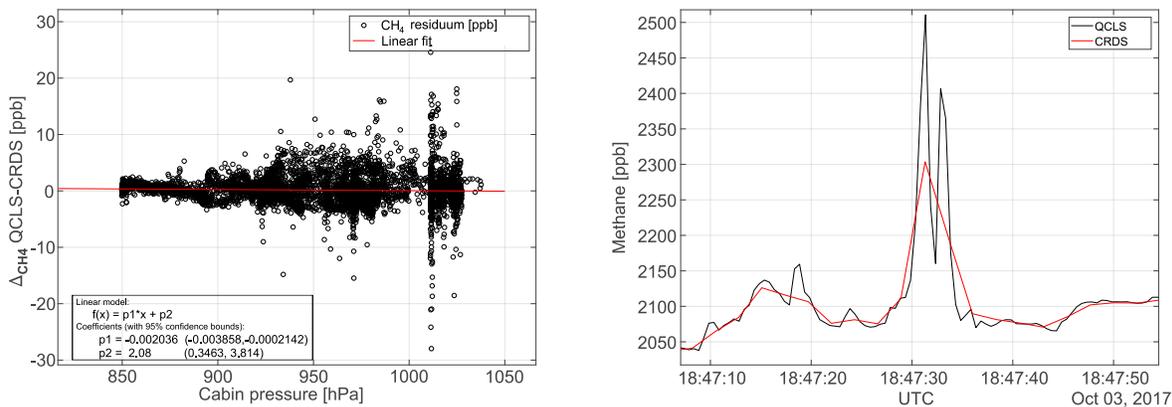


Figure 12. The left panel shows the cabin pressure dependence for a typical flight on Oct. 3, 2017. The large cabin pressure dependence in excess of 0.3 ppb hPa^{-1} reported by Pitt et al. (2016) has effectively been minimized using the calibration strategy from Sect. 2.3. The right hand side panel shows a temporal zoom on the CH₄ mole fractions at 18:47 UTC to emphasize the benefit of high-frequency measurements.

concurrently measuring instruments (CRDS & Flasks). The total uncertainties stated for these species do therefore not reflect the intrinsic uncertainties of the instrument, but worst-case values, that may be better given the availability of appropriate standards in future deployments. The uncertainty of calibration sequence evaluation (see Section 2.3) is estimated with the double of the measurement precision and the uncertainty introduced by the H₂O correction is estimated from Eq. (1) using an assumed relative error on retrieved water vapor of 2%. Errors originating from instrument drift are considered negligible due to our frequent calibration strategy (see Section 2.3). The total uncertainty is given by the quadrature sum of the individual contributors, listed in Table 3. Table 3 further includes the WMO compatibility goals for Global Atmosphere Watch (GAW) network compatibility among laboratories and central facilities. Precision figures given in Table 3 can be compared to $2s-1\sigma$ PICARRO G2401-m airborne precision estimates based on ambient measurements at stable conditions of 0.3 ppb, 0.02 ppm and 2.0 ppb for CH₄, CO₂ and CO, respectively.

A severe cabin pressure dependence in excess of 0.3 ppb hPa^{-1} in CH₄ mole fraction has been previously reported for airborne TILDAS instrumentation (Pitt et al., 2016). This instrumentation however physically differs from the one reported in this study. It is not possible to accurately compare the dependencies of one instrument relative to another since many factors/quantities involved are instrument-specific, e.g. the open-path length, the positioning and properties of optical elements, like windows, mirrors, etc., the stiffness and thermal expansion coefficient of the employed optical stands. We were nevertheless able to effectively minimize cabin pressure dependencies during operation of the QCLS instrument aboard the C130 using the calibration strategy from Sect. 2.3. This required a total calibration gas amount of $\sim 3.5 \text{ m}^3$ (excluding zero air) for the 18 research flights. Figure 12 (left panel) shows the difference in CH₄ dry-air mole fraction reported by the QCLS and the PICARRO instrument-CRDS as a function of cabin pressure during the research flight described above. The large scatter results from different sampling patterns among the two instruments, hindering a one-to-one comparison of the QCLS measurements with the PICARRO-CRDS. While the QCLS samples continuously with a frequency of 2 Hz (1.5 kHz sweep frequency), the PICARRO

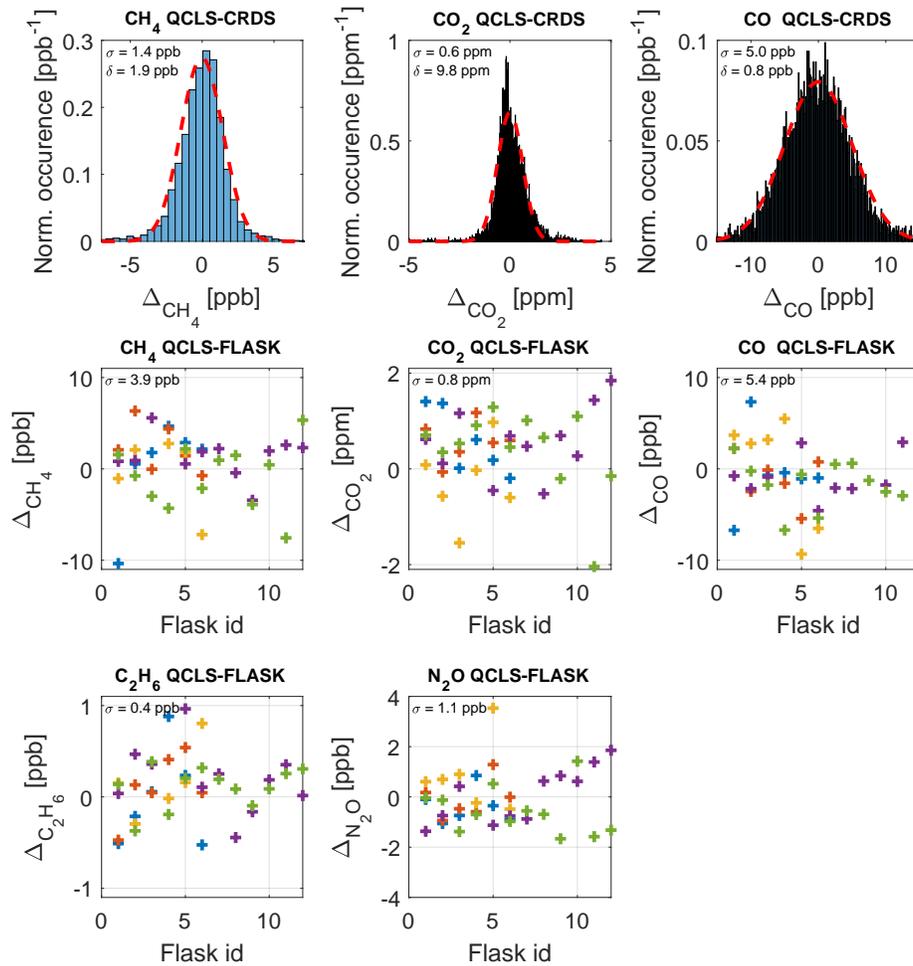


Figure 13. Comparison of QCLS derived mole fractions to well-established in-flight [PICARRO-cavity ring-down](#) data and flask samples after correcting for a bias (δ) constant for the whole measurement series including standard deviations σ . Interpretation of the errors against flask samples is difficult for high-variability flight segments, due to the large flask sampling time. The residual plots show color-coded data from 5 typical flights on 10/03/2017 ([blue](#)), 10/11/2017 ([red](#)), 10/14/2017 ([yellow](#)), 10/18/2017 ([violet](#)) and 10/20/2017-2017 ([green](#)).

[CRDS](#) samples with a frequency of 0.5 Hz one species after the other. For CH₄, for example, the [PICARRO-CRDS](#) uses the first 0.5 s of the 2 s sampling time, implying that, for the later 1.5 s, the [PICARRO-CRDS](#) is insensitive to CH₄. Therefore, it is difficult to mimic the [PICARRO-cavity ring-down](#) sampling by averaging the QCLS data as it would be required for a one-to-one comparison. Instead we decided to linearly interpolate QCLS data to the [PICARRO-CRDS](#) timescale. The fast response time of the QCLS instrument allows for better sampling of spatially narrow plumes, as can be seen from the right hand side panel in Figure 12. This panel zooms in on a relevant portion of the methane data from Figure 10 and demonstrates that two mutually-separated plumes can be identified from the high frequency QCLS data at 18:47 UTC, where only a single enhancement can be seen from [PICARRO-cavity ring-down](#) data. Furthermore, absolute enhancement and area beneath the peak(s) differ for the

two instruments, due to the different sampling patterns. Figure 13 compares the QCLS mole fractions to the [PICARRO cavity ring-down](#) instrument and to the flask samples after correcting for a bias constant for the whole measurement series. The upper panels show differences in retrieved mole fractions between the QCLS and the cavity ring-down instrument for the flight on Oct. 3, 2017, exhibiting a near normal distribution. This hints towards residuals originating from random processes, i.e. noise.

5 Despite the different sampling time and pattern, the measurements exhibit a compatibility to the calibrated cavity ring-down observations of 1.4 ppb in CH₄, 0.6 ppm in CO₂ and 5.0 ppb in CO. Although interpretation of the differences to flask samples is difficult for high-variability flight segments, the lower panels of Figure 13 show a good agreement for five typical flights (10/03/2017, 10/11/2017, 10/14/2017, 10/18/2017, 10/20/2017) during the ACT-America campaign. [The relative deviations are in good agreement with the QCLS-CRDS data, except for CH₄, where QCLS-CRDS compatibility \(1.4 ppb\) differs from the QCLS-FLASK compatibility of 3.9 ppb. This could be related to the different sampling times between the QCLS and flask samples.](#)

10

6 Conclusions

We adapted the commercially-available QCL/ICL based *Dual Laser Trace Gas Monitor* from *AERODYNE RESEARCH INC., Billerica, USA* for airborne flux estimation (e.g. via the mass-balance approach) and demonstrate successful operation for

15 representative research flights aboard NASA Wallops Flight Facility's C-130 during the ACT-America field campaign in fall 2017. Known cabin-pressure dependencies (Gvakharia et al. (2018); Pitt et al. (2016)) on the retrieved mole fractions are effectively minimized using a frequent (5 to ~~10mins~~ [10 min](#) interval) two-point calibration approach obtained by flushing the sample cell with "zero" and "target" gases. This allows for a measurement duty cycle of ~~≥ 90%~~ [≥ 90 %](#) when operating at sample flow rates near 23 SLPM. A custom retrieval software has been developed to learn about possible error sources,

20 mitigation possibilities of instrument dependencies and to be able to extend the instruments capabilities in the future. Apart from low frequency laser instability we identify high frequency "jumps" on the spectral axis, possibly due to the instruments frequency lock mechanism. In-flight performance has been assessed using data obtained during the research flight on the 3rd Oct. 2017 above the eastern ~~U.S.~~ [US](#). We identify two precision regimes whether flying within the planetary boundary layer or above, due to aircraft vibration propagating into the instrument optics and related slight changes in optical alignment. Typical

25 in-flight precision figures for boundary layer flights (standard deviation for 1s averaging) are 740 ppt, 205 ppt, 460 ppb, 2.2 ppb, 137 ppt, 16 ppm for CH₄, C₂H₆, CO₂, CO, N₂O and H₂O respectively. Precision figures improve to approximately the half for flights above the PBL. We estimate a total measurement uncertainty of 1.85 ppb, 1.6 ppb, 1.0 ppm, 7.0 ppb and 0.8 ppb in CH₄, C₂H₆, CO₂, CO and N₂O, respectively. We demonstrate QCLS comparisons to concurrent flask sample and cavity-ringdown measurements within combined measurement uncertainty for all targeted species. The instrument retrieves carbon

30 dioxide mole fractions via a ¹³C¹⁶O₂ absorption line. We find that precise knowledge of the δ¹³C of the working standards and the sampled air is needed to enhance CO₂ compatibility when operating on the 2227.604 cm⁻¹ ¹³C¹⁶O₂ absorption line.

Code and data availability. Software code and data are available from the authors upon request.

Competing interests. The authors are not aware of any competing interests.

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Supplement to "Adaptation and performance assessment of a Quantum / Interband Cascade Laser Spectrometer for simultaneous airborne in situ observation of CH_4 , C_2H_6 , CO_2 , CO and N_2O "

1 Compatibility & Comparison with other instruments

We have computed the differences between flasks and the CRDS in the same way they have been computed for the QCLS in the main manuscript by interpolating high frequent in situ data to the flask end fill times. This has been done to get an idea on what spread can be expected due to the long flask sampling time compared to the fast measurement cycles of CRDS and QCLS. Although the spread in Fig. 1 might be slightly bigger for the QCLS compared to the CRDS it remains unclear if this is due to higher sampling rate and/or response time of the QCLS.

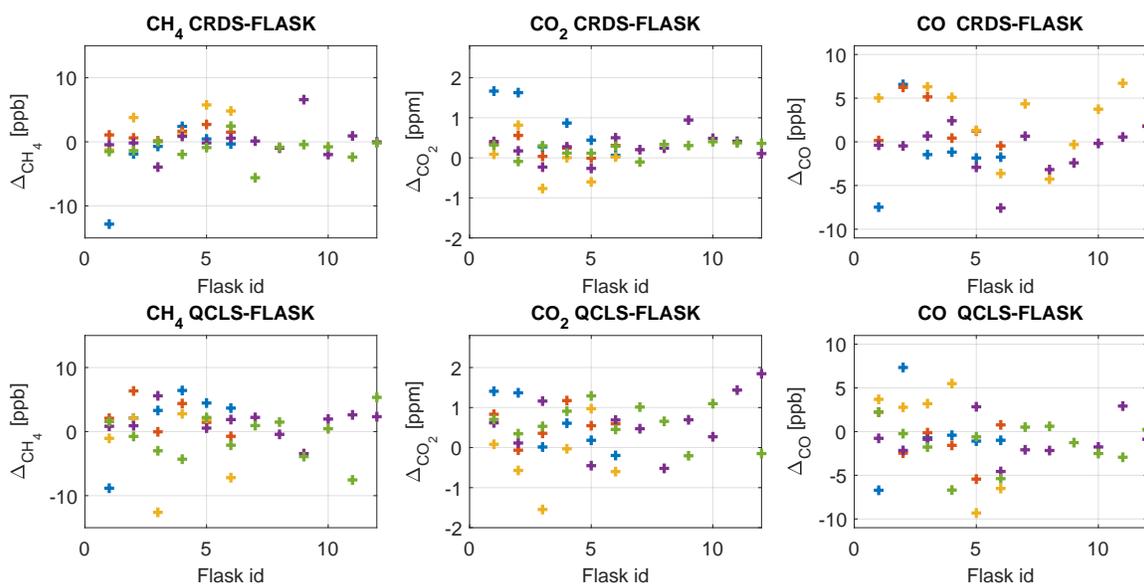


Figure 1. Comparison of CRDS (upper row) and QCLS (lower row) derived mole fractions to flask samples. Interpretation of the errors against flask samples is difficult for high-variability flight segments, due to the large flask sampling time. The residual plots show color-coded data from 5 typical flights on 10/03/2017, 10/11/2017, 10/14/2017, 10/18/2017 and 10/20/2017.

2 Cross-sensitivities

There was doubt if the water vapor correction is deteriorating compatibility between instruments. Figure 2 shows cross sensitivities of the QCLS-CRDS residuals for the flight highlighted in the original manuscript (10/03/2017) with respect to cell pressure, cell temperature and water vapor after correcting for a constant bias. The residuals have been computed by linearly interpolating the higher frequency QCLS to the CRDS time scale, due to different sampling times and patterns. From this figure, we would argue, that the water vapor correction (center row in Figure 2) is not systematically deteriorating compatibility between the instruments.

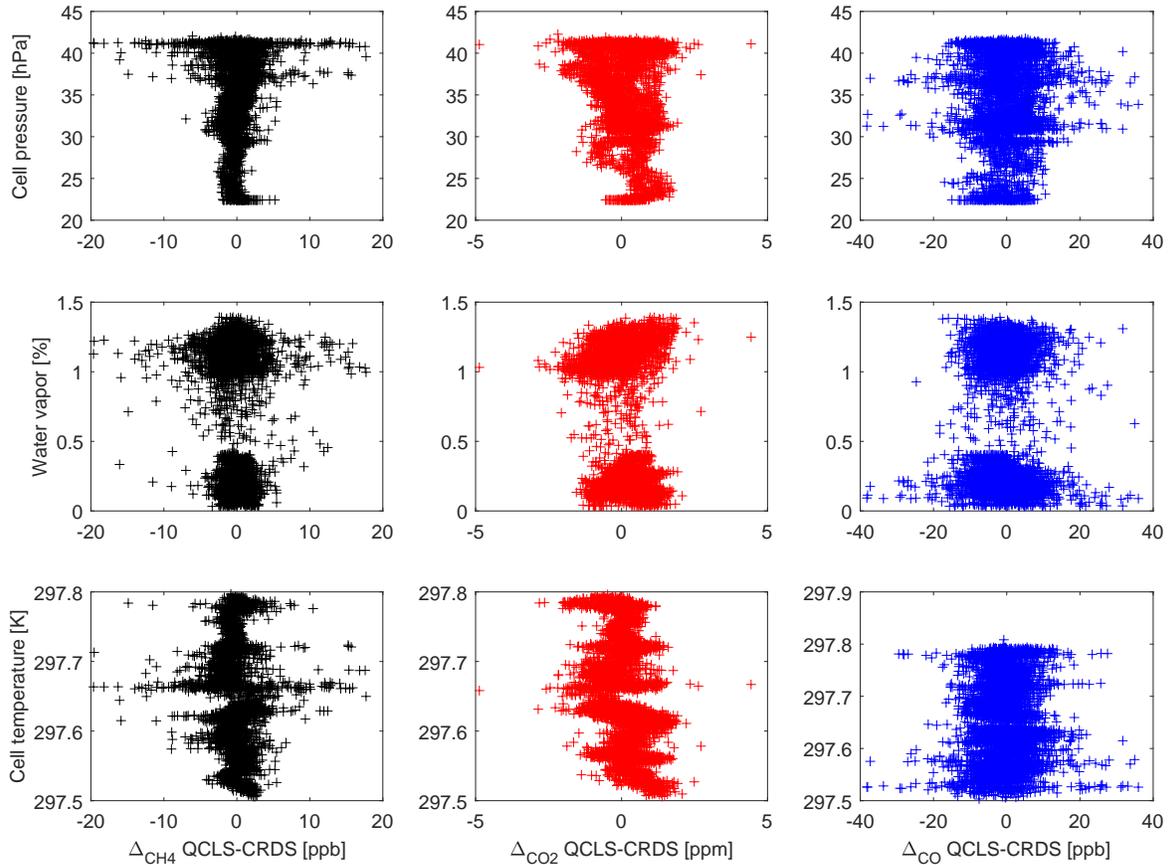


Figure 2. Cross sensitivities of the QCLS-CRDS residuals for the flight highlighted in the original manuscript (10/03/2017) with respect to cell pressure, cell temperature and water vapor after correcting for a constant bias. Due to different sampling times and patterns the higher frequency QCLS data have been linearly interpolated to the CRDS time scale.

3 Large bias in CO₂

Explaining the large bias in retrieved CO₂ requires an estimation of the influence of the isotopic composition of the working standards used and the sampled air within this study. We have used working standards of synthetic nature from *Air Liquide* due to the large amount of needed calibration gas. Usually these are produced with CO₂ from natural gas & oil combustion processes. We determined the CH₄ and CO₂ values of each working standard gas cylinder using a Picarro G-1301m. This has the drawback that we do not know the isotopic composition of our working standards. The reason why we did not send our working standards to a central lab is because the influence of the isotopic composition had been considered negligible at this stage (Chen et al., 2010). It was only in late summer 2018, that we found out (during development of JFIT) when we found that the instrument was using a ¹³C¹⁶O₂ line to derive ambient CO₂. We assume the large bias originating from differences in isotopic composition in our working standards relative to the natural terrestrial abundances. This requires an estimate on the possible influence which will be given here.

It is commonly assumed that differences in isotopic composition only make up for errors on the order of 0.1 ppm in CO₂. This is true if measuring the primary isotopologue, as done with the Picarro CRDS. If the CO₂ concentration is derived from the secondary isotopologue (¹³C¹⁶O₂) the influence of isotopic composition is much larger. Let us take the $\delta^{13}C = -8.6$

$\%o$ reported for the NOAA standard Cert.-Nr. CB11361 as an example to estimate the influence of isotopic composition on retrieved mole fractions. Per definition $\delta^{13}C$ is given by

$$\delta^{13}C = \left(\frac{R_x}{R_{vpdb}} - 1 \right) \times 1000$$

Inserting the values from above and re-arranging this equation yields

$$5 \quad R_{noaa} = (1 - 8.6 \times 10^{-3}) \times R_{vpdb}$$

Inserting the standard ratio for the reference materials of the Vienna Pee Dee Belemnite $R_{vpdb} = 0.011180 \pm 0.000028$ (Tohjima et al., 2009; Chen et al., 2010) yields the corresponding isotopic ratio of

$$R_{noaa} = (1 - 8.6 \times 10^{-3}) \times 0.011180 = 0.011083$$

According to HITRAN the primary isotopologue and secondary isotopologue together make up 99.5261 % of atmospheric CO_2 .

- 10 To satisfy both equations we obtain an abundance of 0.984350 primary isotopologue and 0.010910 $^{13}C^{16}O_2$ for the NOAA standard dealt with here. However, spectral line intensities S_{ij} as defined on <https://hitran.org/docs/definitions-and-units/> are weighted according to the natural terrestrial abundances reported in HITRAN. Retrieved mole fractions are thus scaled by their terrestrial natural abundance from HITRAN. We'll first compute the unscaled $^{13}C^{16}O_2$ using the natural abundance from HITRAN (98.4204 % primary and 1.1057 % secondary CO_2 isotopologue) from a hypothetical 400 ppm background (with a
- 15 natural isotopic composition as defined in HITRAN) resulting in

$$^{13}CH_{4,unscaled}CO_{2,unscaled} = 400 * 0.011057 = 4.4228$$

~~Now we can~~ We can now estimate the influence of the different isotopic composition (NOAA example) from above by scaling the unscaled $^{13}CO_{2,unscaled}$ with the secondary isotopologue abundance computed above. For the given absorption line, a retrieval algorithm based on HITRAN will retrieve an abundance of $CO_{2,retrieved}$ according to

$$20 \quad x_{retrieved}CO_{2,retrieved} = \frac{4.4228}{0.010910} = 405.4 \text{ ppm}$$

From this example we see that the **small perturbation in isotopic composition already has an impact of 5.4 ppm** in retrieved CO_2 .

Chen et al., 2010 reported on synthetic air with added CO_2 from burned petroleum or natural gas with $\delta^{13}C = -37 \pm 11 \%o$. Using this value, and repeating the math from above, we obtain a **possible influence estimate change of 17.2 ppm in retrieved**

- 25 **mole fractions** resulting solely from a different isotopic composition. Given this estimate, we find that, precise knowledge of the $\delta^{13}C$ of the working standards and the sampled air is needed to enhance CO_2 compatibility when operating on the 2227.604 cm^{-1} $^{13}C^{16}O_2$ absorption line. In the absence of other error sources, achieving WMO compatibility using this absorption line at ambient CO_2 concentrations of 400 ppm requires the sum of $\delta^{13}C$ from the working standards and the sampled air to be known better than 4.9 %o. In reality other error sources are not negligible, which will further reduce the stated margin.

4 Calibration cycles

We included distribution diagrams of the calibration cycles during the flight highlighted in the main manuscript (10/03/2017) in Figure 3.

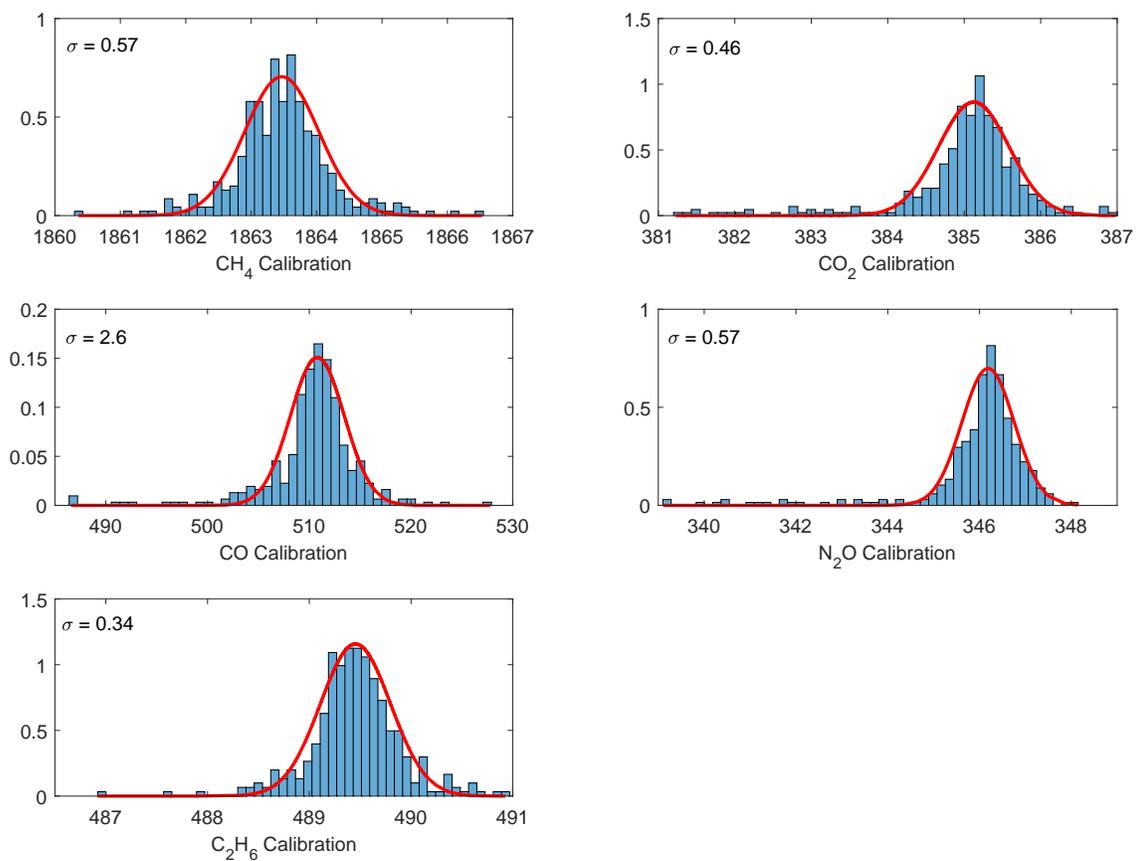


Figure 3. Distribution diagrams of the calibration gas measurements during the flight highlighted in the main manuscript on Oct. 3, 2017.