Towards Laboratory-level Accuracy in the Field: Spectroscopic Uncertainty in Greenhouse Gas Sensing with Frequency Combs

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Abstract. Long-term monitoring of long-lived greenhouse gases (ghgs) requires sub-percent (0.1%) accuracy, and observations should also be dense enough to constrain top-down calculations of ghg emissions. However, logistical difficulties make it costly to expand the current measurement network. Dual Comb Spectroscopy (DCS) has emerged as a cost-effective technique to measure ghgs, like $CH_4$4, $CO_2$2, and $H_2$2O, with high accuracy. By employing laser frequency combs, DCS provides broadband measurements with extremely high spectral resolution (0.0067 cm-1) at open paths with a range of up to 10 km. The lack of an instrument line-shape in DCS systems is appealing as it should allow for self-calibration and stable long-term monitoring without instrument drift. To fully assess the uncertainties in long-path DCS systems, we systematically investigate the impact of spectroscopic uncertainties as well as those induced by temperature, pressure and water vapor variations. Here, we show that retrieved concentrations of ghgs from a multi-month DCS field deployment disagree by up to 76 ppb for CH_4 and 3.5 ppm for CO2 when using different spectroscopic databases, which do not meet the 0.1

1 Introduction

Long-term monitoring of well-mixed greenhouse gases (ghg) requires instruments that can measure at 0.1% accuracy (Keeling et al, 1998). These observations also need to be in spatially representative locations, and observations should be dense enough to provide top-down constraints on calculations of greenhouse gas emissions (Jacob et al., 2016). To this end, the National Oceanic and Atmospheric Administration (NOAA) maintains a global network of flask-sampling sites. Air samples are collected in flasks and shipped for analysis, an expensive and logistically difficult process (Tans et al, 1989; Sweeney et al, 2015). These difficulties limit highly accurate ghg measurements to a limited number of places.

The accuracy of ghg measurements is limited by both instrument capabilities and the accuracy of ghg spectroscopy. Many existing methane sensors are based on infrared spectroscopy, which are limited by their accuracy and portability. Cavity Ringdown Spectroscopy, although highly accurate, have to be continuously calibrated with reference gases, which limit their portability, and only measure at the point-scale, introducing spatial representation error. On the other hand, open path measurements,

such as Fourier Transform Spectroscopy, can measure at longer ranges, but their accuracy can be limited by drifts in the instrument line-shape, in addition to being difficult to deploy. Both automated and accurate measurements directly in the field would therefore open up new possibilities for long-term monitoring by expanding the current ghg measurement network.

Recently, Dual-Comb Spectroscopy (DCS) has emerged as a candidate to augment the NOAA network, because it can remotely measure greenhouse gas concentrations with high accuracy. DCS provides broad-band, high SNR, and high spectral resolution measurements (Rieker et al., 2014; Coddington et al., 2016; Waxman et al., 2017, 2019; Coburn et al., 2018). As a result, DCS could be the ideal instrument for greenhouse gas remote sensing. Its absolute frequency accuracy, ideal instrument line-shape and high SNR allows for highly precise interrogation of molecular line-positions and line-strengths. Its high spectral resolution resolves molecular line-shapes caused by pressure and temperature-induced broadening effects. Its open-path, kilometer-scale measurements can be used to measure at scales relevant for ghg emissions inversions. Finally, its absolute stability and virtual lack of an instrument line-shape means that inter-calibration is not needed for a future network of DCS instruments.

These capabilities have been demonstrated in field-deployments. Reiker et al, 2014, was the first to deploy DCS to measure CH_4, CO_2, and H_2O around the 6050-6300 cm^{-1} (1.6 micron) band by taking advantage of the broadband capabilities of the instrument. Cossel et al, 2017, employed the open-path and high signal-to-noise features of the instrument to detect methane leaks from a natural gas production sites. They were able to detect methane leaks 1,000 times smaller than that of techniques of similar spatial scales. Waxman et al, 2018 utilized the open-path, kilometer-scale measurements to quantify CO_2 traffic emissions in Boulder, Colorado, USA and obtained results that matched with bottom-up inventories. Finally, Waxman et al, 2017, used the absolute calibration inherent in the frequency comb's mode-locked laser and obtained sub-percent agreement of ghg concentrations with two independent DCS setups, despite not being inter-calibrated, demonstrating its capability as part of a future network. These field-deployments show the utility of DCS for future remote sensing applications.

Although DCS is capable of measuring highly resolved spectra with absolute frequency stability, accurately measuring and monitoring ghg concentrations in the atmosphere is challenging due to spectroscopic limitations. The spectroscopic databases, which are used to calculate absorption features of ghgs, do not have the accuracy to reach the 0.1% accuracy required for background monitoring. Additionally, the presence of other gases, mainly water vapor, can confound spectroscopic measurements and ghg retrievals. This is especially true for methane.

For example, Waxman et al, 2017, also found that retrieved methane concentrations disagreed when using different spectroscopic databases. These spectroscopic databases contain the parameters necessary for calculating the absorption cross-sections of gases being measured and their sensitivity to pressure and temperature-induced broadening effects. They found that there was a 20 ppb (1%) difference in methane concentrations that resulted from different spectroscopic databases, which is an order of magnitude greater than what is needed for long-term ghg monitoring. Moreover, these biases also depend on environmental variables, such as pressure, temperature and humidity. This variable error cannot be simply subtracted out, as in the case of systematic error, or averaged out, as in the case of random error. To achieve sub-percent accuracy, the accuracy of the spectroscopic parameters modeling these environmental variables should also be accurate to within a corresponding sub-percent level.

Motivated by achieving long-term monitoring capabilities, We compare ghg retrievals from different spectroscopic databases with measured spectra from a DCS deployment and quantify the biases in these databases . This enables adjustments to spectroscopic parameters to be made for more accurate ghg spectroscopy for future remote sensing applications. Then, we perform numerical experiments on the spectroscopic parameters and analyze these effects on ghg retrievals. We identify and quantify the atmospheric conditions where variable bias is most prevalent. Finally, we assess the ability of the DCS to retrieve vertical gradients of greenhouse gases in the atmosphere through a series of synthetic experiments and quantify the additional information DCS provides in vertical profile retrievals.

2 Dual-Comb Spectroscopy Technique

2.1 Dual-Comb Spectroscopy Technique

The technique of DCS employs laser frequency combs, which were originally designed for pico-second time keeping (see Fortier et al. 2019, for a historical review). Frequency combs emit laser light at about 100,000 distinct frequencies, which are narrowly and evenly spaced apart in frequency space, like the teeth of a comb (Hall et al, 2000). This broad-band, laser-light is the defining feature of a frequency comb. DCS employs two frequency combs so that the destructive interference maps infrared (THz) to radio frequencies (kHz). The resulting radio-frequency comb can be read by commercial radio-frequency detectors, decreasing instrument cost (Coddington et al, 2016).

To achieve laboratory-level accuracy, the frequency combs need to have long-term frequency stability and maintain comb coherence. To do this, mutual comb coherence is enforced by phase-locking each tooth of the two combs to a Continuous Wave (CW) Laser. The resulting destructed comb teeth are referenced to a common quartz microwave oscillator. This ensures that both of generated comb light and resulting destructed light are phase-locked. furthermore, to close the calibration feedback loop, the CW laser and microwave oscillator are also effectively locked via a bootstrapping method. Further details can be found in Truong et al. 2016. This self-referencing protocol results in laboratory-level accuracy and stability in a field setting, which we apply to greenhouse gas remote sensing.

2.2 Field Setup

In this study, our DCS generates light between 6,000 and 6,400 cm^{-1} (1560 - 1660 nm) at 80,000 distinct and stable frequencies, resulting in an equidistant spectral-sampling of 0.0067 cm^{-1} (add spectral resolution here!). Since changes of line-shapes in time can be one reason for re-calibrating instruments, DCS systems should be more stable, as both their frequency positions as well as spectral sampling and resolution are fixed and determined by the physical nature of the measurements.

The DCS design is outlined in Sinclair et al, 2015. In summary, both of the frequency combs are powered by a 10 mW femto-second, mode-locked laser centered at 1550 nm. The light passes through a erbium-doped highly non-linear fiber, which amplifies the light to 300 mW.

The DCS was mounted atop a building at the NIST facility between 21 September to x November, 2016 in Boulder, CO and aimed at a retro-reflector on a nearby hill 1-km away. After traversing this 2-km round-trip path-length, the signal is read on a InGaAs photodetector and saved on the FPGA. After transferring to a computer, post-processing further aggregates the data into 30-second intervals. Finally, the interferogram is Fourier Transformed, which results in a transmission spectra that contains the information for retrieving ghg concentrations. More information on the field setup can be found in Waxman et al., 2017.

A commercial cavity ring-down spectrometer (Picarro Model 3012) was also deployed to the field, alongside a pressure and temperature sensor, to act as a reference for our measurements. The Picarro was calibrated to the WMO error standard by referencing a WMO reference mixed gas that contains known quantities of CO_2, CH_4, and water vapor in a pressure and temperature controlled cavity in the instrument. This results in an instrument uncertainty of 0.7 ppm for CO_2 and 1.5 ppb for C_H4. the instrument was mounted atop a radio tower 30 m above the ground along the path of the DCS beam.

2.3 Spatial representation of point-measurements over an open path

Although the point sensor is acting as a reference for our field measurements, it should be noted that the point-sensor and the open-path DCS will not have exactly matching results, even if the accuracy of both instruments was perfect. This representation error is due to the spatial footprint of the two instruments – where the DCS is measuring the air over a 1 km path and the Picarro is measuring a much smaller point. The point sensor is therefore more sensitive to small-scale enhancements and turbulence-induced fluctuations. However, the Picarro instrument remains a useful benchmark to test our DCS retrievals.

Minimizing spatial representation error is also the reason why we retrieve pressure and temperature from DCS spectra over the path, rather than relying on the nearby point-scale sensors. Accurately retrieving pressure and temperature over the path is important for accurately calculating the dry air column density. Other instruments, such as OCO and TCCON, use ancillary measurements of O_2 in order to infer the dry-air column, because the concentration of oxygen is well known and exhibits very little variation. DCS has also recently been used to measure O_2 concentrations (Malarich et al., 2023). However, due to the high spectral sampling of the DCS, we can instead calculate the dry air column by directly retrieving the pressure, temperature, and water vapor over the light-path.

3 Retrieval Approach

3.1 Problem Statement

The retrieval problem for an open path system is that the depth of the measured absorption lines depends on the ghg column density integrated over the path, typically expressed in units of molecules/cm^2. To convert from column density to volume mixing ratio, we divide the greenhouse gas column density by the dry air column density:

$$[ghg] = \frac{ghg_{cd}}{total_c d - H_2 O_{cd}} \tag{1}$$

$$\tag{2}$$

In Eq. 1, $ctotal_{cd}$ is the column density of air, ghg_{cd} is the column density of ghg molecules, and $H_2 O_{cd}$ is the column density of water vapor, expressed in molecules/cm^2. The column density of dry air can be calculated from a modification of the Ideal Gas Law:

$$\rho_{dry} = \frac{p(1 - [H_2 O])}{rT} \tag{3}$$

$$dry_{cd} = \rho_{dry} \delta x \tag{4}$$

Eq. 3 provides the relationship between the number density of dry air, denoted ρ_{dry}, and the atmospheric state, which is determined by pressure (p), temperature (T), and the water vapor mixing ratio ($[H_2 O]$). To compute the dry air column density, dry_{cd}, we multiply the dry air number density, ρ_{dry}, by the round-trip path-length, δx. Since we are jointly retrieving pressure, temperature, and [H$_2$O] from DCS spectra, errors in modeling the pressure and temperature-dependent absorption cross-sections being measured will propigate into the dry air column and thus the ghg concentration.

Here, we will quantify the biases induced in retrieving greenhouse gas concentrations, for both the retrieval of greenhouse gas column densities as well as its conversion to a column-averaged mixing ratio via the derived dry air column. This constitutes all the steps for retrieving ghg concentrations over the open path.

3.2 Retrieval Algorithm

In order to retrieve the ghg concentrations from the measured spectra, we performed a non-linear inversion using the Lambert-Beer Law:

$$\tau = \sum_i^n [ghg] dry_{cd} \sigma \tag{5}$$

$$I = exp^{-\tau} \tag{6}$$

$$\tag{7}$$

The optical depth, τ, depends on the ghg column density and the absorption cross-section, σ. The cross-section was calculated using the Voigt line-shape from vSmartMOM.jl (citation), which was based off the Hitran API (HAPI) (citation). Eq. 6 gives the relationship between the transmission intensity, I, and the optical depth.

Usually, an instrument operator would then have to be applied in order to convolve the modeled line-by-line simulation to the actual instrument resolution. However, one of the advantages of the DCS is that the instrument's line-shape is negligible, so

this step does not need to be performed. Since changes of line-shapes in time can be one reason for re-calibrating instruments, DCS systems should be more stable, as both their frequency positions as well as spectral sampling and resolution is fixed and determined by the physical nature of the measurements. Thus, the resulting forward model is as follows:

$$f(x) = exp^{-\tau} p(\nu, x_{Legendre}) \tag{8}$$

Evaluations of the forward model map the chemical and thermo-dynamic state (e.g., concentrations, pressure, and temperature) to simulated spectra observed by the instrument. To find the optimal state, the misfit between the simulated spectra and the observed spectra is minimized by iteratively selecting state parameters and evaluating the forward model. Exploration and selection of the state is done by non-linear least squares fitting [Rogers 2000]. The algorithm is as follows:

$$x_{i+1} = x_i + (\mathbf{K^T S}_\epsilon)\mathbf{K^T}(y - f(x)) \tag{9}$$

Here, y is the observed spectra, $f(x)$ is the modelled spectra, $mathbfS_\epsilon$ is the error covariance matrix, and $\mathbf{K}$ is the jacobian matrix. The jacobian is calculated using the ForwardDiff.jl package (citation). Finally, x_i is our state vector at the ith iteration, and it includes the vertical column density (vcd) of each of the gases being retrieved, the 100 shape parameters for each of the Legendre Polynomials, and the pressure and temperature along the path.

A crucial aspect of our retrieval is that our state vector contains the column density (total number of trace gas molecules per unit area), rather than the volume-mixing ratio. This enables the separation of spectroscopic errors from pressure and temperature errors. Errors in pressure and temperature calculations will alias into the dry air column amount seen in the denominator of Eq. **??** and therefore will carry into the derived ghg concentration. On the other hand, fitting only for the column amount will enable us to evaluate the errors sources independently.

3.3 Spectral line-lists

Since we are retrieving pressure and temperature from the shape of the absorption lines, it is necessary to accurately model the pressure, temperature, and wavelength-dependent absorption lines of the molecules being retrieved. The Voigt line-shape model accounts for both pressure and temperature effects by convolving the pressure and temperature-dependent Lorentzian line-shape and the temperature-dependent Gaussian line-shape. More complex profiles than the standard Voigt Profile have recently been used to account for additional physical effects, such as the molecular velocity changes that occur with molecular collisions (known as velocity changes), the speed-dependence on collisional broadening and shifting coefficients (speed dependence), and the interaction of neighboring transitions (line-mixing) [Ngo et al, 2013]. While accounting for these additional processes makes greenhouse gas retrievals more accurate, it has been shown that inaccuracies in the spectroscopic parameters lead to larger errors in modeling line-shapes than the complexity of the line-shape models themselves [citations].

The temperature, pressure, and wavelength absorption features unique to each molecule are calculated from spectral parameters tabulated in line-lists. Spectroscopic parameters are usually empirically fitted from laboratory measurements of molecular spectra.

Table 1 displays the line-lists being used in our study. We use the HITRAN 2008, 2016, and 2020 line-lists, in addition to the TCCON and OCO line-lists. The cross-sections were generated using the Voigt line-shape, except for OCO, which accounts

Species	Line-lists	Retrieval Window
CH_4	TCCON, Hitran 2008, Hitran 2016, Hitran 2020	6050-6115 cm^{-1}
CO_2	OCO, TCCON, Hitran 2016, Hitran 2020	6180-6260 cm^{-1}
H_2O	TCCON	6050-6115, 6180-6260 cm^{-1}

Table 1. Spectroscopic line-lists and retrieval windows used to retrieve greenhouse gas amounts in our experiment.

for velocity changes, speed-dependence, and line-mixing. Using multiple line-lists enables us to quantify how biases vary with pressure and temperature in the most commonly used spectroscopic databases.

4 Field Results

4.1 Methane retrievals disagree more than CO_2

180 Regional-scale gradients of CO_2 in the atmosphere are about 0.25% (1 ppm). Inferring CO_2 sources at this scale requires sub-ppm accuracy. A global network should be capable of this laboratory-level accuracy, which the DCS can provide directly in the field.

Fig 1 shows the retrieved time series for a two-week period in our study. Our algorithm retrieves CO_2 over the window between 6180-6260 cm^{-1}, and we employed the Hitran 2016, Hitran 2020, TCCON, and OcO line-lists. We can see that there 185 is a diurnal cycle, with 40 ppm CO_2 peaks in the time-series, which correspond to rush-hour traffic. The Picarro is also observing CO2, which is displayed as black dots.

Fig. 1C displays the ratio between the CO_2 concentrations retrieved from the DCS and the CO_2 measurements from the Picarro instrument. We can see that the ratio ranges from xx to xx, which indicates an x to x percent disagreement between the DCS retrieval and the Picarro instrument. OCO seems to have the best fits with chi2 ranging from xx to xx. TCCON is the 190 second best, which ranges from xx to xx. Finally, we find that there is not much of a difference between the Hitran 2016 and 2020 line-lists with Chi2 being xx and xx respectively.

Despite the fact that the DCS is solely relying on information from the spectroscopic databases, the ratio between the DCS retrieval and the WMO-calibrated CO_2 concentrations are nearly at unity, indicating very close agreement, and demonstrating the ability of the DCS measurement and retrieval to obtain highly accurate measurements of CO_2.

195 On the other hand, there is considerable disagreement for retrieved methane. Methane's spectroscopy is continuously evolving (Collins et al, 2018; Myer et al, 2016). Fig. 2 shows the retrieved methane time-series. Methane's daily peak is 200 pbb above background concentrations. Although less than the CO_2 diurnal cycle, methane still exhibits a diurnal cycle, which is driven by boundary layer height and urban emissions in Boulder. CO_2 emissions exhibit a more pronounced diurnal cycle, because the sources of CO_2, such as vehicle traffic and electricity production, are diurnally varying (Waxman et al, 2018).

200 We used the Hitran 2008, 2016, and 2020 line-lists , in addition to the TCCON line-list, to retrieve methane concentrations. In contrast to CO_2, the methane concentrations can vary by up to xx pbb, which is due to spectroscopic errors. These errors in

Retrieved CO_2
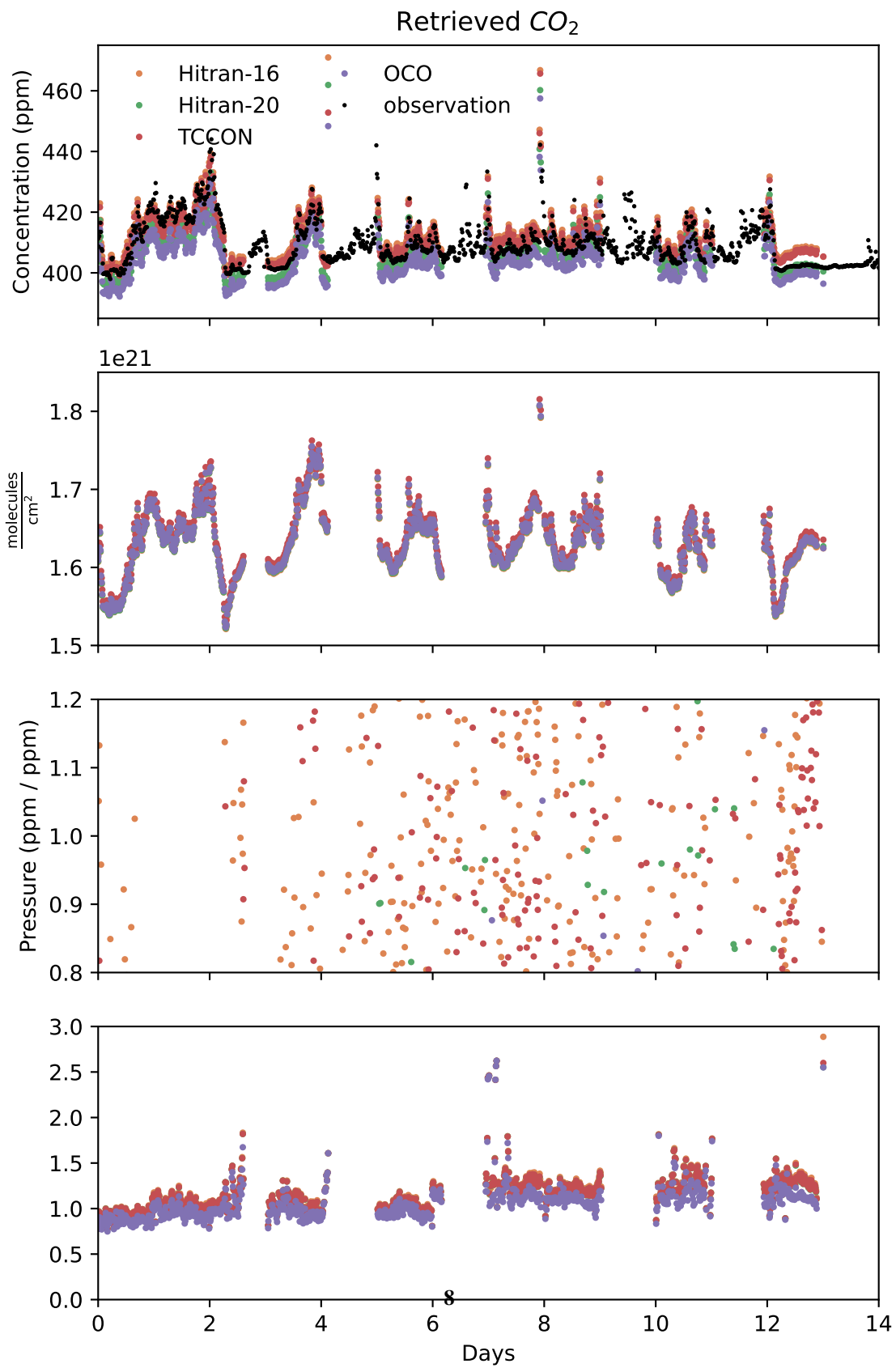
Ch$_4$ Correlations Variable	Hitran 2008	Hitran 2016	Hitran 2020	TCCON
H$_2$O amount				
H$_2$O error				
pressure error				
temperature error				
CO$_2$ correlations				
H$_2$O amount				
H$_2$O error				
pressure error				
temperature error				

Table 2. Error correlations for our retrievels from the field-deployed DCS. The errors were calculated relative to the Picarro instrument.

pressure and temperature-dependent spectroscopic parameters can induce errors in not only the methane column amount, but also the dry air column density, affecting the overall methane concentrations.

Fig. 2C shows the ratio between the retrieved methane from the DCS and the measured concentrations from the Picarro instrument. In contrast to CO$_2$, this ratio for methane exhibits a much larger range, from 0.93 to 1.07, resulting in a 7% disagreement in methane concentrations.

Explain Fig. 3.

4.2 Tracing error sources from field retrievals

In order to trace the error sources, we plotted the relative ghg concentrations error as a function of other parameters of interest. They include relative pressure error, retrieved water vapor columns, and relative water vapor error. The relative errors were calculated by computing the percent difference of the retrieved variable compared to the reference measurement taken by the Picarro, pressure, and temperature sensors on the nearby tower. Figs xx and Table 3 shows these results.

For CO$_2$, we find that there are weak correlations when correlating error terms. The relative error correlations between CO$_2$ and pressure range from 0.02, which is from OCO, to 0.14, which are from the Hitran 2016 and 2020 line-lists. Water vapor seems to have the strongest correlation, which ranges between 0.16 to 0.20.

On the other hand, we find much stronger relationships for methane. From Fig. xx, we can see that there is some correlation between the methane and water vapor relative errors, with a correlation of about 0.49. This indicates that errors in retrieving methane and water are linked. We can trace the source of this error to the pressure retrieval, which has a correlation of -0.33. A negative correlation indicates that high biases in pressure are leading to low bias in retrieved methane. This negative correlation increases when looking at Hitran 2016, which goes up to -0.59, while Hitran 2020 goes back to -0.41. this points to errors from pressure broadening parameters and water vapor spectroscopy aliasing onto the retrieved column.

9

Retrieved CH$_4$

Dry Column Density
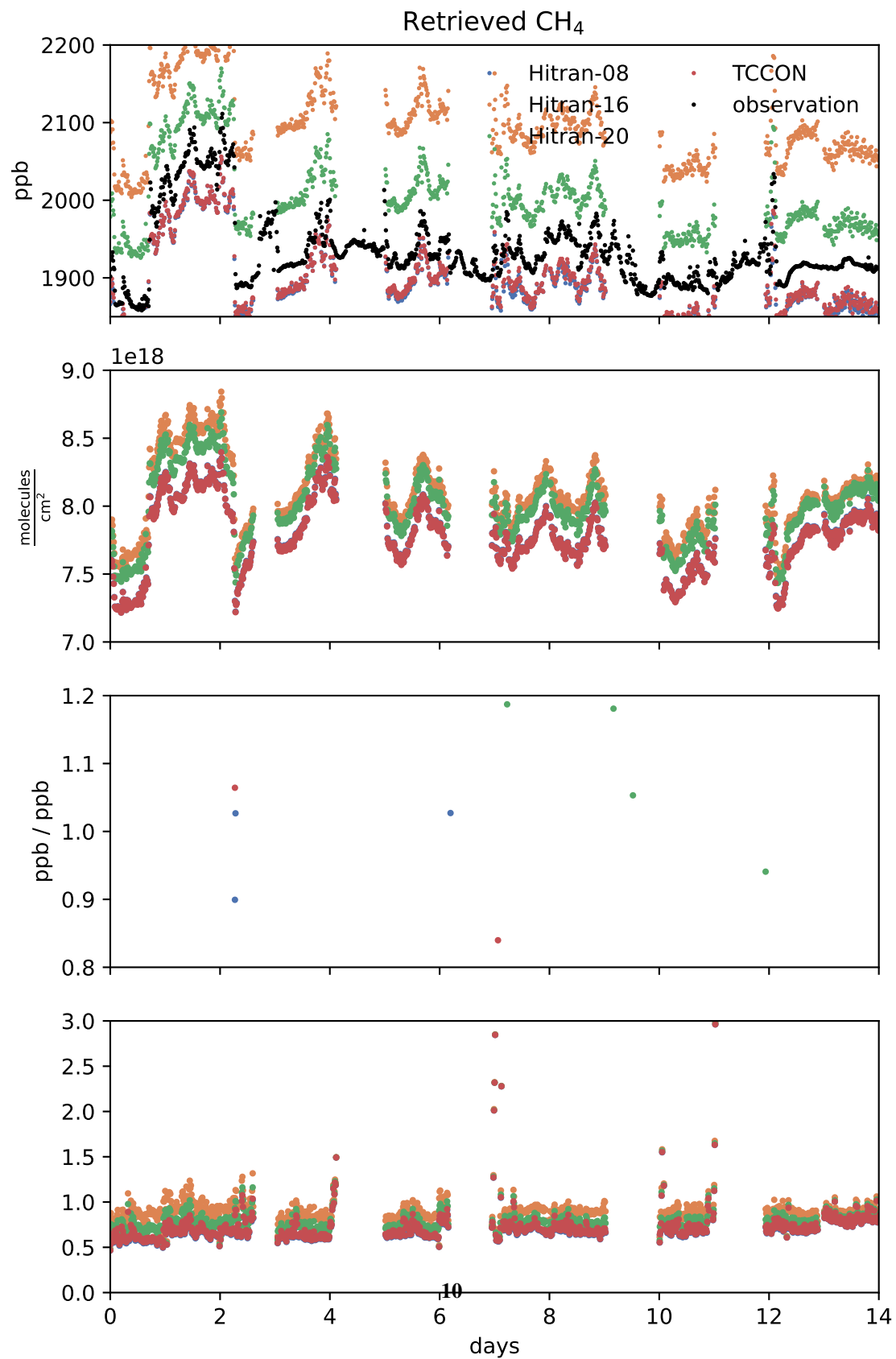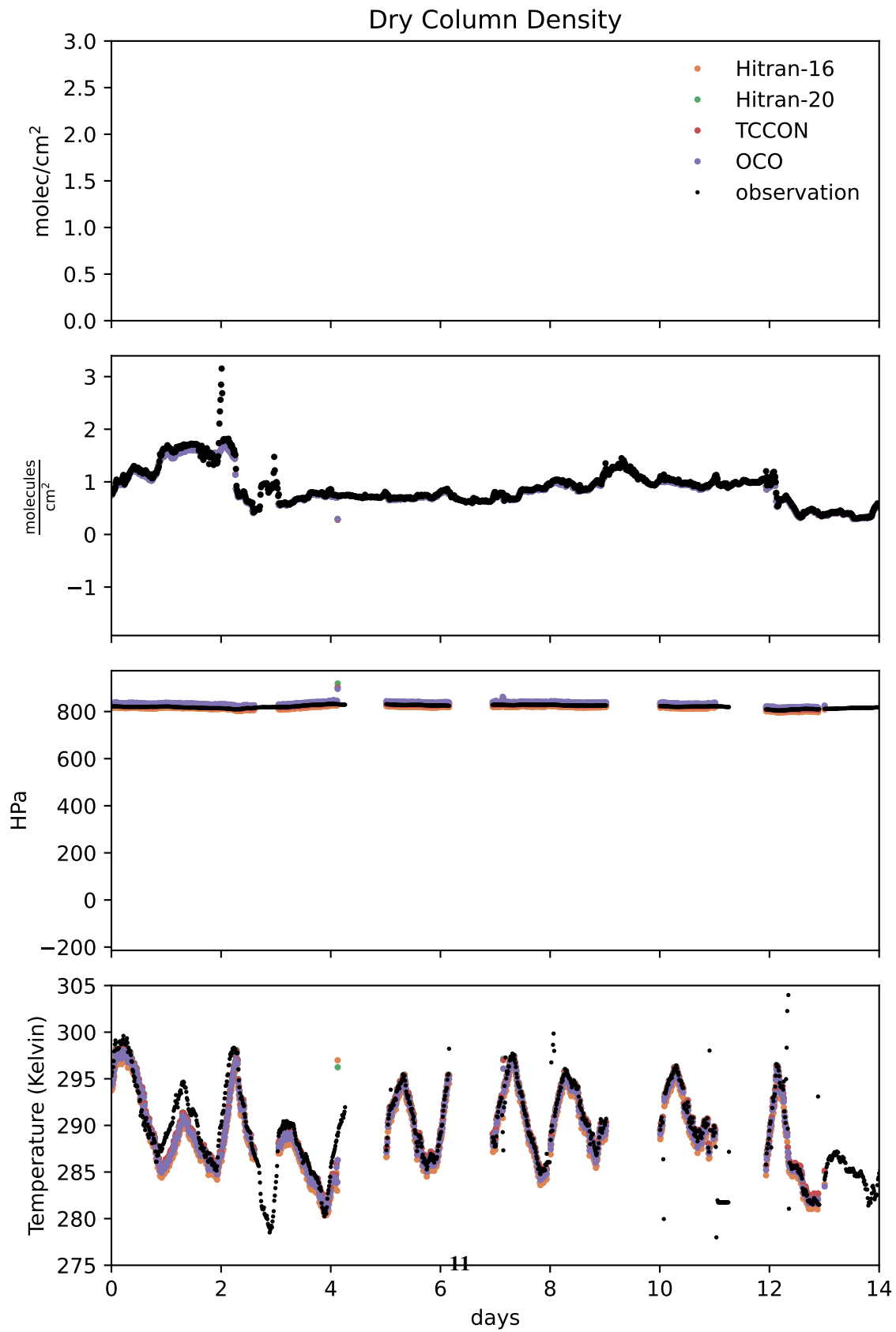
4.3 Comparing spectra from different line-lists

We can examine the accuracy of the CO_2 and methane spectroscopy by looking at the spectral residuals of our retrieval's and comparing them to the measured DCS spectrum. Fig. 4 shows the transmission spectrum, which is the measured transmission divided by the instrument baseline. The data shown in Figs 4 and 5 are obtained from averaging the spectra over a 24 hour period on 21 September, 2016. Spectra were averaged in order to minimize random noise so that individual absorption features can be closely inspected.

In both Figs. 4 and 5, we can see that the residuals between the model and measured spectra only differ by 1e-3, indicating a good model fit to the measured spectra. The root mean squared error for these are xx over the methane window and xx over the CO_2 window.

The CO_2 window, which ranges between 6180 and 6260 cm^{-1}, is also observed by other instruments, such as SCIAMACHY, OCO, and TCCON. We can see from the spectral residuals in Fig XB that OCO performs best, with a chi2 of xx and rmsd of xx. TCCON also performs well with a Chi2 of xx and rmsd of xxx. We also see that there is not much difference among the fits for different Hitran editions, with chi2 ranging from xx to xx and rmsd ranging from xx to xx.

Although there is not a significant difference between each of these spectral residuals, OCO does perform best. This is due to the additional physical processes accounted for in the OCO spectroscopy, which includes line-mixing and other processes beyond just pressure and temperature broadening. Incorporating additional physical processes makes calculations of the dry air column amount more accurate [Hartmann et al., 2008; Long et al., 2022; Malina et al, 2022].

In contrast to CO_2, Fig. 5B shows a large difference in the methane residuals. We can see that Hitran 2008 has the best fit, with a chi2 of xx and rmsd of xx. TCCON performs similarly to Hitran 2008 (chi2=xx and rmsd=xx), because TCCON obtained their parameters from Hitran 2008. Interestingly, the worst performing spectroscopy comes from Hitran 2016 with a chi2 of xx and rmsd of xx. The subsequent update to Hitran 2020 improved the fits to be on par with Hitran 2008 with a chi2 of xx and rmsd of xx.

The Merlin mission will be analyzing the R6 methane transition. Fig. XX shows a zoom into the R6 transition between 6076 to 6079 wavenumbers. We find that here, there are systematic residuals in all the line-lists. This indicates that there are both parameter and model errors in this region. Several studies have more closely examined this specific transition e.g., citations. They find that accounting for additional processes, such as line-mixing and collision induced absorption, through the Hartman Tran Profile improves the fits to xx%. Since the DCS has a broader spectral range, similar analyses and parameter optimizations should be performed over additional transitions over the DCS ranges in order to obtain the most accurate modeled absorptions of methane.

Methane spectroscopy is particularly challenging, because of the manifolds in vibrational and rotational transitions, which creates a blend of overlapping absorption lines, resulting in line-shape asymmetries and additional difficulty in modeling the line-shape. The Voigt Profile does not account for these more complex processes. However, we find that errors that arise from the complexity of the line-shape is outweighed by the errors in the line-shape parameters themselves. This is in agreement with
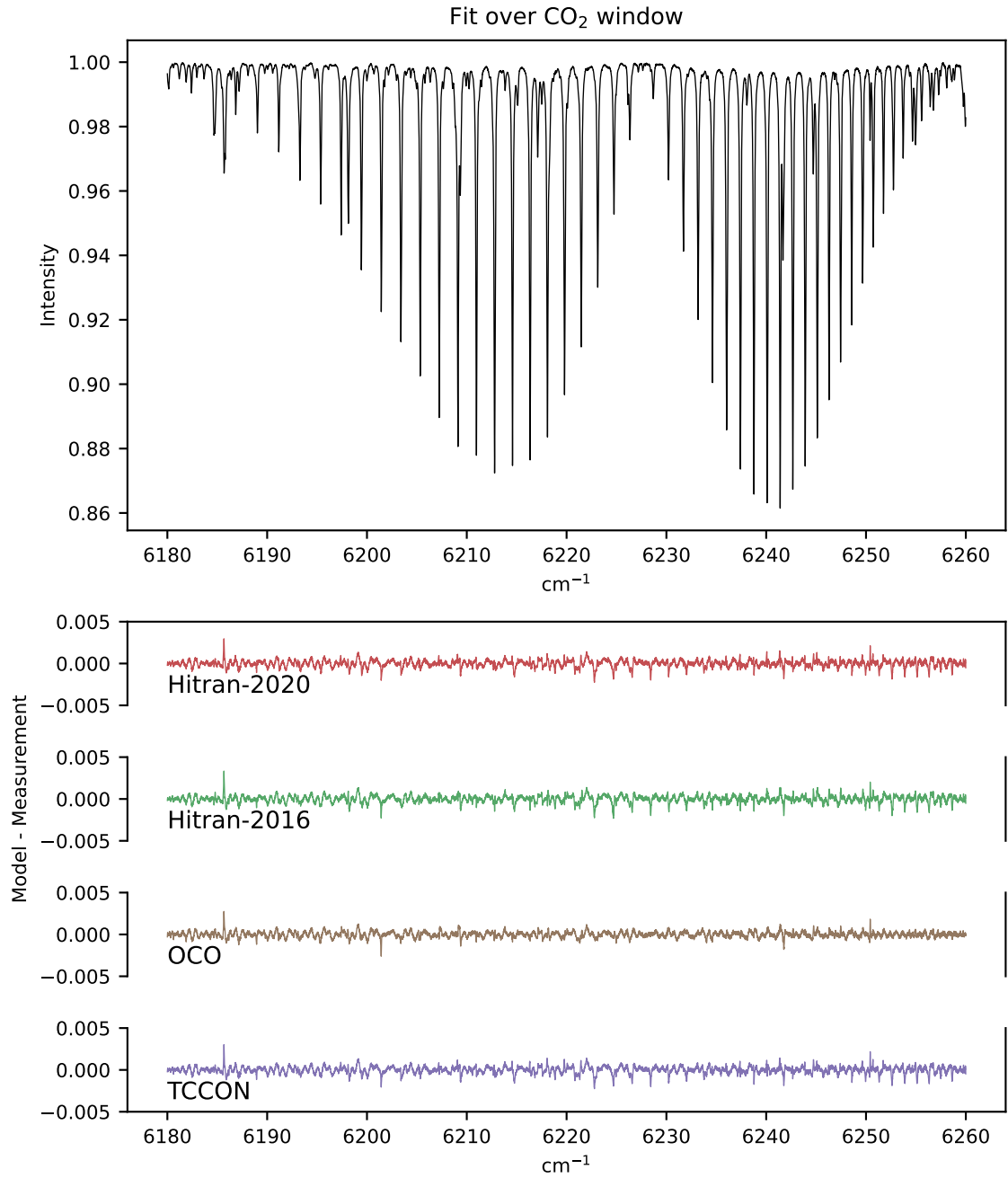
Figure 4. DCS Absorption spectrum (top) over the CO_2 retrieval window (6180-6260 cm^{-1}). The bottom panel shows modelled residuals from the OCO, Hitran 2016, Hitran 2020, and TCCON line-lists, as outlined in Table 1.
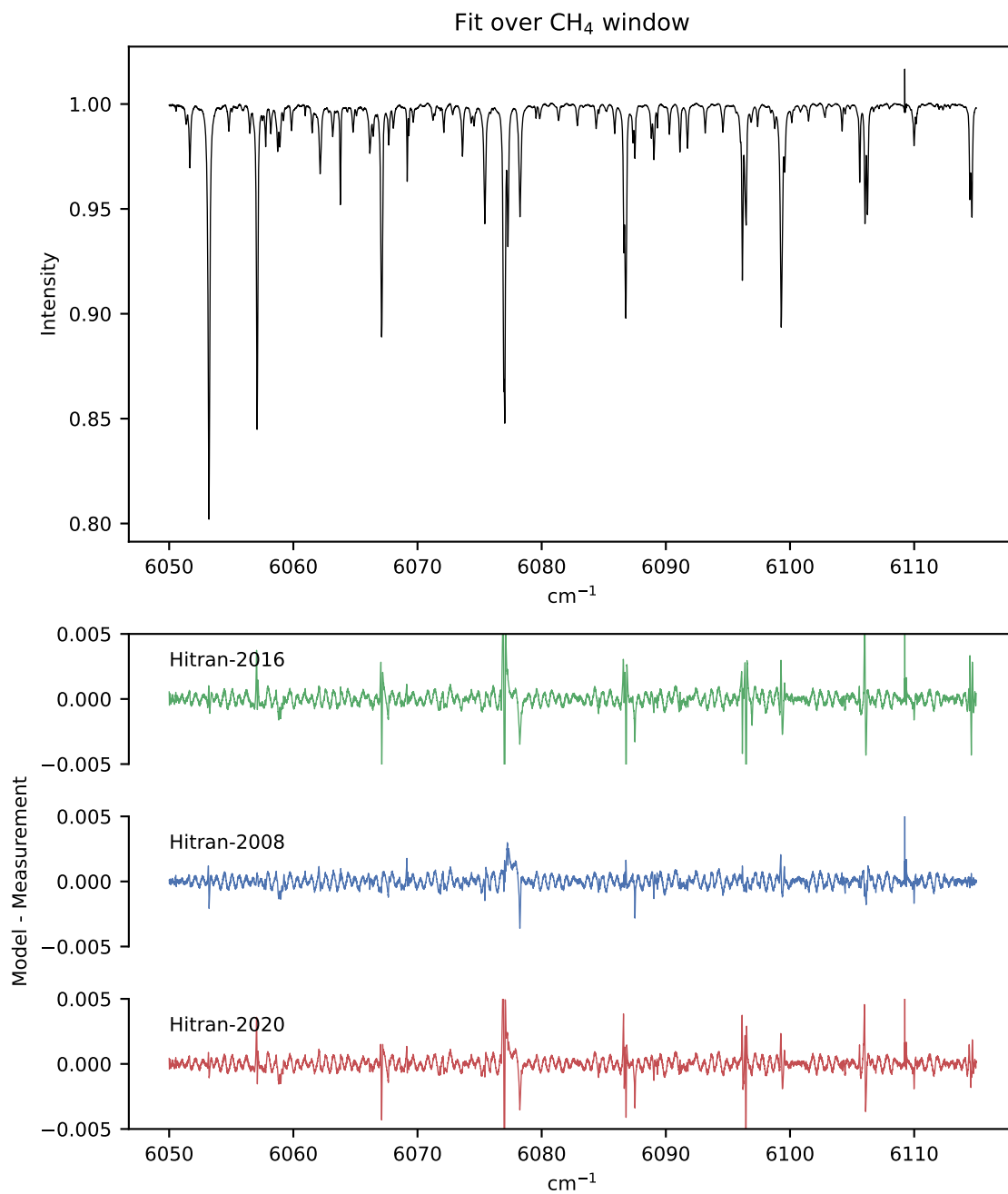
Figure 5. DCS absorption spectrum over the CH$_4$ fitting window (6050-6115 cm^{-1}), on top. The bottom panel shows the residuals with modelled spectra using the Hitran 2008, Hitran 2016, Hitran 2020, and TCCON line-lists.
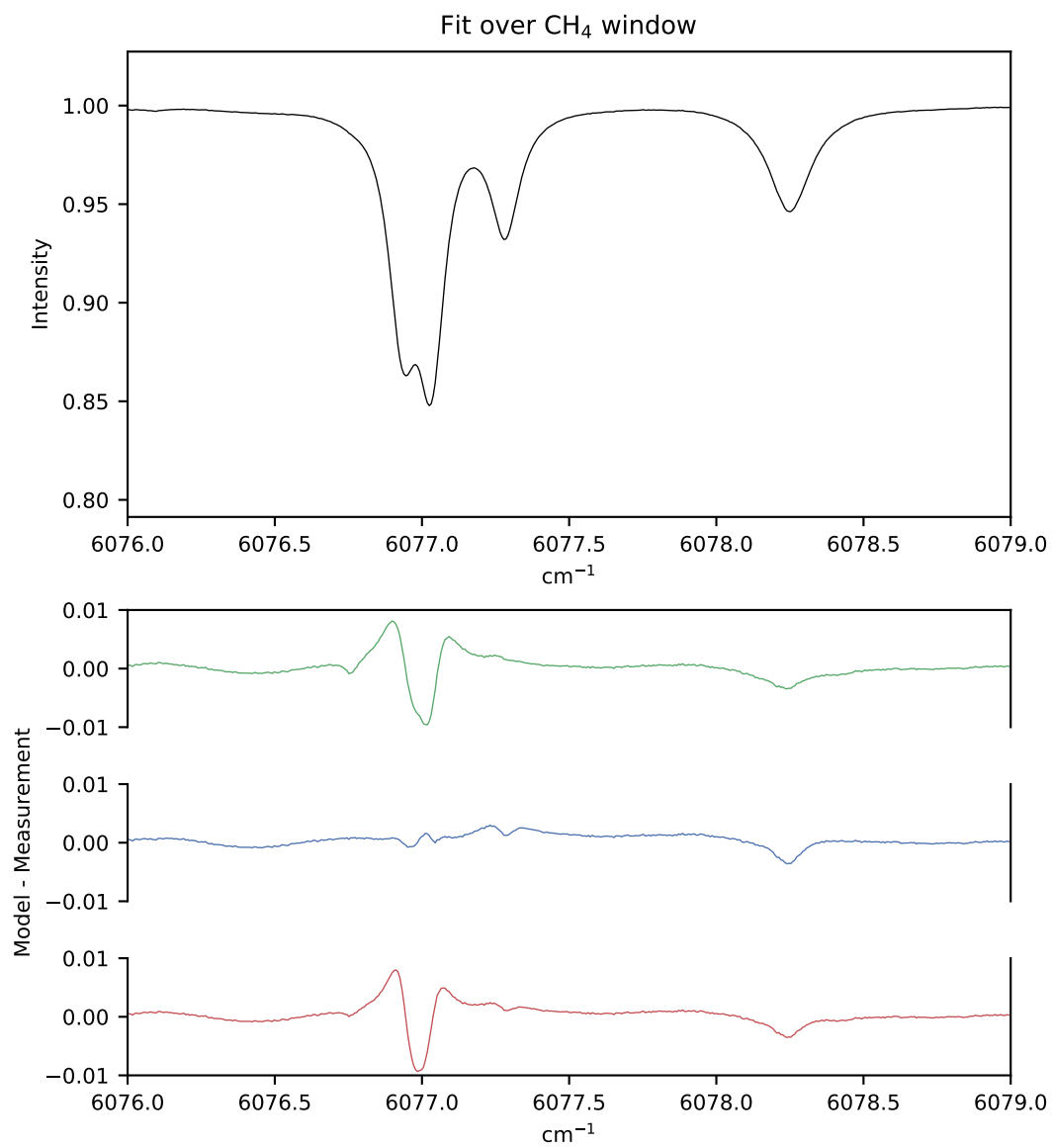
Figure 6. Zoom into the CH$_4$ R6 transition, which will be observed by the Merlin Mission.

255 Reiker et al (2014). Calculating more accurate spectroscopic parameters for methane is an on-going effort, and we find that it is necessary in order to achieve highly accurate methane measurements with the DCS.

5 Synthetic Retrieval Experiments

5.1 Pressure errors cause disagreements among different line-lists

We performed synthetic retrieval's In order to find the disagreement among the line-lists used in this study. Synthetic measure-
260 ments were generated using the most accurate line-lists for the species: OCO line-list for CO_2, TCCON for water vapor, and Hitran 2008 for methane. We generated the synthetic spectra over a range of pressures and temperatures. Then, we performed the retrieval with different line-lists in order to calculate the retrieval error. In our retrievals, we also fitted for pressure and temperature, which enables us to calculate how much the retrieval error of our greenhouse gas concentrations varies with pressure and temperature. Figs **??** and **??** display our results.

265 For methane, we find that errors are large, maxing out at xx ppb at p=xx and T=xx for Hitran 2016 and xx for Hitran 2020. From our synthetic retrievals, we can see that temperature errors are minimal, varying by about 1 degree, while the retrieval error for pressure can be up to xx HPa. This indicates that errors in methane are largely due to errors in modeling pressure effects, which can be traced to either model error or parameter error.

Talk about how these variable bites are a function of pressure and temperature and where the biases is the highest

270 ### 5.2 Quantifying effects of errors in pressure broadening

We can further quantify this with a numerical experiment, where we perturb the pressure broadening parameters. In this case, we perturbed the temperature dependence of pressure broadening, called n_air in Hitran, by 5%, which is within error of that parameter.

Fig. 9 shows the results of our parameter broadening experiment. At temperatures close to the reference temperature of 298
275 K, the retrieval error is minimal, at around 20 ppb, and this is independent of pressure. the retrieval error increases farther from the reference temperature, and it is maximized at very low temperatures and peak at around 45 ppb. This relationship is because of xx reasons.

The biases in this perturbation experiment are also pressure and temperature dependent. describe the relationship with pressure and temperature.

280 In general, this experiment shows two things. First of all, the biases incurred from small errors in these parameters can be substantial. Our results show that a 5% perturbation in this parameter can incur up to a 2.5% error in the retrieved concentrations. Secondly, biases in retrieved greenhouse gas concentrations, specifically methane, are nonlinear and depend on pressure and temperature. The biases are maximized at lower temperatures. Given these results, more certainty is needed for parameters affecting pressure broadening in methane spectroscopy. This is important for fully realizing the technological potential of DCS

Hitran-2016

Hitran-2020

18
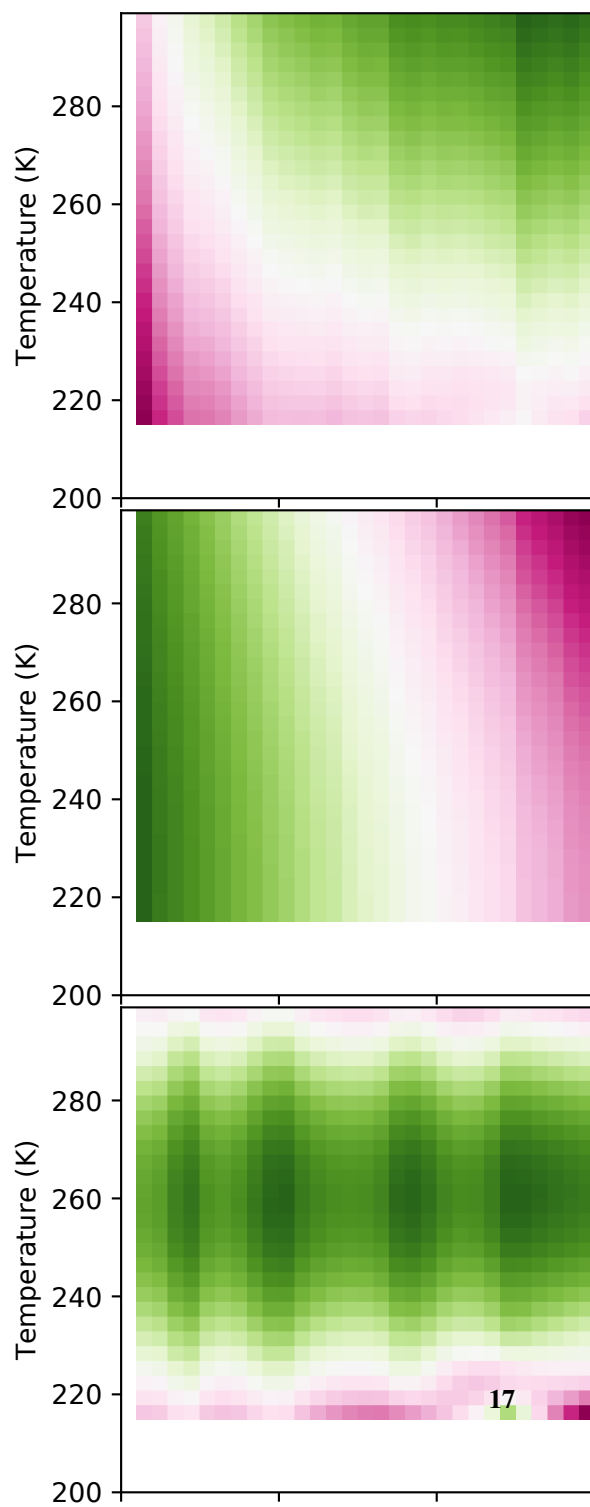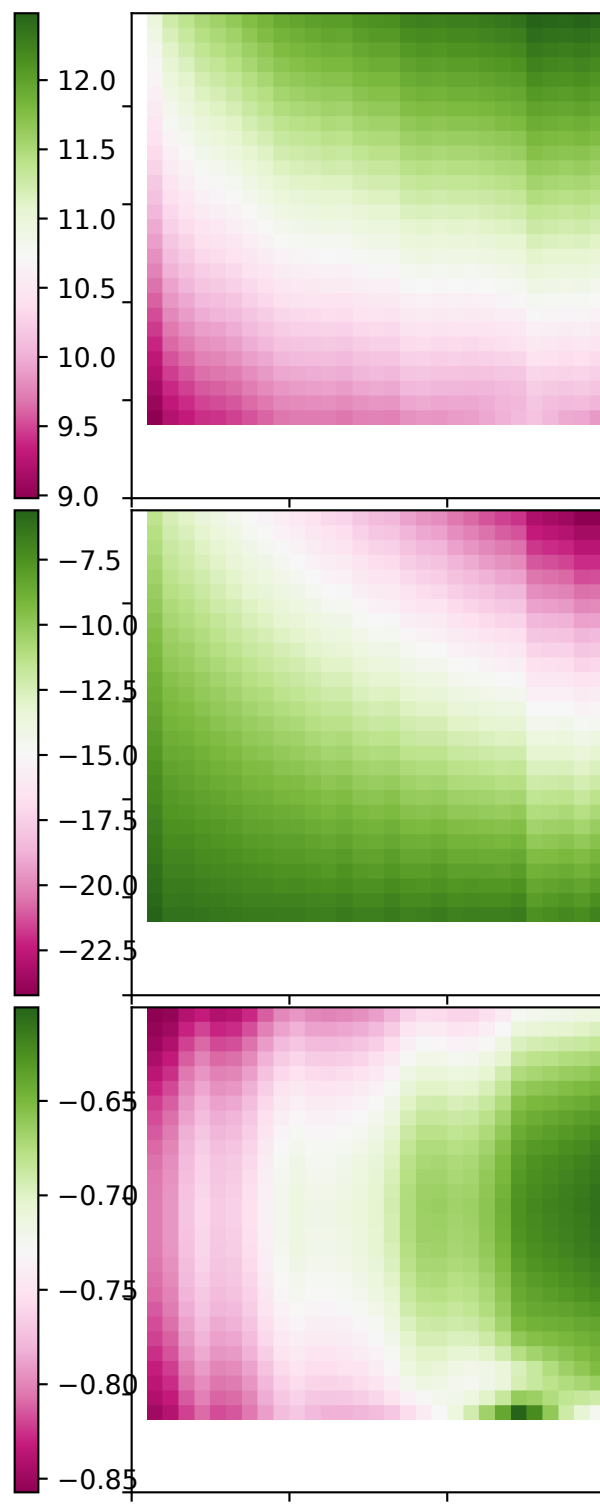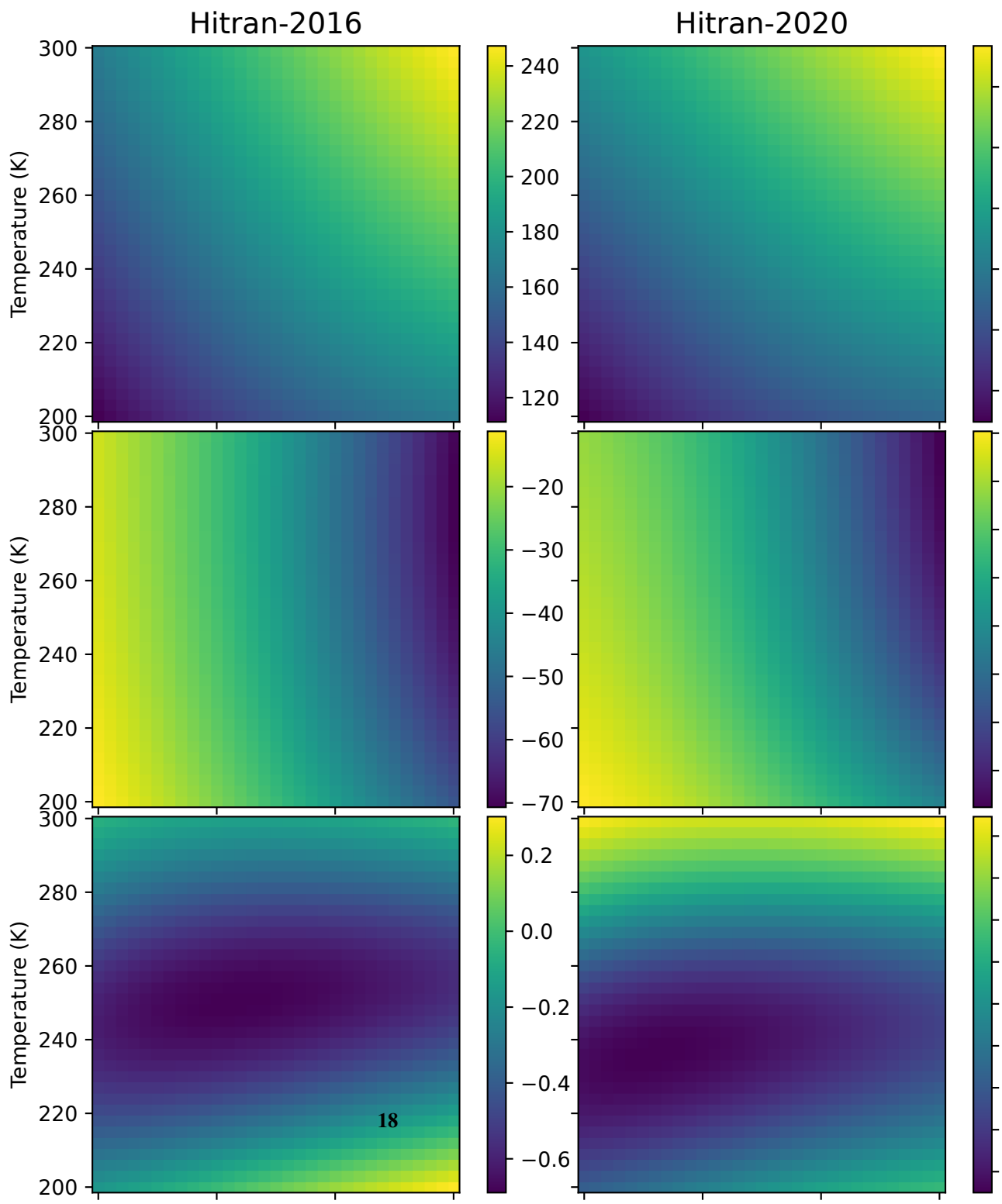
285 to obtain laboratory-level accurate greenhouse gas measurements in the field and for the ability of DCS to measure vertical ghg gradients in the atmosphere – a future DCS application.

6 Vertical Profile Retrievals

6.1 Measuring Vertical Gradient's: A DCS Application

Measuring vertical ghg gradients is a future DCS application. The long-range, open-path, and absolute stability of the active
290 light source enables highly accurate spectra to be measured. The DCS would be on the ground, aimed at a balloon with a mounted retro-reflector, and the return-signal would be measured on the ground. The high spectral sampling of the DCS would enable precise interrogation of narrower absorption features characteristic of the upper atmosphere, and the absolute frequency stability would enable accurate measurements of absorption features through spectral averaging. This makes DCS an excellent candidate for ground-based vertical profile measurements.

295 Vertical profile measurements will provide additional constraints on how greenhouse gases are transported throughout the atmosphere and top-down ghg flux inversions. Moreover, there is considerable disagreement in ghg vertical gradients in chemical transport models. currently, ghg vertical gradients are measured through flasks from air and balloon flights and the NOAA Air Core Program [Karion]. The DCS can augment these measurements with more numerous vertical profile measurements in a future network.

300 There has been recent work on developing vertical profile retrievals from ground-based spectral measurements measured by TCCON (e.g., Kuai et al, 2014, Roche et al, 2021). One of the major error terms was uncertainties in the instrument's line-shape (Roche et al, 2021), which requires constant calibration (Wunsch et al, 2011). The DCS can provide ground-based spectral measurements free from the distortions of an instrument line-shape.

Here, we quantify the additional information that a ground-based DCS vertical profile retrieval can provide. Through calcu-
305 lations of the Degrees of Freedom, which arises from the information content of the retrieval, we can calculate the number of layers that can be retrieved from a vertical profile retrieval. In order to ascertain the importance of pressure and temperature broadening effects, we also quantify the information that variations in pressure and temperature in the atmosphere provides by assuming an isothermal and isobaric atmosphere. In these synthetic experiments, we assume that the DCS is pointing straight up at a balloon at an altitude of 10 km, so the round-trip path length is 20 km.

310 ## 6.2 Retrieval Algorithm and analysis Methods

Our vertical profile retrieval algorithm employs the Optimal Estimation Method developed by Rogers 2000. This Bayesian method is necessary, because the problem is ill-posed. Incorporating prior information about the atmospheric state then transforms the cost function into the following equation:

In equation xx, there are two terms being minimized. the first term is the misfit between the observed and modeled instrument
315 measurement, which is the same as Section 2. The second term is the misfit between the prior (or initial state) and the
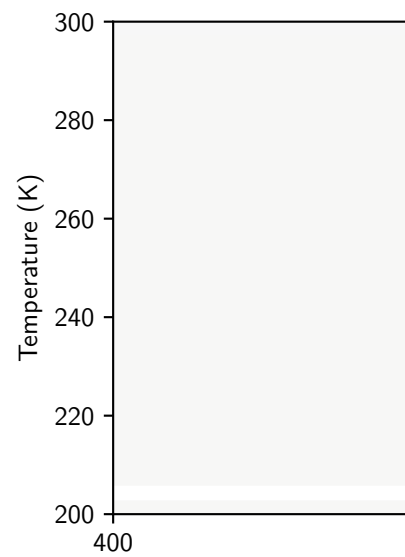
CH_4 Error
(ppb)
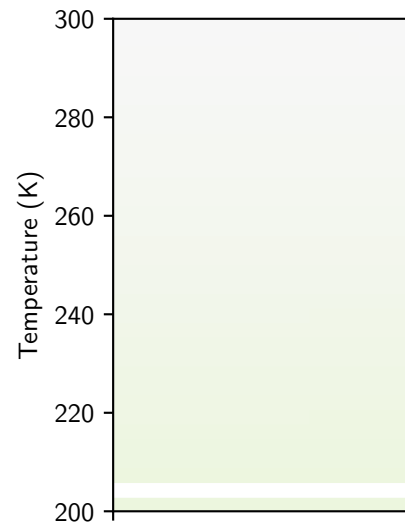
Pressure Error
(HPa)
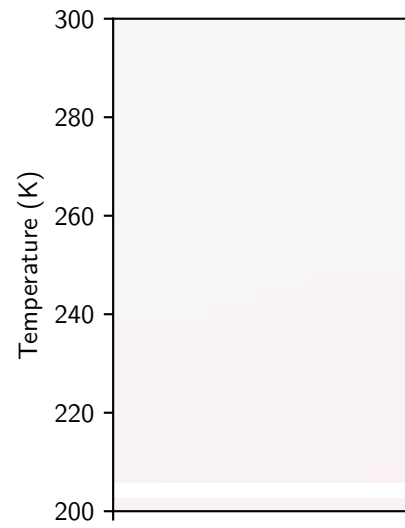
Temperature Error
(K)

400

species	standard	isobaric	isothermal
CH_4			
CO_2			
H_2O			

Table 3. Degrees of Freedom from our synthetic vertical profile experiments.

retrieved state (the solution). Both terms are weighted by an error covariance matrix. The measurement misfit is weighted by the measurement covariance matrix, which contains the instrument errors. The misfit of the prior and retrieved state is weighted by the prior error covariance, which contains the uncertainties for each state variable in the main diagonal elements and the correlation between the variables in the off-diagonal elements. Physically, the off-diagonal terms of the prior error covariance matrix are the correlation between different layers, and we set the correlation length scale to 50 HPa. The off-diagonal elements are calculated using the following equation:

Since the problem is nonlinear, the state vector, x, needs to be iteratively updated, which is calculated by the following equations:

here, γ is a Tikhonov regularization parameter that dictates the importance of the prior knowledge and changes the step-size between each iteration. We enable gamma to adapt to the linearity of the problem at each step, decreasing at near linear states and increasing farther away from linearity.

For the forward model, we also employ the Lambert-Beer law over multiple layers:

here, τ_i is the optical depth of layer i and σ_{ij} is the cross-section for layer i and species j. Since there are additional layers, the problem becomes more nonlinear, so we linearize the problem by solving it in log-space. The forward model then becomes the following:

6.3 High spectral sampling of the DCS enables more retrieved layers

We developed a simulation of DCS measurements in a vertical profile setting for a standard atmosphere. Vertical profile retrievals can be assessed by the Degrees of Freedom (DOF) of the retrieval. The DOF corresponds to the number of atmospheric layers that can be inferred, which is calculated using the following equations:

explain the terms in the equations Table 2 shows the DOF for each the retrieved species. We get about 4 DOF for CO_2, 3 for methane, and about 4.5 for water vapor. This is in comparison to a TCCON retrieval, which contains xx for CO_2 and xx for methane [citations].

6.4 Quantifying retrieved information from pressure versus temperature

We also compute the information that atmospheric variations in pressure and temperature contribute to a vertical profile retrieval. To do this, we model the transmission and absorption through an isothermal and isobaric atmosphere. Table 3 displays our results. We find that for methane, the DOF for pressure variations is xx while temperature is xx. For CO_2, pressure

contributes xx DOF, while temperature contributes xx. finally, for water vapor, pressure contributes xx, while temperature variations contribute xx. Note that the sum of the pressure and temperature DOF does not equal the total DOF for a standard atmosphere, because the information contained in pressure and temperature variations are not orthogonal.

345   In general, pressure variations (the isothermal atmosphere simulations) contribute more information. This is due to the fact that the dynamic range for pressure is higher than that of temperature in an atmospheric profile. Overall, this also underlines the importance of calculating accurate pressure broadening effects of ghg spectra, which is also emphasized in Roche et al (2021).

7   Summary and Discussion

350   Dual Comb spectroscopy brings laboratory-level accurate spectroscopy directly into the field. Its absolute frequency stability and high spectral sampling enables high-resolution interrogation of molecular absorption features. However, we showed that limitations of the spectroscopic parameters of ghgs, mainly methane and water vapor, prevent highly accurate retrievals of greenhouse gas concentrations. With field data, we found that errors in methane spectroscopy can lead to more than a 5% disagreement in retrieved methane concentrations, while CO_2 was xx%.

355   We found that these errors are correlated with pressure errors and water vapor errors, which affect the column density and alias on to the retrieved concentrations. Our numerical experiment, where we calculated the retrieval error as a function of pressure and temperature, indicate that a large portion of the error is due to errors in pressure broadening parameters, while the errors from temperature effects are minimal. Our numerical perturbation experiment showed that an only 5% error in the temperature dependence on pressure broadening can actually incur a 2.5% in retrieved methane, and the bias is also dependent

360   on pressure and temperature.

We also developed a vertical profile retrieval algorithm for the DCS, which is a future application. From these experiments, we find that the high spectral resolution of the DCS can enable additional layers to be retrieved. mOreover, the frequency stability of the DCS also enables higher signal to noise ratios by time-averaging free from instrument drift . We quantified the information that atmospheric pressure and temperature variations bring, and our synthetic isobaric and isothermal atmosphere

365   tests show that a majority of the information comes from variations in atmospheric pressure. This underlines the importance of obtaining more accurate pressure broadening parameters to model these effects.

the dependence of the biases to pressure and temperature prevent simple rescaling, and since the errors are not random, they cannot be simply averaged out. this variable error underlines the necessity of improved ghg spectroscopic parameters. Overall, the DCS will enable highly accurate greenhouse gas measurements from the surface and throughout the atmosphere. However,

370   improvements to ghg spectroscopy should be made in order for DCS measurements to obtain the 0.1% accuracy necessary for ghg monitoring.

8 Conclusions

Dual Comb Spectroscopy has the potential of augmenting our greenhouse gas observation network by bringing laboratory-level accurate spectroscopy directly into the field. To aid in this application, we developed a retrieval algorithm that separates the effects of pressure and temperature from the retrieved greenhouse gas amounts by utilizing the high spectral resolution of the DCS. We found that while there do exist spectroscopic errors in methane and CO_2, it is important to properly model the effects of pressure-broadening on ghgs. We also found that the high spectral sampling of the DCS enables direct retrieval of pressure and temperature from only the shape of the measured absorption cross-sections. In order to have the DCS achieve the 0.1% accuracy necessary for monitoring ambient ghgs and their trends, additional laboratory work should be done to measure and quantify the spectroscopic parameters of methane. The DCS would also be an ideal instrument for obtaining spectroscopic parameters, given that it is free from the distorting effects of the instrument line-shape.

DCS is a novel method of measuring greenhouse gases. By employing the time-keeping stability of the instrument, we can now bring laboratory-level accurate measurements directly into the field. However, without ancillary measurements to quantify the dry air column, the accuracy of the DCS retrieval is not limited by the instrument, but by the accuracy of greenhouse gas spectroscopy itself.

Code availability. TEXT

Data availability. TEXT

Code and data availability. TEXT

Sample availability. TEXT

Video supplement. TEXT

Appendix A

A1

Author contributions. TEXT

Competing interests. TEXT

395 *Disclaimer.* TEXT

Acknowledgements. TEXT

References

REFERENCE 1

REFERENCE 2