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Absolute accuracy and sensitivity analysis of OP-FTIR retrievals of CO₂, CH₄ and CO over concentrations representative of “clean air” and “polluted plumes”

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Abstract

When compared to established point-sampling methods, Open-Path Fourier Transform Infrared (OP-FTIR) spectroscopy can provide path-integrated concentrations of multiple gases simultaneously, in situ and near-continuously. Concentrations can be retrieved from the measured IR spectra using a forward model coupled to a non-linear least squares fitting procedure, without requiring “background” spectral measurements unaffected by the gases of interest. However, few studies have investigated the accuracy of such retrievals for CO₂, CH₄ and CO, particularly across a broad concentration range covering ambient to highly polluted air (e.g. from biomass burning or industrial plumes). Here we perform such an assessment using data collected by a field-portable FTIR spectrometer. The FTIR was positioned to view a fixed IR source placed at the other end of an IR-transparent cell filled with the gases of interest, whose target concentrations were varied by up to two orders of magnitude. Retrievals made using the forward model are complicated by absorption line pressure broadening, the effects of temperature on absorption band shape and by convolution of the gas absorption lines and the instrument line shape (ILS). Despite this, with optimal forward model parameterisation (i.e. the wavenumber range used in the retrieval, gas temperature, pressure and ILS), concentration retrievals for all gases were able to be made to within 5% of the true value. Sensitivity to the aforementioned model inputs was also investigated. CO retrievals were shown to be most sensitive to the ILS (a function of the assumed instrument FOV), which is due to the narrow nature of CO absorption lines and their consequent sensitivity to convolution with the ILS. Conversely, CO₂ retrievals were most sensitive to assumed atmospheric parameters, particularly temperature. The analysis suggests that trace gas concentration retrieval errors can remain well below 10%, even with the uncertainties in atmospheric pressure and temperature that might arise when studying plumes in field situations (e.g. at uncertain altitudes or temperatures). Our findings provide confidence that FTIR-derived trace gas retrievals of CO₂, CH₄ and CO based on forward modeling can yield accurate results, even over very

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large concentration ranges that can prove difficult to retrieve via standard classical least squares (CLS) techniques.

1 Introduction

In many applications, remote sensing of gas species presence and concentrations offer advantages over established point-sampling and/or laboratory analysis methods. Open-path (OP) Fourier Transform Infrared (FTIR) spectroscopy can be used to detect and quantify a wide range of gases simultaneously; can operate in situ, eliminating contamination from tubing or sample handling; can operate continuously, providing real-time data at a relatively high temporal resolution (seconds); and can be used over long path lengths, providing path-integrated gas concentrations less prone to artefacts induced by point-based sampling and which cannot easily be acquired using alternative approaches.

A variety of analysis techniques are available to retrieve trace gas concentrations from measured single-beam spectra acquired by FTIR instrumentation. These generally involve comparing the measured spectra with reference spectra of the gas of interest under known conditions of temperature, pressure and concentration. Reference spectra may come from laboratory measurements of gases, or may be synthetically generated (e.g., Griffith, 1996) from molecular absorption databases, such as HITRAN (Rothman et al., 2009). One retrieval technique involves converting the measured spectra into absorbance units and fitting the reference spectra using classical least squares (CLS) or partial least squares methods over a spectral window within which the trace gas of interest has significant features (Haaland, 1990). One difficulty with this approach can be the necessity to obtain “background” single beam spectra unaffected by the gases of interest, these being combined with the single-beam observations of interest to derive the values of absorbance (Bacsik et al., 2004). Alternatively, the single-beam reference spectra may be forward modelled and iteratively fitted to the measured spectra using nonlinear least squares (NLLS) (e.g., Griffith et al., 2003). The accuracy

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of both methods is generally gauged via a goodness-of-fit measure between the measured and modelled/reference spectra. However, only a few published studies have determined absolute retrieval accuracies via independent accuracy assessments based on experimental methods using cells containing known gas concentrations (see Esler et al., 2000; Horrocks et al., 2001). This is surprising given the sensitivity of retrieval methods to analysis parameters such as spectral window position and extent, gas temperature and pressure, and instrument line shape (Hart et al., 1999; Horrocks et al., 2001). OP-FTIR spectroscopy is being used increasingly as a method for monitoring key carbonaceous greenhouse and tracer species such as CO₂, CH₄ and CO. Given that OP-FTIR spectroscopy of these and other trace gas species is being applied in an ever-increasing range of applications, including volcanology (Horrocks et al., 1999; Oppenheimer et al., 2002); urban and aircraft pollution assessment (Grutter, 2003; Grutter et al., 2003; Hong et al., 2004; Schäfer et al., 1995, 2003) agricultural emission estimation (Childers et al., 2001; Griffith et al., 2002); and biomass burning investigations (Griffith et al., 1991; Yokelson et al., 1997), it is important that the true accuracy of the method is established over the wide range of potential concentrations found in these applications. Here we use an experimentally-based laboratory setup to determine the absolute accuracy of OP-FTIR retrievals of carbon dioxide (CO₂), carbon monoxide (CO) and methane (CH₄) made using the forward modelling approach across a concentration range encompassing both ambient air and highly polluted plumes (such as those emanating from vegetation fires, vehicle pollution or biogenic sources).

2 Background

In some cases, the accuracy of FTIR retrievals has been inferred via comparisons of the retrieved concentrations to those from more established point-sampling techniques, such as nondispersive infrared (NDIR) spectroscopy for CO₂ and CO (e.g., Gerlach et al., 1998), or gas chromatography (GC) (e.g., Goode et al., 1999) or wet chemistry (e.g., von Bobruzki et al., 2010) for other gases. For laboratory biomass burning,

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Goode et al. (1999) compared FTIR concentration retrievals made using synthetic reference spectra and CLS analysis, with those from GC. CO₂ retrievals from FTIR were shown to agree to within 1% of the GC results, although FTIR retrievals of CO and CH₄ were shown to generally underestimate concentrations by ~6% when compared with GC. Gerlach et al. (1998) compared CO₂/SO₂ ratios derived from FTIR, NDIR and GC, finding general agreement between all three methods. Whilst these results are encouraging in terms of the apparent agreement between FTIR and alternative approaches, they only represent intercomparisons between methods essentially employing rather different sampling strategies.

To achieve a true absolute accuracy assessment for FTIR retrievals, it is necessary to measure the IR spectra of well characterised, laboratory prepared, calibrated gas mixtures and compare the gas concentrations retrieved from these measurements to the known true concentrations. Only a limited number of studies have undertaken such a procedure (e.g., Horrocks et al., 2001; Esler et al., 2000; Lamp et al., 1997). Esler et al. (2000) were primarily interested in determining the precision of OP-FTIR gas analysis of CO₂, CH₄, CO and N₂O, using a sample of clean air (Southern Hemisphere “baseline” air) introduced into a 9.8 m White cell, analysing the measured spectra using a CLS approach and synthetically generated absorbance spectra. For CO₂, the method proved to be highly accurate giving a retrieval accuracy of 0.006% compared to GC analysis of the same sample, and for CH₄, CO and N₂O, 0.03%, 1.0% and 0.1%, respectively. These excellent accuracy statistics for ambient air unfortunately were not extended to measurements covering a broader range of concentrations. Optimal retrievals made at higher concentrations (and equivalently longer pathlengths, since the method actually responds to the number of gas molecules present in the optical path) might require use of different parameterisations of the forward model (for example the spectral window). This maybe due, for example, to absorption saturation or deviations from the standard Beer-Lambert law caused by deviations in absorptivity coefficients at high concentrations due to interactions between molecules in close proximity (Zhu and Griffiths, 1998).

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Lamp et al. (1997) generated gas mixtures using mass flow controllers to yield a broad concentration range of CH₄ (8–1900 ppm-m) and CO (10–3120 ppm-m) in a 20 m White cell. CLS analysis of the resulting IR absorbance spectra showed a significant nonlinear relationship between measured and known concentrations. For CH₄, retrieved values were within 5% of the true concentrations below 700 ppm-m, but accuracy halved at higher concentrations. Lamp et al. (1997) demonstrated that use of strong absorption regions, such as the CH₄ Q-branch at 3017 cm⁻¹, can lead to reduced accuracy as concentration increases, and a switch to other spectral windows might be more appropriate. CO retrievals were shown to suffer from similar nonlinearities, with concentration underestimated by more than 50% at concentrations higher than 1000 ppm-m.

An alternative to CLS-based methods is to use a nonlinear least squares (NLLS) fitting procedure (Marquardt, 1963). This approach can fit single-beam spectra directly and requires no assumption of Beer-Lambert linearity, allowing for the use of both weak and strong absorption regions (Griffith et al., 2003). In a comparison between retrievals made using CLS and NLLS methods, Childers et al. (2002) found that for CO₂, CH₄, NH₃ and N₂O, the CLS method generally underestimated at higher gas concentrations. To demonstrate this effect, Fig. 1 illustrates retrievals made here using the CLS and NLLS approach from spectra of a gas cell containing CO₂ gas of varying concentrations, topped up with nitrogen to maintain ambient pressure (the experimental method is described fully in Sect. 3 of this paper). The underestimation of high CO₂ concentrations when using the CLS method is clearly evident, and is due to the aforementioned nonlinear deviation from the Beer-Lambert law.

For volcanological applications, Horrocks et al. (2001) used a similar experimental setup and spectral forward modelling approach to that employed here to test the accuracy of OP-FTIR retrievals of SO₂ over a wide range of absorber amounts (125 ppm-m–10 500 ppm-m). As is the case here, instead of using a White cell to increase path-length, Horrocks et al. (2001) chose to use higher mixing ratios (ppm) of SO₂, which

are equivalent to a longer path according to the Beer-Lambert law:

$$\tau = \alpha Lc \quad (1)$$

where optical depth (τ , unitless) is equal to the product of the absorption coefficient of the sample (α , [ppm·m]⁻¹), the path length of the sample (L , m) and the mixing ratio of the sample (c , ppm). Optical depth is related to the true transmission (T , unitless) following Eq. (2):

$$T = e^{-\tau} \quad (2)$$

The measured transmittance is the true transmittance convolved with the instrument line shape (ILS). Horrocks et al. (2001) found that increased retrieval accuracies were achieved as concentrations of SO₂ increased, improving from ~5.6% at 125 ppm·m to within 1.0% at 10 500 ppm·m. This study builds on this work by using a similar approach to establish the OP-FTIR retrieval accuracies for CO₂, CO and CH₄ at mixing ratios ranging from those found in ambient air to those found in polluted cities, biomass burning smoke and volcanic plumes, a much broader range than investigated by Esler et al. (2000). We follow Horrocks et al. (2001) and analyse the collected IR spectra using an iterative NLLS method coupled to a forward modelling approach, specifically the Multi-Atmospheric Layer Transmission (MALT) model described in Griffith (1996) and Griffith et al. (2003). The work of Lamp et al. (1997) showed how Beer-Lambert law divergence can impact retrieval accuracy when investigating high concentration gases using spectral regions containing strong IR absorbance features. Generating retrievals from forward modelled synthetic spectra fitted to the measured spectra in the way conducted here should avoid these problems and the associated concentration underestimation illustrated in the CLS-derived results displayed Fig. 1.

3 Instrumentation and setup

Our study utilised facilities of the UK's Natural Environment Research Council's Molecular Spectroscopy Facility, part of the Rutherford Appleton Laboratory. A stainless steel

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gas cell of circular cross section was fitted with IR transparent KBr windows at each end and was filled with the sample gas at the concentration of interest before each spectral measurement. Gas cell length was 1.05 m, diameter 160 mm and IR window diameter 135 mm. The spectrometer used was a MIDAC Corporation FTIR Air Monitoring system, fitted with a mercury cadmium telluride (MCT) detector and ZnSe optics. The spectrometer was optically coupled to a 76 mm Newtonian telescope and placed to view an IR source through the IR transparent windows of the gas cell. The IR source used was a SiC globar operating at 1100 K, positioned at the focus of a 150 mm collimator. This setup, shown in Fig. 2, is very similar to that used by Horrocks et al. (2001), with a total pathlength of ~ 1.5 m, 0.5 m of which consisted of free air between the cell and spectrometer and cell and IR source, together with air inside the spectrometer housing. The CO₂ and H₂O mixing ratios in the ambient air outside of the cell were monitored using a calibrated LICOR 840 NDIR gas analyser. An attenuator was fitted to the FTIR spectrometer telescope to avoid MCT detector saturation, and the temperature of the gas inside the gas cell measured using a platinum resistance thermometer (PRT).

Table 1 lists the gas mixtures investigated. As described by the Beer-Lambert law (Eq. 1), it is possible to simulate a longer OP measurement pathlength by increasing the mixing ratio of the gas sample inside the cell, since pathlength (L) and mixing ratio (c) equivalently increase the number of gas molecules in the open path over which the IR spectra are acquired. The mixing ratios used here were chosen to represent a range covering those from clean air measured over short-to-long pathlengths in the natural environment (e.g. 10–1000 m), as well as polluted air across the same pathlength range, and range up to mixing ratios that might be found in pollutant plumes (e.g. from industrial sources or biomass burning). For example, six different CO₂ pathlength-concentration products (hereafter called pathlength amount) were used, spanning $\sim 12\,500$ ppm-m to $\sim 360\,000$ ppm-m. If these pathlength amounts are expressed as mixing ratios using pathlengths typically employed in the field, both the lowest and highest cell mixing ratios yield a CO₂ mixing ratio of ~ 420 – 450 ppm for a 30 m

and 800 m path, respectively, equivalent to typical ambient CO₂ conditions found in urban settings (e.g., Rigby et al., 2008).

Gas mixtures were prepared barometrically using high purity (99.9%) component gases. The barometric mixing method relied on three MKS Baratron (type 690) pressure capacitance manometers operated at three precision levels of 0.1 Pa, 10 Pa and 100 Pa with a stated accuracy of $\pm 0.05\%$. The manometers were also used to test the sealing of the gas cell, recording a $< 1\%$ change in cell pressure over 18 h when filled to ambient pressure (1000 hPa). For each gas concentration to be studied, the cell was evacuated before the sample gas (CO₂, CO or CH₄) was slowly released into the cell until the desired mixing ratio was reached. After waiting for the pressure to stabilise and noting the final pressure, the cell was filled with nitrogen to ambient pressure (1000 hPa) and allowed to stabilise once more. After stabilisation, 10 IR spectra were measured with the FTIR spectrometer, each consisting of 8 co-added scans (a total of ~ 9 s scan time per spectra) in order to increase signal-to-noise. The relative standard deviations among each set of 10 replicate single beam spectral measurements ranged from 0.1–1.2%, with standard errors of the means of 0.03–0.4% for these measurement conditions. The partial pressure of the sample gas was used to calculate the true sample mixing ratio (ppm) by dividing the partial pressure of the sample gas by the final ambient pressure of the gas cell. To avoid contamination by gas from the previous mixture, the lowest concentration of each gas was mixed first, working up to higher concentrations.

4 Procedure for gas concentration retrieval

4.1 Spectrum simulation and fitting algorithm

Spectra were analysed using a NLLS method combined with a forward modelling approach, whereby NLLS was used to fit a forward modelled spectrum to a measured spectrum, thus solving the inverse problem of returning gas concentrations from the observations. The method is quite commonly applied in OP-FTIR studies, and exam-

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ples include SFIT2 (Rinsland et al., 1998), often used to retrieve total atmospheric column trace gas abundances (e.g., Hase et al., 2006; Fu et al., 2007; Senten et al., 2008), but also used for ground-based open-path studies (e.g., Briz et al., 2007). A similar procedure (Burton et al., 1998) has been commonly applied to the retrieval of gas concentrations from open path measurements of volcanic plumes (e.g., Oppenheimer et al., 1998; Horrocks et al., 1999; Richter et al., 2002). The specific retrieval procedure used here is based on the Multi-Atmospheric Layer Transmission (MALT) model of Griffith (1996) and Griffith et al. (2003), whose past applications include the analysis of open-path, White cell, and solar occultation spectra (Goode et al., 1999, 2000; Bertschi et al., 2003; Galle et al., 2000; Griffith et al., 2002).

The background theory to the inverse problem is detailed in Rodgers (2000). By denoting the measurement spectrum as vector \mathbf{y} (the measurement vector) and the variables to be retrieved (the trace gas concentrations) as the state vector \mathbf{x} , the measurement and its relation to the state vector, can be described as:

$$\mathbf{y} = f(\mathbf{x}) \quad (3)$$

where $f(\mathbf{x})$ is the forward function, describing the physics of the measurement. It is unlikely that the physics of a system will be known and understood with full accuracy. Hence Eq. (3) is adapted as:

$$\mathbf{y} = F(\mathbf{x}) + \varepsilon \quad (4)$$

$F(\mathbf{x})$, the forward model, approximates the physics of the measurement, and ε is the measurement error. Here $F(\mathbf{x})$ represents the simulated single beam spectrum.

The radiative transfer forward model used to simulate the spectra $F(\mathbf{x})$ is detailed in Griffith (1996). To parameterise the calculation of $F(\mathbf{x})$ for each measured single-beam spectrum \mathbf{y} , the user is required to decide upon an appropriate spectral window for the analysis, and a priori values for component trace gas concentrations, pressure, temperature, pathlength, and instrument line shape. From these, the forward model generates a synthetic single-beam spectrum as a combination of a background spectrum (modelled as a polynomial) and the effect caused by gases having IR absorption

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features within the spectral micro-window of interest. Calculations are performed using the HITRAN database (Rothman et al., 2009), listing absorption line positions and strengths, widths and details of pressure and temperature dependencies for the given species.

A polynomial function (the order of which is defined as a parameter by the user) is fitted to the measured spectrum and is used to simulate the 100% continuum line (i.e. the signal in the absence of the trace gas. Examples of different fitted polynomial functions are shown in Fig. 3. The forward model calculates the optical depth (OD) of the target gas at each wavenumber ν as a function of the absorption coefficient at ν and the pathlength amount of each gas. A necessary parameter for this computation is the Voigt line shape – the convolution of the Doppler broadening Gaussian line shape function and the pressure broadening Lorentzian line shape function. The former is calculated using temperature and molecular weight, and the latter using the pressure dependence given in HITRAN. Convoluting the line strengths from HITRAN with the line shape produces the absorption coefficient used to calculate the optical depth. At wavenumber ν , the overall OD is taken as the sum of all calculated ODs for all absorption lines for all species. The OD is then converted to a transmission measure and convolved with the instrument line shape (ILS) and the 100% continuum line to yield the final synthetic single-beam spectrum for the spectral window of choice (Fig. 3). The ILS is dependent on the apodization function used, the instrument field-of-view (FOV), and any modulation loss or phase error in the interferometer. These parameters can be retrieved during the NLLS fitting procedure.

The difference between the synthetic and measured spectrum yields a residual spectrum (Fig. 3, bottom); and the chi-squared (χ^2) statistic and the partial derivatives for each of the input parameters are calculated. The Levenburg-Marquardt method (Levenburg, 1944; Marquardt, 1963; Press et al., 1992) is used to find the least-squares linear best fit, and thus the set of optimum gas concentrations that minimise the residual spectrum, based on pre-determined convergence criterion (χ^2 minimum).

4.2 Reported error

As with other spectrally-based retrieval approaches based on forward modelling and nonlinear fitting methods (e.g., Burton, 1998), MALT reports the standard error for each of the retrieved trace gas amounts and the a priori input parameters (this metric is termed the reported error hereafter). For each iteration of the NLLS fitting procedure, the covariance matrix is determined from the standard deviation of the residual spectrum (i.e. the synthetic spectrum subtracted from the measured spectrum). The reported error for parameter x_i is defined as the square root of the i th diagonal element of the covariance matrix, and is influenced by choice of a priori fixed input parameters, model errors/lack of fit, measurement noise, amount of information (the width of the spectral window and intensity of signal within that window) and degrees of freedom (which reduces with increasing number of parameters).

The reported error is based on the quality of the fit between the measured and modelled spectra, and is in part designed to provide the user with information potentially useful in gauging the quality of the retrieval process. Most ideally the user would like to know the actual retrieval error, i.e. the true difference between the amount of trace gas present in the optical path and that reported by the retrieval procedure. This retrieval error can have both random and systematic components, and improved understanding of the relationship between the reported error and retrieval error is one of the key aims of this work, along with an appreciation of the absolute accuracies able to be obtained from the method, and their sensitivity to model parameterisation uncertainty.

5 Methodology

5.1 Determination of input parameters

When performing a spectral fit, the input parameters required by the spectral forward model (MALT) can be stated as fixed constants or can be included in the fitting pro-

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cess. These parameters relate to the composition of the sample atmosphere (i.e. which gases are present in the sample and have absorption lines in the spectral window of interest, the concentration of these gases, and the temperature and pressure of the composition) and to the instrument line shape (i.e. spectral shift, resolution, apodisation, FOV, phase and zero-line offset). In our experiment, whilst the gas concentration was fitted, the temperature and pressure of the sample were taken from the gas cell PRT and Baratron readings, respectively. Determination of instrument line shape parameters was, however, less straight forward:

- the spectral shift (correction for fractional wavenumber shifts in the position of absorption lines caused by inaccurate knowledge of the position of the interferometer moving mirror) was fitted
- the spectral resolution was fixed at the manufacturer's specification (0.5 cm^{-1})
- asymmetry in the line shape influenced by small changes in spectrometer alignment was also fitted through a variable phase error
- the field-of-view (determined by the spectrometer's collimator focal length) was initialised at the manufacturer's specification and fitted as described below to determine the effective value.

Horrocks et al. (2001) demonstrate that their MIDAC spectrometer's effective field-of-view of 52 mrad differed significantly from the nominally quoted 20 mrad. We followed the methodology of Horrocks et al. (2001) to determine the field-of-view of the instrument used here, measuring the spectrum of CO gas with narrow absorption lines at low pressure (401 hPa) so that the resulting measurement is primarily a function of the absorption feature convolved with the instrument line shape. 80 scans were co-added to create one particularly low-noise spectrum. A series of MALT retrievals were run for a single absorption line at 2082 cm^{-1} , and the field-of-view parameter optimised to give the lowest reported error, whilst all other parameters remained fixed. The FOV parameter yielding the smallest reported error for the low-pressure CO absorption line

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was used as a fixed input for all other retrievals conducted here. Sensitivity to this parameter was also investigated (see Sect. 5.3). To determine the retrieval error of the reported concentrations, it is necessary to compare the retrieved concentrations with the true concentration (i.e. to the cell concentrations listed in Table 1). Retrieval error is therefore here defined as the true concentration subtracted from the reported concentration, divided by the true concentration and expressed as a percentage.

One further consideration for the retrieval procedure is to account for any zero-baseline spectral offset that may result from photometric errors associated with the use of an MCT detector (Müller et al., 1999). Two factors might lead to a non-zero signal in spectral regions that should otherwise exhibit complete absorption. The first is caused by scattering of radiation that has not originated from the lamp source, potentially related to imperfections in instrument optics, such as dirty mirrors. This is a common occurrence in well used field spectrometers, particularly when deployed to dusty or corrosive environments. Furthermore, if the gas cell was at a different temperature to that of the interferometer, an effect will appear in the measured spectrum. Whilst laboratory spectrometers often solve this problem by placing the interferometer before the sample cell, this is not of the case for bistatic OP-FTIR field configurations (Müller et al., 1999). Neither the temperature of the gas cell nor spectrometer were controlled in this experiment, but were rather left to equilibrate to ambient temperature, and therefore small differences in temperature may have influenced the recorded spectra. The second factor which might lead to a non-zero baseline is detector saturation. MCT detectors saturate rather easily (Smith, 1995), and whilst efforts were made in this study to prevent detector saturation via use of the attenuator, some detector saturation effect may be present. Any zero-baseline offset caused by stray light or detector saturation will be apparent in spectral regions where the examined gases should absorb all incoming radiation (e.g. the CO₂ saturation band at $\sim 2350\text{ cm}^{-1}$). If an offset was present, this amount was subtracted from the spectrum before quantitative analysis.

5.2 Spectral window and “background” polynomial

MALT requires the user to select a suitable spectral window and an appropriate polynomial for simulating the continuum spectra. To yield the most accurate concentrations, the window must have sufficient information about the gas of interest (i.e. an absorption feature) and should ideally be in a region of the IR spectrum that minimises contaminating absorption features from other gases (though this is not essential). The order of the polynomial used to simulate the continuum spectrum needs to be carefully selected so that it does not fit broad absorption features. In this work, a series of spectral windows were tested for retrieving the concentrations of each gas (Fig. 4 and Table 2), and the window yielding the lowest retrieval errors was thus identified. Similarly, a range of polynomial orders (3rd, 4th and 5th order) were employed. Given that all three gases in this study demonstrate fine absorption structure (a number of clearly defined narrow absorption lines) within the tested spectral windows, it is unlikely that the background polynomial fit will be influenced by these, except perhaps across the narrow CH₄ spectral window.

For CO₂ (Fig. 4a), the widest spectral spectral window used here, 2020–2310 cm⁻¹ (taken from Esler et al., 2000) was split into two sub windows, 2150–2310 cm⁻¹ (location of primary absorption features of ¹³CO₂ and ¹²CO₂) and 2034–2075 cm⁻¹ (location of the weaker ¹²CO₂ feature, see inset in Fig. 4a). For each window, CO₂ retrievals were run using a background continuum spectrum simulated via 3rd, 4th and 5th order polynomials. Given that water vapour was certainly present in the ambient part of the path external to the gas cell and has absorption lines in these spectral windows, H₂O was also included in the retrievals. Whilst CO and N₂O also absorb within these spectral windows, they were not present in sufficient amounts to be significant. In field situations using longer pathlengths, CO and N₂O may affect the measured signal and should therefore be included in any retrieval procedure. For CH₄, Esler et al. (2000) use a broad spectral window, 2810–3150 cm⁻¹. Unfortunately, the majority of this window is affected by a spectrometer artefact (2800–2990 cm⁻¹, see Fig. 4e), believed

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to be caused by residue on the instrument optics. The complexity introduced by the artefact significantly hinders the ability to model the spectrum using a lower-order (<6) polynomial. Two spectral windows were therefore selected so as to exclude the effects of this artefact, a broad window (2980–3090 cm⁻¹), that maximises the number of CH₄ absorption lines, and a narrower window concentrating on the strongest lines (3005–3020 cm⁻¹). In addition, a third window, lying within the region where lines are affected by the detector artefact (2894–3001 cm⁻¹) was also investigated. For CO, Essler et al. (2000) use a broad window encompassing the entire CO absorption feature and a similar window is used here (2000–2230 cm⁻¹). In addition, two narrower windows, one featuring only one branch of the CO absorption feature (2142–2241 cm⁻¹) and the other featuring only four weaker CO absorption lines (2039–2075 cm⁻¹) were also investigated (Fig. 4c).

5.3 Sensitivity analysis and error budget

A sensitivity analysis was performed in order to determine the influence of model parameter uncertainty on retrieval accuracy. Uncertainties in temperature, pressure and spectrometer FOV were considered, which may result from field situations where the measurement conditions are less tightly controlled than is possible in the laboratory. In particular, it can be difficult to measure temperature and pressure precisely in some open-path geometries, particularly when analysing high altitude plumes, or ones where the plume is generated by high temperature volcanological or combustion-related processes. Pressure and temperature are important in the retrieval procedure as they affect the shape of gas absorption features upon which the fit between the measured and modelled spectra depends. Assumed pressure determines the Lorentzian line shape of absorption lines in the simulated spectra. Higher pressures lead to a broadening of line widths, and the maximum line depth is suppressed. Whilst the relatively low (0.5 cm⁻¹) spectral resolution of the FTIR spectrometer used here is responsible for the majority of observed linewidths, this pressure-related broadening does also in-

fluence the retrieval process. Pressure broadening for any sample gas is also related to the other gases contained in the gas mixture.

The influence of assumed temperature is to affect the strengths of individual absorption lines and the band shape of the modelled spectra. Doppler broadening caused by the temperature-dependent distribution of molecular velocities within gases (as well as a minor influence on line broadening) contributes to the temperature dependence of lineshapes. The primary influence of temperature and pressure, however, is in the calculation of the mixing ratio from the retrieved number of gas molecules per square cm (molecules cm^{-2}) output from the retrieval process (the absorption features present in the spectra are a direct function of the number of molecules of the target gas in the optical path). The relationship between the concentration of a particular gas in a sample, in molecules per square centimetre (X , molecules cm^{-2}) and the mixing ratio of the gas (x , ppm), pressure (p , hPa), temperature (T , K) and pathlength of the sample (L , m) is described in Eq. (5), where A is Avogadro's constant ($6.022 \times 10^{22} \text{ mol}^{-1}$) and R is the gas constant ($8.315 \text{ J mol}^{-1} \text{ K}^{-1}$):

$$X = \frac{xLpA}{RT} \quad (5)$$

Any error in assumed pressure or temperature will therefore cause a proportional error in retrieved mixing ratio (x) through Eq. (5); whereas, retrievals in molecules cm^{-2} will only be affected by the influence of pressure and temperature errors on the forward modelled spectra. In many applications, OP-FTIR is used to investigate concentration ratios of two gases, for example $\text{CO}_2:\text{CO}$ in biomass burning studies (Yokelson et al., 1997) or $\text{SO}_2:\text{HCl}$ in volcanological applications (Burton et al., 2007), and in this case it may not be necessary to retrieve volumetric mixing ratios since the ratios of the gas amounts expressed in units of molecules cm^{-2} or ppm-m is identical. Therefore, for the sensitivity analysis conducted here, pressure and temperature-independent amounts (in molecules cm^{-2}) were used for the comparison. Pressure and temperature inputs were varied systematically by up to $\pm 20^\circ\text{C}$ and $\pm 200 \text{ hPa}$, respectively; ranges that might be found over altitude differences of up to 3 km. Retrieved concentrations were

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trieved effect of instrument line shape inaccuracies on individual absorption lines are decreased. The effects of degrading the assumed spectral resolution from the highest 0.5 cm^{-1} value were investigated, but increased the reported errors, and therefore further adjustments to this factor were not required.

6.2 Spectral window and background polynomial

6.2.1 Carbon dioxide

For each gas, three spectral windows were identified containing either a broad absorption feature or a selection of individual absorption lines (Fig. 4 and Table 2). For CO_2 , results shown in Fig. 7 indicate that the absolute retrieval error for 5 of the 6 pathlength amounts tested is at a minimum for the $2150\text{--}2310\text{ cm}^{-1}$ spectral window using a fourth-order polynomial, with retrieved pathlength amounts over the full range tested having a root mean squared (RMS) error of 2.4% (Fig. 7b). Whilst the results show little sensitivity to the use of a fourth or fifth-order polynomial, the use of a third-order polynomial leads to a noticeable increase in retrieval error. A third-order polynomial is insufficient to describe the background shape of a spectral window as wide as $2150\text{--}2310\text{ cm}^{-1}$. Moreover, the background shape of this window is complicated by the CO_2 absorption feature that strengthens to saturation at 2310 cm^{-1} (Fig. 4a). Retrieval errors are highest for the broader, $2020\text{--}2310\text{ cm}^{-1}$ spectral window (Fig. 7a), though the reported error (not shown) is lowest for this window (0.1%, compared with 0.3% for $2150\text{--}2310\text{ cm}^{-1}$ and 0.9% for $2034\text{--}2075\text{ cm}^{-1}$). This apparent contradiction may be explained by the presence of a large featureless baseline across most of this wider spectral window (Fig. 4a) leading to an overall improved fit between the modelled and measured spectrum, though not necessarily the best fit at the wavenumber location of the absorption features. A wider spectral window typically decreases the ability of any particular polynomial to model the background continuum as is the case here. There is also an additional reason why use of the broader spectral window generally leads to greater inaccuracy. This is because the zero-baseline offset can only be cal-

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culated from data collected in the CO₂ absorption saturation region (near 2350 cm⁻¹), and uncertainties in this correction will increase as the offset is applied to more distant spectral locations. The results for the narrowest spectral window (2034–2075 cm⁻¹) used here for CO₂ retrieval are less influenced by the choice of polynomial order, each having RMS errors of less than 3.7% (Fig. 7c). The flatter background continuum in this window, combined with the presence of fine absorption structure in the CO₂ lines, explains the reduced sensitivity to polynomial order. The inaccuracy of the retrievals made at lower pathlength amounts in this spectral window is most likely due to the weaker nature of the absorption lines at 2034–2075 cm⁻¹.

Our results clearly indicate that the choice of spectral window, coupled with an appropriate choice of background polynomial, have a strong influence on CO₂ retrieval accuracy. Broader windows typically contain more information, potentially improving the fit between the forward modelled and measured spectra. However, it is also important to ensure that the background continuum of the spectrum within the window under study can be sufficiently well represented by the chosen polynomial. Our results suggest that whilst the 2020–2310 cm⁻¹ spectral window used for CO₂ retrieval gives the lowest reported errors (based on the fit residuals; Sect. 4.2), it does not result in the lowest retrieval error. The 2150–2310 cm⁻¹ spectral window, used with a fourth-order polynomial actually provides the lowest retrieval error for CO₂, ranging from –1.9% to 4.3% across all pathlength amounts tested. An example spectrum with best-fit modelled spectrum is shown in Fig. 8a.

6.2.2 Methane

As outlined in Sect. 5.2, retrievals of CH₄ were confounded by an instrument artefact in the relevant absorption region. The spectral window tested that covered this region (2894–3001 cm⁻¹) showed both large reported and retrieval errors, regardless of the polynomial order chosen (Fig. 7e). The lowest retrieval errors for CH₄ come instead from the 2980–3090 cm⁻¹ spectral window that excludes the artefact region (Fig. 7d),

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with a fourth-order polynomial yielding an RMS error of 1.4% (Fig. 8b shows an example spectrum with a best-fit modelled spectrum for this spectral window). As was the case with the narrowest (2034–2075 cm⁻¹) CO₂ retrieval window, the polynomial order does not significantly influence retrieval accuracy due to the fine structure of the CH₄ absorption lines and the flat background continuum. However, for the narrowest CH₄ retrieval window tested (3005–3015 cm⁻¹), the polynomial order has a strong influence (Fig. 7f) with only a first order function allowing pathlength amounts to be retrieved within an RMS error of 3.9%. Individual CH₄ absorption lines remain unresolved at the 0.5 cm⁻¹ spectral resolution used here, and instead combine to appear as one large apparent absorption feature, and thus higher order polynomials incorrectly start to fit this feature as well as the background continuum.

6.2.3 Carbon monoxide

Results for CO suggest that the two broadest spectral windows provide very similar retrieval accuracies, with the 2000–2230 cm⁻¹ spectral window used with a fourth-order polynomial achieving an RMS error of 3.6% across all pathlength amounts tested here (slightly better than the RMS error of 3.9% for the 2142–2241 cm⁻¹ spectral window). Figure 8c shows an example spectrum and best-fit modelled spectrum for the spectral window 2000–2230 cm⁻¹. Generally, the two narrower spectral windows overestimated pathlength amounts compared to the 2000–2230 cm⁻¹ window. Retrievals for CO across all spectral windows tested here showed a lower reliance on choice of background polynomial compared to the other gases, reflecting the “flat” background continuum across the whole CO absorption feature (Fig. 4f). Results from the narrower 2039–2057 cm⁻¹ spectral window indicate that it is best suited to retrieval of higher pathlength amounts, with poor retrieval accuracies for pathlength amounts below 1000 ppm·m. High reported errors (based on the fit residuals) suggest that the retrieval process performs poorly with the weak absorption lines in this spectral window, as is also the case for lower pathlength amounts of CO₂ retrieved in the 2034–2075 cm⁻¹ spectral window.

6.3 Sensitivity analysis and error budget

Using the optimum set of retrieval parameters described in Sect. 6.2, a series of sensitivity analyses were performed. In Sect. 6.1, the spectrometer FOV was determined as 22 mrad. The exact FOV is difficult to determine given the fast optics and the absence of a well defined limiting aperture. We compared retrievals made using our optimally determined FOV with those made using a FOV varied by $\pm 10\%$.

Retrievals for all three gases generally show a systematic reliance upon the specified FOV (Fig. 9), with retrieved pathlength amounts generally increasing with assumed FOV. CO demonstrated the greatest sensitivity to FOV since the CO absorption lines are narrower than the instrument's 0.5 cm^{-1} spectral resolution and their representation is therefore strongly influenced by instrument parameters. CO₂ retrieval accuracy appears to be less sensitive to FOV uncertainty at higher pathlength amounts. This may be explained by the increasing saturation (absorption of all source energy) by strong absorption lines at higher CO₂ pathlength amounts, leaving fewer lines in the spectral window affected by errors in FOV.

The retrieval sensitivities to assumed pressure and temperature were calculated from the pressure- and temperature-independent molecular amounts (molecules cm^{-2}), rather than from the volumetric mixing ratios (ppm-m), as the latter are additionally sensitive to these parameters via the relationship used to interconvert between these two concentration units (Eq. 6). Figure 10 shows the sensitivity of the retrievals to assumed gas pressure, where it can be seen that pathlength amounts are generally overestimated when pressure is underestimated, and vice versa. As is the case with the FOV parameter, the forward modelled absorption line widths are affected by the assumed pressure (Fig. 11a,b). When a lower pressure is assumed, narrower lines than are actually present in the measured spectrum are modelled due to inadequate pressure broadening, causing a positive residual between the modelled spectrum and the measurement (similar to the residual spectrum in Fig. 11b). In order to fit the modelled spectrum to the measured spectrum, the NLLS procedure increases the concentration

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of the absorber to minimise this positive residual, leading to an overestimation of gas pathlength amounts, whereas the reverse is true when assumed pressure is overestimated.

For CH₄ and lower pathlength amounts of CO, the error induced by pressure uncertainties was significantly lower than for CO₂ (Fig. 10). As pathlength amounts increase, absorption lines deepen, causing any line shape inaccuracies due to incorrect pressure specification to be exacerbated. For CO₂, line deepening is less of an issue, given that deep absorption lines occur for all pathlength amounts in the spectral window chosen, and this explains why CO₂ retrievals shows a higher sensitivity to pressure uncertainties at all pathlength amounts, with the percentage error relatively independent of actual concentration. We find that the reported errors based on the forward modelled fit residuals show little dependence on pressure ($\pm 0.04\%$, $\pm 0.01\%$ and $\pm 0.002\%$ across ± 100 hPa for CO₂, CH₄ and CO, respectively), whereas retrieval errors show a much greater sensitivity. In field situations, pressure uncertainties are most likely to arise from uncertainty in plume height. Our analysis shows that uncertainties of up to 500 m at sea level (~ 50 hPa) are therefore equivalent to a $\pm 0.5\%$ uncertainty in CH₄ and low CO pathlength amounts, but are closer to $\pm 3\%$ for CO₂ and higher pathlength amounts of CO.

Figure 12 shows the sensitivity of retrieved pathlength amount to assumed temperature. For CH₄ and CO retrievals, temperature increases lead to proportional increases in retrieved pathlength amounts, whilst for CO₂, this effect is not observed at lower pathlength amounts and is reversed for the highest pathlength amounts (above 5×10^{20} molecules cm⁻²). These findings are best explained by the temperature dependence of spectral band shape. Changing temperature affects the envelope of the absorption band (Fig. 11c), with higher temperatures causing more absorption in the weaker lines that lie towards the edge of the band, and reduced absorption in the stronger lines located towards the middle of the band. Therefore, for spectral windows containing strong absorption lines located towards the middle of an absorption band, when assumed temperature is overestimated, a higher gas concentration is required

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for the forward modelled spectrum to best-fit the measured spectrum. When a spectral window containing weaker absorption lines at the edge of an absorption band is used, the opposite is true. For the CH₄ and CO spectral windows, these effects largely cancel each other out as the spectral windows lie across both strong and weaker lines at the middle and edge of their respective absorption bands. The greater influence of the stronger absorption lines leads to a small positive sensitivity for CH₄ and CO in the spectral windows used here. For CO₂, however, the saturation of the strongest lines towards the middle of the band means that the sensitivity of concentration retrievals to temperature is reversed.

6.4 Sensitivity summary

Table 3 summarises the findings of the sensitivity analyses and indicates to what percentage accuracy CO₂, CH₄ and CO can be retrieved assuming optimum parameterisation of the forward model. The “worst-case” scenario (as suggested by Horrocks et al., 2001) indicates that the total error due to uncertainties that could arise from incorrect retrieval parameterisation amounts to less than 8.2% for all tested pathlength amounts, with a mean of 4.8%. Generally these “external” errors are of a similar magnitude to the additional errors that maybe introduced via the uncertainty inherent in the absorption line intensities for each gas. The HITRAN08 absorption line intensity uncertainties are reported to be between 5–10% for CO₂ and CH₄, but are lower for CO at 1–2% (Rothman et al., 2009). Of course, with good meteorological measurements and careful collection of non-saturated single-beam spectra, the magnitude of the external errors can be minimised.

Errors in assumed pressure become increasingly significant at higher pathlength amounts due to the deepening of absorption lines, especially for CO₂ and CO. One solution to this problem would be to use a spectral window with weaker absorption lines; however, the results for temperature sensitivities indicate that this would increase sensitivity to the spectral band shape dependence on temperature. Errors in assumed temperature of less than 10 °C lead to errors in retrieved concentration of below 3%.

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Greater errors are perhaps most likely to occur during studies focused on plumes from hot sources (volcanic, fire or industrial), and care should be taken to minimise sensitivity to these errors by using a broad spectral window encompassing weak and strong absorption lines and ideally targeting plumes once they have cooled to near ambient temperatures at some distance from the source region. Then, the magnitude of errors in assumed pressure and temperature that may be expected in the field should not lead to significant retrieval errors when retrieving molecular amounts (molecules cm⁻²). However, for volumetric mixing ratios (e.g. ppm) the effect of these errors will be exacerbated through Eq. (6).

In our experiment, the spectrometer FOV was determined to be 10% higher than the manufacturer's nominal value of 20 mrad. Unlike gases such as SO₂, ambient and elevated pathlength amounts of CO₂, CH₄ and CO demonstrate deep absorption lines that increase their sensitivity to instrument line shape, and therefore extra care should be taken to preserve instrument optics from degradation if measurements are to target these gases.

7 Summary and implications for field measurements

Our study collected single-beam spectra of a broad range of concentrations of CO₂, CH₄ and CO using OP-FTIR spectroscopy, representing mixing ratios varying from those found in the ambient atmosphere to the highly polluted plumes of biomass burning, volcanoes and industry over the equivalent pathlength of tens to hundreds of metres.

A number of spectral windows were investigated for the concentration retrieval of each gas species via a forward modelling nonlinear least squares fitting approach. Spectral windows that maximised the amount of absorption information for each gas (e.g. the number of absorption lines) typically produced the lowest reported errors (fit residuals) and the lowest actual retrieval errors when compared to the true gas cell pathlength amount. However, if broad spectral windows are to be used it is important to

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ensure a good background polynomial fit (used to represent the continuum radiation), and we found that when wider windows were investigated, containing large regions showing no absorption (e.g. 2020–2310 cm⁻¹ for CO₂), retrieval accuracies were diminished due to poor background fitting. Similarly, it is important to check that broader windows do not contain spectral artefacts, such as those found here in the 2894–3001 cm⁻¹ spectral window when retrieving CH₄. Such artefacts, potentially caused by substances contaminating spectrometer optics, will complicate the simulation of background shape using lower-order polynomials, and should therefore be avoided.

When using optimum parameterisation of the MALT forward model used here, the nonlinear least squares fitting procedure was able to retrieve pathlength amounts within 4.8% of the true values for all gases and pathlength amounts tested (Fig. 13). Mean retrieval errors were 2.4%, 1.4% and 3.6% for CO₂, CH₄ and CO, respectively. A series of analyses was performed to assess the sensitivity of retrievals to uncertainties in instrument (FOV) and environmental (temperature, pressure) parameters. The uncertainties assumed were of a magnitude similar to those expected in many field situations in which OP-FTIR may be deployed. Sensitivities were shown to be different for each gas. Uncertainty in the FOV parameter had most impact on CO retrieval. The shape of the forward modelled absorption feature is therefore highly dependent on the assumed instrument FOV due to the narrowness of the CO absorption lines, which remain unresolved at the 0.5 cm⁻¹ resolution used here. The sensitivity of all retrievals to FOV increased when the spectral window used for the analysis contained strong absorption lines, which occurred at higher pathlength amounts for the CH₄ and CO spectral windows, but at lower pathlength amounts for the CO₂ spectral window (where higher pathlength amounts led to absorption saturation, and therefore, a smaller number of observed absorption lines).

Generally, the results of this study indicate that reported errors, based on the residuals between the best-fit forward modelled spectra and the measured spectra, are smaller than the actual retrieval errors (Table 3). Reported errors should therefore not be used as a proxy for actual retrieval error. Reported errors appear most useful for

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the optimisation of instrument line shape, where minimising the reported error via adjustment of the assumed FOV can improve actual retrieval errors. However, errors in assumed FOV, temperature and pressure can all impart similar effects on the spectral fitting. For example, minimising reported errors by adjusting the assumed pressure could improve the spectral fit, but the same degree of improvement might be achieved by adjusting the FOV, potentially resulting in a quantitatively different retrieved path-length trace gas amount. These sensitivities and uncertainties suggest that proper assessment of gas temperature, pressure and instrument FOV is important for accurate gas concentration retrieval, given that errors induced by one parameter may be compensated for by adjusting the value of another parameter to minimise reported error, but that this may result in retrieval of an incorrect concentration.

Retrieval sensitivity to errors in temperature and pressure were relatively small for the magnitude of parameter uncertainty that might be expected in typical field situations. Assuming a potentially “worst-case” scenario of a 50 hPa and 10°C error in assumed pressure and temperature, and the 10% difference in FOV found here as compared to the manufacturer’s specification, pathlength amount retrievals might vary by up to 8.2% (errors added in quadrature). As discussed by Horrocks et al. (2001), gases that demonstrate individual absorption lines resolved by the spectrometer (as opposed to gases such as SO₂, with broad bands for which individual rotational lines cannot be resolved), are more susceptible to parameter errors affecting spectral line shape. Minimising uncertainty in these parameters is therefore paramount for retrievals of CO₂, CH₄ and CO via a combination of accurate temperature and pressure information, and careful examination of the spectral fit. In particular, as demonstrated in this study, errors due to poor zero-baseline offset correction, incorrect pressure, temperature, and instrument line shape assumptions will all cause a poor fit when a retrieval is performed using a window containing both weak and strong absorption lines, and minimising reported errors in such a window will improve retrieval accuracy.

The results from this study confirm that a forward modelling approach coupled with a nonlinear least squares fitting routine can be a viable and accurate method for re-

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trieving gas concentrations from OP-FTIR data, in this case using an MCT detector covering a wide spectral range (600–6000 cm⁻¹). The concentrations of the three most abundant carbonaceous gases in the atmosphere were retrieved here to accuracies better than 5% over a very wide range of pathlength amounts (Fig. 13). Whilst it remains difficult to provide a quantitative measure of actual concentration retrieval error directly from the forward modelling reported errors (fit residuals), the results from this study provide confidence that carefully undertaken retrievals made using the forward modelling NLLS method can provide high retrieval accuracies.

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Table 1. Cell mixing ratios (ppm) and equivalent pathlength amount (ppm·m) for the 1.05 m gas cell filled with CO₂, CH₄ and CO, respectively, with the equivalent mixing ratios for longer atmospheric paths (assuming the same temperature, ~20 °C, and pressure, ~1000 hPa conditions) also given. For reference, ambient “clean” air mixing ratios of CO₂, CH₄ and CO are circa 385 ppm, 1.8 ppm and 0.15 ppm, respectively.

Cell mixing ratio (ppm)	Pathlength amount (ppm·m)	30 m path equivalent (ppm)	100 m path equivalent (ppm)	800 m path equivalent (ppm)
CO₂				
12 014	12 612	420.4	126.1	15.8
24 991	26 236	874.5	262.4	32.8
45 799	48 080	1602.7	480.8	60.1
100 125	105 112	3503.7	1051.1	131.4
200 200	210 172	7005.7	2101.7	262.7
340 351	357 304	11 910.1	3573.0	446.6
CH₄				
51.94	54.52	1.83	0.55	0.07
92.81	97.43	3.25	0.97	0.12
168.51	176.91	5.90	1.77	0.22
270.85	284.34	9.48	2.84	0.36
490.09	514.50	17.15	5.15	0.64
CO				
18.96	19.90	0.66	0.20	0.03
244.14	256.30	8.54	2.56	0.32
459.13	482.00	16.07	4.82	0.60
1217.05	1277.67	42.59	12.78	1.60
6077.20	6379.91	212.66	63.80	7.98

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Table 2. Spectral windows used here for the retrieval of CO₂, CH₄ and CO and marked in Fig. 4. Also listed are the potentially interfering gases (those in brackets were not included in the forward-model spectral simulation conducted here due to the very short clean air atmosphere path used, but would generally be required over longer pathlengths in the ambient atmosphere).

Target gas	Spectral window	Interfering gases
CO ₂	2020–2310 cm ⁻¹	H ₂ O (N ₂ O, CO)
	2034–2075 cm ⁻¹	H ₂ O
	2150–2310 cm ⁻¹	H ₂ O (N ₂ O, CO)
CH ₄	2894–3001 cm ⁻¹	H ₂ O
	2980–3090 cm ⁻¹	H ₂ O
	3005–3020 cm ⁻¹	H ₂ O
CO	2000–2230 cm ⁻¹	H ₂ O
	2039–2057 cm ⁻¹	H ₂ O
	2142–2241 cm ⁻¹	H ₂ O

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Table 3. Summary of errors associated with parameter uncertainty when retrieving trace gas amounts from OP-FTIR measurements using the MALT forward model (Griffith, 1996) with a NLLS fitting procedure. Errors for choice of polynomial and errors in assumed field-of-view, pressure and temperature are taken from the results presented in Figs. 7, 9–11, and are calculated using the difference between the retrievals made using the best parameter to those using the altered parameter, expressed as a percentage. Uncertainties in the HITRAN08 database (Rothman et al., 2009) refer to the line intensity error specified therein.

Source of error	Retrieval error (%), for CO ₂ pathlength amounts (ppm-m):					
	12 612	26 235	48 080	105 112	210 172	357 304
Choice of polynomial (4th or 5th order)	0.9	0.6	1.7	1.8	1.5	0.9
Field-of-view (best-fit or manufacturer's)	5.2	6.2	5.5	3.2	0.2	1.8
50 hPa error in assumed pressure	2.2	2.8	3.2	2.1	3.4	3.5
10 °C error in assumed temperature	4.2	4.5	1.0	2.5	0.6	4.3
Total (added in quadrature)	7.1	8.2	6.7	4.9	3.8	5.9
Uncertainty in line intensities (HITRAN08)	5.0–10.0	5.0–10.0	5.0–10.0	5.0–10.0	5.0–10.0	5.0–10.0
Mean reported error	0.2	0.3	0.4	0.4	0.3	0.3
Accuracy of retrieved:true (best parameters)	-1.9	3.1	4.3	-1.0	-1.7	2.7
	Retrieval error (%), for CH ₄ pathlength amounts (ppm-m):					
	54.5	97.4	176.9	284.3	514.5	
Choice of polynomial (4th or 5th order)	1.6	0.8	0.6	0.7	1.0	
Field-of-view (best-fit or manufacturer's)	2.4	1.6	1.4	1.3	1.2	
50 hPa error in assumed pressure	0.8	0.4	0.3	0.3	0.6	
10 °C error in assumed temperature	2.8	2.2	2.1	1.9	1.5	
Total (added in quadrature)	4.1	2.9	2.6	2.4	2.2	
Uncertainty in line intensities (HITRAN08)	5.0–10.0	5.0–10.0	5.0–10.0	5.0–10.0	5.0–10.0	
Mean reported error	2.0	0.9	0.6	0.6	0.8	
Accuracy of retrieved:true (best parameters)	0.8	0.2	0.1	4.8	1.3	
	Retrieval error (%), for CO pathlength amounts (ppm-m):					
	19.9	256.3	482.0	1277.7	6379.9	
Choice of polynomial (4th or 5th order)	0.2	0.0	0.0	0.0	0.0	
Field-of-view (best-fit or manufacturer's)	4.0	5.4	5.4	5.1	2.4	
50 hPa error in assumed pressure	1.7	0.5	1.3	2.8	4.3	
10 °C error in assumed temperature	0.2	0.8	0.9	1.0	1.0	
Total (added in quadrature)	4.4	5.5	5.6	5.9	5.0	
Uncertainty in line intensities (HITRAN08)	1.0–2.0	1.0–2.0	1.0–2.0	1.0–2.0	1.0–2.0	
Mean reported error	0.5	0.1	0.1	0.1	0.1	
Accuracy of retrieved:true (best parameters)	-4.0	4.4	4.3	2.0	3.4	

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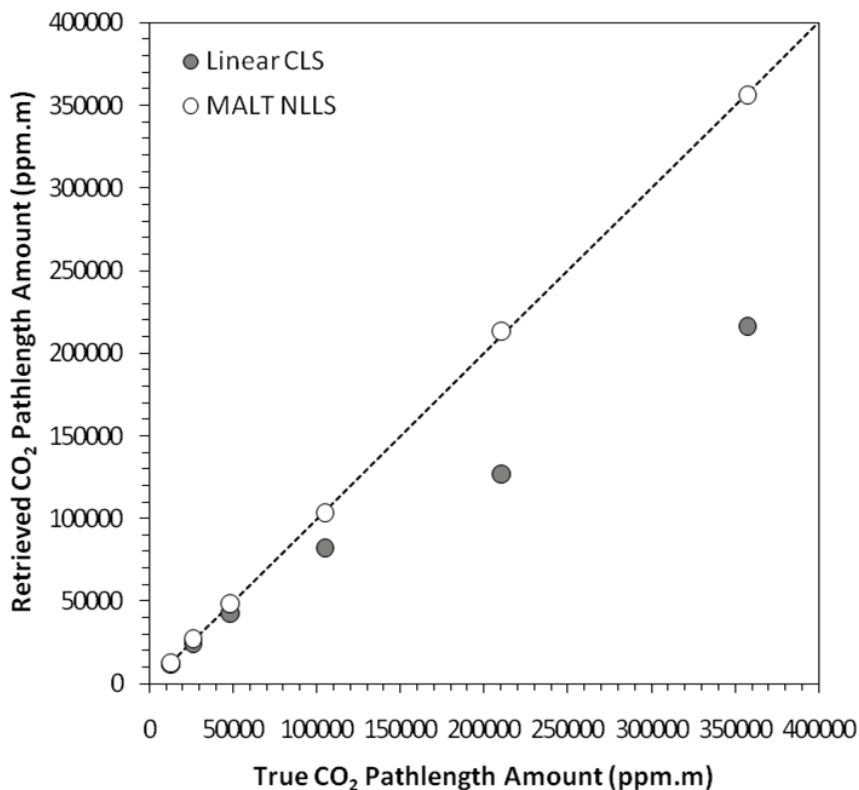


Fig. 1. Comparison of FTIR-derived retrievals of gas-cell CO₂ pathlength amount to the true pathlength amount within the cell. Retrievals were made from the same spectra via two approaches, the Classical Least Squares (CLS) approach described in Haaland (1990) and the MALT forward model and nonlinear least squares (NLLS) fitting procedure described in Griffith (1996) and Griffith et al. (2003). The 1:1 line is shown, and the increasing underestimation of the CLS-based retrievals at higher pathlength amounts is clearly evident.

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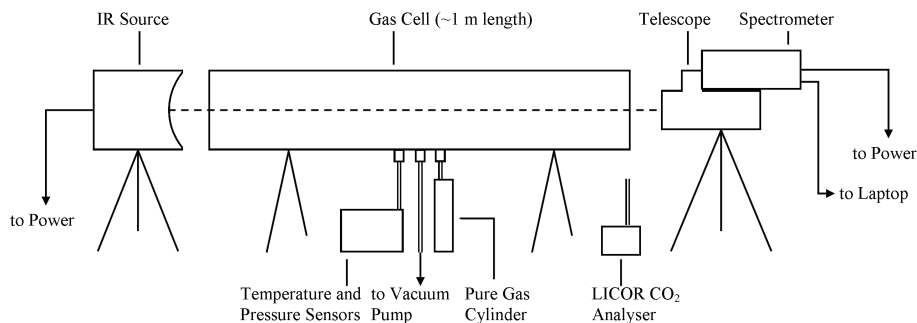
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**Fig. 2.** Schematic of the physical instrumentation arrangement used in the current study.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

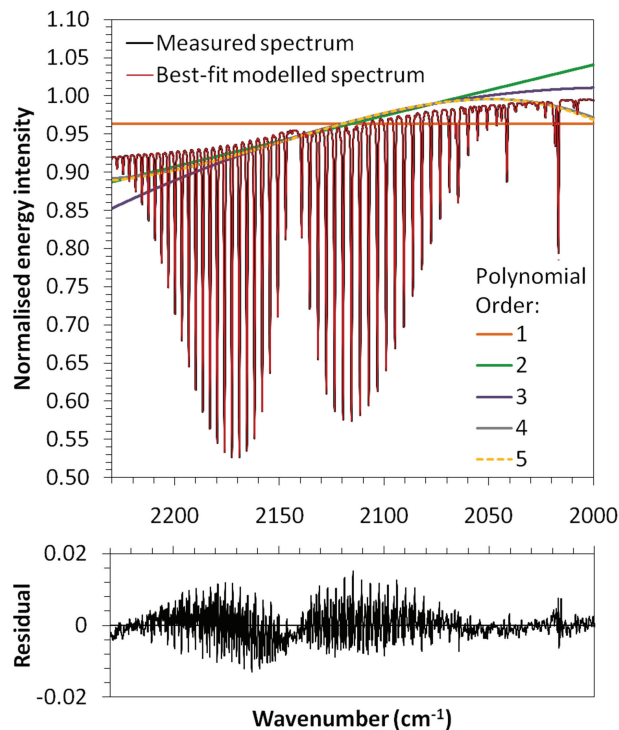


Fig. 3. Examples of results from a measured spectrum and the best-fit modelled spectrum produced using the MALT forward model and nonlinear least squares (NLLS) fitting procedure described in Griffith (1996). The case shown is for 482 ppm-m of CO at a gas pressure of 1000 hPa. (top) The measured and best-fit modelled spectra are shown to be extremely well matched, with the different background polynomial functions (orders 1–5) tested also shown. The fourth order polynomial provided the best match to the measured spectrum, and this was used to simulate the best-fit modelled spectrum shown. (bottom) The residual spectrum (i.e. the measured spectrum subtracted from the modelled spectrum), which is used to provide a measure of fitting accuracy.

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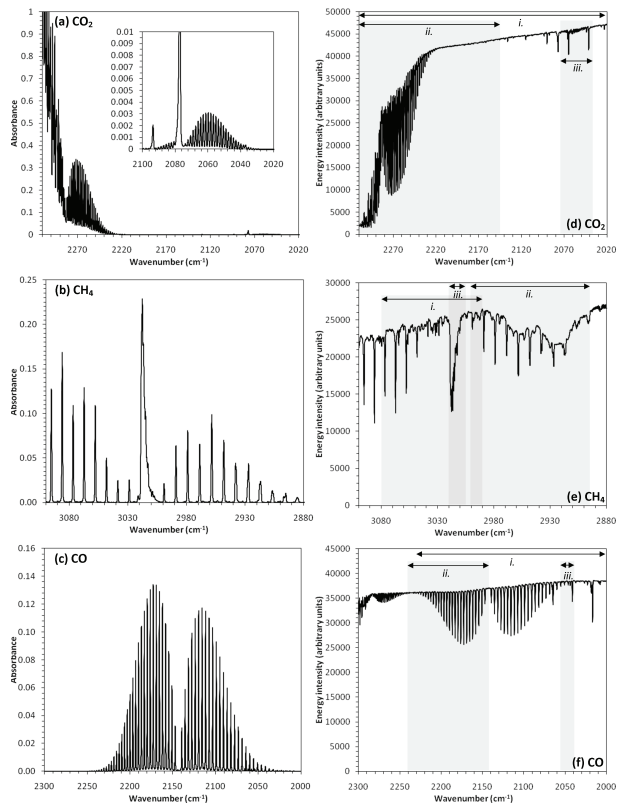


Fig. 4. Modelled and measured spectra at 0.5 cm^{-1} wavenumber resolution for the CO_2 , CH_4 , and CO trace gases considered here. (Left) absorbance spectra modelled using the MALT forward model; (right) measured FTIR single-beam spectra. The various spectral windows used to retrieve the trace gas concentrations from the measured spectra are indicated by the numbered horizontal arrows in (d–f) and are detailed in Table 2.

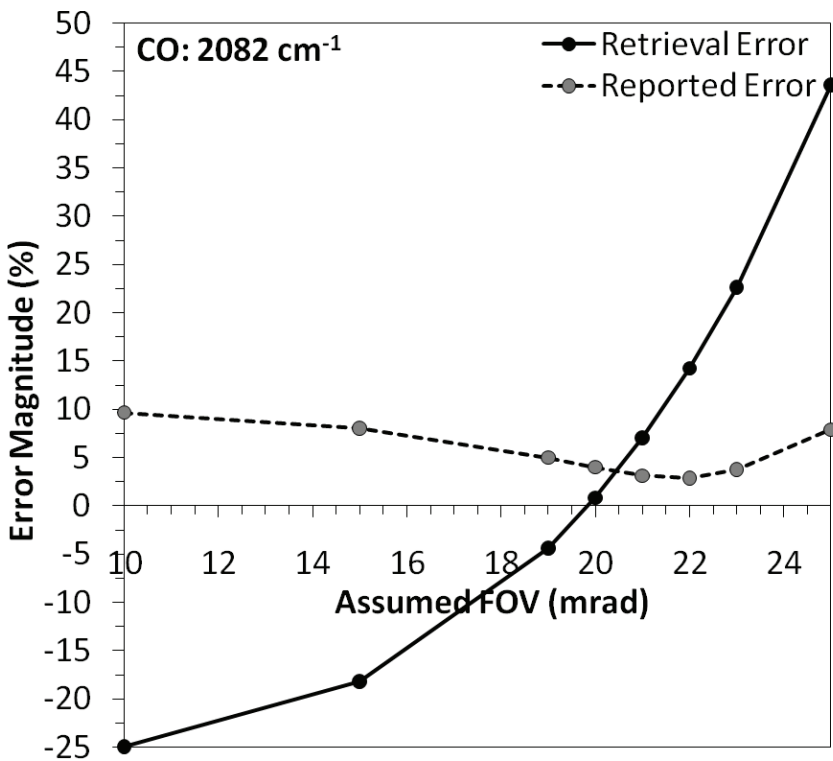


Fig. 5. Sensitivity of the reported error (based on the fit residuals) and retrieval error (based on the difference between retrieved pathlength trace gas amount and actual pathlength trace gas amount) to assumed instrument FOV. The example is shown for CO trace gas retrievals based on the CO absorption line centred at 2082 cm⁻¹ (Fig. 6). Measurements were made at a low pressure of 400.5 hPa with a true CO mixing ratio of 1217.05 ppm. Reported error is minimised at an assumed FOV of 22 mrad, though is relatively insensitive to the FOV variations studied here. Retrieval error is, however significantly more sensitive, and assumed 20 mrad FOV yields the smallest actual retrieval error.

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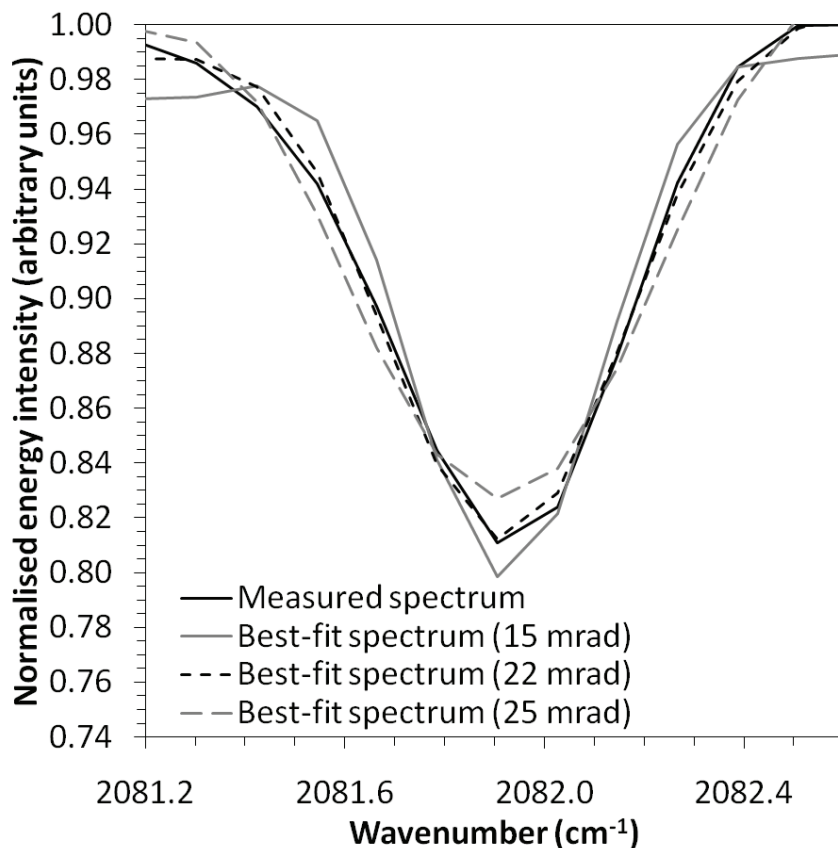


Fig. 6. Measured single-beam spectra and best-fit modelled spectra for the CO absorption line centred at 2082 cm^{-1} at a gas pressure of 400.5 hPa. Modelled spectra were simulated assuming different fields-of-view (15–25 mrad), with the 22 mrad FOV providing the best match between the measured and modelled spectra.

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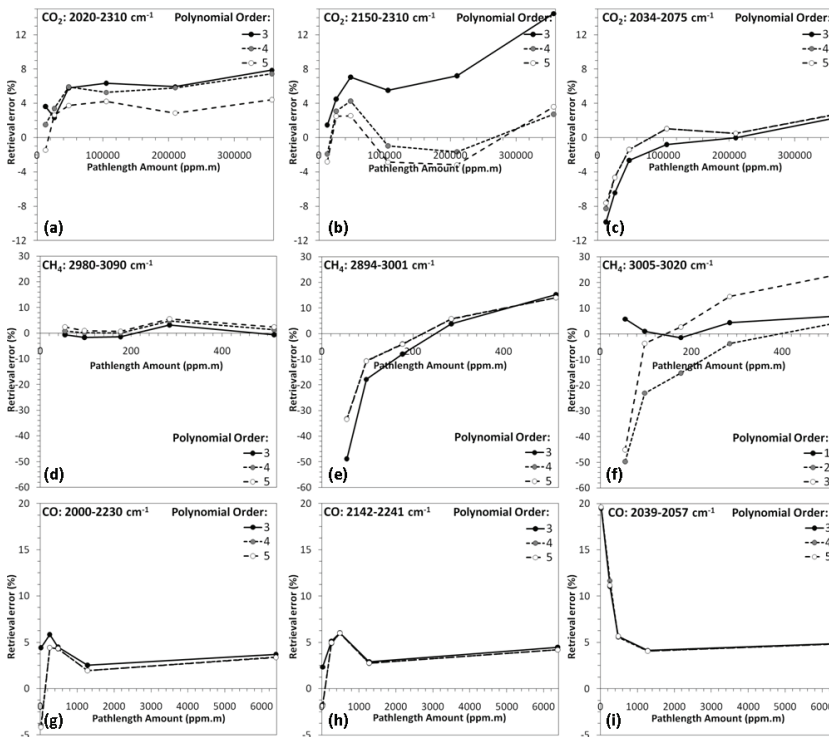


Fig. 7. Retrieval errors for CO₂, CH₄ and CO trace gas retrievals resulting from use of the MALT forward model and NLLS fitting procedure with OP-FTIR spectra from a gas cell containing samples of these three gases over wide concentration ranges. Retrievals were made using three different spectral windows for each trace gas and three different polynomial orders. In order to aid comparison of the error magnitudes for the retrievals of each trace gas, the same y-axis range is used to display the results from the three spectral windows tested. Retrieval error magnitude is seen to vary quite widely between the different spectral windows used to retrieve the pathlength amount of a particular trace gas, and for some windows between the different polynomial orders examined.

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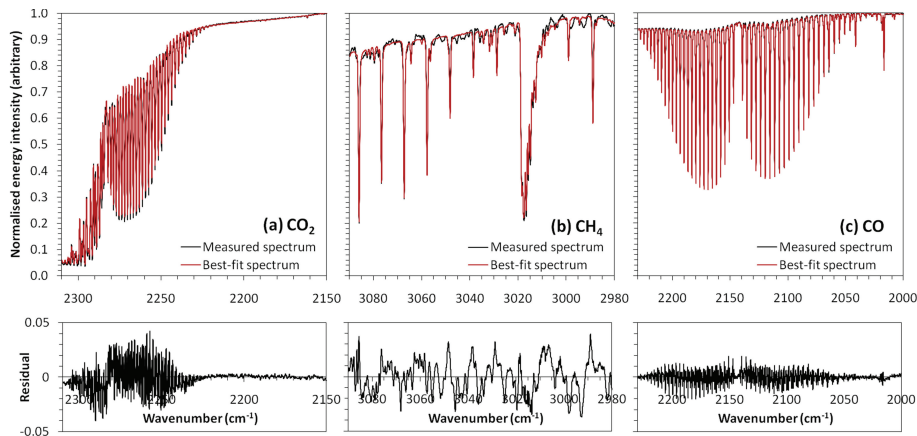


Fig. 8. Examples of measured spectra and best-fit forward modelled spectra made using the optimum spectral windows and a fourth-order polynomial background (top), and the residual between the measured and modelled spectra (bottom) for **(a)** CO₂; **(b)** CH₄; and **(c)** CO. Forward modelled spectra were simulated using MALT and the best-fit modelled spectra were found using the NLLS fitting procedure.

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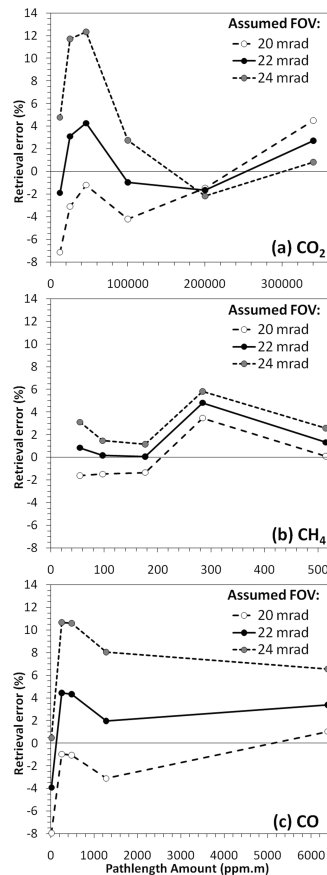


Fig. 9. Sensitivity of trace gas concentration retrieval error to the assumed FOV for **(a)** CO₂, **(b)** CH₄, and **(c)** CO. Retrievals were made using the MALT forward model with a NLLS fitting procedure. The same y-axis range is used in each case to aid comparison of error magnitude between gases.

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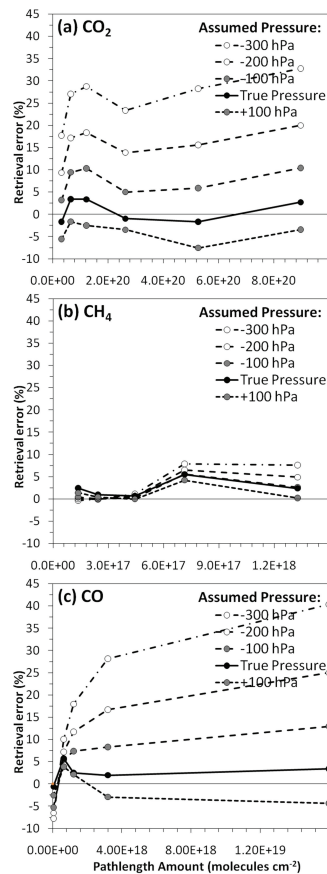


Fig. 10. Sensitivity of trace gas concentration retrieval error to the assumed gas pressure for (a) CO₂, (b) CH₄, and (c) CO. Retrievals were made using the MALT forward model with a NLLS fitting procedure. The same y-axis range is used in each case to aid comparison of error magnitude between gases.

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**Absolute accuracy of
OP-FTIR retrievals of
CO₂, CH₄ and CO
concentrations**

T. E. L. Smith et al.

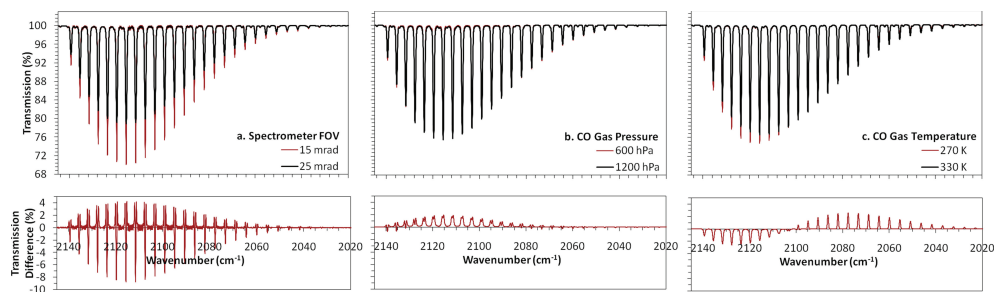


Fig. 11. Simulated transmission spectra for CO gas at a fixed molecular amount of 6.424×10^{17} molecules cm^{-2} , along with percentage difference in transmission between the CO transmission spectra simulated using **(a)** an assumed FOV of 15 mrad and 25 mrad; **(b)** at 600 and 1200 hPa; and **(c)** at 270 K and 330 K. The figure focuses on the p -branch of the CO vibrational stretching mode absorption feature, centred at 2143 cm^{-1} . Increasing FOV leads to broader, but weaker absorption lines; increasing pressure leads to deeper and broader absorption lines; whilst increases in temperature lead to stronger absorption towards the edge of the band (wavenumbers $<2100 \text{ cm}^{-1}$) and weaker absorption towards the band centre (wavenumbers $>2100 \text{ cm}^{-1}$).

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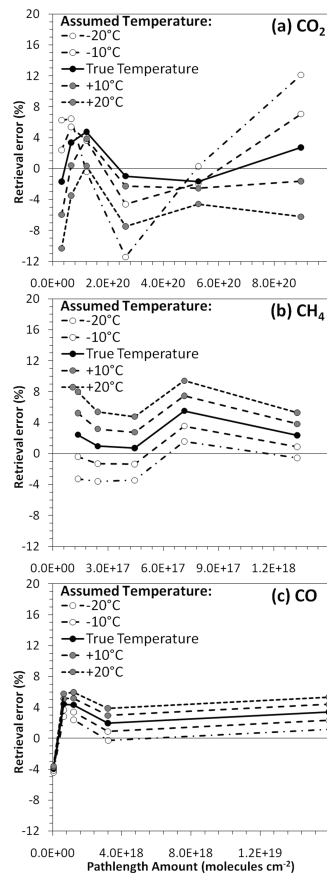


Fig. 12. Sensitivity of trace gas concentration retrieval error to the assumed gas temperature for **(a)** CO₂, **(b)** CH₄, and **(c)** CO. Retrievals were made using the MALT forward model with a NLLS fitting procedure. The same y-axis range is used in each case to aid comparison of error magnitude between gases.

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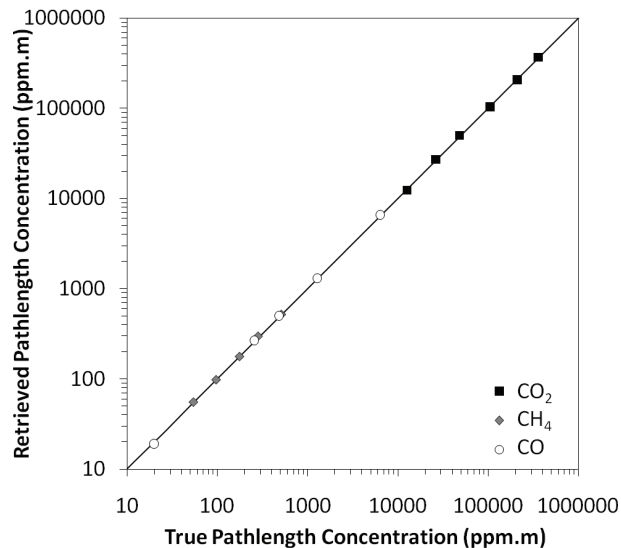


Fig. 13. Relationship between mean retrieved pathlength trace gas amounts made using the optimum parameterisation of the MALT forward model determined herein. The 1:1 line is shown and all retrieved amounts are within 4.8% of true amounts (note logarithmic axes).

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