Improving the Retrievals of Greenhouse Gases from Ground-Based Solar Absorption Spectra

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

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Abstract

A quadratic speed-dependent Voigt (qSDV) line shape with line mixing (LM) has been implemented into the forward model of the spectral fitting software GFIT to improve the retrievals of total columns of CO₂, CH₄, and O₂ from high-resolution ground-based solar absorption spectra. Absorption coefficients were calculated using the qSDV+LM spectral line shape with spectroscopic parameters for the strong 20013 \leftarrow 00001 CO₂ band centered at 4850 cm⁻¹, the weak 30013 \leftarrow 00001 and 30012 \leftarrow 00001 CO₂ bands centered at 6220 cm⁻¹ and 6340 cm⁻¹ respectively, as well as the 2v₃ band of CH₄. Absorption coefficient calculations were validated using laboratory spectra of CO₂ and CH₄. Laboratory spectra were modeled better with the qSDV+LM when compared to using the Voigt spectral line shape. The qSDV was used to fit air-broadened, room-temperature, cavity ring-down spectra of the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ O₂ band. It was shown that the Voigt line shape is inadequate to model the spectral lines of this O₂ band and that speed-dependent effects need to be taken into account. Spectroscopic parameters of the discrete spectral lines of the O₂ $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ band were retrieved and implemented in GFIT.

A year of ground-based solar absorption spectra acquired at Eureka (Nunavut, Canada), Park Falls (Wisconsin, USA), Lamont (Oklahoma, USA), and Darwin (Northern Territory, Australia) were processed using GFIT. Total columns of CO_2 , CH_4 , and O_2 were retrieved using absorption coefficients calculated assuming a Voigt spectral line shape and the qSDV+LM (with LM used when applicable). With the qSDV+LM, spectral fits of CO_2 and CH_4 improved as a function of solar zenith angle. The airmass dependence of the retrieved columns of CO_2 , CH_4 , and O_2 , as well as the column-averaged dry-air mole-fraction of CO_2 (XCO₂) decreased while the accuracy of XCO₂ improved.

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1 Motivation and Background

1.1 Surface Temperature and Radiative Forcing

The globally averaged annual mean surface temperature of the Earth has increased since the Industrial Revolution. In 1824, Joseph Fourier calculated that given the distance between the Earth and Sun, the surface temperature of Earth should be much cooler than it actually is. He didn't know why this was, but one of his suggestions was that the Earth's atmosphere could be absorbing some of the infrared radiation that the Earth emits (after absorbing sunlight) instead of emitting it to space (Fourier, 1824). In 1896, Svante Arrhenius was the first scientist to attempt to calculate how changes in the concentration of carbon dioxide (CO₂) in Earth's atmosphere would affect the Earth's surface temperature. Arrhenius predicted that increased emissions of CO₂ to the atmosphere by human activity would be enough to cause global warming, but given the low rate of CO₂ emission at that time, he postulated that it would take thousands of years to double CO₂ in the atmosphere (Arrhenius, 1896). At that time, no one thought that human activity could have a profound impact on the Earth's atmosphere in a short time frame.

In 1938, Guy Stewart Callendar met with the Royal Meteorological Society and argued that CO_2 in the atmosphere had risen to levels higher than what scientists at the time expected (Callendar, 1938). However, his claims weren't taken seriously since measurements of CO_2 in the atmosphere at the time were not reliable (Weart, 2003). It wasn't until the mid-1950s that the first reliable measurements of CO_2 in the atmosphere were made, showing that the concentration of CO_2 was rising at a rate much faster than thought by most scientists at the time. Scientists took advantage of the improvements made in digital computing to improve on the calculations done by Arrhenius by incorporating more physical processes in their calculations. In 1967, Manabe and Wetherald created a one-dimensional radiative convection model that calculated a 2 °C increase in the global temperature if the atmospheric concentration of CO_2 of 1967 was doubled (Manabe and Wetherald, 1967). However, the model did not take into account processes that were not well understood (such as cloud formation). As time went on, scientists developed a better understanding of the physical and chemical processes that influence the radiative forcing of Earth's climate system.

Radiative forcing, as defined in the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report (2014), is the change in energy flux caused by a driver and is calculated at the tropopause or top of the atmosphere. Figure 1.1 shows a breakdown of the radiative forcing (in Wm⁻²) due to emitted substances and their drivers, relative to their forcing values in 1750. The figure shows that well-mixed greenhouse gases (GHGs) such as CO₂, and methane (CH₄) significantly contribute to the positive radiative forcing of Earth's climate system. When all of these factors are taken into consideration, the total radiative forcing in 2011 relative to 1750 is positive.



Figure 1.1: Breakdown of the radiative forcing due to emitted substances. Shown are the global averaged values (in Wm⁻²) for the emitted substances and their drivers as well as changes in albedo (due to land changes) and solar irradiance, relative to 1750 for 2011. The error bars give the uncertainty for the compound. This figure is SPM.5 from the Summary for Policy Makers found in the IPCC Fifth Assessment Report (2014).

The increase in radiative forcing since 1750 has led to warming of much of the world's oceans, sea level rise, the frequency of warmer days increasing, decreasing snow cover in most regions, shrinking annual average Arctic sea ice extent, and glacier retreat (IPCC, 2014). Changes in the climate system have had an impact on life on Earth through increased droughts, heat waves, stronger storm systems, and flooding. We know that much of the increase in radiative forcing is due to human activity. However, most of these activities produce jobs which are the main source of income for many people. An accurate prediction of how the climate will change given different scenarios is important to governments in order to make informed decisions with regard to the creation of policies that will impact both the environment and economy.

1.2 The Carbon Cycle

All life on Earth contains carbon and requires carbon to grow. The carbon cycle describes the exchange of carbon between the biosphere, atmosphere, hydrosphere and geosphere. Figure 1.2 shows the amount of carbon contained in different reservoirs. The exchange of carbon between these reservoirs can happen quickly (time scales of anywhere between years to millennia) and slowly (time scales of 10,000 years and longer) (Ciais et al., 2014). Most of the carbon on Earth is stored in the geosphere. A series of processes can move carbon slowly between rocks, soil, ocean, and the atmosphere.

The ocean is the largest reservoir of actively cycled carbon, as shown in Figure 1.2, and is stored as dissolved inorganic carbon (DIC) in the form of carbonic acid (H₂CO₃), bicarbonate (HCO₃⁻), and carbonate (CO₃⁻²). At the surface of the ocean where air meets water, CO₂ is absorbed from the atmosphere and turns into H₂CO₃ when it reacts with water. Through the release of a hydrogen atom, the carbonic acid can turn into HCO₃⁻, and through the release of another hydrogen atom, bicarbonate turns into CO_3^{2-} which will react with Ca²⁺ to form calcium carbonate CaCO₃ (Jacob, 1999). When it rains, CO₂ in the atmosphere can combine with water to create carbonic acid. The carbonic acid makes the rain slightly acidic, causing it to dissolve rocks over a long period of time. Weathering of rocks causes the release of calcium (and other) ions which are carried by rivers into the ocean. Calcium is used to create carbonate by organisms, such as plankton, in order to build their shells. Once these organisms die, they can end up on the

ocean floor where over time they turn into limestone from compression by layers of sediment and other dead organisms that have fallen on top of them (Jacob, 1999). Climate models predict, with very high confidence, that ocean uptake of CO_2 will continue for higher concentrations of CO_2 in the atmosphere, although this will lead to the acidity of oceans increasing over time (Stocker et al., 2014).



Figure 1.2: Simplified diagram of how carbon cycles through the biosphere, atmosphere, geosphere, and ocean, from Chapter 6 of the IPCC Fifth Assessment Report (2014) (Ciais et al., 2014). The black numbers and arrows represent the carbon stored in a reservoir and exchange flux respectively. Most black quantities are estimated from a time prior to the Industrial Revolution. Red numbers and arrows represent anthropogenic influences on reservoirs and fluxes after the Industrial Revolution. Reservoirs have units of PgC (1 PgC=10¹⁵ gC), while fluxes are in PgC/year.

In the biosphere, plants and phytoplankton absorb CO_2 from the atmosphere into their cells and using the energy from the sun, convert CO_2 and water into sugar and oxygen (O_2) in a process known as photosynthesis. CO₂ is released into the atmosphere from plants when they decay, are burned, or are consumed by other animals. In all these cases, the opposite chemical reaction happens where sugar and O₂ react to create CO₂ and water, releasing energy. Carbon stored in mud will eventually turn into shale over a long period of time, when heat and pressure are applied to the mud. But sometimes layers of organic matter will build up on top of each other faster than the organic matter can decay, leading to coal, oil, or natural gas being created instead of shale. CO₂ is emitted back into the atmosphere from the geosphere, naturally, through volcanic emissions (Jacob, 1999). By directly tapping into fossil fuels stored in the geosphere, humans have added another pathway for carbon contained in the geosphere to get to the atmosphere. This additional pathway has accelerated the time it takes for carbon to move from the geosphere to the atmosphere. The evolution of the biospheric uptake of CO₂ is less certain than the ocean (Stocker et al., 2014), due to the lack of knowledge of how increasing temperatures and climate change will impact the exchange of carbon between the biosphere and the atmosphere. Monitoring CO₂ in the atmosphere can help determine the influence of climate change on the plant cycle.

The fastest warming region on Earth is the Arctic. For regions north of 62°, the surface air temperature has increased by 0.6 °C per decade since 1985 (McGuire et al., 2009). Scientists view the Arctic as an early warning system, a sort of canary in a coal mine, for the impacts of climate change. Due to rising surface temperatures in the Arctic, the past two decades have seen a decrease in the amount of sea ice that survives the summer melt. Warmer Arctic summers, coupled with higher amounts of an ice-free Arctic ocean, could lead to an increase in CO₂ uptake by the Arctic Ocean. However, the exposed Arctic ocean will absorb the solar radiation that would have been reflected by the sea ice. The extra heat could then be emitted back to the atmosphere, which will lead to higher production of CH₄ from wetlands in the Arctic region (Parmentier et al., 2015). The amount of CH₄ emitted from wetlands is not only dependent on soil temperature, but also on the water table position and carbon available from organic matter. The sensitivity of CH₄ emissions from wetlands to these factors are still unknown (O'Connor et

al., 2010). Formation of new wetlands and strengthening of existing wetlands in the Arctic is of particular concern as it would lead to increased emissions of CH₄ in this region.

The Arctic has been a sink of carbon for a long time, with estimates that it makes up 25% of the Earth's carbon sink (McGuire et al., 2009). When plants and animals die in the Arctic, the decay process is slowed since the organic matter becomes frozen. As soil, sediment and other organic matter is piled on top of the already frozen organic matter, it becomes richer in carbon. If the carbon-rich soil remains frozen for more than two years, it becomes permafrost. Currently it is estimated that 1035 Pg of carbon is stored in the soil of the Northern permafrost carbon pool, of which ~5-15% of it could be released as GHGs during this century (Schuur et al., 2015). However, increasing land surface temperatures have also led to an increase in CO₂ uptake by plants in the Arctic, which might absorb CO₂ released from permafrost. But new studies such as Webb et al. (2016) suggest that the Arctic could be turning from a carbon sink to a carbon source due to increased emissions of carbon to the atmosphere during the winter season.

1.3 Atmospheric Measurements of CO₂

Continuous measurements of the atmospheric concentration of CO₂ were first made in the 1950s by Charles David Keeling at the Mauna Loa Observatory (altitude of 3400 m) located on the island of Hawaii. These measurements were made by collecting samples of air and determining the concentration of CO₂ in these samples. Since these measurements are made at such a high altitude, air measured at the observatory is representative of air from much of the Northern Hemisphere. Figure 1.3 shows the concentration of atmospheric CO₂ at Mauna Loa from flask measurements made between 1990 to summer of 2016. Keeling found that there is a strong seasonal variation in the concentration of CO₂ in the atmosphere as shown by the blue and orange dots in Figure 1.3. The atmospheric concentration of CO₂ was found to be at a maximum in the winter and a minimum in the summer. The seasonal cycle of CO₂ is driven by increased photosynthesis that occurs during the summer, due to the longer days, causing plants to withdraw more CO₂ from the atmosphere than they respire. In the winter, the opposite happens due to the longer nights resulting in plants respiring more CO₂ than they take in. With each successive year, Keeling observed the same seasonal trend but with increased concentrations of CO₂ as shown by

the grey curve (that doesn't pass through the dots) in Figure 1.3. The increasing trend is the result of human activities which emit CO_2 to the atmosphere.



Figure 1.3: In-situ measurements of atmospheric CO_2 made at Mauna Loa from 1990 to 2016. The blue (calibrated data) and orange (uncalibrated data) dots are monthly CO_2 measurements, the grey curve that connects the dots shows seasonality of CO_2 and the other grey curve is when the seasonal trend is removed. This figure was generated and taken from: http://www.esrl.noaa.gov/.

 CH_4 is a more potent GHG than CO_2 , but due to its lower concentration and shorter lifetime in the atmosphere, it has less of an influence on the radiative forcing of the climate than CO_2 . It is the second-most important anthropogenic GHG and like CO_2 , the concentration of CH_4 in the atmosphere has been increasing since the Industrial Revolution. CH_4 emission from wetlands is the most significant natural source of CH_4 in the atmosphere. Anthropogenic sources of CH_4 include fossil fuel burning, waste, rice cultivation, biomass burning, and domesticated ruminants. Figure 1.4 shows the atmospheric concentration of CH_4 measured at Mauna Loa. These are the monthly averages of the concentration of CH_4 from in-situ measurements (given by the blue and orange dots). The smoothed gray line indicates the trend in CH_4 with the seasonal cycle taken out. Reaction of CH_4 with OH in the atmosphere is the major sink of CH_4 and is the cause of the seasonal cycle of CH_4 seen in Figure 1.4.



Figure 1.4: In-situ measurements of atmospheric CH_4 made at Mauna Loa from 1990 to 2016. The blue (calibrated data) and orange (uncalibrated data) dots are monthly CH_4 measurements, the grey curve that connects the dots shows seasonality of CH_4 and the other grey curve is when the seasonal trend is removed. This figure was generated and taken from: http://www.esrl.noaa.gov/

In-situ measurements of CO_2 and CH_4 are extremely accurate and precise (~0.2 ppm and ~1 ppb respectively) but are sparse in certain regions. The current in-situ networks that measure CO_2 and CH_4 are good enough for constraining global emission rates (with knowledge of loss

rates) and the global annual radiative forcing. However, they are not good enough for accurately determining regional-scale emissions and how they change over time (Hartmann et al., 2014).

1.4 Remote Sensing of Greenhouse Gases

Satellite measurements of GHGs can provide observations for regions where there are no in-situ measurements. However, nadir-viewing satellite instruments measure the amount of CO_2 in a column of air, while in-situ instruments measure CO_2 at the surface. Column measurements of CO_2 are sensitive to air in the free troposphere and provide information on regional-scale fluxes while in-situ measurements give information on local sources and sinks (Olsen and Randerson, 2004). Rayner and O'Brien (2001) showed that monthly mean satellite measurements of CO_2 , with an observation foot-print of $8^{\circ}x10^{\circ}$, need a precision better than 2.5 ppm to improve our understanding of the carbon cycle. Miller et al. (2007) found that monthly averaged satellite measurements of XCO_2 that have a precision of 1-2 ppm should be able to detect a 1GtC/yr carbon sink.

The Greenhouse gases Observing SATellite (GOSAT) (Yokota et al., 2009) was launched in January of 2009 and makes observations of total columns of CO₂ and CH₄. In February 2009, the Orbiting Carbon Observatory (OCO) satellite was launched, but the payload did not detach from the rocket and so fell into the ocean. As a consequence, OCO-2 (the replacement for OCO) was launched into Earth orbit in the summer of 2014, and is now making measurements of CO₂ columns. Given the strict accuracy and precision requirements of CO₂ columns from space, the data need to be reliable. There is always the possibility that satellite instruments could be partly damaged on launch, as well as degrade over time. Use of both CO₂ column and in-situ measurements to determine fluxes requires that the CO₂ column measurements be accurately tied to the reference scale of the in-situ measurements. Therefore, validation of these measurements over the lifetime of these missions is essential when assessing their reliability. To validate satellite measurements of GHGs, a network of ground-based remotesensing instruments that measure total columns and are linked to the World Meteorological Organization (WMO) reference scale for in-situ measurements was established.

The Total Carbon Column Network (TCCON) is network of ground-based Fourier Transform Spectrometers (FTSs) that records solar absorption spectra. From these highresolution spectra, precise and accurate total columns of CO₂, CH₄, N₂O, CO, HF, H₂O, and HDO are retrieved. The main goal of TCCON is to be the primary validation data set for satellite measurements of GHGs as well as to understand how GHGs exchange between the atmosphere, biosphere, and ocean. In order to accomplish this, TCCON measurements need to be more precise and accurate then satellite measurements. To improve the precision and accuracy of remote sensing measurements of GHGs, TCCON is constantly improving on measurement techniques and analysis procedures. There are many TCCON sites around the world, as shown in Figure 1.5, with the first TCCON site in Canada located in the high Arctic on Ellesmere Island in Nunavut. The FTS is housed at the Polar Environment Atmospheric Research Laboratory (PEARL), located approximately 15 km away from the Eureka weather station. PEARL is home to many instruments that measure different aspects of the atmosphere. It is run by the Canadian Network for the Detection of Atmospheric Change (CANDAC), which provides on-site support for the operation of the FTS and all other instruments at PEARL.





Understanding how the carbon cycle in the Arctic is changing is important when trying to predict climate change. Satellite measurements from GOSAT and OCO-2 can help with this, but measurements made from sunlight reflected off snow- and ice- covered surfaces are currently

problematic due to the low surface albedo of snow/ice. Boesch et al. (2011) found that the theoretical retrieval errors over a surface of snow/ice were 1 ppm for hypothetical OCO measurements made at low solar zenith angles (SZAs) and increased to 6 ppm as SZA increased. For this reason, most Arctic measurements of CO_2 available from OCO-2 and GOSAT are from the summer months. So there is little information about the Arctic carbon cycle in the spring and fall from satellite measurements of CO_2 and CH_4 .

TCCON CO₂ measurements don't have this problem since TCCON instruments view the sun directly. However, TCCON GHGs retrieved from solar absorption spectra exhibit an artificial airmass dependence that, if left uncorrected, would be aliased into the seasonal cycle of CO₂ and other GHGs, leading to incorrect conclusions about the seasonal cycle of these gases. An empirical correction is applied to TCCON data to take this airmass dependence into account (as described in Section 4.2.1 and Wunch et al. (2011)) but the correction is only applicable to measurements made at SZA < 82°. As shown in Figure 1.6, at 80°N there are approximately three months in a year when the sun does not get above the horizon (polar night shown in Figure 1.6), and another two months when the smallest SZA is larger than 82° (area between the red lines in Figure 1.6). This SZA restriction limits the measurements available from high-latitude sites (such as Eureka) to the period from late March to early September.



Figure 1.6: Minimum and maximum SZA plotted as a function of day of year in 2012 at Eureka. The upper curve is the maximum SZA of the day and the lower curve is the minimum SZA. The horizontal black line is SZA = 90° and the red horizontal line is SZA = 82°. Yellow vertical lines are the start and end of polar day. In between the red vertical lines are days when all measurements are flagged due to SZA > 82°. Polar night is when sun is below the horizon.

Studies by Hartmann et al. (2009) (for CO₂) and Frankenberg et al. (2008) (for CH₄) have shown that the choice of spectral line shapes and spectroscopic parameters used to calculate absorption coefficients in the forward model of the retrieval code impacts the retrieved total columns of gases, with the biggest impact at high latitudes (as shown in Frankenberg et al. 2008 for CH₄) due to the longer path length of sunlight through the atmosphere. This airmass dependence not only effects ground-based measurements but also satellite measurements.

The scientific goal of this thesis is thus to investigate how the choice of spectral line shape and spectroscopic parameters impact:

- 1. The airmass dependence of retrieved columns of CO₂, CH₄, and O₂,
- 2. The spectral fits of these gases,
- 3. The bias in the total column created by the choice of absorption coefficients used in the retrieval.

The work done in this thesis provides a physics-based solution for the airmass-dependent artifact, which improves the retrieval of total columns of GHGs from solar absorption spectra by both ground-based and space-based remote sensing instruments.

1.5 Outline and Contribution to Thesis

The rest of this thesis is structured as follows. In Chapter 2, details about the FTS used to record solar absorption measurements at PEARL will be discussed, along with the theory behind how it works. Solar absorption spectra were recorded by the candidate on site during the Canadian Arctic ACE/OSIRIS Validation Campaigns of 2011, 2012, 2013, 2014, and the CANDAC summer campaign of 2012. When the candidate was not on site, solar absorption spectra were recorded by CANDAC operators, while the candidate helped with remote trouble-shooting of the instrument. In 2014, the candidate worked with Ph.D. students Jonathan Franklin (Dalhousie University) and Dan Weaver (University of Toronto) to establish and refine remote access to the new suntracker installed at PEARL by Jim Drummond (CANDAC PI), Pierre Fogal (PEARL Site Manager), and Anthony Pugliese (University of Toronto). At the same time, the candidate worked with Dan Weaver, Pierre Fogal, and Yan Tsehtik (CANDAC Data Manager) to establish remote access to the FTS at PEARL. From February to September 2014, the candidate recorded solar absorption spectra from Toronto using remote access to the instrument and sun tracker.

Chapter 3 gives details on the spectral fitting software used to retrieve total columns of GHGs from the solar absorption spectra. The spectral fitting software was used to retrieve total columns of GHGs from solar absorption spectra recorded at Eureka. This chapter also discusses how the data were filtered and corrected. The candidate used the spectral fitting software GGG to retrieve total columns of GHGs from 2010-2015. Debra Wunch (Caltech) and Geoff Toon (National Aeronautics and Space Administration (NASA) Jet Propulsion Laboratory (JPL)) provided feedback to the candidate on questions about the spectral fitting software. Jonathan Franklin provided the candidate with the correct SZA values for measurements made with the new suntracker in order to correct the data for the suntracker not being properly coupled to the instrument from 2014 to 2015.

Chapter 4 is a review of how absorption coefficients are calculated. In this chapter, the theory and formulas used for different spectral line shapes are provided.

Chapter 5 details the implementation and testing of a new spectral line shape for CO_2 in the forward model of the spectral fitting software and investigates the impact it has on the retrieved columns of CO_2 . The candidate implemented the speed-dependent Voigt line shape with first-order line mixing in the forward model of the spectral fitting software and fitted laboratory and solar spectra. Laboratory spectra of CO_2 in the spectral bands of interest were recorded by Keeyoon Sung (NASA JPL) and provided to the candidate. Geoff Toon helped the candidate with the fitting of the laboratory spectra. The candidate fitted a year of solar absorption spectra from Darwin, Park Falls, and Lamont using different spectral line shapes. Processing of the solar spectra was done on the Caltech server with access provided by Paul Wennberg (Caltech) and Debra Wunch, who also helped with input on the processing of these spectra. The work in Chapter 5 has been published in Mendonca et al. (2016).

Chapter 6 details the implementation and validation of absorption coefficients for CH₄ in the forward model of the spectral fitting software and the impact these new absorption coefficients have on the retrieved columns of CH₄. For this work, the candidate implemented a full (or strong line mixing) scheme into the forward model of the spectral fitting software to calculate absorption coefficients using spectroscopic parameters from Devi et al. (2015; 2016). Laboratory spectra were fitted by the candidate to test absorption coefficient calculations. The laboratory spectra were recorded at NASA JPL and provided to the candidate by Keeyoon Sung and Malathy Devi (The College of William and Mary), who both also provided guidance when fitting the laboratory spectra. As previously done with CO₂, the candidate retrieved total columns of CH₄ from solar absorption spectra using the new absorption coefficients. This work has been accepted for publication in the Journal of Quantitative Spectroscopy and Radiative Transfer (JQSRT).

In Chapter 7, spectral line shapes for O_2 (in the band of interest) were investigated by fitting high-resolution laboratory cavity ring-down absorption spectra. These spectra were recorded by David Long (National Institute of Standards and Technology (NIST)) and provided to the candidate with help from Paul Wennberg. The candidate created the software code (in Matlab) to fit the laboratory spectra and retrieve the necessary spectroscopic parameters with the different spectral line shapes. Total columns of O_2 from Darwin, Park Falls, and Lamont were retrieved by the candidate using the new absorption coefficients. Using the work done in Chapter 6 for CO_2 , the airmass dependence for the column-averaged dry-air mole fraction (X) of CO_2 using the new CO_2 and O_2 columns was calculated and the impact of the new absorption coefficients on the airmass dependence and accuracy of XCO_2 was investigated. Derbra Wunch provided the candidate the Matlab analysis code developed to compare TCCON measurements with aircraft measurements. A manuscript on this work will shortly be submitted to Atmospheric Measurement Techniques (AMT).

Finally, Chapter 8 summarizes the main conclusions of this thesis and provides suggestions for future work.

2 Instrumentation

2.1 The PEARL Bruker IFS 125HR

The Fourier Transform Spectrometer (FTS) used by all TCCON sites is the Bruker IFS 125HR. It is a commercially available instrument, which is currently the most stable highresolution FTS and meets the TCCON precision requirements (Wunch et al., 2011). In 2006, the Bruker IFS 125HR (which will henceforth be referred to as the PEARL 125HR), was installed at PEARL to replace Environment Canada's Bomem DA8 FTS (Batchelor et al., 2009). From August 2006 onwards, the PEARL 125HR has recorded solar absorption spectra in the midinfrared (MIR) as part of the Network for the Detection of Atmospheric Composition Change (NDACC). In spring of 2010, the PEARL 125HR began recording solar absorption spectra in the near-infrared (NIR) spectral region after the installation of an InGaAs detector (by Rebeca Batchelor) and joined TCCON in the summer of 2010. Since then, by alternating beamsplitters, both MIR and NIR solar absorption spectra have been recorded by the PEARL 125HR.

At the heart of the PEARL 125 HR is a scanning Michelson interferometer, which splits the beam into two equal portions using a beamsplitter, with half of the beam transmitted to a moving mirror and the other half reflected to a stationary mirror. Figure 2.1 is a schematic of the PEARL 125HR setup at Eureka, with each compartment of the instrument numbered. The beamsplitter is permanently aligned in the interferometer compartment (1) and is housed in an enclosure with a locking mount that can be accessed to swap the beamsplitter depending on the type of measurement. Solar absorption spectra are recorded with one of two beamsplitters: the potassium bromide (KBr) for measurements made between 450 to 4800 cm⁻¹ and the calcium fluoride (CaF₂) for measurements made between 1200 to 15000 cm⁻¹. Once the radiation is split in two by the beamsplitter, half of the radiation is directed towards a fixed mirror located in the interferometer compartment (1) while the other half is directed towards the scanning mirror located in the scanning mirror and motor compartment (2).



Figure 2.1: Schematic of PEARL 125HR. The different compartments are given different numbers to distinguish them. The numbers refer to: 1) interferometer, 2) scanning mirror and motor, 3) source, 4) HCl sample, 5) HBr sample, and 6) detector. Figure adapted from Bruker IFS 125HR manual.

The radiation from the fixed and scanning mirrors is reflected back towards the beamsplitter where the two beams recombine. Since there is an Optical Path Difference (OPD) between the two mirrors, the beams are now out of phase and will combine with either constructive or destructive interference, creating an interferogram. When the OPD between the fixed and scanning mirror is zero this is known as Zero Path Difference (ZPD). After the two beams are combined at the beamsplitter, they are directed towards the detectors located in the detector compartment (6) after passing through one of the sample compartments, (4) or (5). MIR interferograms are recorded on one of two liquid-nitrogen-cooled detectors: the mercury-cadmium-telluride (MCT) detector which is sensitive to radiation from approximately 600 to 6000 cm⁻¹ and photovoltaic indium antimonide (InSb) detector which is sensitive to radiation from approximately 1850 to 10000 cm⁻¹. NIR interferograms are recorded on a room temperature InGaAs detector that is sensitive to radiation from approximately 4000 to 11000 cm⁻¹. A helium

neon laser is used to sample the interferogram at regular intervals as OPD increases in order to reconstruct the interferogram.

For a source of radiation that contains multiple wavelengths, the intensity (I) of the recombined beam with a OPD of x is expressed as (Davis et al., 2001a; Griffiths and de Haseth, 2007):

$$I(x) = \int_0^\infty B(v) \cos(2\pi v x) \, dv \tag{2.1}$$

where *B* is the spectral intensity at wavenumber *v*, where wavenumber is the inverse of wavelength and given in units of cm⁻¹. Since Eq. 2.1 represents a superposition of waves that have been added together to construct the interferogram applying a Fourier transform to Eq. 2.1 results in the spectrum *B* (Davis et al., 2001a; Griffiths and de Haseth, 2007):

$$B(v) = \int_0^\infty I(x) \cos(2\pi v x) \, dx. \tag{2.2}$$

The spectrum described by Eq. 2.2 assumes ideal conditions that cannot be achieved in practice. For instance, it assumes that the OPD is infinite, allowing the integration over all x from 0 to ∞ . A practical spectrometer has a finite maximum OPD distance. This can be represented by a *BOXCAR* truncation function which is 1 between 0 and the maximum OPD and 0 every where else:

$$BOXCAR(x)=1, \quad 0 \ge x \le L$$

BOXCAR(x)=0, $x < 0, x > L$ (2.3)

where *L* is the maximum OPD. So the ideal interferogram, given by Eq. 2.1, is multiplied by the boxcar function Eq. 2.3 to get the interferogram. The Fourier transform of the boxcar function from *x* space to *v* space is (Davis et al., 2001a; Griffiths and de Haseth, 2007):

$$SINC(v,L) = 2L \frac{\sin(2\pi vL)}{2\pi vL}.$$
(2.4)

Figure 2.2 is a plot of the SINC function. By the convolution theorem, the Fourier transform of the interferogram will be the spectrum that is the convolution of Eq. 2.2 with Eq. 2.4 and so each
spectral line is now broadened by the instrument. The distance between the zero points (or width) of the central maxima of the SINC function is 1/L and gives the spectral resolution.





$$FOV = \frac{D}{2z},\tag{2.5}$$

where *D* is the diameter of the field stop placed at the focus of the collimating mirror, and z is the focal length of the collimator. An ideal FTS assumes that the source of radiation is a point source, but the sun is an extended source of radiation that will fill the entire aperture. This leads to light entering into the FTS that will diverge from the parallel by an angle α which is related to the distance from the optical axis *d* and the focal length of the collimator by the equation (Davis et al., 2001b):

$$\alpha = \frac{d}{z}.$$
 (2.6)

The effective OPD (x_{eff}) for an off-axis ray of light will be given by (Davis et al., 2001b):

$$x_{eff} = x\cos(\alpha) . \tag{2.7}$$

For very small α , $cos(\alpha)$ can be approximated by $1 - \frac{\alpha^2}{2}$ and substituting this into Eq. 2.7 gives:

$$x_{eff} = x \left(1 - \frac{\alpha^2}{2} \right). \tag{2.8}$$

Substituting x_{eff} in the cosine term of Eq. 2.1 leads to:

$$\cos(2\pi\nu x_{eff}) = \cos(2\pi\nu x \left(1 - \frac{\alpha^2}{2}\right)).$$
(2.9)

This shows us that an off-axis ray at a given v will behave like an on-axis ray given by $v\left(1-\frac{\alpha^2}{2}\right)$. Essentially off-axis rays will be shifted to lower v. If the spectrometer is viewing a monochromatic source, one would expect the resulting interferogram to be a sine wave but this would only be true if the source was a point source. In the case of an extended monochromatic source, a range of v that spans from v to $v\left(1-\frac{1}{2}\left(\frac{D}{2z}\right)^2\right)$ will be measured by the spectrometer. The *RECT* function in v space that models this range is shown in Figure 2.3 and has a width of $\frac{1}{2}vFOV^2$.



Figure 2.3: The *RECT* function with $v_0 = 7850 \text{ cm}^{-1}$ and FOV = 1.2 mrad.

The instrument line shape is given by the convolution of the *RECT* and *SINC* functions:

$$ILS(v, FOV, L) = SINC(v, L) * RECT(v, FOV)$$
(2.10)

where * means convolution. The measured spectrum is the convolution of the real spectrum with the *ILS*. NIR inteferograms measured by the PEARL 125HR are processed with the i2s software that comes with GGG 2014 (Wunch et al., 2015). The interferograms are corrected for solar intensity variations (Keppel-Aleks et al., 2007), phase error (Mertz, 1967), and fast Fourier transformed into spectra (Bergland, 1969).

2.2 Measuring the Instrument Line Shape

When all the optics in the FTS are aligned properly, the ILS is represented by Eq. 2.10. To test the alignment of the FTS, an HCl gas cell, with known pressure and concentration amount (Hase et al., 2013) is placed in compartment (4) of Figure 2.1. A tungsten lamp located in the source compartment (3) is used as the source of radiation and 50 spectra are co-added to produce a spectrum of the HCl absorption. Since the conditions that the spectrum is measured

under are well known, the spectrum convolved with the ILS can be calculated and compared to the measured spectrum. The LINEFIT (version 12) program developed by Hase et al. (1999) compares the measured spectrum to the calculated spectrum and retrieves the modulation efficiency and phase error by minimizing the difference between the measured and calculated spectra. The modulation efficiency refers to the amount of radiation reaching the detector. Ideally, all radiation that is incident on the input aperture reaches the detector at all OPDs but in reality, some loss of radiation will occur as the scanning-arm mirror moves. TCCON requires that the modulation efficiency vary by less than $\pm 5\%$ between 0 and 45 cm OPD. Phase errors arise from phase changes that are induced by the optical components, leading to an asymmetry in the spectral line if the phase changes are constant for every v.

From 2010 onwards, HCl spectra were periodically measured by the PEARL 125HR in order to monitor the alignment of the spectrometer. Figure 2.3 shows the results of four ILS tests performed during the Canadian Arctic ACE/OSIRIS Validation Campaigns from 2012-2014. The four plots in Figure 2.4 show: a) the modulation efficiency plotted as a function of OPD, b) the phase error as a function of OPD, c) the retrieved column of HCl, and d) the retrieved temperature. Figure 2.4 shows the results of the analysis done by LINEFIT12 for spectra recorded on: (1) February 23, 2012, (2) February 26, 2013 (3) March 2, 2014, and (4) March 2, 2014. Spectra 1-3 were recorded using the Eureka Neoplas (NP) cell (cell #32), and show an over modulation (as seen in Figure 2.4a), which indicates a shear misalignment (Wunch et al., 2015). LINEFIT assumes a perfect modulation efficiency at ZPD. A shear misalignment is the result of the lateral displacement of the moving mirror with respect to the fixed mirror at ZPD which reduces the modulation at ZPD (Hase, 2012). The shear misalignment manifests as an over modulation (modulation efficiency greater than 1) as the OPD increases as seen in Figure 2.3a for spectra 1-3. However, the retrieved column of HCl decreases every year for the spectra recorded from the Eureka NP cell, indicating that the cell might be leaking.

In an effort to improve the monitoring of the ILS of all Bruker IFS125HR spectrometers in TCCON, all HCl cells in the network were sent to Frank Hase for calibration (Hase et al., 2013), where an effective pressure was assigned to each cell and the purity of the gas in the cell was also measured. The Eureka NP cell was confirmed to be leaking by Frank Hase, and cell #28 was sent to PEARL to replace it. Spectrum (4) was acquired with cell # 28 and the modulation efficiency was found to be 0.95 at max OPD with the retrieved column amount being close to the measured amount from Hase et al. (2013). Currently, the modulation efficiency is on the border of the acceptable value for TCCON, and the instrument will need to be realigned if the modulation efficiency drops below 0.95.



Figure 2.4: ILS test results obtained for the PEARL 125HR using HCl spectra. (a) The modulation efficiency plotted as a function of OPD. (b) The phase error. (c) The retrieved column amount of HCl in the cell from each microwindow used. (d) The retrieved and actual temperatures used in the fits. The figure shows the results from the tests done on: (1) February 23, 2012, (2) February 26, 2013, and (3) March 2, 2014 done with cell #32, (4) March 2, 2014 with the replacement cell #28.

2.3 Solar Tracker

Sunlight is directed into the PEARL 125HR using a custom-built solar tracker located on the roof of PEARL. From August 2006 to July 2013, the PEARL 125HR recorded solar absorption spectra using a four-quadrant-diode active-tracking system previously installed by Environment Canada for the use with the Bomem DA8 (Batchelor et al., 2009). Two gold-plated mirrors on the roof of PEARL directed a beam of sunlight into compartment (3) of the PEARL 125HR. To set up the tracker, an operator would have to remove the box and covers of the mirrors on the roof, then manually move the tracker mirrors to the sun until the beam fell on the input optics and on a small pick-off mirror that directed a part of the beam towards the diode detector. Throughout the day, the gain setting on the control box would have to be adjusted for the changing solar intensity and the orientation of the detector tube would have to be turned to adjust for the changing polarization of the light. The four-quadrant-diode active-tracking system required constant operator intervention and could only be used while an operator was on site.



Figure 2.5: The Community Solar Tracker (CST) housed in the Robodome on the roof of PEARL (photo taken by Anthony Pugliese) and schematic drawing of the CST from (Franklin, 2015).

In the summer of 2013, the Community Solar Tracker (CST) (Franklin, 2015) at Dalhousie University was installed at PEARL replacing the four-quadrant-diode active-tracking system. The tracker (seen in Figure 2.5) is placed inside a Robodome which is made of fiber glass with a base and a shutter that can be remotely controlled. A python graphical user interface (GUI), developed by Jonathan Franklin, is used to control both the solar tracker and Robodome, which can be accessed through the PEARL network. The CST has two tracking modes: passive and active. Active tracking is done by using a network video camera which periodically takes pictures of the solar disk and then fits an ellipse to the image to determine a correction to the position of the tracking mirrors to maintain tracking the sun. In both passive and active tracking modes, the software will calculate the position of the sun in the sky for the geographical location of tracker at that time of day. This is done so that if there is a loss of signal (e.g., from a cloud) tracking will still continue. With the python GUI, the iris of the camera is automatically adjusted for the camera to remain unsaturated. Control and operation of the CST can be done from any location with the python GUI and access to the PEARL network.

3 Retrieval of Greenhouse Gases at Eureka3.1 GFIT

GFIT is a nonlinear least-squares spectral fitting algorithm that minimizes the difference between a calculated spectrum and the spectrum measured by the FTS. It calculates an atmospheric transmittance spectrum for a given set of atmospheric conditions, then uses an inverse method to compare the calculated spectrum to the measured spectrum and decides how to best adjust a set of parameters in order to decrease the difference between the measured and calculated spectra (Wunch et al., 2011). This is described by the following equation:

$$\chi = \sum_{i}^{n} (y_i - F_i(\vec{\mathbf{x}}))^2 \tag{3.1}$$

where χ is the sum of the squares for the difference between the measured spectrum y and the calculated spectrum $F(\vec{x})$. The difference is calculated at each spectral grid point i for a total of n spectral grid points. \vec{x} is the state vector of parameters retrieved during the inverse process:

$$\vec{\mathbf{x}} = [cl, ct, cc, fs, VSF_k] \tag{3.2}$$

where *cl* is the continuum level, *ct* is the continuum tilt, *cc* is the continuum curvature, *fs* is the frequency shift, and VSF_k is the Volume Scale Factor (VSF) for the k^{th} gas of interest in the spectral window. The *cl*, *ct*, and *cc* parameters will be discussed in Section 3.1.1, VSF_k will be discussed in Section 3.1.2, and *fs* has already been described in Section 2.1.

3.1.1 Forward Model

The atmospheric transmission spectrum at a given v is calculated by the forward model in GFIT as described by:

$$S(v) = cont(v)[ILS * T(v)]$$
(3.3)

where S is the transmittance at v, *cont* is the continuum, and T(v) is the transmittance from the calculated spectrum before the convolution with the ILS (as defined by Eq. 2.10). *cont*(v) is

used to model the solar Planck function and the instrument response due to the optical setup (Wunch et al., 2011). Ideally a spectrum measured outside of the Earth's atmosphere with the FTS, would be used to ratio out the features created by the instrument response and the solar Planck function, but that is not possible so we model these features using cont(v). When calculating the continuum in GFIT, it is assumed that instrument response is a smooth function over the width of the spectral window, and the solar Planck function varies slowly over the width of the spectral window, and the solar Planck function varies slowly over the width of the spectral window, and the solar Planck function varies slowly over the width of the window. The continuum is calculated using a set of orthogonal polynomials, which in GFIT are the Legendre polynomials given by:

$$P_m(x) = \frac{1}{2^m} \sum_{j=0}^m {\binom{m}{j}}^2 (x-1)^{m-j} (x+1)^j$$
(3.4)

where x is the grid point number and m is the polynomial number. The continuum can then be calculated using:

$$cont = cl \left[P_0(x) + ct(P_1(x)) + \sum_{i=2}^m cc_m(P_m(x)) \right].$$
(3.5)

For the standard TCCON retrievals in GGG2014, only cl and ct are retrieved. The option to retrieve more coefficients (cc_m) is possible, but only used when the optical setup is different from the standard TCCON setup (Kiel et al., 2016).

The transmission spectra are calculated taking into account multiple gases in the spectral window of interest:

$$T(v) = \exp\left[-\sum_{G}^{N_{gas}} sN_{G}k_{G}(v)\right]$$
(3.6)

where N_{gas} is the total number of gases in the spectral window, N_G is the number density of gas G, and $k_G(v)$ is the absorption cross-section of gas G. L is the path length through the atmosphere, which is computed by a ray-tracing algorithm. This algorithm calculates the photon slant path from the top of the atmosphere to the location of the instrument for the SZA at the time of the measurement. The spectroscopic parameters used to calculate absorption cross

sections for a gas in Earth's atmosphere are from the atm line list (Toon, 2014a). Absorption cross sections are calculated each day based on the pressure (P), temperature (T) and a priori volume mixing ratio (VMR) profiles that are generated for local noon.

T, P, and H_2O a priori profiles are generated from the National Centers for Environmental Prediction (NCEP) data (Kalnay et al., 1996). A priori profiles for CH₄, N₂O, CO and HF are created using an empirical function which is based on measurements from JPL MkIV FTS balloon flights (Toon, 1991), and the Atmospheric Chemistry Experiment (ACE) FTS instrument aboard SCISAT (Bernath et al., 2005). For CO₂, an empirical model based on fits to in-situ GLOBALVIEW data is used (Wunch et al., 2011). The empirical functions adjust an a priori profile (for the gas of interest) generated at a latitude of 35° N to work at other latitudes. This a priori profile is based on ACE and MkIV measurements made from 2003 to 2007. The adjustment is done by taking into account the secular increase, seasonal cycle, and interhemispheric gradient of the gas. The a priori profile is adjusted using the time difference between the reference a priori profile (2007) and the date of the observation using the secular trend of the gas of interest. The secular trend is also adjusted by altitude, taking the age of air into account. Similarly, the seasonal cycle of the gas of interest is calculated, taking the latitude and altitude dependence into account. When applying the latitude gradient, it is assumed that the gas distribution is anti-symmetric about the equator at the surface. Figure 3.1a shows the antisymmetric function used to represent the gradient value taking into account the latitude of the site. It is also assumed that the gas distribution is symmetrical in the middle stratosphere about the equator. This requires that the gradient be adjusted with altitude as well as taking into account the tropopause height. Figure 3.1b shows the values used to scale the gradient plotted as a function of altitude, for a tropopause altitude of 20 km and 9 km. The calculations are performed for 71 atmospheric layers (0 to 70 km), so all a priori profiles are generated on a vertical grid of 1 km.



Figure 3.1: a) The anti-symmetric function used to represent the latitudinal gradient of the gas of interest at the surface. b) The function used to represent the gradient with altitude while taking into account different tropopause heights. Shown for tropopause heights of 9 and 20 km.

3.1.2 Retrieval

The Jacobian matrix (J) is computed in parallel with the computation of each measured spectrum. To create J, the derivative of the spectrum (Eq. 3.3) is taken with respect to each parameter in the state vector (given in Eq. 3.2). Computing J analytically has two advantages over the finite difference method: (1) it is faster since it reduces the number of redundant calculations (Benner et al., 1995), and (2) it is more accurate than the finite difference method (Wunch et al., 2011). To solve for the optimal values of \vec{x} , an iterative scheme is employed that decreases the difference between the calculated and measured spectrum (Wunch et al., 2011):

$$(\boldsymbol{J}^T \boldsymbol{S}_{\in}^{-1} \boldsymbol{J} + \boldsymbol{S}_a^{-1}) \Delta \boldsymbol{\vec{x}} = \boldsymbol{J}^T \boldsymbol{S}_{\in}^{-1} \boldsymbol{\vec{r}} + \boldsymbol{S}_a^{-1} (\boldsymbol{\vec{x}} - \boldsymbol{\vec{x}}_a)$$
(3.7)

where \vec{x}_a is the a priori state vector, \vec{x} is the value of the state vector on the current iteration, $\Delta \vec{x}$ is the difference that should be added to \vec{x} in the next iteration to decrease the difference between the measured and calculated spectrum given by \vec{r} . S_a is the a priori covariance matrix, which

contains the estimated a priori errors and S_{\in} is the measurement error covariance matrix which is a diagonal matrix consisting of the spectral noise that is assumed to be same for the entire spectrum. GFIT does not do a profile retrieval, since it assumes that the shape of the gas profiles is well known. It scales the a priori profiles using the retrieved VSF. To calculate the column (molecules/cm²) for a given gas (*G*), it uses the following formula (Wunch et al., 2011):

$$column_G = VSF_G \int_{z_s}^{\infty} f_G^{a \ priori}(z) \ ndz$$
(3.8)

where z is the altitude, z_s is the surface altitude, n is the total number density, and $f_G^{a \ priori}(z)$ is the a priori mole fraction of G.

3.2 Column-Averaged Dry-Air Mole Fraction

The column-averaged dry-air mole fraction (X_G) for a gas *G* is calculated by (Wunch et al., 2011):

$$X_G = 0.2095 \frac{column_G}{column_{O_2}} \tag{3.9}$$

where $column_{O_2}$ is the retrieved column of O₂, and 0.2095 is the value of the dry-air mole fraction of O₂ in Earth's atmosphere. The column of O₂ is used instead of surface pressure because errors that are common to *G* and O₂, such as incorrect modeling of the *ILS* and tracker mis-pointing are diminished when using Eq. 3.9 to calculate *X_G*. This happens because all gases are retrieved from the same spectrum, so certain errors will be common to all gases. The disadvantage to this approach is that errors that effect only O₂ will impact all *X_G*.

3.2.1 Airmass Dependence Correction

The retrieved column of O_2 exhibits an airmass dependence whereby the retrieved amount increases as a function of SZA. Other molecules such as CO_2 and CH_4 also exhibit an airmass dependence as a function of SZA, which is thought to be partly due to the absorption coefficients used by the forward model (Chapters 4-7 will go into greater detail on this topic). If this airmass dependence is left uncorrected, it will be aliased into the seasonal cycle of X_G which will lead to differences between TCCON sites that are not physical in nature. This is because the mean SZA at a given site varies through out the year and day. TCCON uses an empirical correction to correct the X_G for this SZA-dependent artifact. The empirical model assumes that the true variation of X_G throughout the day can be modeled using an antisymmetrical function, while a symmetrical function is used to model the artificial variation caused by the airmass dependence of the retrieved column of the gas of interest and O₂. We can, therefore, represent a measurement as (Wunch et al., 2011):

$$y_i = \hat{y}[1 + \beta A(t_i) + \alpha S(\theta_i)]$$
(3.10)

where \hat{y} is the mean value of X_G measured that day, β is the fitted coefficient of the antisymmetric function $A(t_i)$ and α is the fitted coefficient of the symmetric function $S(\theta_i)$. The antisymmetric function is calculated by (Wunch et al., 2011):

$$A(t_i) = \sin(2\pi(t_i - t_{noon}))$$
(3.11)

where t_i is the time of the measurement and t_{noon} is the time at solar noon, both in units of days. The antisymmetric function is calculated by (Wunch et al., 2011):

$$S(\theta_i) = \left(\frac{\theta_i + 13}{90 + 13}\right)^3 - \left(\frac{\theta_i + 13}{90 + 13}\right)^3$$
(3.12)

where θ_i is the SZA in degrees. The empirical correction was orginally developed for XCO₂ but is applied to all X_G . One α value is applied at all TCCON sites, regardless of year, and is the daily averaged value derived from one year of measurements made at Darwin, and the entire measurement set at Park Falls and Lamont (Wunch, et al., 2015; Wunch et al., 2011). There is a separate α derived for XCO₂, XCH₄, XN₂O, and XCO. The correction for X_G is calculated by:

$$X_G^{corrected} = \frac{X_G}{[1 + \alpha_G S(\theta_i)]}$$
(3.13)

where $X_G^{corrected}$ is the corrected value of X_G , and α_G is the coefficient of G used to correct for the symmetric component of the air mass dependence given by $S(\theta_i)$.

3.3 TCCON X_G Measurements at Eureka

NIR solar spectra have been recorded by the PEARL 125HR from 2010-2015. Spectra are recorded at PEARL from late February to mid-October, when the sun is above the horizon. Each year, measurements begin during the springtime Canadian Arctic ACE/OSIRIS Validation Campaign and end in October. Since 2010, all spectra have been processed using the GGG spectral fitting software (versions 2009, 2012, and 2014 (Wunch et al., 2015)). As part of the analysis, data are flagged as bad for a set of conditions found in the quality control data file. Table 3.1 is a list of all the variables and their minimum and maximum allowed values for Eureka. Some of the quality control flag settings are the same for all sites, for instance measurements recorded at a SZA of 82° or higher are flagged because the empirical airmass correction as described in Section 3.2.1 does not work for these measurements when using GGG 2014 (Wunch et al., 2015). This is because the shape of the symmetric function (Eq. 3.12) changes at a SZA of approximately 82°, causing XCO₂ to increase as a function of SZA. Applying the correction to measurements taken at SZA > 82° makes these values higher than they should be as shown in Figure 6 of Wunch et al. (2011).

Most of the quality flags have been set by TCCON, but for some it is possible to change these settings to take into account the measurement conditions at a particular site. Variables such as year, lat, lon, tins, tout and zobs had to be changed to take into account the measurements at Eureka. Some Eureka spectra are recorded under polar vortex conditions, which makes the a priori profiles used by the retrieval software incorrect, since the empirical functions used to generate them do not take into account stratospheric subsidence induced by the polar vortex. HF can be used as a dynamical tracer to identify polar vortex conditions. As suggested by Geoff Toon, if the retrieved XHF is greater than 150 ppt, the measurement is flagged as bad. The maximum for XCO₂ was changed from 400 to 425 ppm since measurements in the spring of 2013 were around 400 ppm. The minimum for X_{Air} was changed from 0.96 to 0.98 since that this value is around 0.99 at Eureka and deviations of more than ±0.01 showed large residuals in the spectral fits. **Table 3.1:** Quality flag variables, with the minimum and maximum allowed values, and description of each variable. Table is modified from <u>https://tccon-</u>

wiki.caltech.edu/Software/GGG/Download/GGG_2012_Release_Notes#Setting_up_the_qc.dat_ file for Eureka. * Indicates max or min variables have been modified to fit site specific characteristics.

Variable	Min	Max	Description of Variable
	Value	Value	
year	2008.0	2016.5	Year*
day	0	367	Day of the year (1-366)
hour	-12.0	36.0	Fractional UT Hour
run	0	999999	Not output
lat	79.0	81.0	Latitude (deg.)*
long	-87	-85	Longitude (deg.)*
zobs	0.60	0.62	Geometric Altitude (km)*
zmin	0.0	0.9	Pressure Altitude (km)
asza	0.0	82.0	Solar Zenith Angle (deg)
azim	-180	360	Solar Azimuth Angle (deg)
osds	-9	9	Observer-Sun Doppler Stretch (ppm)
opd	40.0	50.0	Optical path Difference (cm)
fovi	0.0	0.005	Internal Field Of View (rad)
graw	0.0	0.016	Spectral Point Spacing (cm ⁻¹)
tins	10.0	35.0	Internal Temperature (C)*
pins	0.0	1030.0	Internal Pressure (hPa)
tout	-60.	40.	External Temperature (C)*
pout	940.	1030.	External Pressure (hPa)
hout	0	110.	External Humidity (%)
sia	0.0	9999.	Solar Intensity (Average)
fvsi	0.0	5.	Fractional Variation in Solar Intensity
wspd	0.0	30.0	Wind Speed (m/s)
wdir	-180	360.0	Wind Direction (deg.)
Xair	0.98	1.005	0.2095*column_air/column_O ₂ *
Xair (error)	0.0	0.05	one-sigma precision
XHF	-1	150	0.2095 *column_HF/column_O ₂ *
XHF (error)	0	500	one-sigma precision
XH₂O	-1	15000	0.2095 *column_H ₂ O/column_O ₂
XH₂O (error)	0	5000	one-sigma precision
XHDO	-1	15000	0.2095 *column_HDO/column_O ₂
XHDO (error)	0	5000	one-sigma precision
ХСО	1.	500.	0.2095 *column_CO/column_O ₂
XCO (error)	0	20.	one-sigma precision
XN₂O	100	400	$0.2095*column_N_2O/column_O_2$
XN₂O (error)	0	50	one-sigma precision
XCH ₄	0	2	0.2095*column_CH ₄ /column_O ₂

XCH₄ (error)	0	0.1	one-sigma precision
XCO ₂	350	425	0.2095*column_CO ₂ /column_O ₂ *
XCO ₂ (error)	0	1	one-sigma precision
XO ₂	0.20	0.22	0.2095*(column_O ₂ /column_O ₂)=0.2095
XO₂ (error)	0	0.05	one-sigma precision
XHCL	0	5	0.2095*column_HCL/column_O ₂
XHCL (error)	0	50	one-sigma precision

From the recorded spectra, total columns of CO₂, CH₄, N₂O, CO, H₂O, HDO, and HF

were retrieved. Table 3.2 is a list of the spectral windows used to retrieve each of the trace gases.

Table 3.2: Standard TCCON spectral fitting windows. The first column lists the primary gas of interest in the fitting windows and the interfering species (given in brackets). The second column lists the center of the spectral fitting window and the width of the window (given in brackets).

Primary Gas and Interfering Species	Spectral Window Centre and Width (cm ⁻¹)
CO ₂ (H ₂ O, HDO, CH ₄)	6220(80), 6339(85)
CH4 (H2O, HDO, CH4, N2O)	5938(116), 6002(11), 6076(138)
N ₂ O (H ₂ O, HDO, CH ₄ , CO ₂)	4395(43), 4430(23),4719(73)
CO (H ₂ O, HDO, CH ₄)	4233(48), 4290(56)
HF (H ₂ O)	4038(0.3)
H ₂ O (HDO, CH ₄ , CO ₂ , N ₂ O)	Chapter 1 4565(2.5), 4571(2.5), 4576(1.9), 4611(2.2), 4622(2.3), 4699(4.0), 6076(3.9), 6099(0.9), 6125(1.4), 6177(0.8), 6255(3.6), 6301(7.9), 6392(3.1), 6401(1.1), 6469(3.5)
HDO (H ₂ O, CO, CH ₄)	4054(3.3), 4116(8.0), 4212(1.9), 4232(48), 6330(45), 6377(50)
O ₂ (H ₂ O, HF, CO ₂)	7885(240)

From 2010 until July 2013, spectra were recorded using the four-quadrant-diode active-tracking system until it was replaced by the CST system in July 2013. From February 2010 to October 2011, spectra were recorded by personnel on site. Due to funding issues, from February 2012 until October 2013 there were no fulltime CANDAC operators on site so measurements in this time period were done only during the Canadian Arctic ACE/OSIRIS Validation Campaigns of

2012 and 2013, as well as CANDAC summer campaigns in 2012 and 2013. From 2014 onwards, spectra were recorded both remotely from the University of Toronto and by CANDAC operators at PEARL. Remote access to the Bruker computer as well as the CST-enabled measurements for several hours a day. There was coordination between personnel at the University of Toronto and CANDAC operators at PEARL to maximize the number of spectra recorded. Figure 3.2 shows all individual X_G from July 2010 to September 2015 retrieved with GGG 2014 (Wunch et al., 2015).

3.4 Correcting X_G for Solar Tracker Pointing Error

In 2015, it was discovered that the solar beam from the CST was not properly aligned to the instrument. Using the sun as a source of radiation requires that the interferometer's FOV is pointed at the center of the solar disc. When fitting solar spectra, absorption features associated with the sun must be taken into account. GGG 2014 calculates the absorption from solar lines associated with the outer layer of the sun using the solar line list created by Toon (2014b). From the perspective of the Earth, the sun's rotation produces a Doppler shift in these features. GGG will calculate the expected Doppler shift for the features assuming that the solar beam is properly aligned with the instrument. If the FOV is not pointed at the center of the solar disc, it will create a Doppler shift of the solar lines with respect to the atmospheric absorption lines, which will impact the retrievals. Some retrieval algorithms will fit this Doppler shift but this option is not available in GGG 2014. However, GFIT will calculate a solar gas shift, which is the difference between where the solar lines are expected to be and where they are. The solar gas shift is manually added to the Doppler shift to correct it. Retrievals for the data from 2014 and 2015 were redone with the corrected Doppler shift to account for the incorrect alignment. Figure 3.3a shows XCO₂ retrieved with the originally calculated Doppler shifts (blue squares) and with the new Doppler shifts (red squares) for 2014 and 2015 respectively. Figure 3.3b shows the difference between the two retrieved XCO₂ datasets for 2014 and 2015. The biggest difference between them was 0.3 ppm as seen in Figure 3.3b. The 2014 and 2015 data shown in Figure 3.2 have been corrected for the tracker pointing error.



Figure 3.2: Time series of X_G measured at Eureka from June 2010 to September 2015. (a) to (g) show XCO₂, XCH₄, XN₂O, XCO, XH₂O, XHDO, and XHF respectively.



Figure 3.3: (a) XCO₂ retrieved with the original Doppler shift (blue squares) and the new Doppler shifts (red squares) for 2014 and 2015. The difference between the two retrievals is shown in (b).

A secondary effect of not seeing the center of the solar disc is that the calculation of the viewing SZA will be incorrect, which will affect the calculation of the photon path through the atmosphere and the airmass correction of the gas given by Eq. 3.13. However, this secondary effect is minor because calculating X_G using Eq. 3.9will cancel out tracker mis-pointing (Washenfelder et al., 2006; Wunch et al., 2011). When calculating X_{Air} , which is the ratio of the column of O_2 to the column of dry air divided by the 0.2095, one can see an asymmetry in the X_{Air} data as shown in Figure 3.4a which shows X_{Air} for 2014. With the solar gas shift difference calculated in the retrieval, Jonathan Franklin was able to calculate the actual SZA of most the measurements during 2014 and 2015. Figure 3.4b shows X_{Air} with the new SZA showing that the asymmetry in X_{Air} is now gone. To fix the alignment of the solar beam, the solar gas shift data were used to shift the tracking position of the sun on the CST camera, throughout the year in 2015, as detailed in Franklin, (2015). The SZA correction was applied to 2014 and 2015 data shown in Figure 3.2. The Eureka TCCON data is available on http://tccon.ornl.gov/.



Figure 3.4: (a) X_{Air} for all 2014 data (unfiltered) plotted as a function of hour (UTC) with SZA calculated assuming the instrument is viewing the center of the solar disc. (b) The same data but with the SZA corrected for the pointing problem

4 Calculating Absorption Coefficients

Remote sensing of the Earth's atmosphere relies on measuring the amount of radiation absorbed (and/or emitted) by gases in the atmosphere in order to infer their concentrations of that. In this work, the source of the radiation is the sun and the target molecules are GHGs (Chapter 1). GHGs are active in the infrared spectral region due to having a dipole moment. How each GHG reacts interacts with radiation is determined by the structure of the molecule. In order to retrieve the concentration of the gas of interest, the forward model of the retrieval algorithm ($F(\vec{x})$, from Eq. 3.1) is used to calculate its spectrum for comparison with the measured spectrum. This chapter details how such transmittance spectra are calculated.

4.1 Rovibrational Spectroscopy

The energy spectrum of a given molecule can be determined by using Schrodinger's equation (Schwabl, 2007):

$$\widehat{H}\Psi = E\Psi \tag{4.1}$$

where Ψ is the wavefunction of the molecule, \hat{H} is the Hamiltonian operator (used to characterize the total energy of the system), and E is the energy eigenvalues that solves Schrodinger equation for the given \hat{H} . The \hat{H} that describes the total energy of a molecule takes into account the electronic energy, vibrational energy, and rotational energy of the system simultaneously. Solving for such a \hat{H} is currently impossible. Assuming that the electronic, vibrational, and rotational energies can be decoupled (the Born-Oppenhimer approximation), the total energy (E^{total}) of the system can be described as (Schwabl, 2007):

$$E^{total} = E^{electronic} + E^{vibrational} + E^{rotational}$$
(4.2)

where $E^{electronic}$ is the electronic energy, $E^{vibrational}$ is the vibrational energy, and $E^{rotational}$ is the rotational energy.

In the case of a diatomic molecule, the vibrational motion can be modeled as a spring-like system (or harmonic oscillator). The \hat{H} describing this system would take into account both the

kinetic and potential energy of the harmonic oscillator. The energy eigenvalues that are the solution to such a system are (Schwabl, 2007):

$$E^{vibrational}(\mathbf{v}) = v_e\left(\mathbf{v} + \frac{1}{2}\right) \tag{4.3}$$

where v_e is the vibrational constant of the molecule (cm⁻¹), and v is the vibrational quantum number (v $\in \mathbb{N}$). For an anharmonic oscillator, Eq. 4.1 becomes (Schwabl, 2007):

$$E^{vibrational}(\mathbf{v}) = v_e \left(\mathbf{v} + \frac{1}{2}\right) - \chi_e v_e \left(\mathbf{v} + \frac{1}{2}\right)^2 \tag{4.4}$$

where χ_e is the anharmonicity constant for the molecule.

For a polyatomic molecule having N atoms, there will be N coupled oscillators and when it receives energy it will have some complicated vibrational movement that can be broken down into simpler movements. For example, the vibrational oscillations of CO_2 can be broken down into the symmetrical stretch, bending (doubly degenerate), and asymmetrical stretch vibrations as shown in Figure 4.1. In general, for an N atom system, the number of normal modes of vibration is 3N-5 for a linear molecule and 3N-6 for a non-linear molecule.

For CO₂, which is a linear molecule, there are 3(3) - 5 = 4 fundamental vibrations:



Figure 4.1: The three fundamental vibrational modes of CO₂. The bending mode is doubly degenerate. Figure is from http://bouman.chem.georgetown.edu/S02/lect23/co2.png

In the case of a diatomic molecule, the \hat{H} describing $E^{rotational}$ would only take into account the rotational energy assuming a rigid-rotator model. Solving Eq. 4.1 yields:

$$E^{rotational}(J) = RJ(J+1)$$
(4.5)

where R (cm⁻¹) is the rotational constant of the molecule (which is a function of the reduced mass of the molecule and bond length) and J is the rotational quantum number ($J \in \mathbb{N}$). In the rigid-rotator model, the bond between the atoms is assumed to be rigid but in reality it is more like a spring. So when the rotational velocity increases, the spring will extend, changing the bond length and therefore R. To keep R the same, a centrifugal distortion D term is added to Eq. 4.6, resulting in:

$$E^{rotational}(J) = RJ(J+1) - DJ(J+1)^2.$$
(4.6)

In the infrared range of the electromagnetic spectrum, transitions occur between vibrational states in the same electronic state. In addition, transitions from rotational states, in one vibrational state to rotational states in another vibrational state also occur. Ignoring the electronic state, which stays constant (C), the rovibrational energy of a state (given by Eq. 4.2) can be written as:

$$E^{total}(\mathbf{v}, J) = E^{rotational}(\mathbf{v}) + E^{rotational}(J) + C.$$
(4.7)

For rovibrational transitions, the following selection rules are applied $\Delta v = \pm 1, \pm 2$, etc. and $\Delta J=0, \pm 1$. A transition from *J* in the lower vibrational level to *J*-1 in the higher vibrational results in $\Delta J=-1$ and is known as the "P branch". A transition from *J*-1 to *J* results in $\Delta J=+1$ which is known as the "R branch". The "Q branch" occurs when $\Delta J=0$. The frequency of the transition is the difference between the total energy in the upper vibrational level E'(v, J) and the lower vibrational level E''(v, J).

4.2 Transmittance Spectrum

For a given intensity of light $(B_o(v))$ that passes through an absorbing medium (assuming no emission), the intensity of light absorbed is related to the amount of absorber in the

medium and its absorption cross-section as given by the Beer-Lambert law. The transmittance (T(v)) of the material sample can be calculated using the Beer-Lambert law:

$$T(v) = \frac{B(v)}{B_o(v)} = \exp[-LNk(v)]$$
(4.8)

where *L* is the path length of the sample through which the radiation travels, *N* is the number density (molecules/cm³) assumed to be constant over *L*, and k(v) is the absorption cross-section of the absorbing gas. The number density can be calculated using the Ideal Gas Law:

$$N = \frac{PN_{av}n}{RT}$$
(4.9)

where *P* is the total pressure (atm), N_{av} is Avogadro's number (6.022x10²³ mol⁻¹), *n* is the mole fraction for the gas of interest, *T* is the temperature (K), and *R* is the gas constant (82.057 cm³ atm K⁻¹ mol⁻¹). The absorption cross-section is calculated by:

$$k(v) = \sum_{i}^{N_{line}} S_{i}g(v, v_{i}^{o})$$
(4.10)

where S_i is the line intensity (cm⁻¹/molecule cm⁻²) for the spectral line centered at v_i^o , and $g(v, v_i^o)$ is the function that describes the shape of the spectral line. The value of S_i reported in spectroscopic line parameter databases such as the high-resolution transmission molecular absorption database (HITRAN) (Rothman et al., 2005) is given at the reference temperature $T^o = 296$ K. To take into account the temperature dependence of S_i , the following formula is used (Rothman et al., 2005):

$$S_{i}(T) = S_{i}(T^{o}) \frac{\exp(-hE_{i}^{"}c/k_{B}T) Q_{T}(T^{o})[1 - \exp(-hv_{i}^{o}c/k_{B}T)]}{\exp(-hE_{i}^{"}c/k_{B}T^{o}) Q_{T}(T)[1 - \exp(-hv_{i}^{o}c/k_{B}T^{o})]}$$
(4.11)

where *h* is Planck's constant (6.626x10⁻³⁴ m² kg/s), E''_i is the lower state energy (cm⁻¹), *c* is the speed of light (2.998x10¹⁰ cm/s), k_B is Boltzmann's constant (1.380x10⁻²³ m² kg s⁻² K⁻¹), and Q_T is the total internal partition function.

4.3 Spectral Line Shape Theory

4.3.1 Collisional Broadening

An isolated molecule that is excited from E'' to higher state E' will stay in its higher state for a finite amount of time and decay spontaneously. The difference between E' and E'' (or ΔE) gives the spectral line position v at which one would assume to see a sharp feature when measured by a spectrometer. But given the Heisenberg Uncertainty Principle ($\Delta E \Delta t > h/2\pi$) there will be an uncertainty in the measured line position which results in the natural broadening of the spectral line (Lévy et al., 1992).

If the molecule is in a gaseous mixture, the natural lifetime of the molecule in its excited state can be shortened by collisions with other molecules. As the pressure increases, the rate of collision between molecules also increases and natural broadening becomes inconsequential due to the dominance of collisional (or pressure) broadening. The line shape due to collisional broadening is the Lorentz line shape (g^L) calculated by (Lévy et al., 1992):

$$g^{L}(v, v_{i}^{o}) = \left(\frac{1}{\pi}\right) \frac{\gamma_{L_{i}}}{(v - v_{i}^{o} - P\delta_{i}^{o})^{2} + {\gamma_{L_{i}}}^{2}}$$
(4.12)

where δ_i^o is the pressure-shift coefficient and γ_{L_i} is the Lorentz half-width at half-maximum (HWHM). The Lorentz half-width, γ_{L_i} , is calculated by:

$$\gamma_{L_i}(T) = \frac{P}{P^o} \gamma_{L_i}^o \left(\frac{296}{T}\right)^n \tag{4.13}$$

Where $\gamma_{L_i}^o$ is the Lorentz half-width coefficient (atm⁻¹ cm⁻¹ at reference temperature 296 K and pressure P^o) and *n* is the value of the temperature-dependence exponent.

4.3.2 Line Mixing

The Lorentz line shape assumes that spectral lines are collisionally isolated. To show how this changes when lines are not collisionally isolated, we follow the discussion of Lévy et al. (1992). Figure 4.2 shows two spectral lines centered at v_1 and v_2 . Collisions have broadened the spectral lines so that they overlap. At frequency v, collisions have perturbed the energy levels of

the spectral line centered at v_1 so that a photon of energy v can be absorbed by this transition. Similarly, for the spectral line centered at v_2 , collisions will perturb the initial and final energy levels of the transition so that it can also absorb a photon of energy v. So the absorption of a photon of energy v could be due to either transition.



Figure 4.2: Two spectral lines centered at v_1 and v_2 . Both lines are broadened so that they overlap at v. Figure is modified from Berman (1998).

When spectral lines are coupled, inelastic collisions can transfer population from one rotational level to another rotational level within the same vibrational state. This effectively transfers intensity from one part of the spectrum to another part of the spectrum and is known as line mixing (Gentry and Strow, 1987). For line mixing (LM) to occur, certain conditions must be met. One, the energy difference between rotational levels (within the same vibrational state) must be less than the thermal energy (k_BT) so that inelastic collisions can transfer a molecule from one rotational level to another (Lévy et al., 1992). Two, the spectral lines must be broadened enough to overlap (Lévy et al., 1992). To take line mixing into account in the absorption cross-section calculation, the following equation is used (Lévy et al., 1992):

$$k(v) = \frac{1}{\pi} \sum_{i} S_{i}^{eff} \left(\frac{\gamma_{L_{i}}}{(v - v_{i}^{eff} - P\delta_{i}^{o})^{2} + {\gamma_{L_{i}}}^{2}} + \frac{Y_{i}(v - v_{i}^{eff} - P\delta_{i}^{o})^{2}}{(v - v_{i}^{eff} - P\delta_{i}^{o})^{2} + {\gamma_{L_{i}}}^{2}} \right)$$
(4.14)

where S_i^{eff} is the effective line intensity, v_i^{eff} is the effective line center frequency, and Y_i is the line mixing parameter. These parameters can be calculated following the method described in Lévy et al. (1992). First one needs to construct the relaxation matrix W which models the coupling of rotational levels. The diagonal elements of the relaxation matrix are γ_{L_i} and off-diagonal elements ϵ_{ij} are the rate of transfer from rotational level *i* to *j*. Then the matrix ($v_o + iW$) is diagonalized, where v_o is the diagonal matrix of all v_i^o , using:

$$\boldsymbol{A}^{-1}(\boldsymbol{v}_{\boldsymbol{o}} + i\boldsymbol{W})\boldsymbol{A} = \boldsymbol{\Lambda} \tag{4.15}$$

where A is the matrix of eigenvectors whose eigenvalues are diagonal elements of Λ . The real values of Λ are v_i^{eff} . The column vector of effective line strengths, \vec{S}^{eff} , is calculated by:

$$\vec{S}^{eff} = Re[(\vec{\mu}^T A)(A^{-1}\boldsymbol{\rho}\vec{\mu})]$$
(4.16)

where ρ is a diagonal matrix of populations of lower state energies, and $\vec{\mu}$ is a column vector of transition dipole moments calculated by taking the square root of S_i divided by the population ρ_i . \vec{S}^{eff} contains the effective line strength for each spectral line S_i^{eff} . The column vector \vec{Y} contains the line mixing parameter for each line (Y_i) and is calculated using the formula:

$$\vec{Y} = Im[(\vec{\mu}^T \boldsymbol{A})(\boldsymbol{A}^{-1}\boldsymbol{\rho}\vec{\mu})]_i / S_i^{eff}.$$
(4.17)

Essentially line mixing takes into account the change in line strength, line position, and line shape when spectral lines are not isolated. By examining Eq. 4.13 one can see that the spectral line shape due to line mixing is a combination of the Lorentz line shape and an asymmetric line shape that is scaled by Y_i (given by the term on the right hand side of Eq. 4.14. An example of the asymmetric line shape is shown in Figure 4.3b.

4.3.3 Doppler Broadening

For a molecule moving towards or away from an observer, the emitted radiation will be Doppler shifted to a higher or lower frequency as measured by the observer. Molecules in a gaseous mixture will follow a Maxwell-Boltzmann speed distribution and different velocities of the emitted radiation will result in different Doppler shifts. When all these Doppler shifts are taken into account, they result in a broadening of the spectral line. The spectral line shape due to Doppler broadening ($g^{G}(v, v_{i}^{o})$) takes on a Gaussian shape calculated by:

$$g^{G}(v, v_{i}^{o}) = \left(\frac{1}{\gamma_{D_{i}}\sqrt{\pi}}\right) e^{-\frac{(v-v_{i}^{o})^{2}}{\gamma_{D_{i}}^{2}}}$$
(4.18)

where γ_{D_i} is the Doppler width:

$$\gamma_{D_i} = \frac{v_i^o}{c} \sqrt{\frac{2k_B T}{m}},\tag{4.19}$$

where *m* is the mass of the molecule, and all other terms were previously defined. The Doppler width half-width at half-maximum (HWHM) is Eq. 4.19 multiplied by $\sqrt{\ln(2)}$.

4.3.4 The Voigt Spectral Line Shape

At atmospheric pressures, both Doppler and collisional broadening must be taken into account in the spectral line shape. The Voigt line shape (g^{voigt}) is the convolution of the Doppler and Lorentz line shapes (Lévy et al., 1992):

$$g^{voigt}(v, v_i^o) = \left(\frac{1}{\gamma_{D_i}}\right) \left(\frac{\ln(2)}{\pi}\right)^{1/2} Re[err(v, x_i, y_i)]$$
(4.20)

where err is the complex error function,

$$x_i = \frac{(v - v_i^o - P\delta_i^o)}{\gamma_{D_i}} (\ln(2))^{1/2}, \text{ and } y_i = \frac{\gamma_{L_i}}{\gamma_{D_i}} (\ln(2))^{1/2}.$$
(4.21)

The Voigt line shape assume that spectral lines are collisionaly isolated. This means that the Voigt line shape only works when inelastic collisions do not transfer intensity from one part of the spectrum to another (or in other words cause line mixing). Absorption coefficients calculated using spectroscopic parameters from the HITRAN database (HITRAN 2012 (Rothman et al., 2013) and older) assume a Voigt line shape.

When taking line mixing into account, the Voigt line shape with line mixing $(g^{voigt+LM})$ is (Edwards and Strow, 1991):

$$g^{voigt+LM}(v,v_i^o) = \left(\frac{1}{\gamma_{D_i}}\right) \left(\frac{\ln(2)}{\pi}\right)^{1/2} \left(Re[err(v,x_i,y_i)] + Y_i Im[err(v,x_i,y_i)]\right) \quad (4.22)$$

where all terms are as defined before. Figure 4.3a shows the $Re[err(v, x_i, y_i)]$ part of Eq. 4.22 and Figure 4.3b shows $Im[err(v, x_i, y_i)]$ part of Eq. 4.22 for the Voigt line shape calculated for an arbitrary spectral line.



Figure 4.3: (a) Real part of spectral line shape using the Voigt, speed-dependent Voigt (qSDV), hard collision (HC), and partially-correlated quadratic-speed-dependent hard collision (pCqSDHC). Legend indicates the colours for the different models. (b) Same as (a) but shows the imaginary part used when taking line mixing into account. (c) The difference between the real part of a given model and the real part of the Voigt. (d) Same as (c) but for the imaginary part.

4.3.5 The Speed-dependent Voigt Line Shape

Another assumption made when using the Voigt line shape is that the rate of collision is due to the perturbing molecule. This assumption holds true when there is a heavy absorbing molecule in a mixture of light fast-moving perturbing molecules. But for a light-absorbing molecule in a mixture of heavy slower molecules (or even close to the same mass), the collision rate depends on the speed of the absorbing molecule. Different velocity groups of the absorbing molecule will experience their own homogenous broadening (Rohart et al., 1994). The Lorentz half-width coefficient and pressure shift coefficient then become a function of speed and can be modeled using the following expression given in Rohart et al. (1994):

$$\gamma_{L_i}(V_a) = \gamma_{L_i} \left(1 + a_{\gamma_{L_i}}(V^2 - 1.5) \right), \text{ and } \delta_i^o(V_a) = \delta_i^o(1 + a_{\delta_i^o}(V^2 - 1.5))$$
(4.23)

where V_a is the absolute speed of the absorber, V is the ratio of the absorbing molecule speed to the most probable speed of the absorbing molecule, $a_{\gamma L_i}$ is the speed-dependent Lorentz width parameter (unitless) for line *i*, and $a_{\delta_i^o}$ is the speed-dependent shift parameter. This results in a Lorentz line shape for each absolute speed of the absorbing molecule, which must be taken into account in the Voigt line shape calculations. However, the speed distribution of the absorbing molecule follows Maxwell-Boltzmann statistics and so each Lorentz line shape is weighted by the Maxwell-Boltzmann probability distribution when adding the Lorentz contribution from each absolute speed to the line shape. The speed-dependent Voigt line shape (g^{SDV+LM}) with line mixing becomes (Wehr, 2005):

$$g^{SDV+LM}(v,v_i^o) = \left(\frac{2}{\pi^{\frac{3}{2}}}\right) \int_{-\infty}^{\infty} e^{-V^2} V\left(tan^{-1}\left[\frac{x_i+V}{y_i}\right] + Y_i \frac{1}{2}ln\left[\left(\frac{x_i+V}{y_i}\right)^2 + 1\right]\right) dV \quad (4.24)$$

with γ_{L_i} replaced with $\gamma_{L_i}(V)$ in Eq. 4.21, and δ_i^o replaced with $\delta_i^o(V_a)$ in Eq. 4.21, and all other terms as defined above. To enhance computational efficiency, one can use the quadratic-speeddependent Voigt line shape with line mixing $(g^{qSDV+LM}(v, v_i^o))$ (Ngo et al., 2013; Tran et al., 2013):

$$g^{qSDV+LM}(v,v_i^o)$$

$$= \sum_j \left(\frac{1}{\gamma_{D_j}}\right) \left(\frac{\ln(2)}{\pi}\right)^{1/2} \left(Re\left[err(v,iZ_1^j) - err(v,iZ_2^j)\right]\right)$$

$$+ Y_i Im\left[err(v,iZ_1^j) - err(v,iZ_2^j)\right]\right)$$
(4.25)

where:

$$Z_1^j = \sqrt{X_j + Y_j} - \sqrt{Y_j}$$
 and $Z_2^j = \sqrt{X_j + Y_j} + \sqrt{Y_j}$, (4.26)

$$X_{j} = \frac{i(v - v_{j}^{o}) + \widecheck{C_{o}}}{\widecheck{C_{2}}} \text{ and } Y_{j} = \left(\frac{\sqrt{\ln(2)}}{2\gamma_{D_{j}}\widecheck{C_{2}}}\right)^{2}, \tag{4.27}$$

$$\widetilde{C_o} = C_o - \frac{3}{2}C_2,$$
(4.28)

$$C_o = \gamma_{L_j}(T) + iP\delta_j^o \text{ and } C_2 = \gamma_{L_j}(T)a_{\gamma_{L_i}} + iP\delta_j^o a_{\delta_i^o}.$$
(4.29)

The quadratic-speed-dependent Voigt line shape with line mixing will be referred to as the qSDV+LM. Figures 4.3a and 4.3b show the symmetric and asymmetric shapes for the qSDV+LM, while Figures 4.3c and 4.3d show the difference between the speed-dependent Voigt and Voigt for the symmetric and asymmetric shapes respectively. Figure 4.3c shows that the speed-dependent Voigt is narrower than the Voigt and a "W" shaped residual results when speed dependence is not taken into account. The qSDV+LM (Eq. 4.25) can reproduce the SDV+LM (Eq. 4.24) (Tran et al., 2013) with the difference between the two models being the computation time. The SDV+LM requires a numerical integration scheme where the tan^{-1} and ln have to be evaluated multiple times at a given v, while the qSDV+LM requires that the *err* function be calculated twice at a given v.

4.3.6 Collisional Narrowing

Dicke (1953) showed that collisions that do not contribute to the pressure broadening of an isolated spectral line could affect the Doppler broadening of the spectral line. The Doppler spectral line shape (Eq. 4.11) assumes that molecules travel in a straight line at a constant speed during the lifetime of their excited state. At high enough pressures, collisions with other molecules (that don't change the internal state) will change the velocity of the molecule (slowing it down) resulting in a diffuse type of motion. This, in turn, will decrease the Doppler contribution to the line width. This collisional (or Dicke) narrowing of the spectral line shape is taken into account by two different spectral line shapes, which depend on the type of collision.

The soft collision (SC) model, developed by Galatry (1961), assumes that the absorbing molecule is much heavier than the perturbing molecule so that numerous collisions are needed to change its velocity. The Galatry spectral line shape is given by:

$$g^{SC}(v, v_i^o) = \frac{1}{\pi} Re\left[\frac{1}{\frac{1}{2z} + y_i - ix_i} M\left(1; 1 + \frac{1}{2z^2} + \frac{y_i - ix_i}{z}; \frac{1}{2z^2}\right)\right]$$
(4.30)

where M(...) is the confluent hypergeometric function, $z = \frac{\beta_{soft}}{\gamma_{D_i}}$, and β_{soft} is the Dicke narrowing parameter assuming soft collisions.

The hard collision (HC) model, developed by Rautian and Sobel'man (1967) assumes that the absorbing molecule is light relative to the colliding molecule. In this situation, the absorbing molecule will have no memory of its initial velocity after the collision.

$$g^{HC}(v, v_i^o) = \left(\frac{1}{\gamma_{D_i}}\right) \left(\frac{\ln(2)}{\pi}\right)^{1/2} \frac{Re[err(v, x_i, y_i + z)]}{1 - \sqrt{\pi}zRe[err(v, x_i, y_i + z)]}$$
(4.31)

where $z = \frac{\beta_{hard}}{\gamma_{D_i}}$, and β_{hard} is the Dicke narrowing parameter assuming hard collisions. The hard collision model is compared to the Voigt model in Figures 4.3c and 4.3d showing that an upside down "W" will appear when Dicke narrowing (HC case) needs to be taken into account when modeling the spectral line shape.

The hard and soft collision models assume that collisions can either change the molecules' velocity or their rotational state, but never the two simultaneously. Wehr et al. (2006) showed that the contribution from Dicke narrowing was less than expected for CO buffered by argon. This was attributed to the possibility that some collisions change both the velocity and rotational state of the molecule. Joubert et al. (1999) adapted the HC model to take into account the correlation between velocity and state-changing collisions. Pine (1999) included speed dependence of the collision width as well as the correlation between velocity and state-changing collisions in the HC model to create the partially-correlated speed-dependent hard collision spectral line shape or speed-dependent Nelkin-Ghatak spectral line shape (Ciuryło, 1998).

The biggest obstacle to incorporating a spectral line shape that takes speed dependence or Dicke narrowing (or both) into radiative transfer codes is that these line shapes are computationally intensive mainly because the speed-dependent Voigt calculation requires a numerical integration scheme. Since the qSDV (Eq. 4.25) does not require a numerical integration scheme, it has been incorporated into the partially-correlated speed-dependent hard collision spectral line shape to create the partially-correlated quadratic-speed-dependent hard collision (pCqSDHC) spectral line shape (Ngo et al., 2013; Tran et al., 2013). The pCqSDHC takes into account speed dependence, Dicke narrowing, and partially correlated collisions in a computationally efficient manner and can be reduced to the qSDV, HC model, or Voigt spectral line shapes. Figure 4.3c shows the difference between the pCqSDHC and the Voigt. The residual shown is a combination of the individual residuals of the speed-dependent and hard collision models. Tennyson et al. (2014) recommended that the pCqSDHC spectral line shape replace the Voigt line shape.

4.4 Summary and Conclusion

Fitting of laboratory spectra (for many years now) has shown that the Voigt spectral line shape is not good enough to describe the spectral line shape of some molecules under certain conditions. Studies have shown that speed-dependence of the collisional width and shift, as well as Dicke narrowing, alter the spectral line shape and produce large systematic residuals when not taken into account. Inclusion of speed dependent effects, in the spectral line shape, for atmospheric spectra of molecules such as CO₂, O₂, and CH₄ is necessary because the mass ratio of these molecules in a buffer gas such as air is 1.5, 1.06, and 0.55 and so the speed at the time of collision cannot be ignored. Neglecting line mixing, which alters both the spectral line shape and the intensity, also impacts the calculated absorption coefficient, leading to large systematic residuals. The need to include line mixing in the absorption coefficient calculation of CO₂ in a retrieval algorithm was shown as far back as 1991 for spectra from the Atmospheric Trace Molecule Spectroscopy experiment (ATMOS) (Edwards and Strow, 1991). CH₄ spectral lines are blended at atmospheric pressures greater than 0.3 atm, so line mixing needs to be taken into account when calculating absorption coefficients. Due to the high precision and accuracy requirements for space-based measurements of CO₂ and other GHGs, studies have shown the need to go beyond the Voigt spectral line shape when calculating absorption coefficients (Hartmann et al., 2009; Tran et al., 2010; Thompson et al., 2012). In Chapters 5-7 of this work the forward model of GFIT is updated (for CO₂, CH₄, and O₂) to take into account speed

dependence and line mixing in the absorption coefficient calculation. The retrievals with the new absorption coefficients are compared to the retrievals with the old absorption coefficients and the implications of these results have on remote sensing measurements are discussed.

5 Improving Atmospheric CO₂ Retrievals using Line Mixing and Speed Dependence when Fitting High-Resolution Ground-Based Solar Spectra

5.1 CO₂ Spectral Bands

Laboratory studies of CO₂ spectroscopic parameters and spectral line shapes (Devi et al., 2007; Predoi-Cross et al., 2007a, 2007b) for the weak $30013 \leftarrow 00001 \text{ CO}_2$ band (referred to as "weak CO₂ band 1", centered at 6220 cm⁻¹) and the weak 30012 \leftarrow 00001 CO₂ band centered at 6340 cm⁻¹ (referred to as "weak CO₂ band 2" below) assert that the Voigt spectral line shape is insufficient for modeling the spectral line shape of CO₂ to attain the precision and accuracy necessary for carbon cycle studies. These studies claim that speed dependence and line mixing need to be taken into account when calculating absorption coefficients for both weak CO₂ bands. Hartmann et al. (2009) used two days of solar absorption spectra, measured at Park Falls (Wisconsin, USA), and fitted the spectra with absorption coefficients calculated with a Voigt line shape that included line mixing. Total columns of CO₂ were retrieved using the strong CO₂ band (20013←00001 CO₂ band) centered at 4850 cm⁻¹ and the weak CO₂ band 1. The authors showed that taking line mixing into account improved the spectral fits and decreased the airmass dependence of the dry-air mole fraction (XCO₂) for both bands, with the greatest impact on the strong CO₂ band. Hartmann et al. (2009) further showed that the airmass dependence of XCO₂ retrieved with a Voigt spectral line shape is not geophysical in nature but is due to the inadequacy of the Voigt spectral line shape. If this is not taken into account, it could lead to incorrect inferences about regional sources and sinks.

Thompson et al. (2012) compared the absorption coefficients calculated using the software of Lamouroux et al. (2010) with those obtained using the OCO-2 approach, which takes both line mixing and speed dependence into account. Validation of these absorption coefficients was done by simulating laboratory spectra for the measurement conditions and fitting high-resolution ground-based solar absorption spectra. By taking into account both speed dependence and line mixing, fits to solar absorption spectra were improved and the airmass dependence of XCO₂ decreased. However, residual structure in the spectral fits still existed in both the
laboratory and solar spectra. This may have been due to neglecting speed dependence when calculating absorption coefficients using the software of Lamouroux et al. (2010) and not taking the temperature dependence of line mixing into account in Thompson et al. (2012).

5.2 Line Mixing for CO₂

Recall Section 4.2.2 where it was shown that when inelastic collisions transfer population from one rotational level to another, line mixing needs to be taken into account in absorption coefficient calculations. The relaxation matrix (W) is used to describe the coupling of spectral lines. The diagonal elements of W are Lorentz widths and the off-diagonal elements are the collisional transfer rate ϵ_{jk} , which represents the transfer of population from lower rotational level k to higher rotational level j. For a molecule in thermodynamic equilibrium, the rate of upward transfer is related to the rate of downward transfer through the detailed balance condition:

$$\rho_k \epsilon_{jk} = \rho_j \epsilon_{kj} \tag{5.1}$$

where ρ_k is the population of rotational level k and ρ_j is the population of rotational level j (Lévy et al., 1992). The off-diagonal elements of W are related to the diagonal elements of W through the sum rule, resulting in the equation:

$$W_{kk} = \gamma_k = \frac{1}{2} \left[\sum_{j \neq k} \epsilon_{jk} \right]_{Upper} + \frac{1}{2} \left[\sum_{j \neq k} \epsilon_{jk} \right]_{Lower}$$
(5.2)

where *Upper* denotes the upper vibrational level and *Lower* denotes the lower vibrational level as stated in Predoi-Cross et al. (2007a). The sum rule states that the columns of the W should add up to be zero. This means that the ϵ_{jk} is negative and the rate of transfer cannot be greater than rate of collision given by γ_k .

The ϵ_{jk} for CO₂ can be modeled using the exponential power gap (EPG) law (Gentry and Strow, 1987):

$$\epsilon_{jk} = a_1 \left[\frac{\Delta E_{jk}}{k_B T} \right]^{-a_2} e^{\left(\frac{-a_3 \Delta E_{jk}}{k_B T} \right)}$$
(5.3)

where ΔE_{jk} is the difference between rotational energy levels *j* and *k*, k_B is the Boltzmann constant, *T* is the temperature, and a_1 , a_2 , and a_3 are coefficients that need to be determined (refer to Section 5.3 for details on how they are calculated). Once the coefficients are determined, the EPG law is used to calculate the off-diagonal elements of **W** using the equation:

$$W_{jk}_{\substack{jk\\j\neq k}} = -\beta\epsilon_{jk} \tag{5.4}$$

where $\beta = 0.56$ is the parity bias (Predoi-Cross et al., 2007a). Once *W* has been determined, the line mixing coefficient Y_i , used in Eqs. 4.13, 4.15, and 4.18 to calculate the line shape, can be calculated. Assuming that the spectral lines have weak mixing, the first order (or Rosenkranz) approximation can be used to calculate Y_i (Rosenkranz, 1975):

$$Y_{i} = 2\sum_{j \neq i} \frac{\mu_{j}}{\mu_{i}} \frac{W_{ji}}{\nu_{i} - \nu_{j}},$$
(5.5)

where μ_i is the transition dipole moment of line *i*. The transition dipole moment is calculated by taking the square root of the intensity of the spectral line (S_i) divided by ρ_i .

5.3 Calculating the Line Mixing Coefficient

The line mixing coefficient for a given CO₂ band is calculated using the EPG law (Eq. 5.3) to model the rate of transfer between rotational levels. In order to use Eq. 5.3, the coefficients a_1 , a_2 , and a_3 need to be determined. When constructing W, the columns of the matrix should sum to zero (Eq. 5.2). Substituting Eq. 5.3 into Eq. 5.2 and also taking detailed balance into account (Eq. 5.1) results in an over-determined system of equations, with n equations (where n is the number of spectral lines), and three unknowns. The coefficients a_1 , a_2 , and a_3 are determined by solving the system of non-linear equations using the Levenberg-Marquardt algorithm. It should be noted that we assume only coupling between lines in the same branch, following Predoi-Cross et al. (2007a; 2007b). Once a_1 , a_2 , and a_3 are determined, all

off-diagonal elements of W are calculated by substituting Eq. 5.3 into Eq. 5.4. Eq. 5.5 is then used to determine Y_i .

Given that the Lorentz width changes with temperature (Eq. 4.13), the line mixing coefficient (Y_i) will also have a temperature dependence. The line mixing coefficient of each line was thus calculated for a temperature range between 250-350 K at 2 K intervals. Figure 5.1 shows the line mixing coefficient plotted as a function of $\left(\frac{296}{T}\right)$, for the P(24) spectral line of the weak CO₂ band 1. A quadratic line is fitted to the data, showing that Y_i can be accurately modeled by a quadratic equation, similar to Edwards and Strow (1991), making it easy to use in any retrieval algorithm:

$$Y_i(T) = a_i \left(\frac{296}{T}\right)^2 + b_i \left(\frac{296}{T}\right) + c_i$$
(5.6)

where a_i , b_i , and c_i are the coefficients for line *i* determined by fitting a quadratic line to the $Y_i(T)$ data. The coefficients a_i , b_i , and c_i are then stored in a list with the other spectroscopic parameters for line *i* so that Y_i can be easily calculated using Eq. 5.6.



Figure 5.1: Temperature dependence of the P(24) line mixing coefficient calculated using spectroscopic parameters from Devi et al. (2007). A quadratic line is fitted to the data, and the coefficients of the line can be used to calculate the line mixing coefficient at any given temperature.

However, the calculated $Y_i(T)$ will be different for collisions of CO₂ with air, itself, and H₂O. To adequately take into account all types of collisions, the total line mixing coefficient $Y_{total}^i(T)$ for a given line will be calculated using:

$$Y_i^{total}(T) = X_{air}Y_i^{air}(T) + X_{self}Y_i^{Self}(T) + X_{H20}Y_i^{H20}(T)$$
(5.7)

where X is the dry-air mole fraction of the collision partner (air, self, or H₂O), $Y_i^{air}(T)$, $Y_i^{Self}(T)$, and $Y_i^{H2O}(T)$ are the line mixing coefficients calculated for the different collision partners and modeled by Eq. 5.6. The Lorentz widths from collisions with H₂O are assumed to be 1.35 times the air-broadened widths, as used in GGG2014. So when calculating $Y_i^{H2O}(T)$, the air-broadened Lorentz widths are increased by 35% to calculate the rate of transfer between rotational levels. In order to calculate $Y_i^{total}(T)$, there will be nine parameters for each CO₂ line. In the case when speed dependence has to be taken into account in the spectral line shape calculation, the Lorentz width is not only a function of *T* but also *V*. Berman (1998) showed that there is negligible difference between using speed-dependent and speed-independent line mixing coefficients. So in $\frac{58}{58}$

this study, Y_i is simply a function of T when speed dependence is taken into account in the spectral line shape.

5.4 Fitting CO₂ Laboratory Spectra

TCCON total columns of CO₂ are retrieved from both weak CO₂ bands, while OCO-2 and GOSAT retrieve CO₂ from weak CO₂ band 1 and the strong CO₂ band. To assess the absorption coefficients calculated for CO₂ using the spectral line shapes described in Section 4 for both the strong and weak CO₂ bands, spectra calculated using the forward model of GFIT were compared to laboratory spectra recorded at known laboratory conditions (temperature, humidity) and known CO₂ amounts in a temperature-controlled absorption cell with an optical path length of 29.30 m. The absorption coefficients were calculated using spectroscopic parameters from different laboratory studies that retrieved the parameters using three spectral line shapes: Voigt (Eq. 4.20), Voigt+LM (Eq. 4.22), and the qSDV+LM (Eq.4.25). The line mixing coefficients for a given set of spectroscopic parameters were calculated as described in Section 5.3. The different spectral line shapes were compared and the best spectral line shape was chosen as the new standard to calculate CO₂ absorption coefficients when fitting solar spectra based on the ability to model laboratory spectra.

5.4.1 Fitting a CO₂ Laboratory Spectrum for the Strong CO₂ Band

For the strong CO₂ band, a laboratory spectrum was recorded at the NASA JPL using a Bruker 125HR FTS at a resolution of 0.0044 cm⁻¹. The cell contained a total gas pressure of 0.7892 atm at 296.1 K with 4.96% being ¹²C-enriched ¹⁶O¹²C¹⁶O (Thompson et al., 2012). Figure 5.2a shows the measured laboratory spectrum. The forward model of GFIT was used to simulate the measured spectrum by calculating the absorption coefficients using three different line shapes: (1) Voigt, (2) Voigt+LM, and (3) qSDV+LM. The spectroscopic parameters used to calculate the absorption coefficients with the different spectral line shapes are from HITRAN 2008 (Rothman et al., 2009) and HITRAN 2012 (Rothman et al., 2013). How the HITRAN 2008 and HITRAN 2012 spectroscopic parameters were modified for appropriate use with the qSDV+LM will be explained later in this section. It should be noted that the different spectral line shapes were only used to calculate the absorption coefficients for CO₂ lines for the strong CO₂ band. Absorption coefficients for all other spectral lines were calculated assuming a Voigt line shape and spectroscopic parameters from the default spectral line list, atm (Toon, 2014a), which is provided with the GGG software package. The atm line list is a combination of spectroscopic parameters from HITRAN and other studies that use a Voigt spectral line shape when calculating absorption coefficients. The assumption made about all other CO_2 lines in this window is adequate because the strengths of the CO_2 lines in the strong CO_2 band are approximately 15 times greater than the other CO_2 lines, and including speed dependence and line mixing for these weak lines had no effect on the quality of the spectral fits.



Figure 5.2: (a) Laboratory spectrum of air-broadened CO₂ for the strong CO₂ band. The next six panels show the residuals (measured minus calculated spectra) obtained using the following line shapes. (b) Voigt line shape with HITRAN 2008. (c) Voigt line shape with HITRAN 2012 parameters. (d) Voigt line shape with line mixing and HITRAN 2008. (e) Voigt line shape with line mixing and HITRAN 2012 parameters, with the air-broadened widths scaled by 0.985 and self-broadened widths divided by 0.978. (f) qSDV+LM and HITRAN 2008 parameters, with air-broadened widths divided by 0.985 and self-broadened widths divided by 0.978. The same speed-dependent parameter $\alpha^i = 0.11$ is used for all lines. (g) qSDV+LM with HITRAN 2012 parameters with, $\alpha^i = 0.11$ for all lines.

Figures 5.2b and 5.2c show the residuals (measured minus calculated spectra) for absorption coefficients calculated using a Voigt line shape and spectroscopic parameters from HITRAN 2008 (Figure 5.2a) and HITRAN 2012 (Figure 5.2b). The overall fit, given by the RMS (root mean square) residual, shows no improvement when using HITRAN 2012 spectroscopic parameters compared to HITRAN 2008. However, both residuals show the same systematic structure. Figures 5.3a and 5.3c are plots of the P-branch residuals from 4832.5-4836.6 cm⁻¹ and Figures 5.3b and 5.3d show the R-branch residuals from 4870-4874 cm⁻¹ using a Voigt line shape with HITRAN 2008 and HITRAN 2012, respectively. These residuals clearly show an asymmetric structure regardless of the spectroscopic parameters used to calculate the absorption coefficients.

Figures 5.2d and e show the residuals for absorption coefficients calculated using a Voigt line shape that includes line mixing with HITRAN 2008 and HITRAN 2012 parameters respectively. HITRAN 2012 CO₂ Lorentz widths were calculated by adjusting intermolecular parameters from Gamache and Lamouroux (2013) and Lamouroux et al. (2012a; 2012b) to model the speed-dependent Voigt widths that were measured in Devi et al. (2007a; 2007b). Lamouroux et al. (2015) have shown that the HITRAN 2012 air- and self-broadened widths need to be adjusted in order to calculate absorption coefficients with a Voigt line shape with line mixing. In this work (as well as Lamouroux et al., 2015), the adjustment was done by determining the transition-averaged ratio of Lorentz widths measured using a Voigt line shape to the speed-dependent Voigt line shape, and then multiplying by this factor. In studies by Predoi-Cross et al. (2007a; 2007b), air- and self-broadened Lorentz widths were measured using the Voigt and speed-dependent Voigt line shapes. The average ratio of all the air-broadened Lorentz widths measured in Predoi-Cross et al. (2007a) using a Voigt line shape to those measured using the speed-dependent Voigt line shape is 0.985 (as determined in Lamouroux et al., 2015). For self-broadened Lorentz widths (measured in Predoi-Cross et al., 2007b) this ratio is 0.978 (as determined in Lamouroux et al., 2015). So to convert from Voigt air-broadened Lorentz widths to speed-dependent Voigt air-broadened Lorentz widths, the Voigt air-broadened Lorentz widths were divided by 0.985 (and self-broadened Lorentz widths were divided by 0.978). Since the HITRAN 2012 Lorentz widths represent speed-dependent air- and self-broadened Lorentz widths (Lamouroux et al., 2015), they were converted from speed-dependent Voigt to speedindependent Voigt by multiplying the air- and self-broadened widths by 0.985 and 0.978, respectively. Figure 5.2e shows the residual obtained with the adjusted HITRAN 2012 widths and a Voigt+LM. The overall spectral fit was improved for both HITRAN 2008 and HITRAN

2012, but slightly better for HITRAN 2008 than HITRAN 2012. Figures 5.3e and 5.3f show that the asymmetry has been substantially diminished when using HITRAN 2008 with a Voigt line shape and line mixing. The result is the same for HITRAN 2012 (Figures 5.3g and 5.3h) but a "W" structure remains at line center for all the lines shown in the plots irrespective of line parameters.



Figure 5.3: Same as Figure 5.2, showing details of the residuals for P(24)-P(26) (panels a,c,e,g,i, and k) and R(22)-R(26) (panels b,d,f,h,j, and l).

Multiple laboratory studies have shown that in addition to line mixing, speed dependence should also be taken into account for CO₂ (Devi et al., 2007a, 2007b; Predoi-Cross et al., 2007a, 2007b). To do this empirically, the same speed-dependent parameter $\alpha^i = 0.11$ was used for all lines. This is the average value of α from the measurements of Predoi-Cross et al. (2007a, 2007b). It was assumed that α is the same for both air- and self-broadened widths as done in Devi et al., (2007a; 2007b). In order to use HITRAN 2008 parameters with the speed-dependent Voigt line shape, the air- and self-broadened widths were multiplied by 1/0.985 and 1/0.978 respectively, while HITRAN 2012 parameters were returned to their original values. Figures 5.2f and 5.2g show the residuals obtained using the qSDV+LM to calculate the absorption coefficients with HITRAN 2008 and HITRAN 2012 parameters respectively. The overall spectral fit improved for both sets of spectroscopic parameters when speed dependence was taken into account in addition to line mixing. Figures 5.3i and 5.3j show that the residual at line center was reduced when using qSDV+LM and the empirically scaled HITRAN 2008 spectroscopic parameters. The results were similar for HITRAN 2012 (Figures 5.3k and 5.3l), but the empirical HITRAN 2008 parameters fitted the spectrum better than the empirical HITRAN 2012 parameters. Therefore when fitting solar spectra for the strong CO₂ band, the new CO₂ absorption coefficients will be calculated using qSDV+LM and the empirically scaled HITRAN 2008 spectroscopic parameters.

5.4.2 Fitting a CO₂ Laboratory Spectrum for the Weak CO₂ Bands

Currently, the forward model of GFIT uses spectroscopic parameters from the atm line list for the weak CO₂ bands with a Voigt spectral line shape. These CO₂ spectroscopic parameters are an earlier version of parameters from Toth et al. (2008) that consistently produced the best fits to multiple high-resolution solar absorption spectra recorded at multiple TCCON sites. Figures 5.4a and 5.5a show the measured spectra for both bands, recorded at JPL using a Bruker 125HR FTS at a resolution of 0.00667 cm⁻¹. The total gas pressure is 0.7892 atm at 295.3 K with 9.03% being 12C-enriched ¹⁶O¹²C¹⁶O (Thompson et al., 2012). Figures 5.4b and 5.5b show the difference between the measured and calculated spectra, the latter using a Voigt line shape with spectroscopic parameters from the atm line list for both bands. Figures 5.4c and 5.5c show the residual when a Voigt line shape with line mixing and spectroscopic parameters from the atm line list are used to calculate the absorption coefficients. The overall fit (given by the RMS residual), and the systematic structure in the residual has improved as a result of including line mixing.



Figure 5.4: Panel (a) shows the measured laboratory spectrum for the weak CO₂ band 1. The next six panels show the residuals for a given spectral line shape and set of spectroscopic parameters used to calulate the CO₂ absorption coefficients for the weak CO₂ band 1. (b) Voigt with atm (Toon, 2014a). (c) Voigt+LM and atm (Toon, 2014a). (d) Voigt with Predoi-Cross et al. (2007a, 2007b, and 2009). (e) Voigt with line mixing and Predoi-Cross et al. (2007a, 2007b, and 2009). (f) qSDV+LM and Predoi-Cross et al. (2007a, 2007b, and 2009). (g) qSDV+LM and Devi et al. (2007a).



Figure 5.5: Same as Figure 5.4, but for absorption coefficients calculated for weak CO₂ band 2.

A series of studies by Predoi-Cross et al. on the CO₂ spectral line shape were published starting in 2007. Predoi-Cross et al. (2007a) fitted laboratory spectra using both a Voigt and speed-dependent Voigt with line mixing spectral line shape. Air-broadened half-widths, pressure shifts, and line mixing coefficients were measured in this study. Line intensity, self-broadened half-widths, pressure shifts, and line mixing coefficients were measured by Predoi-Cross et al., (2007b). In both these studies, line positions and the speed-dependent parameters were taken from Devi et al. (2007a) for the weak CO₂ band 1, and Devi et al. (2007b) for the weak CO₂ band 2. The temperature dependence of air-broadened half-widths was determined in Predoi-Cross et al. (2009). Figures 5.4d, 5.4e, and 5.4f show the spectral fits with a Voigt, Voigt with line mixing, and qSDV+LM line shape respectively for the weak CO₂ band 1. Figures 5.5d, 5.5e, and 5.5f are the same as Figure 5.4 but for the weak CO₂ band 2. For both weak CO₂ bands, the fits get better when line mixing is used and improve further when speed dependence is also taken into account. Including speed dependence and line mixing with spectroscopic parameters from Predoi-Cross et al. (2007a; 2007b; 2009) results in better fits to the laboratory spectra than the atm spectroscopic parameters with a Voigt line shape.

Finally, the spectrum was calculated using the spectroscopic parameters from Devi et al. (2007a) for the weak CO_2 band 1, and Devi et al. (2007b) for the weak CO_2 band 2, using qSDV+LM. The residuals of the fits are shown in Figures 5.4g and 5.5g for both windows. In this case, the fits for both windows are better than all other line shape models. Therefore, when fitting solar spectra, the new absorption coefficients will be calculated using the qSDV+LM and spectroscopic parameters from Devi et al. (2007a; 2007b).

5.5 Fitting Solar Spectra

High-resolution solar absorption spectra were recorded at four TCCON stations: Eureka, Canada; Park Falls, USA; Lamont, USA; and Darwin, Australia. Total columns of CO₂ were retrieved from the strong and weak CO₂ bands using GFIT. Two different retrievals were performed: (1) using the Voigt line shape with spectroscopic parameters from the atm line list and (2) using the qSDV+LM line shape with the best set of spectroscopic parameters that modeled the laboratory spectra as described in Sections 5.4.1 and 5.4.2.

5.5.1 Fitting the Strong CO₂ Band

A typical Eureka (eu) solar spectrum recorded at SZA 84.39° on March 17, 2014 was fitted using the Voigt with HITRAN 2012 CO₂ spectroscopic parameters and qSDV+LM and the empirical HITRAN 2008 parameters for the strong CO₂ band (see Figure 5.6). All other spectral lines, except solar lines, were fitted using a Voigt line shape with parameters from the atm line list. Solar lines were calculated using the empirical solar line list (Toon, 2014b). Figure 5.6 shows two residual spectra (measured minus calculated) in the top panel, where the red line indicates the residual for the current retrieval and the blue indicates the residual taking speed dependence and line mixing into account. The bottom panel shows the measured and calculated spectra, as well as the contribution from the various other absorbing species in this window. Taking both speed dependence and line mixing into account reduces the structure in the residual and decreases the RMS residual, but some structure remains.



Figure 5.6: A typical Eureka spectrum recorded at a SZA of 84.39° on March 17, 2014 for the strong CO₂ band, as shown in red dots on the bottom panel. The calculated spectrum, using qSDV+LM, is shown with black dots and the contribution from all species follows the colour code of the legend on the right. The top panel shows the two residuals (measured minus calculated spectrum). The red line is the residual for CO₂ absorption coefficients calculated using HITRAN 2008 parameters with a Voigt line shape. The percent RMS for the red residual is 0.80% (RMS1 in plot). The blue line is the residual when CO₂ absorption coefficients are calculated using the adjusted HITRAN 2008 parameters with qSDV+LM. The corresponding RMS residual is 0.61% (RMS2 in plot).

For a more robust test, solar spectra from Eureka, Park Falls (pa) (Washenfelder et al., 2006), Lamont (oc), and Darwin (db) (Deutscher et al., 2010) were fitted with the qSDV+LM spectral line shape. All four sites record spectra in accordance with TCCON standards and represent a large range of atmospheric conditions (hot, cold, wet, dry, etc.). Figure 5.7 shows the log of the percent RMS residual for the spectral fits plotted as a function of SZA. Figure 5.7a shows the log of the percent RMS residual resulting from fitting the spectra using the Voigt spectral line shape with HITRAN 2012 parameters. Figure 5.7b shows the log of the percent RMS residual for the qSDV+LM and the empirical HITRAN 2008 parameters. Figure 5.7c shows the percent difference of the percent RMS residual between the qSDV+LM and Voigt spectral line shapes for the different sites, given by the formula (Voigt –

(qSDV+LM))/Voigt. The spectral fits improve as a function of SZA with the greatest improvement at SZA of 82° using the new CO₂ absorption coefficients. Above 82° SZA, the difference decreases as a function of SZA. The average RMS residual using a Voigt line shape is $0.60 \pm 0.21\%$ and that using qSDV+LM is $0.49 \pm 0.22\%$.



Figure 5.7: The percent RMS residuals for solar spectra fitted with (a) a Voigt and HITRAN 2012 and (b) qSDV+LM and the empirical HITRAN 2008 parameters, for the strong CO₂ band as a function of SZA. (c) The percent difference, (Voigt - (qSDV+LM))/Voigt, between the RMS residual obtained using the Voigt and qSDV+LM spectral line shapes. Eureka measurements are in green, Park Falls in light blue, Lamont in red, and Darwin in dark blue.

Figure 5.8a shows XCO₂ calculated using the CO₂ column retrieved with a Voigt line shape and Figure 5.8b shows XCO₂ calculated from the CO₂ column retrieved using qSDV+LM. Figure 5.8c shows the percent difference, $(XCO_2^{qSDV+LM}- XCO_2^{Voigt})/XCO_2^{Voigt}$, for the XCO₂ retrieved using the different spectral line shapes. At the lowest SZA, 0.1% more CO₂ is retrieved with the new absorption coefficients with the difference decreasing until SZA of approximately 20° where there is no difference in CO₂ between the two retrievals. Less CO₂ is retrieved using the qSDV+LM as a function of SZA (for SZA>20°) peaking at about 2% less at SZA of 85°. For SZA greater than 85°, the retrieval with the Voigt line shape has less CO₂ (i.e., the airmass dependence changes) and so the difference between the spectral line shapes decreases. The absolute mean percentage difference in XCO_2 retrieved using the two sets of absorption coefficients is $0.40 \pm 0.42\%$ using measurements from all four sites and for all SZA.



Figure 5.8: XCO₂ (using CO₂ column retrieved from the strong CO₂ band) plotted as a function of SZA. (a) XCO₂ calculated using CO₂ column retrieved using a Voigt line shape. (b) XCO₂ calculated using CO₂ column retrieved using a qSDV+LM. (c) The percent difference $((XCO_2^{qSDV+LM}-XCO_2^{Voigt})/XCO_2^{Voigt})x100.$

5.5.2 Fitting the Weak CO₂ Bands

Figure 5.9 shows a typical spectral fit for the weak CO_2 band 1 for a measurement taken at Eureka at a SZA of 84.39°. The top panel shows the residual using a Voigt line shape (red) with spectroscopic parameters from the atm line list and using qSDV+LM (blue) with parameters from Devi et al. (2007a). Figure 5.10 shows the same spectrum but for the weak CO_2 band 2. Systematic structure seen in the Voigt residual is reduced in both windows when using the qSDV+LM spectral line shape. However, some systematic structure in the spectral fits remains.



Figure 5.9: A Eureka spectrum recorded at a SZA of 84.39° on March 17, 2014 for the weak CO₂ band 1, as shown in red dots on the bottom panel. The calculated spectrum using, qSDV+LM, is shown with black dots and the contribution from all species follows the colour code of the legend on the right. The top panel shows the two residuals (measured minus calculated spectrum). The red line is the residual for CO₂ absorption coefficients calculated using parameters from the atm line list with a Voigt line shape. The percent RMS for the red residual is 0.35% (RMS1 in plot). The blue line is the residual using parameters from Devi et al. (2007a) with qSDV+LM. The corresponding percent RMS residual is 0.29% (RMS2 in plot).



Figure 5.10: Same as Figure 5.9, but for the weak CO₂ band 2. The blue line is the residual using parameters from Devi et al. (2007b) with qSDV+LM.

Figures 5.11 and 5.12 are the same as Figure 5.7 but for the weak CO₂ bands 1 and 2 respectively. For both windows, as the SZA increases, the spectral fits are best when the qSDV+LM is used. The impact of the new absorption coefficients on the RMS residuals increases with SZA. At a SZA of 85°, the RMS residual at Eureka decreased by 25% while at Darwin it only decreased by 5%. The mean RMS residual from all measurements for the weak CO₂ band 1 was found to be $0.47 \pm 0.19\%$, and $0.51 \pm 0.20\%$ for the weak CO₂ band 2 when using a Voigt spectral line shape. Using the qSDV+LM, the mean RMS residual is $0.47 \pm 0.20\%$ for the weak CO₂ band 1 and $0.51 \pm 0.20\%$ for the weak CO₂ band 2.



Figure 5.11: Same as Figure 5.7 except log of percent RMS residual is for the weak CO_2 band 1 that was fitted with (a) the Voigt line shape and the atm line list parameters and (b) the qSDV+LM and line parameters from Devi et al. (2007a).



Figure 5.12: Same as Figure 5.7 except log of percent RMS residual is for the weak CO_2 band 2 that was fitted with (a) the Voigt line shape and the atm line list parameters and (b) the qSDV+LM and line parameters from Devi et al. (2007b).

Figure 5.13 shows XCO₂ for the CO₂ column that is the weighted average of CO₂ columns retrieved from the weak CO₂ bands as a function of SZA for all four sites, in the same way as in Figure 5.8. At all four sites, the column of CO₂ retrieved using qSDV+LM is 0.5% greater than the Voigt retrieval at a SZA of 1°. As the SZA increases, so does the amount of CO₂ retrieved with qSDV+LM compared to the Voigt line shape. At 70° SZA, the column of CO₂ retrieved with qSDV+LM is 0.6% greater compared to the Voigt retrievals. For SZA greater than 70°, the difference between the two retrievals decreases until a SZA of approximately 85°. Less CO₂ is retrieved with the qSDV+LM compared to the Voigt line shape for SZA greater than 85°. The absolute mean % difference in XCO₂ retrieved using the two sets of absorption coefficients is 0.57 ± 0.09% using measurements from all sites.



Figure 5.13: Same as Figure 5.8 except XCO_2 is calculated using CO_2 columns retrieved from the weak CO_2 bands.

To compare the two weak CO_2 bands, we look at the correlations between retrieved VSFs. Figure 5.14a shows the correlation between the VSFs retrieved using a Voigt spectral line shape. Figure 5.14b shows the correlation between the VSFs retrieved using the qSDV+LM. The line of best fit (black line) is also shown in each plot along with the correlation coefficient (r). The correlation between the weak bands is good as indicated by r, which is 0.88 for both spectral line shapes.



Figure 5.14: Correlations between the VSF retrieved using the weak CO₂ bands with the absorption coefficients calculated using: (a) the Voigt spectral line shape and the line parameters from the atm line list, (b) the qSDV+LM line shape and line parameters from Devi et al. (2007a; 2007b).

5.6 Discussion of Results

The use of speed dependence and line mixing was shown to improve the accuracy of fits to laboratory spectra for the strong and weak CO₂ bands. The EPG law was used to model offdiagonal relaxation matrix elements because Predoi-Cross et al. (2007a) showed that it gives better results for modeling first-order line mixing coefficients than the Energy Corrected Sudden (ECS) law (Lévy et al., 1992). Using the EPG law has two advantages: (1) the full relaxation matrix can be constructed to take into account mixing between multiple lines in the branch of a band; and (2) the temperature dependence of the first-order line mixing coefficient can be calculated (shown in Section 3). Off-diagonal relaxation matrix elements from Devi et al. (2007a; 2007b) were not used to construct the relaxation matrix because the temperature dependence of the sparameters is not available. Thompson et al. (2012) mention that neglecting the temperature dependence of line mixing could be one of the sources of the remaining residual structure in their modeling of laboratory spectra of the strong and weak CO₂ bands. First-order line mixing was used instead of full line mixing for two reasons: first, the studies by Predoi-Cross et al. (2007a; 2007b) fitted laboratory spectra using first-order line mixing, and second, to address the need to decrease the computation time for absorption coefficient calculations. To compute full line mixing requires calculation of the relaxation matrix and then diagonalization and inversion, which are computationally expensive processes. With this approach, there is no need to compute the relaxation matrix, as this is done off-line: all that is required is Eq. 5.7 to take into account first-order line mixing for air, self, and H₂O collisions.

One of the assumptions made when computing Lorentz widths of CO_2 is that the H₂Obroadening is 1.35 times the air-broadening. However, the study by Sung et al. (2009) shows that it is more likely to be twice the air-broadened width for rotational quantum number *J* higher than 10. This might have a small impact on measurements made through a wet atmosphere. If a study is done to determine the H₂O-broadened Lorentz width of CO₂ for the strong and weak CO₂ bands, the first-order line mixing coefficient for collisions with H₂O can be recalculated.

There are two differences between the empirical parameters that were used for the strong CO_2 band compared to those used for the weak CO_2 bands. The first is that the line intensity was not changed and since the line intensity represents the integrated line absorption, the choice of spectral line shape affects the line intensity. Long et al. (2011) showed that the integrated area of the spectral line obtained using a Voigt line shape was 2% lower than the speed-dependent hard collision line shape. Since not much is known about the intensity changes between the Voigt and speed-dependent Voigt, the intensities were left unchanged. The second difference is that the same speed-dependent parameter for all CO_2 lines was used for the strong band. The studies by Devi et al. (2007a) and Devi et al. (2007b) show that the speed-dependent parameter has a *J* (which here is the rotational quantum number for the lower energy state of the spectral line) dependence. If a study similar to Devi et al. (2007a) and Devi et al. (2007b) were done for the strong CO_2 band, it would be easy to incorporate those spectroscopic parameters into the absorption coefficient calculations to check if the spectral fits improve and the airmass dependence of the CO_2 from the strong band decreases.

The qSDV (Eq. 4.25) was used to take speed dependence into account instead of the numerical integration scheme (Eq. 4.24) in order to minimize absorption coefficient computing

time. In Tran et al. (2013), the numerical integration scheme was compared to the qSDV and the difference between calculated values was found to be on the order of 10^{-9} . When fitting solar spectra, absorption coefficients are calculated on our server at the University of Toronto. Daily absorption coefficient calculations are performed using an Intel(R) Xeon(R) CPU E5-2643 v2 @ 3.50GHz processor and takes approximately 4.5 s for a day's worth of solar spectra for the Voigt calculation for the weak CO₂ band 1. With the qSDV+LM, these absorption coefficient calculation twice when calculating the qSDV+LM.

In Section 5.4, we show that the airmass dependence of XCO₂ is different for the different spectral line shapes used for absorption coefficient calculations in the retrieval of CO₂ total columns. Currently, TCCON XCO₂ is retrieved from both weak CO₂ bands using the Voigt spectral line shape and the airmass dependence is corrected using an empirical formula detailed in Appendix A, Section (e) of Wunch et al. (2011). This airmass dependence must be corrected, otherwise this artifact would alias into the seasonal cycle and lead to spurious biases between sites, as the mean SZA changes throughout the year and with latitude. The empirical correction works well for XCO₂ recorded up to a SZA of 82° but fails to fit the shape of the airmass dependence for measurements taken at higher SZA (Figure 6 of Wunch et al., 2011). Using the qSDV+LM spectral line shape, the empirical airmass correction can be extended to measurements made at SZA \geq 82°. This would result in more data available from all TCCON sites.

6 Using High-Resolution Laboratory and Ground-Based Solar Spectra to Assess CH₄ Absorption Coefficient Calculations

6.1 Background on the $2v_3$ Band of CH₄

Total columns of CH₄ are retrieved from the $2v_3$ band of CH₄, which is centered at 6002 cm⁻¹. This is the same band used by SCIAMACHY and GOSAT to retrieve total columns of CH₄. Frankenberg et al. (2008) showed that incorrect spectroscopic line parameters led to a 1% bias in SCIAMACHY retrievals, with the greatest impact on high-latitude retrievals, and they proposed a new line list that improved fits to their atmospheric spectra. In that study, the Lorentz half-width coefficients and pressure-shift coefficients of each CH₄ line were left unconstrained in order to give the best fit in the multi-spectral fitting process. This resulted in a line list that significantly improved the spectral fits, but it does not properly describe the spectral line shape of CH₄. Tran et al. (2010) showed that taking into account full line mixing between CH₄ lines in the same manifold of a given branch (P and R branches of the $2v_3$ band) when fitting laboratory and solar spectra performed as well as the Voigt line shape with the spectroscopic line parameters of Frankenberg et al. (2008). This also resulted in a decrease in the airmass dependence of CH₄ total columns retrieved from ground-based solar absorption spectra.

Since then, significant improvements have been made to the CH₄ line list between 5500-6240 cm⁻¹, with new measurements of spectroscopic line parameters and the inclusion of weaker CH₄ lines (not used in Frankenberg et al., 2008) in studies such as Campargue et al. (2013) and Nikitin et al. (2010). The most recent study by Nikitin et al. (2015) has further improved on the work done in Nikitin et al. (2010) by including six new spectra in the retrieval of spectroscopic line parameters during the multi-spectral fitting process. Nikitin et al. (2015) used a Voigt spectral line shape when deriving spectroscopic line parameters for CH₄ to create the GOSAT 2014 CH₄ spectral line list. Direct spectral line shape studies of the P, Q, and R branches of the $2v_3$ band were recently performed by Devi et al. (2015; 2016). Both Devi et al. studies used an interactive multi-spectrum fitting process to retrieve line shape parameters with a speeddependent Voigt line shape and full line mixing. Off-diagonal relaxation matrix element coefficients were retrieved for lines in the P(10)-P(1), Q(10)-Q(1), and R(0)-R(10) manifolds for the first time. Laboratory spectra were used to test the calculation of absorption coefficients using different line shapes and spectroscopic parameters.

6.2 Assessing Absorption Coefficients using Laboratory Spectra

In order to validate CH₄ absorption coefficients calculated with different spectral line shapes and their corresponding spectroscopic line parameters, the forward model of the GFIT spectral fitting software is used to simulate laboratory spectra. The laboratory spectra were recorded at JPL, using a Bruker IFS 125HR FTS spectrometer at a resolution of 0.0056 cm⁻¹. All three spectra were obtained using dilute mixtures of CH₄ in air (with commercially available dry air from Airgas) using a 20.941 m coolable multi-pass Herriot cell (Mantz et al., 2014). Each spectrum was recorded with 99.999% ¹²C-enriched CH₄ to minimize interferences from other isotopologues. Table 6.1 lists the laboratory conditions for each spectrum.

Table 6.1: Experimental conditions for the air-broadened CH₄ laboratory spectra recorded with the Bruker IFS 125HR FTIR at JPL.

Spectrum name	Temperature (K)	Total pressure (atm)	CH ₄ volume mixing ratio
B0087.4a	170.0	0.38388	0.00238
B0087.5a	210.2	0.33643	0.00292
B0087.6b	248.1	0.40230	0.00371

The P branch window covers the spectral range of 5880-5995 cm⁻¹, the Q branch window spans 5996-6008 cm⁻¹, and the R branch window covers 6010-6145 cm⁻¹. Figures 6.1a, 6.2a, and 6.3a show the measured laboratory spectra for the P, Q, and R branches respectively. Currently, GFIT calculates absorption coefficients using a Voigt line shape (Eq. 4.20) and using spectroscopic line parameters from the atm line list (Toon, 2014a). For the spectral region 5880-6145 cm⁻¹, the spectroscopic line parameters for CH₄ are from HITRAN 2008 (Rothman et al., 2009), with the parameters for the 2v₃ band based on the study by Frankenberg et al. (2008), with *n* in Eq. 4.13 set to 0.85 in HITRAN 2008, which was not measured in Frankenberg et al. (2008). Additionally, the air-broadened widths for all CH₄ spectral lines in the interval of 5800 - 6000 cm⁻¹ are slightly adjusted by subtracting $0.002-0.01(E''/800)^2$ from the original value found in HITRAN 2008. This was done to improve the consistency of CH₄ retrievals from the three windows. Since the work by Frankenberg et al. (2008) the spectroscopic parameters for CH_4 in this region have been updated (as previously mentioned) with the recent measurements of Nikitin et al. (2015) to create the GOSAT 2014 CH_4 spectral line list using a Voigt line shape. Before comparing the performance of the Voigt line shape to the qSDV+LM, we first evaluated the atm and GOSAT 2014 CH_4 spectral line lists.

In these windows, the most intense CH₄ transitions (HITRAN intensity > 7.5×10^{-23} cm⁻¹/ (molecule cm⁻²)) belong to the $2v_3$ band. However, weak CH₄ transitions (HITRAN intensity < 7.5×10^{-23} cm⁻¹/(molecule cm⁻²)) are visible in the laboratory spectra and should be included in the simulation. When simulating the laboratory spectra using the GOSAT 2014 CH₄ spectral line list, it was found that the RMS residuals were worse than those obtained using the atm line list for both the P and R branch windows. This is because absorption coefficients calculated with the atm line list simulated some weak CH₄ transitions better than the GOSAT 2014 CH₄ spectral line list (not shown). These transitions were identified and the relevant GOSAT 2014 spectroscopic line parameters were replaced with those from the atm line list. This resulted in a better simulation of the laboratory spectra by the modified GOSAT 2014 CH₄ line list. When using a Voigt line shape, for the Q branch, with the original GOSAT 2014 CH₄ spectral line list the weak CH₄ transitions were simulated better than the atm line list (not shown).



Figure 6.1: (a) Laboratory spectra for the P branch of the $2v_3$ band of CH₄ with the colour for each spectrum indicated in the legend. (b) Residual (measured minus calculated spectra) using the Voigt line shape with spectroscopic line parameters from atm line list for all CH₄ lines. (c) Residual for the qSDV+LM and spectroscopic line parameters from Devi et al. (2015) for lines belonging to the $2v_3$ CH₄ band. For CH₄ transitions that do not belong to the $2v_3$ band, a combination of parameters from the GOSAT 2014, atm, and Devi et al. (2015) line lists with the Voigt line shape was used to calculate absorption coefficients as described in the text.



Figure 6.2: The same as Figure 6.1 but for the Q branch of the $2v_3$ band of CH₄.



Figure 6.3: The same as Figure 6.1 but for the R branch of the 2v₃ band of CH₄.

Figures 6.1b, 6.2b, and 6.3b show the residuals (measured minus calculated spectra) for the P, Q, and R branches respectively, when using a Voigt line shape with the spectroscopic line parameters from the atm line list used to simulate the spectral lines belonging to the P, Q, and R branch manifolds (labeled in each figure) of the $2v_3$ CH₄ band (as summarized in Table 6.2). For all three branches, the Voigt line shape cannot properly model most of the manifolds, as shown by the residual structure in Figures 6.1b, 6.2b, and 6.3b, which corresponds to transitions in the $2v_3$ band. This is because $2v_3$ band spectroscopic parameters in the atm line list are based on Frankenberg et al. (2008), who retrieved these parameters from room temperature laboratory spectra.

In Figures 3 to 5 of Frankenberg et al. (2008), the fitting residuals are between -0.01 and 0.01 for the 900.5 hPa (~0.89 atm) and 500.6 hPa (~0.49 atm) laboratory spectra. However, fits to the 240.1 hPa (~0.24 atm) and 126.1 hPa (~0.12 atm) spectra show residual structure that exceeds ± 0.01 . This suggests that some residual structure might be expected when trying to model low-pressure laboratory spectra using the parameters from Frankenberg et al. (2008) to calculate absorption coefficients. Figure 6 of Frankenberg et al. (2008) shows the fitted laboratory spectra (at 240.1 hPa and 126.1 hPa) for the R(6) manifold, with a maximum residual of ~0.01 and a minimum residual of ~-0.015. In Figure 6.3b of this study, the maximum residual is between 0.015 and 0.0175, while the minimum is between -0.0175 and -0.02 depending on the spectrum. So the peak-to-peak residuals in this study are larger than those of Frankenberg et al. (2008). Figure 6.3b also shows that the RMS residual increases as temperature decreases. The larger peak-to-peak residuals found in this study are due in part to the temperature dependence of some of the spectroscopic parameters and in part to the assumption of a perfect ILS. When Devi et al. (2015; 2016) fitted the laboratory spectra used in this study, the ILS distortion was taken into account to minimize the residual; this is not possible with GGG2014. Some of the residual structure for the P branch and the Q(11) to Q(9) manifolds is due to the air-broadened widths for CH₄ spectral lines being adjusted between 5800-6000 cm⁻¹ (as previously stated). This is also why the RMS residuals in the P and Q branches (Figures 6.1b and 6.2b) don't have the temperature dependence seen in the R branch (Figure 6.3b). However, the cause of the systematic residuals for the R(9) and R(10) manifolds (Figure 6.3b) is currently unknown. Spectroscopic parameters used to calculate the absorption coefficients for the R(9) and R(10)

manifolds in the atm line list are the same as those found in the supplementary file for Frankenberg et al. (2008).

Table 6.2: Summary of spectral line shapes and spectroscopic line lists used to calculate CH_4 absorption coefficients as shown in Figures 6.1b, 6.2b, 6.3b for the laboratory spectra and the red residuals in Figures 6.4a, 6.5a, and 6.6a.

Spectral range (cm ⁻¹)	Spectral line shape	Spectral line list parameters	HITRAN intensity cutoff cm ⁻¹ / (molecule cm ⁻²)
5880-5995	Voigt	atm	>1.0x10 ⁻²⁹
5996-6008	Voigt	atm	>1.0x10 ⁻²⁹
6010-6145	Voigt	atm	>1.0x10 ⁻²⁹

Devi et al. (2015; 2016) provide spectroscopic line parameters to calculate CH₄ absorption coefficients using the qSDV+LM line shape for CH₄ lines that belong to the P, Q, and R branches of the 2v₃ band. In order to take line mixing into account, it is necessary to construct the relaxation matrix (W) using the off-diagonal elements (ϵ_{ij}), measured in Devi et al. (2015; 2016). The temperature dependence of off-diagonal element coefficients was also taken into account using the temperature-dependent parameters in Devi et al. (2015; 2016). To calculate the rates of upward transfer (W_{ij}) we use the following formula:

$$W_{ij} = -P\left(X_{air}\epsilon_{ij}^{air}\left(\frac{296}{T}\right)^{n_{ij}^{air}} + X_{self}\epsilon_{ij}^{self}\left(\frac{296}{T}\right)^{n_{ij}^{self}}\right)$$
(6.1)

where n_{ij} is the temperature-dependent exponent of the off-diagonal relaxation matrix element coefficient ϵ_{ij} , air refers to collisions with air, and self refers to collisions with CH₄. In order to satisfy the detailed balance relationship (Lévy et al., 1992), we use the following formula:

$$W_{ji} = \left(\frac{\rho_j}{\rho_i}\right) W_{ij} \tag{6.2}$$

where ρ_j is the population of line *j* and ρ_i is the population of line *i*. The diagonal elements of **W** are the Lorentz widths given by Eq. 4.13. **W** is used with Eq. 4.15-4.17 to calculate v_i^{eff} , S_i^{eff} , and Y_i .

When taking full line mixing into account, the relaxation matrix (W) was calculated assuming a speed-independent relaxation matrix. This is because calculating a speed-dependent relaxation matrix is computationally costly, requiring that for every speed a v_i^{eff} , S_i^{eff} , and Y_i be calculated using Eq. 4.15-4.17 and used in Eq. 4.24, which is calculated using a numerical integration scheme. To save time v_i^{eff} , S_i^{eff} , and Y_i are calculated from the speed-independent relaxation matrix, with diagonal elements fixed to γ_{L_i} measured in Devi et al. (2015; 2016) and the qSDV+LM (Eq. 4.25) is used instead of the SDV+LM (Eq. 4.24).

Devi et al. (2015; 2016) also measured the temperature dependence of the pressure-shift coefficients for the $2v_3$ transitions with the pressure-shift coefficient calculated as:

$$\delta_i = \delta_i^o + \delta_i' \times (T - 296) \tag{6.3}$$

where δ_i replaces δ_i^o (which was defined before in Eq. 4.12, and δ'_i is the temperature dependence of the pressure-shift coefficient (in units of cm⁻¹ atm⁻¹ K⁻¹). Figures 6.1c, 6.2c, and 6.3c show the residuals using the qSDV+LM line shape when calculating the absorption coefficients for the 2v₃ transitions (as summarized in Table 6.3).

Table 6.3: Summary of new spectral line shapes and spectroscopic parameters used to calculate CH_4 absorption coefficients as shown in Figures 6.1c, 6.2c, 6.3c for the laboratory spectra and in Figures 6.4a, 6.5a, and 6.6a for the blue residuals.

Spectral range (cm ⁻¹)	Spectral line shape	Spectral line list parameters	HITRAN intensity cutoff cm ⁻¹ / (molecule cm ⁻²)
5880-5995	qSDV+LM	Devi et al. (2015)	>7.5x10 ⁻²³ (i.e. 2v ₃ P branch transitions)
	Voigt	Combination of GOSAT 2014 CH₄ spectral line list, atm, and Devi et al. (2015)	<7.5x10 ⁻²³
5996-6008	qSDV+LM	Devi et al. (2016)	>7.5x10 ⁻²³ (i.e. 2v ₃ Q branch transitions)
	Voigt	GOSAT 2014 CH₄ spectral line list, and Devi et al. (2016)	<7.5x10 ⁻²³
6010-6145	qSDV+LM	Devi et al. (2015)	>7.5x10 ⁻²³ (i.e. 2v ₃ R branch transitions)
	Voigt	Combination of GOSAT 2014 CH₄ spectral line list, atm, and Devi et al. (2015)	<7.5x10 ⁻²³

When first simulating the laboratory spectra, we found that there was residual structure in some of the $2v_3$ manifolds. On closer inspection of the structure, it was realized that some of the structure was not due to the spectral lines of the $2v_3$ band; rather it was caused by weaker transitions from other nearby bands. In order to reduce the differences between the calculated and measured spectra, spectral lines from the supplementary line list of Devi et al. (2015;2016) were substituted for the GOSAT 2014 CH₄ spectral line list. All manifolds of the $2v_3$ band were better simulated with the qSDV+LM when compared to the Voigt line shape, with some small residuals (less than ±0.01 difference) remaining in some manifolds.

6.3 Fitting Solar Spectra

TCCON solar spectra were fitted using GFIT, with the spectral line parameters from Devi et al. (2015; 2016) and qSDV+LM line shape used to calculate absorption coefficients. Figures 6.4, 6.5, and 6.6 show spectral fits for the P, Q, and R branches of the 2v₃ band of CH₄. This spectrum was recorded at Eureka on March 31, 2015, at a SZA of 77.43° (airmass of 4.4). The lower panel (b) in each figure shows the measured spectrum (red circles), the calculated spectrum (black circles), and transitions from all gases in the window (coloured lines, refer to the legend for different gases). The upper panel (a) in each figure shows the residuals for absorption coefficients calculated using: (i) in red, the Voigt line shape with spectroscopic line parameters from the atm line list for all CH₄ lines, as summarized in Table 6.2 (henceforth refered to as Voigt absorption coefficients), and (ii) in blue, the qSDV+LM with spectroscopic parameters from Devi et al. (2016; 2015) for transitions that belong to the $2v_3$ band. The weak CH₄ lines (HITRAN intensity $<7.5 \times 10^{-23}$ cm⁻¹/(molecules cm⁻²)), in the blue residual, were calculated using the Voigt line shape with a combination of spectroscopic line parameters from the GOSAT 2014 CH₄, atm and Devi et al. (2015; 2016) line lists, as summarized in Table 6.3. For both the blue and red residuals, spectral lines for all the other gases (except solar lines) were fitted with a Voigt line shape and spectroscopic line parameters from atm line list. Solar lines were fitted using the GGG2014 solar line list (Toon, 2014b). For all three windows, the spectral fits improved (blue lines) when absorption coefficients were calculated with the line shape and spectroscopic line parameters as described in Table 6.3 (henceforth refered to as qSDV+LM absorption coefficients) with the RMS residual equal to 0.274, 0.335, and 0.247 for the P, Q and R branches respectively (blue residuals in Figures 6.4, 6.5, and 6.6). These are improvements on the RMS residuals of 0.394, 0.597, and 0.321 for the P, Q, and R branches, respectively, obtained using the Voigt absorption coefficients (red lines).



Figure 6.4: Spectral fits to the P branch of the $2v_3$ band of CH₄ for a solar absorption spectrum recorded at Eureka at a SZA of 77.43° on March 31, 2015. (a) The residual (measured minus calculated) for the Voigt line shape with line parameters as given in Table 6.2 (in red, RMS1) and the qSDV+LM with line parameters as given in Table 6.3 (in blue, RMS2). (b) The measured (red circles, Tm) and calculated using the qSDV+LM (black circles, Tc) spectra, along with the gases included in the fit (refer to the legend to the right) in the spectral window.



Figure 6.5: Same as Figure 6.4 but for the Q branch of the $2v_3$ band of CH₄.



Figure 6.6: Same as Figure 6.4 but for the R branch of the $2v_3$ band of CH₄.

Frankenberg et al. (2008) tested the Voigt parameters (also measured in Frankenberg et al., 2008) on high-resolution ground-based spectra recorded at the TCCON site located in Bremen, Germany. The black residual shown in Figure 8 of Frankenberg et al. (2008) is the residual with no temperature dependence of the Lorentz width. As noted in Section 3, HITRAN 2008 gives the temperature-dependence exponent of the air-broadened Lorentz width of each line belonging to the $2v_3$ band (0.85 for all lines in the $2v_3$ band). So the red residual in Figures 6.4-6.6 is obtained using the Voigt line shape calculated using the spectroscopic parameters of Frankenberg et al. (2008) but with the temperature dependence of the Lorentz width set to 0.85 for all lines in the $2v_3$ band. When one compares the red residual in Figures 6.5 and 6.6 (Voigt with temperature dependence) to the black residual of Frankenberg et al. (2008) (Voigt without temperature dependence) there seems to be a slight improvement for the Q(1)-Q(7) manifolds, but large residuals still remain for the Q(8)-Q(10) manifolds, which are significantly reduced by the qSDV+LM line shape and the spectroscopic parameters from Devi et al. (2016). The inclusion of temperature dependence for the Voigt parameters does not impact the residual structure of the R branch (when comparing Figure 8 of Frankenberg et al. (2008) to Figure 6.6 in this study). However, with the qSDV+LM line shape and the spectroscopic parameters from Devi et al. (2015), the residual structure decreases for most of the R branch manifolds except for the R(10) manifold.

To further evaluate the qSDV+LM absorption coefficients, a year of solar spectra from Eureka, Park Falls, Lamont, and Darwin were used to retrieve total columns of CH₄. Figures 6.7a, 6.7b, and 6.7c show the percent difference of the RMS residual, (Voigt minus (qSDV+LM))/Voigt, for the P, Q, and R branches, respectively. This figure shows that the spectra are fitted better with the qSDV+LM absorption coefficients, with the greatest impact on measurements recorded at SZA > 70° for all three branches. The RMS residuals decrease by approximately 45% for the P branch, 60% for the Q branch, and 40% for the R branch, at a SZA of almost 90°. The average RMS residuals using all spectra are 0.457 \pm 0.160, 0.563 \pm 0.182, and 0.435 \pm 0.169, for the P, Q, and R branches, respectively, using the Voigt line shape and the atm line list to calculate absorption coefficients, where error bars represent 1 σ . With the qSDV+LM absorption coefficients, the average RMS residuals are 0.434 \pm 0.153, 0.491 \pm 0.177, and 0.422 \pm 0.165, for the P, Q, and R branches, respectively.


Figure 6.7: The percent difference of the RMS residuals (qSDV+LM fit minus the Voigt fit, divided by the Voigt fit) of the fitted solar spectra for the: (a) P branch, (b) Q branch, and (c) R branch for spectra from Eureka (eu), Park Falls (pa), Lamont (oc), and Darwin (db).

Each CH₄ window, corresponding to one of the branches of the $2v_3$ band, is used to retrieve a VSF that is applied to the a priori profile to calculate the total column of CH₄. Figure 6.8 shows the correlations between the VSFs retrieved in the three spectral fitting windows. Figures 6.8a, 6.8b, and 6.8c show the correlations between the P and R, Q and P, and Q and R branches, respectively. For these figures, the VSF was retrieved using the Voigt absorption coefficients. Figures 6.8d, 6.8e, and 6.8f are the same as Figures 6.8a, 6.8b, and 6.8c respectively, but the retrievals were done using the qSDV+LM absorption coefficients for transitions in the $2v_3$ band. The correlation between each pair of windows using the Voigt absorption coefficients is good as indicated by the line of best fit and the correlation coefficient (r) shown in the plots. With the qSDV+LM absorption coefficients, the correlation between each pair of windows is also good, indicating that regardless of the choice of spectral line shape, the VSFs retrieved from the different windows are similar.



Figure 6.8: Correlations between CH_4 VSF retrieved using the three spectral fitting windows. (a) R vs P, (b) P vs Q, and (c) R vs Q for VSFs retrieved with the Voigt line shape. (d) R vs P, (e) P vs Q, and (f) R vs Q for VSFs retrieved with the qSDV+LM. Each panel also shows the equation for the line of best fit as well as the correlation coefficient (r). The green dots indicate Eureka, cyan for Park Falls, red for Lamont, and dark blue for Darwin.

The average ratio of total column CH₄ retrieved from all spectra using the qSDV+LM absorption coefficients is 1.011 ± 0.003 relative to the Voigt absorption coefficients. Figure 6.9 shows the average ratio of the total columns retrieved using the two spectral line shapes plotted as a function of SZA for each site. All the data have been sorted into 10° SZA bins for each site and each marker on the plot is the mean of the binned data with the error bar representing 1σ . Figure 6.9 shows that at very low SZA (i.e., $1-10^{\circ}$), 1.2% more CH₄ is retrieved with qSDV+LM absorption coefficients than with the Voigt absorption coefficients, but as the SZA increases the difference between the two retrievals decreases to approximately 0.5% or less. Although the performance of the different spectral line shapes is similar at small SZA (as given by the percent difference in RMS residual shown in Figure 6.7), the spectroscopic parameters used to calculate the absorption coefficients are different. Chesnokova et al. (2016) showed that the total column of CH₄ retrieved using a Voigt line shape will differ with the choice of spectral line list has a greater influence on the retrieved column of CH₄ than the line shape.



Figure 6.9: Ratio of total column CH₄ retrieved using the qSDV+LM to that retrieved using the Voigt line shape plotted as a function of SZA for all four sites. The data were put into 10° SZA bins , with each marker indicating the mean of the ratio for all data in the 10° bin, with error bars indicating 1σ .

Figure 6.10 shows the column-averaged dry-air mole fraction of CH₄ (XCH₄) plotted as a function of SZA for solar absorption spectra recorded at Park Falls on June 30, 2013 for the entire day. Figure 6.10a shows XCH₄ for the column of CH₄ retrieved using a Voigt absorption coefficients (red crosses) and the qSDV+LM absorption coefficients (blue squares). Total columns of CH₄ retrieved using the Voigt absorption coefficients increase as a function of SZA. At a SZA of approximately 82° the retrieved column of CH₄ for both retrievals are almost equal. To examine just the shape of the airmass dependence, the total columns retrieved using the Voigt line shape (red crosses in Figure 6.10b) were adjusted by multiplying the column amounts by 1.012 (the average bias for measurements at SZA 1-10°) to remove the bias between the two retrievals. The retrievals performed with the Voigt absorption coefficients have an airmass dependence, with XCH₄ decreasing as a function of SZA from 10°-30° and remaining almost constant until about 60° after which it increases. In contrast, the XCH₄ retrieved using the qSDV+LM absorption coefficients (blue squares in Figure 6.10b) decreases monotonically as a function of SZA. This is because the CH₄ column retrieved with the qSDV+LM absorption

coefficients decreases as a function of SZA (as shown in Figure 6.9) while the retrieved O_2 column increases as a function of SZA, so when taking the ratio of CH₄ to O_2 , XCH₄ further decreases as a function of SZA.



Figure 6.10: Example of the airmass dependence of XCH₄ from one day of measurements at Park Falls (June 30, 2013) using the absorption coefficients calculated with the Voigt (red crosses) and qSDV+LM (blue squares). (a) Airmass dependence of XCH₄ from retrievals with the Voigt line shape and the qSDV+LM. (b) is the same as (a) but XCH₄ retrieved with the Voigt line shape are multiplied by 1.012.

In order to identify which aspects of the spectral line shape have the greatest impact on the airmass dependence of XCH₄, CH₄ total columns were retrieved using the spectroscopic parameters from Devi et al. (2015; 2016) and different line shapes. Figure 6.11 shows the airmass dependence for solar absorption spectra recorded at Park Falls on June 30, 2013 with six different spectral line shapes. (i) The orange stars indicate the CH₄ total column retrieved with a Voigt line shape (Eq. 4.20) and no temperature dependence (n=0 in Eq. 4.13 and δ'_i =0 in Eq. 6.3). (ii) The red squares indicate the columns retrieved with the qSDV (Eq. 4.25) with no line mixing and no temperature dependence (denoted as TD in the figure). The airmass dependence for the qSDV is not much less than that for the Voigt line shape at SZA < 60°, but more XCH₄ is retrieved with the qSDV for SZA > 60°. (iii) The cyan stars indicate the retrieval done with a Voigt line shape with line mixing (Voigt+LM) and (iv) the green squares indicate the retrieval with the qSDV with line mixing (qSDV+LM). For both of these retrievals, the temperature dependence of the spectroscopic parameters (including line mixing Eq. 6.1, $n_{ij}^{air}=0$ and $n_{ij}^{self}=0$) was not taken into account. The inclusion of line mixing for both of these retrievals significantly decreases the airmass dependence of XCH₄, which is consistent with what was shown in Tran et al. (2010). The temperature dependence was taken into account for (v) the Voigt+LM+TD retrievals (black stars) and (vi) the qSDV+LM+TD retrievals (blue squares). Including the temperature dependence results in less CH₄ retrieved (compared to disregarding temperature dependence) for SZA < 70°, and more for SZA > 70°. Therefore, line mixing has the greatest impact on the retrieval of CH₄ from the 2v₃ band, with speed dependence and temperature dependence affecting measurements made at SZA greater than approximately 60° and 70°, degrees respectively.



Figure 6.11: The airmass dependence of XCH₄ from one day of Park Falls solar absorption spectra recorded on June 30, 2013 retrieved using spectrosopic parameters from Devi et al. (2015; 2016) with a Voigt, Voigt+LM, Voigt+LM+TD, qSDV, qSDV+LM, and qSDV+LM+TD.

6.4 Discussion of Results

Absorption coefficients calculated using different spectral line shapes and spectroscopic parameters were tested using high-resolution laboratory spectra recorded in the $2v_3$ band of CH₄. The spectra calculated using the qSDV+LM and spectroscopic line parameters from Devi et al. (2016; 2015) reproduced the laboratory spectra better than the Voigt with spectroscopic line parameters from the atm line list for the P, Q, and R branches of the $2v_3$ band of CH₄. This was expected because the same laboratory spectra were used to retrieve the spectroscopic line parameters using the speed-dependent Voigt line shape with line mixing in the studies by Devi et al. (2015; 2016). However, the laboratory spectra were useful for testing the implementation of a speed-dependent Voigt with full line mixing scheme in the forward model of the GGG software.

In the studies by Devi et al. (2015; 2016), residual differences of less than ± 0.005 between the measured and calculated laboratory spectra were achieved. In this study, the manifolds of the P, Q, and R branches were simulated with a difference of less than ±0.01 (with most within ± 0.005). The reason we are not able to calculate the laboratory spectra as well as Devi et al. (2015; 2016) can be attributed to the differences between GGG and the spectral fitting software used in Devi et al. (2015; 2016). There are many differences between the two spectral fitting routines, with two major differences in particular. First, in the multi-spectrum fitting procedure used in Devi et al. (2015; 2016) the ILS distortion including residual phase error correction is taken into account to minimize the fitting residuals. This was not done in this study because the GGG software cannot fit the ILS distortion. Secondly, three spectral line lists (as detailed in Table 6.3) were combined to create one line list. While the Devi et al. (2015; 2016), studies used a single line list. It was necessary to create a new line list in this study because the line list that is given in Devi et al. (2016; 2015) does not include some weak CH₄ lines in the spectral range of the TCCON windows. As shown in Figures 6.4-6.6, not only has the residual structure for the 2v₃ manifolds decreased for the solar spectra but so has the structure in between the manifolds, which is due to the inclusion of the GOSAT 2014 CH₄ spectral line list.

This work shows that there is an airmass dependence for the retrieved total column of CH₄ regardless of choice of spectral line shape. If left uncorrected, this airmass dependence artifact would lead to unrealistic differences in the seasonal cycle of XCH₄ from different

geographical regions because the mean SZA varies seasonally and with latitude. To correct for this airmass dependence, TCCON uses an empirical formula detailed in Appendix A, Section (e) of Wunch et al. (2011), which works well for measurements made with a Voigt line shape up to a SZA of about 82°. At large SZAs, the shape of the airmass dependence of the retrieved column of CH₄ changes (from decreasing as a function of SZA to increasing), making the simple function used to model the symmetrical component no longer valid, since the function only takes into account the column decreasing as a function of SZA. This poses a problem for polar sites (like Eureka) which do not go through a full range of SZA throughout the day. At Eureka, there are four months of no sunlight, followed by two months of the sun being above 82° SZA. This limits the data available from high-latitude sites, and thus limits our ability to monitor CH₄ in the polar regions. With the qSDV+LM, the airmass dependence of XCH₄ decreases monotonically as a function of SZA, so the airmass correction can be expanded to include all SZA, resulting in more data available from TCCON sites, especially at high latitudes. The remaining airmass dependence is due to the airmass dependence of the O₂ column used to calculate XCH₄.

TCCON measurements of XCH₄ have been compared to aircraft profile measurements of XCH₄ made with instruments calibrated to meet World Metrological Organization (WMO) standards as detailed in Wunch et al. (2010). When comparing TCCON measurements of XCH₄ to aircraft profiles (Wunch et al., 2010) found a bias of 0.978 ± 0.002 (i.e. TCCON measurements were 2.2% lower than the aircraft measurements). In this study, we have shown that with the qSDV+LM absorption coefficients we retrieve on average 1.1% more CH₄ than with the Voigt absorption coefficients, with the implication being that half of the bias between TCCON and aircraft measurements of XCH₄ is due to the choice of absorption coefficients used in the retrieval of CH₄ total columns.

7 Decreasing the Airmass Dependence of TCCON XCO₂ Measurements

7.1 Background

In the study by Mlawer et al. (1998), ground-based solar absorption spectra were recorded in the NIR region to study the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ band of O₂ centered at 1.27 µm (which will be referred to as the 1.27 µm band). The spectra were compared to a line-by-line radiative transfer model and the differences between the measured and calculated spectra showed the need for better absorption coefficients in order to accurately model the 1.27 µm band (Mlawer et al., 1998). Subsequently, spectroscopic parameters needed to calculate the absorption coefficients from discrete transitions of the 1.27 µm band were measured in multiple studies by Cheah et al. (2000), Newman et al. (1999; 2000), and Smith and Newnham (2000). Collision-induced absorption (CIA) parameters were measured by Maté et al. (1999), and Smith and Newnham (2000), while Smith et al. (2001) validated the work done by Smith and Newnham (2000).

The 1.27 μ m band is of particular importance to TCCON because the O₂ column retrieved from this band is used to calculate X_G. This band is used because of its close proximity to the spectral lines used to retrieve CO₂, thereby reducing the impact of solar tracker mispointing and an imperfect ILS (Washenfelder et al., 2006). To improve the retrievals of O₂ from the 1.27 μ m band Washenfelder et al. (2006) found the need to adjust the spectroscopic parameters in HITRAN 2004 (Rothman et al., 2005). This decreased the airmass and temperature dependence of the O₂ column. These revised spectroscopic parameters were included in HITRAN 2008 (Rothman et al., 2009). Atmospheric solar absorption measurements from this band made at Park Falls by Washenfelder et al. (2006) were the first measurements to observe the electric-quadrupole transitions (Gordon et al., 2010). Leshchishina et al. (2011; 2010) subsequently used cavity-ring-down spectra to retrieve spectroscopic parameters for the 1.27 μ m band using a Voigt spectral line shape and these parameters were included in HITRAN 2012 (Rothman et al., 2013). The need to include non-Voigt effects when calculating absorption coefficients for the O_2 1.27 µm band was first shown by Hartmann et al. (2013) and then by Lamouroux et al. (2014). In both studies, Lorentz widths were calculated using the re-quantized classical molecular-dynamics simulations (rCMDSs) and used to fit cavity-ring-down spectra with a Voigt line shape for some isolated transitions in the O_2 1.27 µm band. The studies concluded that a Voigt line shape is insufficient for modeling the spectral lines of the O_2 1.27 µm band and that effects such as speed dependence should be included in the line shape calculation.

7.2 Fitting Laboratory Spectra

O₂, unlike CO₂ and CH₄, cannot produce an electric dipole moment and therefore should not be infrared active. However, O₂ has two unpaired electrons in the ground state that produce a magnetic dipole moment. Due to the unpaired electrons in the ground state $(X^3\Sigma_g^-)$ the rotational state (*N*) is split into three components which are given by J = N-1, J = N, and J = N+1. While in the upper state $(a^1\Delta_g)$, J = N. When labeling a transition, the following nomenclature is used $\Delta N(N'')\Delta J(J'')$ (Leshchishina et al., 2010), where ΔN is the difference between *N* in the upper state and *N* in the lower state, (*N*) is *N* in the lower state, ΔJ is the difference between *J'* in the upper state and *J''* in the lower state. The magnetic transitions of $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ allow for $\Delta J=0$, ± 1 . This leads to 9 branches observed: P(N'')Q(J''), R(N'')Q(J''), and Q(N'')P(J''), for $\Delta J=0$, O(N'')P(J''), P(N'')P(J''), and Q(N'')P(J''), for $\Delta J=-1$, and S(N'')R(J''), R(N'')R(J''), and Q(N'')R(J''), for $\Delta J=1$ (Leshchishina et al., 2010).

Absorption coefficients for three room temperature air-broadened (79.28% N_2 , 20.72% O_2 , 0.0029% Ar, 0.00015% H_2O) spectra were measured at NIST using the cavity-ring-down spectroscopy (CRDS) technique (Long et al., 2010). A cavity-ring-down instrument consists of a cell with two highly reflective mirrors on each end, a laser, and a detector. The beam from the laser enters the cavity and reaches resonance with a cavity mode. Intensity inside the cavity builds up due to constructive interference. Once the laser is turned off (or pulsed), the intensity leaks out through one of the mirrors that is less reflective than the other. The detector placed behind the less reflective mirror measures the intensity of the radiation leaking out as a function of time. The intensity escaping from the cavity can be determined as an exponential function of time. This is done twice, once with an empty cell and once with the absorbing gas in the cell. The

relationship between empty and full cell decay times (the time it takes for the intensity to drop by 1/e) is dependent on the absorption coefficient of the gas in the cell. Absorption spectra were acquired at pressures of 1.29 atm, 0.98 atm, and 0.66 atm, at temperatures of 296.28 K, 296.34 K, and 296.30 K respectively. Figure 8.1a shows the three measured absorption spectra.



Figure 7.1: (a) Cavity-ring-down absorption coefficients measured at three pressures indicated in the legend at approximately room temperature and a volume mixing ratio of 0.2072 for O_2 . (b) The difference between measured absorption coefficients and those calculated using a Voigt line shape. (c) Difference between the measured absorption coefficients and those calculated using the qSDV.

The spectra were fitted individually using a Voigt line shape (Eq. 4.20) with no line mixing), with S_i , $\gamma_{L_i}^o$, and δ_i^o retrieved for the main isotope of the magnetic dipole lines of the O₂ 1.27 µm band for lines with an intensity greater than 7.0x10⁻²⁸ cm⁻¹/(molecule cm⁻²). The spectroscopic parameters measured by Leshchishina et al. (2010) were used as the a priori for the retrieved spectroscopic parameters for the spectral lines of interest. The v_i^o were left fixed to the values measured by Leshchishina et al. (2010), and all other O₂ spectral lines (intensity < 7.0x10⁻²⁸ cm⁻¹/(molecule cm⁻²)) were calculated using a Voigt line shape with spectroscopic parameters from HITRAN 2012. Spectral fits were done using the lsqnonlin function in Matlab, with a user-defined Jacobian matrix. The Jacobian was constructed by taking the derivative of

the absorption coefficients with respect to the parameters of interest. Using an analytical Jacobian instead of the finite difference method is both computationally faster and more accurate. The Voigt line shape was calculated using the Matlab code created by Abrarov and Quine (2011) to calculate the complex error function and its derivatives.

In addition to transition from the discrete lines CIA is also observed (Rothman et al., 2013). CIA happens when inelastic collisions induce a dipole moment which lasts for a very short time allowing the molecule to absorb a photon. Since CIA is due to collisions from translational motion, discrete lines are not seen rather a continuum is formed. To take CIA into account, a set of 50 Legendre polynomials were added together by retrieving the weighting coefficients needed to add the polynomials to fit the CIA for each spectrum. Figure 7.1b shows the residual (measured minus calculated absorption coefficients) when using a Voigt line shape with the retrieved spectroscopic parameters. The plot shows that residual structure still remains for all three spectra. The RMS residual values for the spectra are given by the legend at the side of the plot.

Figure 7.2 is the same plot as Figure 7.1 but for the P(11)P(11), P(11)Q(10), P(9)P(9), and P(9)Q(8) spectral lines only. Figure 7.2b shows that for all four spectral lines there is a "W" shaped residual at the line center. The P(11)P(11) line was also measured by Hartmann et al. (2013) at pressures ranging from 50 to 800 Torr. Figure 5 of Hartmann et al. (2013) shows the P(11)P(11) line at a pressure of 500 Torr, which is approximately the pressure of the 0.66 atm spectrum (blue spectrum in Figures 8.1 and 8.2). Comparing the blue residual of the P(11)P(11) line in Figure 7.2b to that of the residual of the left panel of Figure 5 of Hartmann et al. (2013), one can see that the residuals are the same. Figure 6 of Hartmann et al. (2013) shows that the amplitude of the residual increases with decreasing pressure, which is also seen in Figure 7.2b. Figure 3 of Lamouroux et al. (2014) shows the same "W" residual for the P(9)P(9) lines and that the amplitude of residual increases with decreasing pressure (although for lower pressures than this study) confirming the results for the P(9)P(9) line shown in Figure 7.2b.



Figure 7.2: The same as Figure 7.1 but zoomed to show four spectral lines in the P branch of the $O_2 1.27 \mu m$ band.

Figure 7.1c shows the residual when using the speed-dependent Voigt line shape (Eq. 4.24 with no line mixing) to fit each spectrum individually. To use Eq. 4.24 requires integration over all possible speeds, which is not computationally practical, so we employ the simple numerical integration scheme as done by Wehr (2005). When fitting the spectra, parameters S_i , $\gamma_{L_i}^o$, δ_i^o , $a_{\gamma_{L_i}}$ and $a_{\delta_i^o}$ were fitted for lines of intensity greater than 7.0x10⁻²⁸ cm⁻¹/(molecule)/cm, while all other O₂ lines were calculated using a Voigt line shape and spectroscopic parameters from HITRAN 2012. The Jacobian matrix was created by taking the derivative with respect to each parameter of interest, as done with the Voigt fits. By taking speed-dependent effects into account, the residuals were reduced to as much as 25 times smaller than those for the Voigt fits and the RMS residuals (given in the legend of Figure 7.1c) are 10 times smaller. However, some residual structure still remains, which is more evident in the Q and R branches than in the P branch. Figure 7.2c shows the four lines in the P branch, as discussed when analyzing the Voigt fits. A small residual "W" remains at line center, as well as residuals from weak O₂ lines.

Figure 7.3 shows the averaged S_i , $\gamma_{L_i}^o$, δ_i^o , and $a_{\delta_i^o}$, retrieved from the three spectra, plotted as a function of rotational quantum number J. The intensity, Lorentz widths, and pressure shifts show a *J* dependence for these parameters for the P and R branches. The measured Lorentz widths and pressure shifts for the Q branches show a I dependence but are not as strong as the P and R branches. This is because the Q branch lines are broadened enough to blend with each other since they are spaced closer together than the P or R branch lines. Figure 7.1c shows that some of the residual structure in the Q branch increases with pressure and is partly due to the blending of these transitions as the pressure increases. The weak O₂ absorption lines also blend in with the Q branch, contributing to the residual structure in Figure 7.1c. The spectroscopic parameters for the weak O₂ absorption lines were not retrieved since they were blended with the strong O₂ lines. Figure 7.4a shows the average $a_{\gamma_{L_i}}$ retrieved from the three spectra, plotted as a function of rotational quantum number *J*, showing that it increases with *J*. Error bars correspond to the 1σ standard deviation and are large regardless of sub-branch. Figure 7.4b shows the retrieved speed-dependent width for the PQ sub-branch for the different pressures. The retrieved speed-dependent width parameter shows the same J dependence regardless of pressure, but it also increases with decreasing pressure. This is the case for all other sub-branches.



Figure 7.3: The averaged retrieved spectroscopic parameters from the O₂ laboratory spectra: (a) intensity (S_i ,). (b) Lorentz width ($\gamma_{L_i}^o$), (c) pressure shift (δ_i^o), and (d) speed-dependent pressure shift ($a_{\delta_i^o}$). All data are plotted as a function of lower state rotational quantum number *J* and error bars are 1 σ .



Figure 7.4: (a) The average speed-dependent Lorentz width parameter $(a_{\gamma L_i})$, retrieved from the O₂ laboratory spectra, plotted as a function of lower state rotational quantum number J. (b) The measured speed-dependent width parameter for spectral lines that belong to the PQ sub-branch plotted as a function of lower state rotational quantum number J.

7.3 Fitting Solar Spectra

The forward model of GFIT calculates absorption coefficients for the discrete lines of the O_2 1.27 µm band using a Voigt line shape and spectroscopic parameters from Washenfelder et al. (2006) and Gordon et al. (2010). To take CIA into account, absorption coefficients are calculated using a Voigt line shape and spectroscopic parameters from the foreign-collision-induced absorption (FCIA) and self-collision-induced absorption (SCIA) spectral line lists provided with the GGG software package (Wunch et al., 2015). Spectroscopic parameters in the FCIA and SCIA line lists were retrieved by Geoff Toon by fitting the laboratory spectra of Smith and Newnham (2000). This was done by retrieving the integrated absorption at every 1 cm⁻¹ of the spectrum and using a Voigt line shape, with fixed Lorentz width and no pressure shift. In GFIT, a volume scale factor is retrieved for the CIA and discrete lines separately so that the O_2 column is derived from the discrete lines of the 1.27 µm band only. The continuum level and tilt of the 100% transmission level is fitted using a weighted combination of the first two Legendre

polynomials. Absorption coefficients for all other trace gases are calculated using a Voigt line shape and spectroscopic parameters from the atm line list. Solar lines are fitted using the solar line list (Toon, 2014b).

Figure 7.5 shows the spectral fit to a solar absorption spectrum recorded at Eureka on March 31, 2015, at a SZA of 77.43° (airmass of 4.4). The measured spectrum (red circles), calculated spectrum (black circles) and transitions from all gases in the window (coloured lines, refer to the legend for different gases) are shown in Figure 7.5b. The residual using a Voigt line shape with spectroscopic parameters from the atm line list to calculate the discrete lines of the O₂ $1.27 \,\mu\text{m}$ band is shown in red in Figure 7.5a. The blue residual is the result of using a speeddependent Voigt line shape with the spectroscopic parameters retrieved from fitting the absorption coefficients in Section 7.2. To decrease the amount of time it takes to calculate the absorption coefficients Eq. 4.25 was used instead of Eq. 4.24, since it requires the Voigt calculation only twice, while Eq. 4.25 requires a numerical integration scheme that calculates the term in the integrand 33 times. The temperature-dependent parameter of the Lorentz width of the discrete lines of the O₂ 1.27 µm band reported in HITRAN 2012 was used to take temperature dependence into account for $\gamma_{L_i}(T)$. There was only a slight improvement with the new absorption coefficients (using the qSDV), as seen in Figure 7.5a. Absorption coefficients calculated with the qSDV were used to retrieve total columns of O₂ from a year of solar spectra recorded at Eureka, Park Falls, Lamont, and Darwin. In total 131,124 spectra were fitted using the qSDV and the RMS residual of the fit only decreased by 0.5% relative to fits using the Voigt line shape.



Figure 7.5: (a) The residuals (measured minus calculated) for a spectrum measured at Eureka on March 31, 2015 at a SZA of 77.43°. The red residual is the result of using the Voigt line shape and the blue is from using the qSDV. (b) The measured (red dots) and calculated (black dots), with the qSDV spectrum, along with the gases included in the fit (refer to the legend to the right) in the spectral window.

7.4 Impact of O₂ Columns on XCO₂ Measurements

The O_2 column retrieved from the 1.27 µm band with a Voigt line shape and spectroscopic parameters from the atm line list increases as a function of solar zenith angle and thus exhibits an airmass dependence. Using a years' worth of spectra from Eureka, Park Falls, Lamont, and Darwin, total columns of O_2 were retrieved using (1) a Voigt spectral line shape with spectroscopic parameters from the atm line list and (2) the qSDV with the spectroscopic parameters determined in Section 7.2. Figure 7.6 shows the percent difference calculated as the column from the qSDV retrieval minus the column from the Voigt retrieval, which was then divided by the latter and multiplied by 100, plotted as a function of SZA. At the smallest SZA, the qSDV retrieves 0.75% less O_2 than the Voigt, with the difference increasing to approximately 1.8% as the SZA reaches 90°.



Figure 7.6: The percent difference between the O_2 column retrieved with the Voigt line shape and the qSDV for a year of measurements from Eureka (eu), Park Falls (pa), Lamont (oc), and Darwin (db).

7.4.1 Airmass Dependence of XCO₂

Recall that Eq. 3.13 is used to correct the XCO₂ data for the airmass dependence of XCO₂, but requires determining the correction factor α for XCO₂. To determine α for the different line shapes, total columns of CO₂ were retrieved using the Voigt line shape and the qSDV+LM (described in Section 5.5.2). Henceforth, XCO₂ calculated from O₂ and CO₂ both retrieved using the Voigt line shape will be referred to as "XCO₂ Voigt". Also, XCO₂ calculated by using CO₂ retrieved with qSDV+LM, as described in Section 5.5.2, and O₂ retrieved with the qSDV, will be referred to as "XCO₂ qSDV". For each day of XCO₂ data from Darwin, Lamont, and Park Falls Eqs. 3.10-3.12 are used to determine α for XCO₂ Voigt and XCO₂ qSDV.

Figure 7.7 shows the average α calculated for each season at Darwin, Lamont, and Park Falls. Eureka XCO₂ cannot be used to determine α because Eureka measurements do not go through the same range of SZAs as the other three sites due to its geolocation. The average α for XCO₂ Voigt are represented by stars in Figure 7.7, while the squares indicate XCO₂ qSDV. At all three sites, α is closer to 0 when the qSDV line shape is used in the retrieval compared to the Voigt retrieval, regardless of the season. The average α for XCO₂ Voigt calculated from a year of measurements from Darwin, Lamont, and Park Falls is -0.0071±0.0057 (1 σ) and that for XCO₂ qSDV is -0.0012±0.0054.



Figure 7.7: The average airmass-dependent correction (α) factor for XCO₂ derived from a year of spectra measured at Darwin, Lamont, and Park Falls for different seasons. The dashed lines with stars are XCO₂ retrieved using a Voigt line shape for both CO₂ and O₂ columns. The solid lines with squares are from XCO₂ retrieved using the qSDV for both CO₂ and O₂ columns.

For all four sites, $\alpha = -0.0071$ is used to correct XCO₂ Voigt measurements. Figure 7.8a shows the XCO₂ Voigt anomalies plotted as a function of SZA. The data are expressed as the daily XCO₂ anomaly, which is the difference between the XCO₂ value and the daily median value, in order to remove the seasonal cycle. When XCO₂ is left uncorrected, there is a clear airmass dependence whereby the amount of XCO₂ decreases as a function of SZA up to a SZA of approximately 82°, at which point XCO₂ increases as a function of SZA. Figure 7.8b shows XCO₂ Voigt corrected for the airmass dependence. This airmass correction works well up to a SZA of approximately 82°, after which the correction only serves to increase the airmass dependence. Figure 7.8c is the same as 7.8a but for the XCO₂ qSDV measurements corrected with $\alpha =$

-0.0012. When the airmass correction is applied to XCO_2 qSDV, there is a small difference between XCO_2 qSDV corrected and uncorrected, with the difference only noticeable for the Darwin measurements recorded at SZA > 60°. For XCO_2 qSDV measurements made at SZA > 82°, XCO_2 does not increase with SZA as it does with the Voigt.



Figure 7.8: (a) XCO₂ Voigt anomaly for a year of measurements from the four TCCON sites indicated by the different colours given in the legend. The XCO₂ anomaly is the difference between each XCO₂ value and the daily median XCO₂. (b) The XCO₂ Voigt anomaly after the airmass dependence correction is applied to the XCO₂ Voigt data. (c) XCO₂ qSDV anomaly. (d) XCO₂ qSDV anomaly after correction for the airmass dependence.

7.4.2 Accuracy of XCO₂

To assess the accuracy of TCCON XCO₂ measurements, they are compared to aircraft XCO₂ profile measurements using the method described in Wunch et al. (2010). Figure 7.9a shows the comparison between the aircraft XCO₂ measurements (legend on the top details the different aircraft) and TCCON XCO₂ Voigt measurements for 13 TCCON sites (given by the colour-coded legend on the bottom right). The gray line indicates the one-to-one line and the dashed line is the line of best fit. There is a bias of 0.9897 ± 0.0005 , as given by the slope of the line of best fit in Figure 7.9a, for the XCO₂ Voigt measurements. Figure 7.9b is the same as 7.9a but for the XCO₂ qSDV measurements. The bias between the aircraft XCO₂ measurements and $\frac{110}{110}$

the XCO₂ qSDV measurements is 1.0041 ± 0.0005 as given by the slope of the line of best fit in Figure 7.9b. Using the qSDV to retrieve total columns of CO₂ and O₂ thus reduces the difference between TCCON XCO₂ and aircraft XCO₂ measurements by 0.62%.



Figure 7.9: (a) Correlation between TCCON and aircraft XCO_2 Voigt measurements for 13 TCCON sites. Each aircraft type is indicated by a different symbol given by the legend in the top left corner. Each site is represented by a different colour given by the legend in the bottom right corner. The grey line indicates the one-to-one line and the dashed line is the line of best fit for the data. The slope of the line of best fit as well as the error on the slope are given in the plot. (b) The same as (a) but for $XCO_2 qSDV$.

TCCON XCO₂ measurements are divided by the scale factors (or bias determined in Figure 7.9) to calibrate to the WMO scale. So for all XCO₂ measurements retrieved with a Voigt line shape, the airmass correction is applied to the data and the result is divide by 0.9897. Figures 7.10a to 7.10d show XCO₂ Voigt (for Eureka, Park Falls, Lamont, and Darwin respectively) indicated by red square boxes in the plots. XCO₂ Voigt measurements made at SZA > 82° have been filtered out because they cannot be corrected for the airmass dependence. The blue boxes are XCO₂ qSDV corrected for airmass dependence and scaled by 1.0041. No filter was applied to the XCO₂ qSDV measurements for SZA since the airmass dependence correction works at all SZA. Figures 7.10e to 7.10h show the difference between XCO₂ Voigt and XCO₂ qSDV for

Eureka, Park Falls, Lamont, and Darwin respectively. The shape in the difference throughout the year is due to the seasonality of the SZA of the measurements. Since Darwin is in the southern hemisphere it has the opposite season compared to the TCCON sites in the norther hemisphere. This is why the Darwin has the opposite shape comapre to Eureka, Park Falls, and Lamont. The mean differences for the data shown in Figures 7.10e to 7.10h are 0.113±0.082, -0.102±0.223, -0.132±0.241, and -0.059±0.231 ppm for Darwin, Park Falls, Lamont, and Eureka respectively. The difference throughout the day at Park Falls, Lamont, and Darwin varies between -0.6 to 0.2 ppm and is SZA dependent.



Figure 7.10: (a) to (d) XCO_2 plotted as a function of day of the year for Eureka (2014), Park Falls (2013), Lamont (2010), and Darwin (2006) respectively. Red indicates XCO_2 Voigt line shape and blue indicates XCO_2 qSDV. (e) - (h) The corresponding differences between XCO_2 Voigt and XCO_2 qSDV.

Figure 7.11a shows XCO₂ Voigt corrected for the airmass dependence, as well as XCO₂ qSDV, uncorrected and corrected for the airmass dependence. These XCO₂ measurements were retrieved from Park Falls spectra recorded on June 18, 2013. For all three XCO₂ measurements, the amount of XCO₂ decreases throughout the day. Figure 7.11b shows the difference between the corrected Voigt XCO₂ and the uncorrected qSDV XCO₂, as well as the difference between the corrected Voigt XCO₂ and the corrected qSDV XCO₂. The difference between the Voigt and

the qSDV (corrected and uncorrected) shows that at the start and end of the day, more XCO_2 is retrieved with the qSDV, while at midday less is retrieved with the qSDV. The range in the differences seen in Figure 7.10e to 7.10h varies with SZA throughout the day as shown in Figure 7.11b.



Figure 7.11: (a) XCO_2 from Park Falls retrieved from spectra recorded on June 18, 2013. Plotted is XCO_2 retrieved: (1) with a Voigt line shape and corrected for the airmass dependence (red squares), (2) with the qSDV (cyan circles), and (3) with the qSDV corrected for the airmass dependence (blue squares). (b) The difference between the Voigt XCO_2 corrected and the qSDV XCO_2 (cyan circles), and the difference between the Voigt XCO_2 corrected and the qSDV XCO_2 corrected (blue squares).

7.5 Discussion of Results

Using cavity-ring-down spectra, it was shown that the Voigt line shape is insufficient to model the line shape of O_2 for the 1.27 µm band, consistent with the results of by Hartmann et al. (2013) and Lamouroux et al. (2014). By using the speed-dependent Voigt when calculating the absorption coefficients, we were better able to reproduce the measured absorption coefficients than using the Voigt line shape. However, some residual structure still remains as seen Figures 7.1c and 7.2c. This is partly due to not being able to retrieve the spectroscopic parameters for

weak O_2 transitions because of the blending of spectral lines. Fitting low-pressure spectra would help with isolating spectral lines and decrease the uncertainty on the retrieved spectroscopic parameters for the Q branch lines. The pressure dependence of the retrieved speed-dependent width parameter is an indication that Dicke narrowing needs to be taken into account, as shown by Bui et al. (2014) for CO₂. When dealing with both speed dependence and Dicke narrowing, a multispectrum fit needs to be used due to the correlation between the parameters (Bui et al., 2014). Therefore, the speed-dependent width parameter derived from averaging a_{γ_L} retrieved from each spectrum is not the true value of $a_{\gamma_{L_i}}$. However, using the average $a_{\gamma_{L_i}}$ with the quadratic speed-dependent Voigt line shape to calculate absorption coefficients for O₂ has led to the decrease of the airmass dependence of the retrieved O₂ column, resulting in the decrease in the airmass dependence of XCO_2 and an increase in the accuracy of XCO_2 . The temperature dependence of the Lorentz width coefficients of this band has never been measured before, which could have an impact on the airmass dependence of O₂. Combining high-pressure cavityring-down absorption coefficient measurements with those for low pressures and different temperatures, as done for CH₄ in Devi et al. (2015; 2016), would provide more accurate line shape parameters for O_2 .

By taking speed dependence into account for both CO₂ and O₂, we were able to significantly decrease the airmass dependence of TCCON XCO₂ and the bias between TCCON and aircraft XCO₂. With the qSDV line shape, XCO₂ measurements made at SZA > 82° no longer have to be filtered out, resulting in more XCO₂ measurement available from all TCCON sites. This is particularly important for high-latitude TCCON sites, such as Eureka, because measurements made from late February to late March and from late September until mid-October are made at SZA > 82°. Filtering out these large SZA measurements thus limits the knowledge of the seasonal cycle of XCO₂ at high latitudes. The airmass dependence of the O₂ column not only affects XCO₂ but all trace gases measured by TCCON, and in the future the airmass dependence of all X_G will be determined with these new O₂ columns.

8 Summary, Conclusions, and Future Work

8.1 Summary and Conclusions

In order to improve the retrievals of GHGs from solar absorption spectra, the absorption coefficients calculated by the forward model of GFIT have been improved. A speed-dependent Voigt line shape with line mixing was implemented into the forward model of GFIT along with the best set of spectroscopic parameters that are used to calculate absorption coefficients for CO₂, O₂, and CH₄. High-resolution laboratory and ground-based solar spectra were used to test the performance of the forward model.

The calculation of absorption coefficients using the qSDV+LM with its corresponding set of optimized spectroscopic parameters was tested on laboratory spectra of CO₂ and CH₄. It was shown that when the forward model of GFIT uses a Voigt line shape to calculate absorption coefficients, it cannot reproduce the laboratory spectra of CO₂ and CH₄ within the noise level of the spectra. The forward model of GFIT can now better reproduce the laboratory spectra of CO₂ and CH₄ due to more accurate absorption coefficient calculations. Cavity ring-down spectra were used to show that the Voigt line shape is insufficient to model the spectral line shape of O₂ for the 1.27 μ m band. Spectroscopic parameters for the speed-dependent Voigt line shape were retrieved from air-broadened, room-temperature laboratory spectra and put into the forward model of GFIT to improve the retrieval of O₂ from TCCON spectra.

A year of spectra recorded at Eureka, Park Falls, Lamont, and Darwin (total of 131,124 spectra) were fitted using new absorption coefficients for CO₂, O₂, and CH₄. By taking speed dependence and line mixing into account for CO₂, the spectral fits showed an overall greater improvement for the strong band compared to the weak CO₂ bands. However, fits of the weak bands improved as much as ~20% as SZA approached 90°. The new absorption coefficients for CH₄ reduced the RMS residual for the P, Q, and R branch windows by 5%, 13%, and 3%, respectively when compared with spectra fitted using a Voigt line shape and the atm line list. The improvement increased as a function of SZA with the RMS residual decreasing by ~45%,

60%, and 35%, for the P, Q, and R branch windows respectively, as the SZA approached 90°. The new absorption coefficients had little impact on the quality of the spectral fits of O₂.

It is evident that neglecting line mixing in the absorption coefficient calculation leads to an airmass dependence of the retrieved columns of CO₂ and CH₄. As previously stated, line mixing occurs when spectral lines are broadened enough to overlap and inelastic collisions transfer intensity from one part of the spectrum to another (Lévy et al., 1992). This transfer of intensity is evident when modeling the strong CO₂ band with a Voigt spectral line shape that excludes line mixing. In Figure 5.2b, if one focuses on the P-branch (4805-4850 cm⁻¹), the asymmetrical structure from ~4805-4835 cm⁻¹ is opposite to the asymmetrical structure from ~4840-4850 cm⁻¹, and at ~4840 cm⁻¹ the structure is no longer asymmetrical. This is because the intensity is moving towards the spectral transitions with the highest intensity in the branch, which are at ~4840 cm⁻¹. By neglecting line mixing, an asymmetrical residual structure appears in the trough of the spectral line, which can be seen in Figure 5.2b. When retrieving CO₂ from solar spectra, neglecting line mixing leads to absorption coefficients for the strong lines being smaller than they should be and absorption coefficients in the weak lines being larger than they should be. To compensate for the strong lines having weaker absorption than they should, more CO₂ is retrieved.

Neglecting line mixing for CH₄, on the other hand, results in less CH₄ retrieved as airmass increases as seen in Figure 6.11. For CH₄ it is harder to see the residual structure from neglecting line mixing in fits to the laboratory spectra because even at the low pressure of the laboratory spectra used in this study, spectral lines within the same manifold are broadened enough to significantly overlap. Tran et al. (2010) give a good explanation of the effect of line mixing on the manifolds, stating that neglecting line mixing leads to more absorption in the far wings of the manifold and less in the center. This is because in the studies by Devi et al. (2015; 2016), line mixing was found to occur only for pairs of spectral lines (with the same rotational symmetry, Tran et al. 2010) within the same manifold, leading to less absorption in the far wings of the manifold. Figure 6.11 shows how XCH₄ decreases as a function of SZA when neglecting line mixing because as SZA increases the lines get more saturated and more weight is put on the far wings of the manifolds. Since absorption is higher in the far wings of the manifolds than it

should be, due to neglecting line mixing, the retrieval will try and compensate by retrieving less CH₄, leading to the airmass dependence seen in Figure 6.11.

The difference between the speed-dependent Voigt and the Voigt spectral line shape is that the speed-dependent Voigt is narrower than the Voigt as shown in Figure 4.3c. This is because when calculating the Voigt, the Lorentz component is calculated with the Lorentz width at the average speed of the absorbing molecule. However, when calculating the speed-dependent Voigt, more weight is put on the Lorentz component that has a width at the most probable speed of the absorbing molecule, which is smaller than the Lorentz width of the average speed of the absorbing molecule. This causes the speed-dependent Voigt to be narrower than the Voigt line shape so that the absorption in the far wings of the spectral line is less when compared to the Voigt. This can be seen in Figure 6.11 when comparing the Voigt line shape to the qSDV for XCH₄. As SZA increases, more CH₄ is retrieved with the qSDV compared to the Voigt line shape because absorption is less in the far wings of the spectral lines with the qSDV.

The absorption coefficients used in the forward model of GFIT have been shown to impact the airmass dependence of the retrieved columns of CO₂, O₂, and CH₄. CO₂ columns retrieved from the weak CO₂ bands no longer increase for measurements taken at SZA > 82°, rather they follow the same trend as measurements made at SZA < 82°. XCO₂ calculated with the O₂ column retrieved with the qSDV results in a decrease in the airmass dependence of XCO₂ with the correction factor decreasing by 80%. The SZA restriction for TCCON measurements of > 82° can now be removed, which will lead to more measurements available from TCCON sites, especially those at high latitudes.

Satellite observations in the Arctic can help monitor how the Arctic carbon cycle is changing with climate change. However, XCO₂ and XCH₄ measurements made at high-latitudes during the spring and fall seasons are sparse due to complications with the retrievals from spectra of sunlight reflected from snow-covered surfaces (Boesch et al., 2011). By removing the SZA restriction on TCCON XCO₂, there will be data available from high-latitude TCCON sites during early spring and late fall which can be used in Arctic carbon cycle studies.

Continued monitoring of the Arctic carbon cycle and understanding of how climate change influences the Arctic carbon cycle is important when trying to predict how the climate

will change in the future. Currently, the Arctic is a sink for carbon but if temperatures continue to increase and the Arctic becomes dryer this will decrease the amount of CO_2 taken out of the atmosphere by the biosphere because H₂O is needed for photosynthesis. However, as the Arctic gets dryer, wetlands would turn into grasslands, decreasing wetland emissions of CH₄ and increasing the uptake of CO₂. Winter conditions are of particular concern because as the temperature increases in the winter, ecosystem respiration will increase, as well as microbial decomposition of organic matter, leading to more CO₂ put into the atmosphere by the Arctic biosphere. A combination of these two factors could offset the carbon taken in by the biosphere in the summer and result in the Arctic turning from a sink to a source of atmospheric carbon. This means that the Arctic carbon cycle needs to be monitored year round.

To overcome the shortcomings of satellite missions that use the sun as the source of radiation (e.g. GOSAT and OCO-2), two space-based GHG lidar missions have been proposed. NASA has proposed the Active Sensing of CO₂ Emissions over Night, Days and Seasons (ASCENDS) mission, which will measure total columns of CO₂ using one of the CO₂ spectral lines from either the strong CO₂ band or weak CO₂ band 2 (Kawa et al., 2010). The proposed German-French climate-monitoring mission called the Methane Remote Lidar Mission (MERLIN) will measure total columns of CH₄ from R(6) manifold of the $2v_3$ branch of CH₄ (Kiemle et al., 2011). Validation of these measurements will be needed if these missions are to achieve their desired accuracy of better than 1%. Both ASCENDS and MERLIN are supposed to make measurements where and when GOSAT and OCO-2 cannot. Measurements made at high-latitude TCCON sites during early spring and late fall will be vital for validation of both the ASCENDS and MERLIN measurements.

The work done in this thesis shows that the choice of absorption coefficients used by the forward model of the retrieval algorithm can create a bias in the retrieved total columns. It was shown that the bias between the TCCON measurements and the integrated aircraft profile measurements was reduced. The slope increased from 0.9897 ± 0.0005 to 1.0041 ± 0.0005 for XCO₂ retrieved with the Voigt and speed-dependent Voigt line shapes respectively. The average total column of CH₄ retrieved from the solar spectra with the qSDV+LM was $1.1 \pm 0.3\%$ higher than the retrievals performed using a Voigt and the atm line list. TCCON eliminates this bias by comparing their measurements to integrated aircraft profile measurements and scaling the

measurements accordingly. The bias created by the choice of absorption coefficients is relevant to satellite observations. By eliminating the bias due to the choice of absorption coefficients, other possible measurement biases can be quantified.

With the new absorption coefficients for CO₂, CH₄, and O₂, the retrievals of XCO₂ and total columns of CH₄ have been improved in three ways: (1) by reducing the RMS fitting residual of CO₂ and CH₄ and hence the derived uncertainties, (2) significantly decreasing the airmass dependence of XCO₂, and (3) improving the accuracy of XCO₂ and CH₄ total columns. The work in this thesis gives a physics-based solution to the airmass dependence of XCO₂ retrieved from remote sensing measurements.

8.2 Future Work

The work in this thesis can be extended to other molecules and spectral regions to improve retrievals. Retrievals of N₂O can be improved by using the qSDV+LM and spectroscopic parameters from Hashemi et al. (2016) for CH₄ since CH₄ is the major interfering species in the N₂O windows. JPL MKIV FTS balloon measurements of CH₃Cl and N₂O have shown the need to include line mixing in the absorption coefficient calculations (Geoff Toon, personal communication). The study by Bray et al. (2012) showed the need to take line mixing into account when fitting laboratory spectra of the Q branch of the v₁ band of CH₃Cl. To take line mixing into account, the relaxation matrix was constructed using the exponential power gap (EPG) law in Bray et al. (2012), which is the same law that was used to construct the relaxation matrix for CO₂ in Section 5.3. The Matlab code developed in this work can be easily adapted to calculate off-diagonal elements of the relaxation matrix for the Q branch of the v₁ band of CH₃Cl, which can then be used to calculate absorption coefficients in GFIT. Similarly, this can also be done for the Q branch of N₂O, near 2798 cm⁻¹, as shown in Strow and Pine (1988).

The airmass dependence and accuracy of XCH₄ calculated with the new absoprtion coefficients for CH₄ and O₂ needs to be determined following the methodology of Section 7.4. The airmass dependence correction factors for XN₂O, and XCO need to be determined for the columns of O₂ retrieved with the qSDV and the accuracy of XN₂O, XCO, and XH₂O also needs to be determined as done in Section 7.4 for XCO₂.

Using speed dependence and line mixing to calculate absorption coefficients in the manner described here could be beneficial for CO_2 vertical profile retrievals. Vertical profile information comes from the spectral line shape: the wings of the spectral line carry information about CO_2 near the surface and the line center has information primarily about the higher altitudes (Kuai et al., 2012). The wings of the line are sensitive to effects like line mixing, while the center of the line can be affected by speed dependence. A spectral line shape that takes these effects into account will allow more accurate profile retrievals. Partial columns of CO_2 have been retrieved using the weak CO_2 band 1 (Kuai et al., 2012; Connor et al., 2015) and the strong CO_2 band (Dohe, 2013). Use of the qSDV+LM should be tested with a vertical profile retrieval algorithm to assess the impact of speed dependence and line mixing on the quality of the profile retrieval. Studies of vertical profile retrievals can then be extended to other GHGs like CH₄.

Appendix

Appendix A

Table A.1: Spectroscopic parameters for the strong CO_2 band. The line center, intensity, Lorentz width, E'', temperature dependence of the Lorentz width (T-dependence), and pressure shift. The spectroscopic parameters are from the atm line list (Toon, 2014a) from GGG2014. Lorentz widths were adjusted as described in Section 5.4.1 to take speed dependence into account. The same speed-dependent parameter (SD parameter) was used for all transitions. Parameters a, b, and c for air, self, and H₂O collisions are calculated following the method in Section 5.3.

ΔIJ	Line Center	Intensity	Lorentz Width	T-Dependence	E''	Pressure Shift	SD Lorentz width	a(air)	b(air)	c(air)	a(self)	b(self)	c(self)	a(H2O)	b(H2O)	c(H2O)
P 56	4803.344561	4.06E-24	0.0657	0.74	1244.22	-0.006709	0.11	-0.00161	0.014457	-0.00232	-0.00636	0.02479	-0.0055	-0.00718	0.026685	-0.00597
P 54	4805.395807	5.89E-24	0.0662	0.75	1157.774	-0.006639	0.11	-0.00122	0.01261	-0.00365	-0.00535	0.021218	-0.00652	-0.00596	0.02259	-0.00687
P 52	4807.425473	8.41E-24	0.0666	0.75	1074.431	-0.006568	0.11	-0.0008	0.011601	-0.00389	-0.00447	0.019421	-0.00661	-0.00501	0.020689	-0.00697
P 50	4809.433944	1.18E-23	0.067	0.76	994.1911	-0.006497	0.11	-0.00057	0.011022	-0.00392	-0.00389	0.01833	-0.00652	-0.0044	0.019557	-0.0069
P 48	4811.421596	1.63E-23	0.0673	0.77	917.0572	-0.006426	0.11	-0.00041	0.01058	-0.00385	-0.00344	0.017427	-0.00633	-0.00391	0.018623	-0.0067
P 46	4813.388794	2.22E-23	0.0676	0.77	843.03	-0.006354	0.11	-0.00028	0.010146	-0.00371	-0.00301	0.016527	-0.00604	-0.00345	0.017687	-0.00642
P 44	4815.33589	2.97E-23	0.0678	0.78	772.1106	-0.006282	0.11	-0.00014	0.009663	-0.00352	-0.00256	0.015553	-0.00568	-0.00297	0.016674	-0.00605
P 42	4817.263226	3.90E-23	0.0681	0.78	704.3004	-0.006209	0.11	0.000023	0.009107	-0.00328	-0.00207	0.014481	-0.00526	-0.00245	0.015557	-0.00563
P 40	4819.17113	5.04E-23	0.0683	0.78	639.6003	-0.006136	0.11	0.000211	0.008472	-0.00301	-0.00154	0.013305	-0.0048	-0.00189	0.014333	-0.00516
P 38	4821.059917	6.41E-23	0.0685	0.78	578.0115	-0.006063	0.11	0.00043	0.007752	-0.0027	-0.00097	0.012018	-0.0043	-0.00127	0.012993	-0.00466
P 36	4822.929889	8.00E-23	0.0687	0.78	519.535	-0.00599	0.11	0.000679	0.006948	-0.00238	-0.00034	0.010621	-0.00378	-0.0006	0.011537	-0.00412
P 34	4824.781332	9.82E-23	0.0689	0.78	464.1717	-0.005917	0.11	0.000957	0.006063	-0.00204	0.000332	0.009111	-0.00323	0.000119	0.009964	-0.00356
P 32	4826.614521	1.18E-22	0.0692	0.78	411.9225	-0.005843	0.11	0.001263	0.005102	-0.00169	0.001053	0.00749	-0.00266	0.000894	0.00827	-0.00298
P 30	4828.429712	1.40E-22	0.0696	0.78	362.7883	-0.00577	0.11	0.001592	0.00407	-0.00134	0.001822	0.005754	-0.00207	0.001721	0.006451	-0.00238
P 28	4830.227149	1.62E-22	0.0701	0.78	316.7698	-0.005697	0.11	0.00194	0.002974	-0.001	0.002636	0.003902	-0.00148	0.002603	0.004502	-0.00176
P 26	4832.007056	1.85E-22	0.0706	0.78	273.868	-0.005624	0.11	0.002298	0.001824	-0.00067	0.003489	0.001935	-0.00088	0.003533	0.002418	-0.00114
P 24	4833.769646	2.06E-22	0.0712	0.78	234.0833	-0.005551	0.11	0.002659	0.000634	-0.00038	0.004375	-0.00015	-0.00029	0.004509	0.000199	-0.00051
P 22	4835.515112	2.24E-22	0.0719	0.77	197.4166	-0.005477	0.11	0.003011	-0.00058	-0.00014	0.005285	-0.00233	0.000287	0.005523	-0.00216	0.000117
P 20	4837.24363	2.39E-22	0.0728	0.76	163.8684	-0.005401	0.11	0.003337	-0.00179	0.000034	0.006201	-0.00462	0.000835	0.00656	-0.00466	0.000729
P 18	4838.955361	2.49E-22	0.0739	0.74	133.4393	-0.005324	0.11	0.003612	-0.00297	0.000115	0.00709	-0.00698	0.001331	0.007593	-0.00729	0.001312
P 16	4840.650447	2.52E-22	0.0751	0.71	106.1297	-0.005243	0.11	0.003799	-0.00407	0.000064	0.007895	-0.00936	0.001737	0.008568	-0.00999	0.001832
P 14	4842.329013	2.47E-22	0.0765	0.69	81.9401	-0.005157	0.11	0.003844	-0.00501	-0.00017	0.008516	-0.01164	0.001984	0.009387	-0.01268	0.002228
P 12	4843.991167	2.34E-22	0.0783	0.69	60.8709	-0.005061	0.11	0.00366	-0.00565	-0.00067	0.008774	-0.0136	0.001952	0.009869	-0.01516	0.00239
P 10	4845.636997	2.13E-22	0.0802	0.7	42.9225	-0.00495	0.11	0.003091	-0.00578	-0.00158	0.008287	-0.01473	0.001382	0.009612	-0.0169	0.002061
P 8	4847.266576	1.83E-22	0.0823	0.71	28.0951	-0.004817	0.11	0.001847	-0.00495	-0.00315	0.006224	-0.01386	-0.00031	0.007713	-0.01668	0.00064
P 6	4848.879955	1.45E-22	0.0849	0.73	16.389	-0.004648	0.11	-0.0007	-0.0022	-0.00593	0.000441	-0.00776	-0.00465	0.001755	-0.01094	-0.00354
P 4	4850.477169	1.01E-22	0.0876	0.74	7.8043	-0.004414	0.11	-0.00627	0.005233	-0.01139	-0.01633	0.015106	-0.01704	-0.0168	0.013709	-0.01667
P 2	4852.058235	5.17E-23	0.0907	0.75	2.3413	-0.003958	0.11	-0.02301	0.030842	-0.02657	-0.09348	0.138127	-0.07623	-0.11025	0.161986	-0.08701
RO	4854.399544	2.62E-23	0.0963	0.74	0	-0.002425	0.11	0.036555	-0.05286	0.03123	0.073504	-0.10275	0.053669	0.084174	-0.11676	0.059859
R 2	4855.940186	7.78E-23	0.089	0.75	2.3413	-0.002469	0.11	0.021411	-0.02657	0.020444	0.034282	-0.03765	0.026238	0.037263	-0.03953	0.027294
R 4	4857.46459	1.27E-22	0.0862	0.74	7.8043	-0.002863	0.11	0.006765	-0.00457	0.009415	0.006731	0.001239	0.008096	0.006279	0.003554	0.007433
R 6	4858.972688	1.70E-22	0.0836	0.72	16.389	-0.003225	0.11	0.000193	0.004118	0.004452	-0.003	0.012266	0.002198	-0.00408	0.01476	0.001484
R 8	4860.464395	2.08E-22	0.0812	0.7	28.0951	-0.003537	0.11	-0.00305	0.007599	0.001951	-0.0068	0.014836	0.000073	-0.00788	0.016822	-0.00043
R 10	4861.939606	2.37E-22	0.0792	0.69	42.9225	-0.003809	0.11	-0.00466	0.008667	0.000639	-0.00816	0.014285	-0.00061	-0.00908	0.015699	-0.00089
R 12	4863.3982	2.58E-22	0.0774	0.69	60.8709	-0.004052	0.11	-0.0054	0.008496	-2.4E-05	-0.0084	0.012482	-0.00066	-0.00914	0.013393	-0.00075
R 14	4864.840035	2.70E-22	0.0758	0.7	81.9401	-0.004274	0.11	-0.00563	0.007635	-0.0003	-0.00808	0.010162	-0.00041	-0.00865	0.010658	-0.00036
R 16	4866.264953	2.73E-22	0.0745	0.73	106.1297	-0.004478	0.11	-0.00554	0.006373	-0.00031	-0.00746	0.007647	0.000003	-0.00787	0.007805	0.000164
R 18	4867.672779	2.69E-22	0.0733	0.75	133.4393	-0.004669	0.11	-0.00526	0.004876	-0.00016	-0.00668	0.005088	0.000498	-0.00697	0.004973	0.000745
R 20	4869.063318	2.58E-22	0.0724	0.76	163.8684	-0.004849	0.11	-0.00485	0.003239	0.000113	-0.00583	0.002553	0.001045	-0.006	0.002213	0.001355
R 22	4870.436359	2.42E-22	0.0715	0.77	197.4166	-0.005019	0.11	-0.00435	0.001521	0.000477	-0.00494	0.00007	0.001626	-0.00501	-0.00046	0.001985
R 24	4871.791674	2.21E-22	0.0709	0.78	234.0833	-0.005182	0.11	-0.0038	-0.00024	0.000909	-0.00404	-0.00235	0.00223	-0.00403	-0.00303	0.002627
R 26	4873.129019	1.99E-22	0.0703	0.78	273.868	-0.005338	0.11	-0.00323	-0.00202	0.001393	-0.00314	-0.0047	0.002855	-0.00305	-0.00552	0.00328
R 28	4874.44813	1.75E-22	0.0697	0.78	316.7698	-0.005488	0.11	-0.00263	-0.00381	0.001919	-0.00225	-0.007	0.003495	-0.00209	-0.00793	0.003943
R 30	4875.748732	1.50E-22	0.0694	0.78	362.7883	-0.005632	0.11	-0.00203	-0.00558	0.002477	-0.00138	-0.00923	0.004148	-0.00116	-0.01026	0.004614
R 32	4877.03053	1.27E-22	0.0691	0.78	411.9225	-0.005771	0.11	-0.00143	-0.00733	0.003056	-0.00052	-0.0114	0.00481	-0.00025	-0.01253	0.005291
R 34	4878.293216	1.06E-22	0.0688	0.78	464.1717	-0.005905	0.11	-0.00084	-0.00905	0.00365	0.000307	-0.01352	0.00548	0.000637	-0.01474	0.005975
R 36	4879.536465	8.62E-23	0.0686	0.78	519.535	-0.006035	0.11	-0.00026	-0.01075	0.004255	0.001117	-0.01559	0.006154	0.001497	-0.01689	0.006661
R 38	4880.759939	6.91E-23	0.0684	0.78	578.0115	-0.00616	0.11	0.000307	-0.0124	0.004861	0.001903	-0.01761	0.006825	0.002331	-0.01899	0.007344
R 40	4881.963286	5.44E-23	0.0682	0.78	639.6003	-0.006282	0.11	0.000855	-0.01402	0.005461	0.002665	-0.01957	0.007487	0.003139	-0.02103	0.008016
R 42	4883.146138	4.22E-23	0.068	0.78	704.3004	-0.006399	0.11	0.001386	-0.01558	0.006044	0.003403	-0.02148	0.008126	0.003921	-0.02302	0.008664
R 44	4884.308118	3.21E-23	0.0677	0.77	772.1106	-0.006514	0.11	0.001903	-0.01711	0.0066	0.004121	-0.02334	0.008727	0.004682	-0.02495	0.009272
R 46	4885.448833	2.40E-23	0.0674	0.77	843.03	-0.006624	0.11	0.002421	-0.01862	0.00711	0.004832	-0.02515	0.009263	0.005434	-0.02682	0.009811
R 48	4886.567878	1.77E-23	0.0671	0.76	917.0572	-0.006732	0.11	0.002968	-0.02014	0.007552	0.005565	-0.02695	0.009699	0.006207	-0.02869	0.010241
R 50	4887.664839	1.28E-23	0.0668	0.76	994.1911	-0.006836	0.11	0.003617	-0.02182	0.0079	0.006404	-0.02888	0.009989	0.007085	-0.03068	0.010511
R 52	4888.739289	9.15E-24	0.0664	0.75	1074.431	-0.006938	0.11	0.004528	-0.02397	0.008113	0.007558	-0.03134	0.010077	0.008291	-0.0332	0.010561
R 54	4889.790791	6.42E-24	0.066	0.74	1157.774	-0.007037	0.11	0.006025	-0.0275	0.008091	0.00958	-0.0357	0.009949	0.01043	-0.03773	0.010393
R 56	4890.818899	4.43E-24	0.0655	0.73	1244.22	-0.007133	0.11	0.007634	-0.03394	0.006541	0.013039	-0.04652	0.009274	0.014383	-0.04969	0.00992

Table A.2: Spectroscopic parameters for the weak CO_2 band 1. The spectroscopic parameters are from Devi et al. (2007a). Parameters a, b, and c for air, self, and H₂O collisions are calculated following the method in Section 5.3.

ΔJJ	Line Cente	Intensity	Lorentz W	T-Depend	E''	Pressure S	SD Lorenta	a(air)	b(air)	c(air)	a(self)	b(self)	c(self)	a(H2O)	b(H2O)	c(H2O)
P 56	6173.169	2.37E-25	0.0647	0.74	1244.22	-0.00834	0	-0.00138	0.012865	-0.00212	-0.00556	0.02191	-0.00496	-0.00644	0.02393	-0.00546
P 54	6175.528	3.45E-25	0.0652	0.75	1157.774	-0.00825	0.1	-0.00107	0.011312	-0.00329	-0.00474	0.018942	-0.00586	-0.0054	0.020425	-0.00625
P 52	6177.856	4.96E-25	0.0673	0.75	1074.431	-0.00402	0.1	-0.00072	0.010479	-0.00351	-0.004	0.017432	-0.00594	-0.00459	0.018806	-0.00633
P 50	6180.153	7.00E-25	0.0681	0.76	994.1911	-0.0053	0.1	-0.00053	0.010012	-0.00354	-0.00351	0.016516	-0.00587	-0.00406	0.017849	-0.00627
P 48	6182.418	9.73E-25	0.0673	0.77	917.0572	-0.00477	0.1	-0.0004	0.009656	-0.00348	-0.00312	0.015754	-0.00569	-0.00364	0.017054	-0.00609
P 46	6184.652	1.33E-24	0.0669	0.77	843.03	-0.00616	0.06	-0.00029	0.0093	-0.00336	-0.00274	0.014984	-0.00543	-0.00324	0.016248	-0.00584
P 44	6186.856	1.79E-24	0.0672	0.78	772.1106	-0.00625	0.099	-0.00017	0.008896	-0.00319	-0.00235	0.014146	-0.00511	-0.00281	0.015369	-0.00551
P 42	6189 029	2 36F-24	0.0679	0.78	704 3004	-0.00665	0 108	-2 6F-05	0.008424	-0.00298	-0.00192	0.013217	-0.00473	-0.00234	0.014394	-0.00513
P 40	6191 172	3 07F-24	0.0682	0.78	639 6003	-0.00588	0.088	0.000143	0.007872	-0.00273	-0.00144	0.012186	-0.00432	-0.00183	0.013314	-0.00471
P 38	6193 284	3 92F-24	0.0681	0.78	578 0115	-0.00674	0.000	0.000342	0.00724	-0.00246	-0.00093	0.011049	-0.00387	-0.00127	0.012122	-0.00425
P 36	6195 367	4 91F-24	0.0686	0.78	519 535	-0.00675	0.055	0.000571	0.006525	-0.00240	-0.00036	0.011045	-0.00339	-0.00065	0.010817	-0.00376
D 3/	6107 /2	6.05E-24	0.0000	0.78	464 1717	-0.00678	0.100	0.0000071	0.000523	-0.0018/	0.000361	0.003004	-0.00333	0.00003	0.010017	-0.00374
1 34 D 37	6100 ///	7 32F-24	0.0002	0.78	/11 0225	-0.00661	0.105	0.0000001	0.003731	-0.00152	0.000201	0.000440	-0.00235	0.000745	0.003334	-0.00324
P 30	6201 / 38	8 60F-24	0.0001	0.78	362 7883	-0.00001	0.105	0.001110	0.004033	-0.00132	0.000528	0.000373	-0.00233	0.000743	0.007843	-0.0027
P 28	6203 403	1.01E-24	0.0701	0.78	316 7608	-0.00077	0.100	0.00143	0.003313	-0.00113	0.001044	0.003533	-0.00101	0.001327	0.000177	-0.00214
D 26	6205.405	1 165 22	0.0703	0.70	272 060	0.00075	0.11	0.001704	0.002301	0.00056	0.002400	0.003032	0.00120	0.002303	0.004303	0.00137
F 20	6203.335	1.101-23	0.0703	0.78	273.000	0.00008	0.107	0.002111	0.001829	0.00030	0.003210	7 25 05	0.0007	0.00320	0.002421	0.00038
F 24	6207.240	1.291-23	0.072	0.78	107 4166	-0.00038	0.129	0.002400	0.00071	4 05 05	0.004003	-7.3L-03	-0.00013	0.004208	0.000323	-0.00038
F 22	6210.074	1.411-23	0.0728	0.77	162 9694	0.00034	0.13	0.002810	-0.00044	-4.91-03	0.00494	-0.00213	0.000410	0.005205	-0.00193	0.000228
F 20	6210.374	1.511-25	0.074	0.70	122 4202	0.00030	0.131	0.003143	-0.00101	0.000120	0.005825	-0.0043	0.000342	0.000233	0.00434	0.000827
P 10	6212.795	1.576-25	0.0752	0.74	106 1207	-0.00629	0.141	0.003431	-0.00275	0.000212	0.000701	-0.00050	0.001421	0.007271	-0.00089	0.001404
P 10	0214.300	1.002-25	0.0702	0.71	100.1297	-0.00629	0.120	0.003037	-0.00565	0.000174	0.007502	-0.00665	0.001810	0.006272	-0.00956	0.00195
P 14	6216.352	1.5/E-23	0.078	0.69	81.9401	-0.0061	0.147	0.003712	-0.00477	-4.1E-05	0.008139	-0.01106	0.002062	0.009142	-0.01226	0.002349
P 12	6218.089	1.49E-23	0.0797	0.69	42.0225	-0.00574	0.143	0.003566	-0.00544	-0.00052	0.008429	-0.01298	0.002035	0.009699	-0.01478	0.002547
P 10	6219.797	1.35E-23	0.0813	0.7	42.9225	-0.00549	0.14	0.003048	-0.00562	-0.00139	0.00801	-0.01413	0.001484	0.009557	-0.01664	0.002278
P 8	6221.477	1.16E-23	0.0831	0.71	28.0951	-0.00486	0.132	0.001867	-0.00488	-0.00292	0.006069	-0.01333	-0.00016	0.007821	-0.01663	0.000948
P 6	6223.129	9.25E-24	0.085	0.73	16.389	-0.00519	0.131	-0.00061	-0.00223	-0.00565	0.000514	-0.00746	-0.00441	0.002079	-0.0112	-0.00311
P 4	6224.753	6.43E-24	0.0875	0.74	7.8043	-0.00399	0.124	-0.0061	0.005075	-0.01109	-0.01572	0.014/33	-0.01654	-0.01625	0.013077	-0.0161
P 2	6226.349	3.31E-24	0.0917	0.75	2.3413	-0.00371	0.117	-0.02284	0.03063	-0.02629	-0.09022	0.1336	-0.07397	-0.10996	0.161743	-0.08669
RO	6228.69	1.68E-24	0.0955	0.74	0	-0.00366	0.091	0.036009	-0.0521	0.031082	0.072515	-0.10162	0.053397	0.084093	-0.11683	0.060134
R 2	6230.216	4.98E-24	0.0886	0.75	2.3413	-0.0044	0.125	0.021494	-0.02676	0.020812	0.034667	-0.03848	0.026905	0.037998	-0.04065	0.028116
R 4	6231.713	8.10E-24	0.0852	0.74	7.8043	-0.00417	0.114	0.007043	-0.00496	0.009902	0.00732	0.000384	0.008794	0.006877	0.002871	0.008099
R 6	6233.183	1.09E-23	0.0836	0.72	16.389	-0.00435	0.139	0.00042	0.003877	0.004895	-0.00261	0.011881	0.002723	-0.00378	0.014632	0.001947
R 8	6234.624	1.33E-23	0.082	0.7	28.0951	-0.00415	0.137	-0.00293	0.007566	0.002316	-0.00665	0.014876	0.00044	-0.00785	0.017107	-0.00012
R 10	6236.037	1.51E-23	0.0798	0.69	42.9225	-0.00456	0.134	-0.00468	0.008831	0.000926	-0.00823	0.014651	-0.00036	-0.00927	0.01627	-0.00068
R 12	6237.421	1.64E-23	0.0782	0.69	60.8709	-0.00484	0.132	-0.00553	0.008813	0.000199	-0.00865	0.013061	-0.00049	-0.0095	0.014131	-0.0006
R 14	6238.777	1.72E-23	0.0765	0.7	81.9401	-0.00493	0.135	-0.00587	0.00806	-0.00012	-0.00846	0.010861	-0.00028	-0.00912	0.011467	-0.00023
R 16	6240.104	1.74E-23	0.0749	0.73	106.1297	-0.00541	0.127	-0.00587	0.006861	-0.00018	-0.00795	0.008389	0.000109	-0.00844	0.00861	0.000293
R 18	6241.403	1.71E-23	0.0737	0.75	133.4393	-0.00546	0.12	-0.00566	0.005377	-4.1E-05	-0.00725	0.0058	0.000611	-0.00759	0.005702	0.000897
R 20	6242.672	1.63E-23	0.0726	0.76	163.8684	-0.00545	0.114	-0.0053	0.003705	0.000233	-0.00644	0.003169	0.001189	-0.00665	0.002804	0.001554
R 22	6243.912	1.53E-23	0.072	0.77	197.4166	-0.00574	0.126	-0.00484	0.001904	0.000615	-0.00557	0.000529	0.001821	-0.00567	-6.3E-05	0.00225
R 24	6245.123	1.39E-23	0.0709	0.78	234.0833	-0.00587	0.108	-0.00431	0.000013	0.001084	-0.00466	-0.00211	0.0025	-0.00466	-0.00289	0.002979
R 26	6246.305	1.25E-23	0.0702	0.78	273.868	-0.00595	0.104	-0.00374	-0.00195	0.001625	-0.00374	-0.00473	0.003218	-0.00364	-0.00569	0.00374
R 28	6247.456	1.09E-23	0.0695	0.78	316.7698	-0.00609	0.092	-0.00313	-0.00395	0.002226	-0.0028	-0.00735	0.003974	-0.00262	-0.00847	0.004531
R 30	6248.578	9.39E-24	0.0692	0.78	362.7883	-0.00608	0.097	-0.00251	-0.006	0.002879	-0.00186	-0.00997	0.004765	-0.0016	-0.01123	0.005353
R 32	6249.669	7.92E-24	0.0687	0.78	411.9225	-0.00581	0.086	-0.00187	-0.00807	0.003576	-0.00091	-0.01259	0.00559	-0.00058	-0.01399	0.006206
R 34	6250.73	6.55E-24	0.068	0.78	464.1717	-0.00682	0.071	-0.00122	-0.01017	0.004311	0.000031	-0.01522	0.006447	0.000436	-0.01675	0.007088
R 36	6251.761	5.32E-24	0.0682	0.78	519.535	-0.00669	0.096	-0.00057	-0.01229	0.005078	0.000972	-0.01786	0.007332	0.001447	-0.01952	0.007999
R 38	6252.761	4.25E-24	0.067	0.78	578.0115	-0.00593	0.074	0.000081	-0.01442	0.005869	0.00191	-0.02051	0.008241	0.002455	-0.0223	0.008933
R 40	6253.729	3.33E-24	0.0678	0.78	639.6003	-0.0072	0.076	0.000728	-0.01657	0.006677	0.002845	-0.02318	0.009165	0.00346	-0.0251	0.009881
R 42	6254.666	2.57E-24	0.0666	0.78	704.3004	-0.00714	0.082	0.001373	-0.01873	0.00749	0.00378	-0.02587	0.01009	0.004464	-0.02792	0.01083
R 44	6255.572	1.95E-24	0.0668	0.77	772.1106	-0.0078	0.096	0.002024	-0.02092	0.008294	0.004721	-0.02859	0.010997	0.005474	-0.03077	0.011758
R 46	6256.445	1.45E-24	0.0666	0.77	843.03	-0.00785	0.104	0.002699	-0.02316	0.009068	0.005686	-0.03135	0.011851	0.006508	-0.03365	0.012627
R 48	6257.287	1.06E-24	0.0675	0.76	917.0572	-0.0074	0.1	0.003442	-0.02552	0.009782	0.006721	-0.03421	0.012604	0.007611	-0.03664	0.013383
R 50	6258.095	7.67E-25	0.0666	0.76	994.1911	-0.00828	0.1	0.004357	-0.02819	0.010394	0.007948	-0.03737	0.013186	0.00891	-0.03992	0.013947
R 52	6258.872	5.44E-25	0.0647	0.75	1074.431	-0.00852	0.1	0.005685	-0.03167	0.010847	0.009679	-0.04144	0.013518	0.010734	-0.04414	0.014232
R 54	6259.615	3.80E-25	0.065	0.74	1157.774	-0.00866	0	0.007912	-0.0373	0.010978	0.01273	-0.04844	0.013562	0.013988	-0.05146	0.014222
R 56	6260.325	2.61E-25	0.0645	0.73	1244.22	-0.00877	0	0.010331	-0.04731	0.00879	0.017897	-0.06501	0.012704	0.019969	-0.06989	0.013702

Table A.3: Spectroscopic parameters for the weak CO_2 band 2. The spectroscopic parameters are from Devi et al. (2007b). Parameters a, b, and c for air, self, and H₂O collisions are calculated following the method in Section 5.3.

ΔJJ	Line Center	Intensity	Lorentz W	T-Depend	E''	Pressure Shift	SD Lorentz	a(air)	b(air)	c(air)	a(self)	b(self)	c(self)	a(H2O)	b(H2O)	c(H2O)
P 56	6292.996791	1.96E-25	0.0647	0.74	1244.22	-0.008337	0	-0.00145	0.013449	-0.0023	-0.00584	0.022915	-0.00528	-0.00678	0.025064	-0.00581
P 54	6295.31976	2.91E-25	0.0652	0.75	1157.774	-0.008247	0.1	-0.00113	0.011839	-0.00346	-0.00499	0.019826	-0.00615	-0.0057	0.021412	-0.00657
P 52	6297.618696	4.23E-25	0.0686	0.75	1074.431	-0.00682	0.1	-0.00079	0.010963	-0.00366	-0.00422	0.018221	-0.0062	-0.00485	0.019687	-0.00661
P 50	6299.893138	6.06E-25	0.0678	0.76	994.1911	-0.00573	0.1	-0.0006	0.01046	-0.00367	-0.00371	0.017224	-0.00608	-0.00431	0.018641	-0.0065
P 48	6302.142651	8.54E-25	0.0681	0.77	917.0572	-0.00703	0.1	-0.00047	0.010065	-0.00359	-0.0033	0.016382	-0.00586	-0.00386	0.017757	-0.00629
P 46	6304.366818	1.18E-24	0.0669	0.77	843.03	-0.00835	0.1	-0.00036	0.009669	-0.00345	-0.00291	0.015536	-0.00556	-0.00343	0.016867	-0.00599
P 44	6306.565245	1.61E-24	0.0667	0.78	772.1106	-0.00671	0.1	-0.00024	0.009226	-0.00325	-0.00249	0.014626	-0.00521	-0.00298	0.015909	-0.00562
P 42	6308.737559	2.15E-24	0.0678	0.78	704.3004	-0.0064	0.1	-8.9E-05	0.008714	-0.00302	-0.00205	0.01363	-0.0048	-0.00249	0.014861	-0.00521
P 40	6310.883404	2.82E-24	0.068	0.78	639.6003	-0.00656	0.1	0.000085	0.008126	-0.00275	-0.00156	0.012538	-0.00436	-0.00196	0.013714	-0.00476
P 38	6313.002446	3.64E-24	0.0682	0.78	578.0115	-0.00684	0.097	0.000289	0.007458	-0.00246	-0.00102	0.011347	-0.00388	-0.00138	0.012464	-0.00428
P 36	6315.094369	4.61E-24	0.0686	0.78	519.535	-0.00648	0.095	0.000524	0.006712	-0.00215	-0.00044	0.010054	-0.00338	-0.00075	0.011107	-0.00376
P 34	6317.158873	5.74E-24	0.0689	0.78	464.1717	-0.00627	0.102	0.000788	0.005888	-0.00182	0.000189	0.008657	-0.00286	-6.6E-05	0.009639	-0.00323
P 32	6319.195679	7.00E-24	0.0695	0.78	411.9225	-0.0067	0.114	0.001081	0.004991	-0.00149	0.000866	0.007153	-0.00232	0.000672	0.008056	-0.00267
P 30	6321.204523	8.38E-24	0.0698	0.78	362.7883	-0.00689	0.094	0.001398	0.004024	-0.00115	0.00159	0.00554	-0.00176	0.001464	0.006351	-0.0021
P 28	6323.185158	9.83E-24	0.0703	0.78	316.7698	-0.00673	0.108	0.001736	0.002993	-0.00082	0.002361	0.003815	-0.0012	0.002312	0.004518	-0.00151
P 26	6325,137354	1.13E-23	0.0709	0.78	273.868	-0.00692	0.112	0.002088	0.001906	-0.00051	0.003175	0.001975	-0.00063	0.003214	0.002548	-0.00091
P 24	6327.060897	1.27E-23	0.0716	0.78	234.0833	-0.00669	0.109	0.002446	0.000773	-0.00022	0.004026	0.000018	-0.00006	0.004169	0.000433	-0.0003
P 22	6328.955587	1.40E-23	0.0727	0.77	197.4166	-0.00654	0.122	0.0028	-0.00039	0.00002	0.004906	-0.00205	0.000495	0.005171	-0.00183	0.000306
P 20	6330 821242	1 50F-23	0.0741	0.76	163 8684	-0.00627	0 124	0.003133	-0.00156	0.000199	0.0058	-0.00423	0.001024	0.006208	-0.00425	0.00091
P 18	6332 657693	1 58F-23	0.075	0.74	133 4393	-0.00639	0.127	0.003422	-0.00272	0.000289	0.006675	-0.00649	0.001507	0.007255	-0.00682	0.001492
P 16	6334 464787	1 61F-23	0.0766	0.71	106 1297	-0.00639	0 144	0.003633	-0.0038	0.000254	0.007482	-0.00878	0.001905	0.008264	-0.0095	0.002024
P 14	6336 242384	1 58F-23	0.0781	0.69	81 9401	-0.0059	0 144	0.003712	-0.00474	0.000042	0.008126	-0.011	0.002155	0.009147	-0.01221	0.00245
P 12	6337 990359	1.50E 25	0.0701	0.69	60 8709	-0.00587	0.143	0.00357	-0.00542	-0.000042	0.000120	-0.01293	0.002133	0.009147	-0.01221	0.00245
P 10	6339 708601	1 38F-23	0.0737	0.05	42 9225	-0.00571	0.143	0.003057	-0.00561	-0.0013	0.000420	-0.01200	0.002100	0.000721	-0.01475	0.002037
D 8	6341 397014	1 10F-23	0.0013	0.7	28 0051	-0.00575	0.132	0.001870	-0.00/87	-0.00283	0.006101	-0.01332	_4 9E-05	0.0050	-0.01668	0.0024
P 6	6343.055514	0 //F-2/	0.005	0.71	16 3 80	-0.00323	0.135	-0.001075	-0.00487	-0.00283	0.000101	-0.01332	-4.56-05	0.007834	-0.01008	-0.001088
P /	6344 684032	6 57E-24	0.0873	0.73	7 80/13	-0.00403	0.127	-0.0000	0.00222	-0.00337	-0.01557	0.0073	-0.00428	-0.01609	0.01131	-0.00234
P 2	6346 282512	3 38F-24	0.0073	0.74	2 3/13	-0.00304	0.113	-0.00011	0.0001110	-0.01102	-0.01337	0.01458	-0.01030	-0.01003	0.012075	-0.01551
	6240.202312	1 715 24	0.052	0.73	2.3413	0.00341	0.125	0.02235	0.050855	0.02031	0.00070	0.10201	0.05350	0.10304	0.101301	0.06031
	6250 147040	E 00E 24	0.0933	0.74	2 2412	-0.00331	0.097	0.030213	-0.03239	0.031202	0.072979	0.10222	0.03303	0.004424	-0.11720	0.000309
R /	6351 640149	9 26E-24	0.0004	0.73	7 80/13	-0.00414	0.122	0.02103	-0.02032	0.020001	0.034002	0.003800	0.020303	0.0050178	0.04001	0.020102
D 6	6252 102126	1 115 22	0.0000	0.74	16 200	0.00477	0.122	0.000416	0.00433	0.003313	0.007340	0.000433	0.000700	0.000505	0.002313	0.000078
	6254 525009	1.110-23	0.0838	0.72	20.305	-0.00477	0.120	0.000410	0.00392	0.004674	0.00207	0.012033	0.002039	-0.00363	0.014702	0.001007
по В 10	6255 029709	1.536-25	0.0810	0.7	42 0225	-0.00402	0.131	-0.00237	0.007048	0.002273	-0.00073	0.013038	0.000335	-0.00793	0.01/2/2	-0.0002
n 10 n 12	6257 21157	1.556-25	0.08	0.09	42.5225	-0.00431	0.130	-0.00474	0.008933	0.000807	-0.00855	0.014051	-0.00043	-0.00939	0.010439	-0.00077
R 12 P 14	6357.31157	1 725 22	0.0766	0.09	91 0401	-0.00474	0.132	-0.00501	0.00892	0.000126	-0.00878	0.013221	-0.00058	-0.00962	0.014265	-0.0007
R 14	6356.054375	1.73E-23	0.0700	0.7	106 1207	-0.00496	0.134	-0.00596	0.006159	-0.00021	-0.00859	0.010986	-0.00038	-0.00925	0.011565	-0.00033
R 10	6359.967286	1.74E-23	0.0747	0.75	100.1297	-0.00551	0.117	-0.00596	0.00694	-0.00027	-0.00807	0.006465	0.000017	-0.00857	0.006079	0.000197
K 18	6361.250392	1.70E-23	0.0738	0.75	153.4393	-0.00535	0.124	-0.00575	0.005423	-0.00013	-0.00736	0.005814	0.000525	-0.0077	0.005707	0.000807
R 20	6362.503794	1.02E-23	0.0727	0.70	107.4166	-0.00590	0.110	-0.00558	0.003700	0.000142	-0.00055	0.003109	0.00111	-0.00675	0.002732	0.001475
R 22	0303.72701	1.516-25	0.0718	0.77	197.4100	-0.00577	0.125	-0.00491	0.001849	0.000529	-0.00504	0.000385	0.001754	-0.00575	-0.00022	0.00218
R 24	6364.921972	1.3/E-23	0.071	0.78	234.0833	-0.00594	0.111	-0.00437	-0.00011	0.001006	-0.0047	-0.00235	0.002446	-0.00469	-0.00315	0.002923
R 20 D 20	6267 222044	1.22E-23	0.0703	0.78	2/3.868	-0.0061	0.111	-0.003//	-0.00215	0.001559	-0.00373	-0.00508	0.00318	-0.00363	-0.00606	0.003699
K 28	6367.222941	1.06E-23	0.07	0.78	316.7698	-0.00608	0.112	-0.00313	-0.00424	0.002175	-0.00275	-0.00781	0.003954	-0.00256	-0.00895	0.004508
R 30	6368.32989	9.01E-24	0.0694	0.78	362.7883	-0.0063	0.101	-0.00247	-0.00639	0.002846	-0.00176	-0.01055	0.004765	-0.00149	-0.01184	0.005349
R 32	6369.408071	7.53E-24	0.0689	0.78	411.9225	-0.00627	0.099	-0.001/9	-0.00856	0.003565	-0.00076	-0.0133	0.005611	-0.00042	-0.014/3	0.006223
R 34	6370.457696	6.18E-24	0.0685	0.78	464.1/1/	-0.00657	0.092	-0.0011	-0.01077	0.004323	0.000238	-0.01605	0.00649	0.00066	-0.01762	0.007126
R 36	63/1.4/8994	4.9/E-24	0.0689	0.78	519.535	-0.00655	0.121	-0.0004	-0.013	0.005113	0.00124	-0.01882	0.007397	0.001/34	-0.02051	0.008057
R 38	63/2.4/2213	3.93E-24	0.0678	0.78	5/8.0115	-0.00708	0.088	0.000297	-0.01524	0.005929	0.002242	-0.0216	0.008326	0.002807	-0.02342	0.00901
к 40	63/3.43/618	3.05E-24	0.0683	0.78	639.6003	-0.00713	0.112	0.000995	-0.01749	0.006759	0.003241	-0.02439	0.009268	0.003877	-0.02634	0.009974
R 42	6374.375493	2.33E-24	0.0668	0.78	/04.3004	-0.00599	0.1	0.001692	-0.01975	0.007593	0.004239	-0.02718	0.010209	0.004946	-0.02926	0.010936
R 44	6375.286142	1.74E-24	0.0675	0.77	/72.1106	-0.00663	0.1	0.002392	-0.02201	0.008414	0.00524	-0.02997	0.011126	0.006016	-0.03219	0.011871
R 46	6376.169887	1.28E-24	0.0669	0.77	843.03	-0.00698	0.1	0.003111	-0.0243	0.0092	0.006257	-0.03278	0.011987	0.007102	-0.03512	0.012745
R 48	6377.027072	9.29E-25	0.0663	0.76	917.0572	-0.00755	0.1	0.003887	-0.02667	0.009919	0.007331	-0.03565	0.012742	0.008244	-0.03811	0.013502
R 50	6377.858062	6.61E-25	0.0649	0.76	994.1911	-0.00811	0.1	0.004813	-0.02929	0.010533	0.008568	-0.03875	0.013325	0.009551	-0.04132	0.014068
R 52	6378.663242	4.63E-25	0.0654	0.75	1074.431	-0.008536	0	0.006106	-0.0326	0.010983	0.010251	-0.04263	0.013661	0.011322	-0.04533	0.014359
R 54	6379.443021	3.18E-25	0.065	0.74	1157.774	-0.008655	0	0.008204	-0.03781	0.01112	0.01312	-0.0491	0.013713	0.014377	-0.0521	0.014362
R 56	6380.197829	2.15E-25	0.0645	0.73	1244.22	-0.00877	0	0.010446	-0.04694	0.009117	0.017899	-0.06426	0.012934	0.019889	-0.06894	0.013887

ΔN(N)	Line Center	Intensity	Lorentz Width	T-Dependence	E''	Pressure Shift	SD Lorentz width
0 15	7797.42	1.22E-26	0.0469	0.83	343.9694	-0.003244	0.046
P 25	7798.85	2.70E-27	0.0361	0.79	933.5309	-0.003311	0.038
P 25	7800.63	3.10E-27	0.0361	0.79	931.7432	-0.003285	0.038
P 23	7806.42	4.83E-27	0.0378	0.8	793.2087	-0.003174	0.041
P 23	7808.23	5.60E-27	0.0381	0.8	791.4032	-0.003126	0.041
0 13	7809.89	1.51E-26	0.0488	0.84	260.6824	-0.003028	0.048
P 21	7813.84	8.16E-27	0.0402	0.8	664.2595	-0.003145	0.042
P 21	7815.67	9.54E-27	0.0402	0.8	662.4359	-0.003106	0.042
P 19	7821.11	1.29E-26	0.0421	0.81	546.7042	-0.003041	0.043
0 11	7822.22	1.69E-26	0.0505	0.84	188.8531	-0.002919	0.05
P 19	7822.95	1.52E-26	0.0421	0.81	544.8622	-0.002912	0.043
P 17	7828.22	1.89E-26	0.0441	0.83	440.5618	-0.00295	0.044
P 17	7830.08	2.27E-26	0.0441	0.83	438.701	-0.002926	0.044
09	7834.4	1.66E-26	0.0524	0.84	128.492	-0.002666	0.051
P 15	7835.18	2.57E-26	0.0459	0.83	345.8495	-0.002793	0.045
P 15	7837.06	3.15E-26	0.0458	0.83	343.9694	-0.002783	0.045
P 13	7841.99	3.22E-26	0.0476	0.83	262.5827	-0.002784	0.048
P 13	7843.89	4.07E-26	0.0475	0.83	260.6824	-0.002707	0.048

Table A.4: The retrieved spectroscopic parameters for the O₂ $a^1 \Delta_g \leftarrow X^3 \Sigma_g^-$ band as described in Section 7.3.

07	7846.43	1.34E-26	0.0546	0.84	79.607	-0.002515	0.052
P 11	7848.64	3.68E-26	0.0492	0.84	190.7748	-0.002691	0.049
P 11	7850.56	4.82E-26	0.0491	0.84	188.8531	-0.002635	0.049
Q 39	7850.83	1.72E-29	0.0225	0.72	2232.0828	-0.005118	0.029
Q 37	7854.01	4.75E-29	0.0238	0.73	2012.8914	-0.005075	0.03
Р9	7855.13	3.75E-26	0.0508	0.84	130.4375	-0.002521	0.05
Q 35	7857.01	1.24E-28	0.0252	0.74	1804.8746	-0.005028	0.03
Р9	7857.08	5.16E-26	0.0506	0.84	128.492	-0.002439	0.05
05	7858.32	7.32E-27	0.0581	0.84	42.2001	-0.002208	0.055
Q 35	7858.71	3.37E-29	0.0252	0.74	1803.1738	-0.00503	0.03
Q 35	7859.29	2.90E-29	0.0252	0.74	1802.592	-0.00503	0.03
Q 33	7859.83	3.03E-28	0.0268	0.75	1608.0662	-0.004978	0.033
Р7	7861.47	3.27E-26	0.0528	0.84	81.5805	-0.002472	0.051
Q 33	7861.55	8.28E-29	0.0268	0.75	1606.3483	-0.004979	0.033
Q 33	7862.1	7.09E-29	0.0268	0.75	1605.8013	-0.004979	0.033
Q 31	7862.49	7.15E-28	0.029	0.76	1422.4984	-0.003532	0.034
Р7	7863.44	4.96E-26	0.0526	0.84	79.607	-0.002396	0.051
Q 31	7864.22	1.93E-28	0.0285	0.76	1420.7631	-0.004924	0.034
Q 31	7864.73	1.64E-28	0.0285	0.76	1420.2512	-0.004924	0.034
Q 29	7864.97	1.56E-27	0.0311	0.77	1248.2013	-0.003465	0.035

Q 29	7866.72	4.24E-28	0.0305	0.77	1246.4487	-0.004863	0.035
Q 29	7867.2	3.53E-28	0.0305	0.77	1245.9719	-0.004863	0.035
Q 27	7867.28	3.18E-27	0.0328	0.78	1085.2033	-0.003674	0.036
Р 5	7867.65	2.20E-26	0.0557	0.84	44.2117	-0.002166	0.054
Q 27	7869.05	9.29E-28	0.0342	0.78	1083.4332	-0.003395	0.036
Q 25	7869.42	6.22E-27	0.0356	0.78	933.5309	-0.002878	0.037
Q 27	7869.49	8.32E-28	0.0355	0.78	1082.9917	-0.003565	0.036
Р 5	7869.67	3.93E-26	0.0555	0.84	42.2001	-0.002323	0.054
Q 25	7871.21	1.79E-27	0.0353	0.78	931.7432	-0.00312	0.037
Q 23	7871.39	1.13E-26	0.0377	0.79	793.2087	-0.002989	0.04
Q 25	7871.61	1.42E-27	0.0359	0.78	931.3373	-0.003142	0.037
Q 23	7873.2	3.37E-27	0.037	0.79	791.4032	-0.0029	0.04
Q 21	7873.2	1.93E-26	0.0405	0.8	664.2595	-0.004	0.042
Q 23	7873.57	2.51E-27	0.0368	0.79	791.0331	-0.003178	0.04
Р 3	7873.68	6.96E-27	0.061	0.84	18.3372	-0.000912	0.057
Q 19	7874.85	3.10E-26	0.0414	0.81	546.7042	-0.003003	0.043
Q 21	7875.03	5.69E-27	0.0397	0.8	662.4359	-0.003	0.042
Q 21	7875.36	4.29E-27	0.0391	0.8	662.1021	-0.002992	0.042
P 3	7875.77	1.90E-26	0.0597	0.84	16.2529	-0.001286	0.057
Q 17	7876.33	4.65E-26	0.0434	0.81	440.5618	-0.002637	0.043
Q 19	7876.69	9.16E-27	0.041	0.81	544.8622	-0.002801	0.043
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Q 19	7876.99	6.79E-27	0.0409	0.81	544.5651	-0.002666	0.043
Q 15	7877.65	6.51E-26	0.0451	0.83	345.8495	-0.002495	0.045
Q 17	7878.19	1.40E-26	0.043	0.81	438.701	-0.002805	0.043
Q 17	7878.45	1.00E-26	0.0427	0.81	438.4413	-0.002785	0.043
Q 13	7878.81	8.47E-26	0.0467	0.83	262.5827	-0.002357	0.046
Q 15	7879.53	2.01E-26	0.0451	0.83	343.9694	-0.003027	0.045
Q 15	7879.75	1.41E-26	0.0454	0.83	343.7481	-0.002638	0.045
Q 11	7879.8	1.01E-25	0.049	0.84	190.7748	-0.001741	0.048
Q 9	7880.64	1.12E-25	0.0501	0.84	130.4375	-0.002741	0.05
Q 13	7880.71	2.66E-26	0.0462	0.83	260.6824	-0.003763	0.046
Q 13	7880.89	1.77E-26	0.0467	0.83	260.5009	-0.002354	0.046
Q 7	7881.31	1.10E-25	0.0509	0.84	81.5805	-0.002121	0.051
Q 11	7881.72	3.31E-26	0.0481	0.84	188.8531	-0.002943	0.048
Q 5	7881.83	9.35E-26	0.053	0.84	44.2117	-0.0016	0.052
Q 11	7881.86	2.07E-26	0.0484	0.84	188.7134	-0.002781	0.048
Q 3	7882.19	6.02E-26	0.0574	0.84	18.3372	-0.001505	0.055
Q 9	7882.58	3.82E-26	0.0494	0.84	128.492	-0.002126	0.05
Q 9	7882.68	2.18E-26	0.0505	0.84	128.3977	-0.002086	0.05
Q 7	7883.29	4.10E-26	0.0523	0.84	79.607	-0.002327	0.051

Q 7	7883.33	2.01E-26	0.0519	0.84	79.5646	-0.001575	0.051
Q 5	7883.82	1.53E-26	0.0532	0.84	42.224	-0.000797	0.052
Q 5	7883.84	4.05E-26	0.0542	0.84	42.2001	-0.001819	0.052
Q 3	7884.14	7.66E-27	0.06	0.84	16.3876	-0.001304	0.055
Q 3	7884.27	3.78E-26	0.0579	0.84	16.2529	-0.001425	0.055
R 1	7888.06	6.69E-26	0.0567	0.84	3.9611	-0.00141	0.057
R 1	7889.93	1.74E-26	0.0605	0.84	2.0843	-0.000453	0.057
R 3	7893.53	7.79E-26	0.0558	0.84	18.3372	-0.001086	0.054
R 3	7895.48	4.09E-26	0.0562	0.84	16.3876	-0.000833	0.054
S 1	7898.44	3.49E-26	0.0586	0.84	2.0843	-0.000263	0.055
R 5	7898.84	8.54E-26	0.0525	0.84	44.2117	-0.001179	0.051
R 5	7900.83	5.57E-26	0.0527	0.84	42.224	-0.001108	0.051
R 7	7903.99	8.59E-26	0.0505	0.84	81.5805	-0.001305	0.05
R 7	7906	6.24E-26	0.0505	0.84	79.5646	-0.001249	0.05
R 9	7908.97	7.95E-26	0.049	0.84	130.4375	-0.001489	0.049
S 3	7909.65	4.24E-26	0.055	0.84	16.3876	-0.000259	0.052
R 9	7911.01	6.16E-26	0.0491	0.84	128.3977	-0.00141	0.049
R 11	7913.8	6.82E-26	0.0476	0.83	190.7748	-0.00164	0.048
R 11	7915.86	5.52E-26	0.0476	0.83	188.7134	-0.001591	0.048
R 13	7918.45	5.43E-26	0.0461	0.83	262.5827	-0.001749	0.045

R 13	7920.53	4.53E-26	0.0459	0.83	260.5009	-0.001604	0.045
S 5	7920.67	4.63E-26	0.0521	0.84	42.224	-0.000593	0.051
R 15	7922.94	4.06E-26	0.0444	0.83	345.8495	-0.002166	0.044
R 15	7925.04	3.46E-26	0.0444	0.83	343.7481	-0.002187	0.044
R 17	7927.25	2.83E-26	0.0426	0.81	440.5618	-0.00237	0.043
R 17	7929.37	2.45E-26	0.0425	0.81	438.4413	-0.002418	0.043
R 19	7931.4	1.86E-26	0.0408	0.8	546.7042	-0.002418	0.042
S 7	7931.51	4.63E-26	0.0502	0.84	79.5646	-0.001037	0.05
R 19	7933.54	1.63E-26	0.0407	0.8	544.5651	-0.002582	0.042
R 21	7935.37	1.14E-26	0.0388	0.8	664.2595	-0.002848	0.041
R 21	7937.53	1.00E-26	0.0377	0.8	662.1021	-0.002606	0.041

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