Using a Speed-Dependent Voigt Line Shape to Retrieve O$_2$ from Total Carbon Column Observing Network Solar Spectra to Improve Measurements of XCO$_2$ Improving the Retrieval of XCO$_2$-from Total Carbon Column Network Solar Spectra

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Abstract. High-resolution absorption spectra of the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ oxygen(O$_2$) band measured using cavity ring-down spectroscopy were fitted using the Voigt and speed-dependent Voigt line shapes. We found that the speed-dependent Voigt line shape was better able to model the measured absorption coefficients than the Voigt line shape. We used these line shape models to calculate absorption coefficients to retrieve atmospheric total columns abundances of O$_2$ were retrieved from ground-based high-resolution absorption spectra from four Fourier transform spectrometers that are apart of the Total Carbon Column Observing Network (TCCON) sites using both Voigt and speed-dependent Voigt line shapes to calculate absorption coefficients. All lower O$_2$ concentration total columns were retrieved with the speed-dependent Voigt line shape, with the difference between the total columns retrieved using the Voigt and speed-dependent Voigt line shapes increasing as a function of solar zenith angle. Previous work has shown that carbon dioxide (CO$_2$) total columns were also retrieved from the same spectra using a Voigt line shape and are better retrieved using a speed-dependent Voigt line shape with line mixing. The column-averaged dry-air mole fraction of CO$_2$ (XCO$_2$) was calculated using the ratio between the columns of CO$_2$ and O$_2$ columns retrieved (from the same spectra) with both line shapes from measurements made over a one-year period at the four sites, and compared. The inclusion of speed dependence in the O$_2$ retrievals significantly reduces the airmass dependence of XCO$_2$. The TCCON empirical airmass correction factor for XCO$_2$ derived from a year of measurements from TCCON sites at Darwin, Lamont, and Park Falls for XCO$_2$ improved from 0.9971±0.0057 to 0.9912±0.0051 when speed dependence was included. XCO$_2$ retrieved with the Voigt and speed dependent Voigt line shapes was compared to aircraft profiles measured at 13 TCCON sites. The bias between the TCCON measurements and the calibrated integrated aircraft profile measurements was reduced from 0.9897±0.0005 1% to 1.0041±0.0005 4%. for XCO$_2$ retrieved with the Voigt and speed dependent Voigt line shapes respectively. These results suggest that speed dependence should be included in the forward model when fitting near-infrared CO$_2$ and O$_2$ spectra to improve the accuracy of XCO$_2$ measurements.
1. Introduction

Accurate remote sensing of greenhouse gases (GHGs), such as CO$_2$, in Earth’s atmosphere is important for studying the carbon cycle in order to better understand and predict climate change. The absorption of solar radiation by O$_2$ in the Earth’s atmosphere is important because it can be used to study the properties of clouds and aerosols, and to determine vertical profiles of temperature and surface pressure. Wallace and Livingston (1990) were the first to retrieve total columns of O$_2$ from some of the discrete lines of the $a^1\Delta_g\leftarrow X^3\Sigma_g^+$ band of O$_2$ centered at 1.27 $\mu$m (which will be referred to bellow as the 1.27 $\mu$m band) using atmospheric solar absorption spectra from the Kitt Peak observatory. Mlawer et al. (1998) recorded solar absorption spectra in the near-infrared (NIR) region to study collision-induced absorption (CIA) in the $a^1\Delta_g\leftarrow X^3\Sigma_g^+$ band of O$_2$ centered at 1.27 $\mu$m (which will be referred to as the 1.27 $\mu$m band), as well as two other O$_2$ bands. 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 $\mu$m band (Mlawer et al., 1998). Subsequently, spectroscopic parameters needed to calculate the absorption coefficients from discrete transitions of the 1.27 $\mu$m band were measured in multiple studies (Cheah et al., 2000; Newman et al., 1999, 2000; Smith and Newnham, 2000), as was collision-induced absorption (CIA) (Maté et al., 1999; Smith and Newnham, 2000), while Smith et al. (2001) validated the work done in Smith and Newnham (2000) using solar absorption spectra.

The 1.27 $\mu$m band is of particular importance to the Total Carbon Column Observing Network (TCCON) (Wunch et al., 2011). TCCON is a ground-based remote sensing network that makes accurate and precise measurements of GHGs for satellite validation and carbon cycle studies. Using the O$_2$ column retrieved from solar absorption spectra, the column-averaged dry-air mole fraction of CO$_2$ (XCO$_2$) has been shown to provide better precision than using the surface pressure to calculate XCO$_2$ (Yang et al., 2002) (Washenfelder et al., 2006). The O$_2$ column is retrieved from the 1.27 $\mu$m band because of its close proximity to the spectral lines used to retrieve CO$_2$, thereby reducing the impact of solar tracker mis-pointing and an imperfect instrument line shape (ILS) (Washenfelder et al., 2006). To improve the retrievals of O$_2$ from the 1.27 $\mu$m band, Washenfelder et al. (2006) found that adjusting the spectroscopic parameters in HITRAN 2004 (Rothman et al., 2005) decreased the airmass and temperature dependence of the O$_2$ column. These revised spectroscopic parameters were included in HITRAN 2008 (Rothman et al., 2009). Atmospheric solar absorption measurements from this band made at the Park Falls TCCON site 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 $\mu$m band using a Voigt spectral line shape and these parameters were included in HITRAN 2012 (Rothman et al., 2013). Spectroscopic parameters for the discrete spectral lines of the O$_2$ 1.27 $\mu$m band from HITRAN 2016 (Gordon et al., 2017) are very similar to HITRAN 2012 except that HITRAN2016 includes improved line positions reported by Yu et al. (2014).

Extensive spectral line shape studies have been performed for the O$_2$ A-band, which is centered at 762 nm and used by the Greenhouse Gases Observing Satellite (GOSAT) (Yokota et al., 2009) and the Orbiting Carbon Observing

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Observatory-2 (OCO-2) satellite (Crisp et al., 2004) to determine surface pressure. Studies have shown that the Voigt line shape is inadequate to describe the spectral line shape of the discrete \( \text{O}_2 \) lines in the A-band. Dicke narrowing occurs when the motion of the molecule is diffusive due to collisions changing the velocity and direction of the molecule during the time that it is excited. This diffusive motion is taken into account by averaging over many different Doppler states resulting in a line width that is narrower than the Doppler width (Dicke, 1953). The need to take into account Dicke narrowing was shown in Long et al. (2010) and Predoi-Cross et al. (2008) found it necessary to use a spectral Line shape model that accounted for Dicke narrowing when fitting the discrete lines of the \( \text{O}_2 \) A-band, and Line mixing, which occurs when collisions transfer intensity from one part of the spectral band to another (Lévy et al., 1992), was shown to be prevalent in multiple studies (Predoi-Cross et al., 2008; Tran et al., 2006; Tran and Hartmann, 2008). Tran and Hartmann (2008) showed that including line mixing when calculating the \( \text{O}_2 \) A-band absorption coefficients reduced the airmass dependence of the \( \text{O}_2 \) column retrieved from TCCON spectra. When fitting cavity ring-down spectra of the \( \text{O}_2 \) A-band, Drouin et al. (2017) found it necessary to use a speed-dependence Voigt line shape, which takes into account different speeds at the time of collision (Shannon et al., 1986), with line mixing to properly fit the discrete spectral lines of the \( \text{O}_2 \) A-band.

The need to include non-Voigt effects when calculating absorption coefficients for the \( \text{O}_2 \) 1.27 \( \mu \text{m} \) band was first shown in Hartmann et al. (2013) and Lamouroux et al. (2014). Lorentzian widths were calculated using the re-quantized classical molecular-dynamics simulations (cCMDs) and used to fit cavity-ring-down spectra with a Voigt line shape for some isolated transitions in the \( \text{O}_2 \) 1.27 \( \mu \text{m} \) band. The studies concluded that a Voigt line shape is insufficient for modeling the spectral lines of the \( \text{O}_2 \) 1.27 \( \mu \text{m} \) band and that effects such as speed dependence and Dicke narrowing should be included in the line shape calculation.

In this study, air-broadened cavity-ring-down spectra of the \( \text{O}_2 \) 1.27 \( \mu \text{m} \) band were fitted using a spectral line shape that takes into account speed dependence. The corresponding spectroscopic parameters for the speed-dependent Voigt line shape were used to calculate absorption coefficients when fitting high-resolution solar absorption spectra. Using these new \( \text{O}_2 \) total columns, and the simultaneously measured \( \text{CO}_2 \) total columns, from using the updated line shape model described by Mendonça et al. (2016), to calculate \( \text{XCO}_2 \) and compared these results with \( \text{XCO}_2 \) retrieved using a Voigt line shape. Section 2 details the formulas used to calculate absorption coefficients using different spectral line shapes. In Section 3, we describe the retrieval of spectroscopic parameters from three air-broadened cavity-ring-down spectra fitted with a speed-dependent Voigt line shape. For Section 4, the speed-dependent line shape along with the retrieved spectroscopic parameters is used to fit solar absorption spectra from four TCCON sites and retrieve total columns of \( \text{O}_2 \), which is compared to \( \text{O}_2 \) retrieved using a Voigt line shape. In Section 5, we investigate the change in the airmass dependence of \( \text{XCO}_2 \) with the new \( \text{O}_2 \) parameters retrievals. In Section 6, we discuss our results and their implications for remote sensing of greenhouse gases.

2. Absorption Coefficient Calculations

2.1 Voigt Line Shape
The Voigt line shape is the convolution of the Lorentz and the Gaussian Doppler line shapes profiles, which model pressure and Doppler broadening of the spectral line respectively. The corresponding absorption coefficient, $k$, at a given wavenumber $v$ becomes:

$$
k(v) = N \sum_j S_j \left( \frac{1}{\gamma_{D,j}} \right) \left( \frac{\ln(2)}{\pi} \right)^{1/2} \left( \text{Re} \left[ c(v, x_j, y_j) \right] \right)
$$

where $N$ is the number density, $S_j$ is the line intensity of spectral line $j$, $\gamma_{D,j}$ is the Doppler half-width (HWHM), $c$ is the complex error function, and

$$
x_j = \frac{(v - v_j^0 - P \delta_j^0)}{\gamma_{D,j}} \left( \frac{\ln(2)}{\pi} \right)^{1/2}, \quad y_j = \frac{\gamma_{L,j}}{\gamma_{D,j}} \left( \frac{\ln(2)}{\pi} \right)^{1/2}.
$$

Here, $v_j^0$ is the position of the spectral line $j$, $P$ is the pressure, and $\delta_j^0$ is the pressure-shift coefficient. The Lorentz half-width, $\gamma_{L,j}$, is calculated using:

$$
\gamma_{L,j}(T) = P \gamma_{L,j}^0 \left( \frac{T}{296} \right)^n
$$

where $\gamma_{L,j}^0$ is the air-broadened Lorentz half-width coefficient (at reference temperature 296 K) and $n$ is the exponent of temperature dependence. The Voigt line shape assumes that pressure broadening is accurately represented by a Lorentz profile calculated for the statistical average velocity at the time of collision.

### 2.2 Speed-Dependent Voigt Line Shape

The speed-dependent Voigt line shape refines the pressure broadening component of the Voigt by calculating multiple Lorentz profiles for different speeds at the time of collision. The final contribution from pressure broadening to the speed-dependent Voigt is the weighted sum of Lorentz profiles (weighted by the Maxwell-Boltzmann speed-distribution) calculated for different speeds at the time of collision. To take speed dependence into account, we use: The speed-dependent Voigt line shape (Ciuryło, 1998) with the quadratic representation of the Lorentz width and pressure shift (Rohart et al., 1994) is:

$$
k(v) = N \left( \frac{2}{\pi \gamma_{L,j}} \right) \sum_j S_j \int_{-\infty}^{\infty} e^{-V^2} \left( \tan^{-1} \left[ \frac{x_j - B \alpha_j(4V^2 - 1.5) + V}{y_j(1 + \alpha_{\gamma_{L,j}}(4V^2 - 1.5))} \right] \right) dV
$$

where $\alpha_{\gamma_{L,j}}$ is the speed-dependent Lorentz width parameter (unitless) for line $j$, $\alpha_j$ is the speed-dependent pressure-shift parameter (unitless), $B$ is $\frac{\left( \frac{\ln(2)}{\pi} \right)^{1/2}}{\gamma_{D,j}}$, $V$ is the ratio of the absorbing molecule’s speed to the most probable speed of the absorbing molecule, and all other variables are defined before.

### 3. 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 (\(X^3Σ_g^-\)) 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 (\(a^1Δ_g\), \(J = N\). When labeling a transition, the following nomenclature is used \(ΔN(N''\Delta J(J'')\) (Leshchishina et al., 2010), where \(ΔN\) is the difference between \(N'\) in the upper state and \(N''\) in the lower state, \(ΔJ\) is the difference between \(J'\) in the upper state and \(J''\) in the lower state. The magnetic transitions of \(a^1Δ_g ← X^3Σ_g^-\) allow for \(ΔJ = 0, \pm 1\). This leads to 9 branches observed: \(P(N'')Q(J''),\) \(R(N'')Q(J''),\) and \(Q(N')Q(J'')\), for \(ΔJ = 0, O(N'')P(J''), P(N'')P(J''),\) and \(Q(N'')P(J''),\) for \(ΔJ = 1,\) and \(S(N'')R(J''), R(N'')R(J''),\) and \(Q(N'')R(J''),\) for \(ΔJ = 1\).

Absorption coefficients for three room temperature air-broadened (NIST Standard reference material® 2659a containing 79.28 % N₂, 20.720(43) % O₂, 0.0029 % Ar, 0.00015 % H₂O, and 0.001 % other compounds) spectra were measured at the National Institute of Standards and Technology (NIST) using the frequency-stabilized cavity-ring-down spectroscopy (FS-CRDS) technique (Hodges et al., 2004; Hodges, 2005). The absorption spectra were acquired at pressures of 131 kPa, 99.3 kPa, and 66.9 kPa, at temperatures of 296.28 K, 296.34 K, and 296.30 K respectively. Figure 1a shows the three measured absorption spectra. A more detailed discussion of the present FS-CRDS spectrometer can be found in Lin et al. (2015).

The spectra were fitted individually using a Voigt line shape (Eq. 1), with \(S_J, γ_{LJ}^J,\) and \(δ_J^P\) for the main isotope of the magnetic dipole lines of the O₂ 1.27 μm band for lines with an intensity greater than \(7.0 \times 10^{-28} \text{ cm}^{-1}/(\text{molecule cm}^2)\). The spectroscopic parameters measured in Leshchishina et al. (2011) for the spectral lines of interest were used as the a priori for the retrieved spectroscopic parameters. The line positions were left fixed to the values measured in Leshchishina et al. (2011), and all other O₂ spectral lines (intensity less \(7.0 \times 10^{-28} \text{ cm}^{-1}/(\text{molecule cm}^2)\)) were calculated using a Voigt line shape with spectroscopic parameters from HITRAN 2012 (Rothman et al., 2013). 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. To take collision-induced absorption (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 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 Root Mean Square (RMS) residual values for the spectra are given by the legend at the side of the plot.

Figure 2 is the same plot as Figure 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 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 6.7 to 107 kPa. Figure 5 of Hartmann et al.
(2013) shows the P(11)P(11) line at a pressure of 66.7 kPa, which is approximately the pressure of the 66.9 kPa spectrum (blue spectrum in Figure 1 and 2). When one compares the blue residual of the P(11)P(11) line in Figure 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) show that the amplitude of the residual increases with decreasing pressure, which is also seen in Figure 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 the residual increases with decreasing pressure (although for lower pressures) consistent with the results for the P(9)P(9) line in Figure 2b.

Figure 1c shows the residual when using the speed-dependent Voigt (Eq. 4) to fit each spectrum individually. To use Eq. (4) requires integration over all possible speeds, which is not computationally practical, so we employ the simple numerical integration scheme as was done by Wehr (2005). When fitting the spectra, parameters $S_j$, $\gamma_{Lj}^0$, $\delta_j^0$, $a_{\gamma L}$, and $a_{\delta j}$ were retrieved for lines of intensity greater than $7.0 \times 10^{-28} \text{ cm}^{-1}/($molecule cm$^2$), while all other $O_2$ lines were calculated using a Voigt line shape and spectroscopic parameters from HITRAN 2012 (Rothman et al., 2013b).

The Jacobian matrix was created by taking the derivative with respect to each parameter of interest, as was done with the Voigt fits. By taking speed-dependent effects into account, the residuals were reduced to 25 times smaller than those for the Voigt fit and the RMS residuals (given in the legend of Figure 1c) are 10 times smaller. However, some residual structure still remains, which is more evident in the in the Q and R branches than the P branch. Figure 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 $O_2$ lines.

Figure 3 shows the averaged intensity, Lorentz width coefficient, pressure shift coefficient, and speed-dependent shift coefficient of the 1.27 $\mu$m $O_2$ band, retrieved from the three spectra, plotted as a function of $J''m$ quantum number $m$ which is $m=J$ (where $J$ is the lower state rotational quantum number) for the P-branch lines, $m=J+1$ for the Q-branch lines, and $m=J+1$ for the R-branch lines. The intensity, Lorentz widths, and pressure shifts show a $J''m$ dependence for these parameters for the P and R sub-branches. The measured Lorentz widths and pressure shifts for the Q sub-branches show a $J''m$ dependence but are not as strong as the P and R sub-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 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 $O_2$ absorption lines also blend in with the Q branch, contributing to the residual structure in Figure 1c. We tried retrieving the spectroscopic parameters for the weak $O_2$ absorption lines, but since they were overlapping with the strong $O_2$ lines, it was not possible. Figure 4a shows the retrieved speed-dependent width parameter averaged over the three spectra, plotted as a function of $J''m$, showing that it increases with $J''m$. Error bars correspond to the $2\sigma$ standard deviation and are large regardless of sub-branch. Figure 4b shows the retrieved speed-dependent width for the PQ sub-branch for the different pressures. The speed-dependent width shows the same $J''m$ dependence regardless of pressure, but also increases with decreasing pressure as is the case for sub-branches. It should be noted that the speed-dependent width parameter should be independent of pressure.
4. Fitting Solar Spectra

High-resolution solar absorption spectra were measured at four TCCON sites using a Bruker IFS 125HR FTIR spectrometer with a room temperature InGaAs detector at a spectral resolution of 0.02 cm\(^{-1}\) (45 cm maximum optical path difference). The raw interferograms recorded by the instrument were processed into spectra using the I2S software package (Wunch, D. et al., 2015) that corrects for solar intensity variations (Keppel-Aleks et al., 2007), phase errors (Mertz, 1967), and laser sampling errors (Wunch, D. et al., 2015), and then performs a fast Fourier transforms to convert the interferograms into spectra (Bergland, 1969). The GGG software package (Wunch, D. et al., 2015) is used to retrieve total columns of atmospheric trace gases. GFIT is the main code that contains the forward model, which calculates a solar absorption spectrum using a line-by-line radiative transfer model and an iterative non-linear least square fitting algorithm that scales an a priori gas profile to obtain the best fit to the measured spectrum. A priori profiles for GHGs are created by an empirical model in GGG that is based on measurements from the balloon-borne JPL MkIV Fourier Transform Spectrometer (FTS) (Toon, 1991), the Atmospheric Chemistry Experiment (ACE) FTS instrument aboard SCISAT (Bernath et al., 2005), and in situ GLOBALVIEW data (Wunch et al., 2011). Temperature and pressure profiles, as well as H\(_2\)O a priori profiles are generated from the National Centers for Environmental Prediction (NCEP) data. The calculations are performed for 71 atmospheric layers (0 km to 70 km), so all a priori profiles are generated on a vertical grid of 1 km.

In the current GGG software package (Wunch, D. et al., 2015), the forward model of GFIT calculates absorption coefficients for the discrete lines of the O\(_2\) 1.27 \(\mu\)m band using a Voigt line shape and spectroscopic parameters from Washenfelder et al. (2006a) 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, D. 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 \(\mu\)m band only. Airglow is not considered when fitting the 1.27 \(\mu\)m band since the spectrometer views the sun directly, and airglow is overwhelmed by such a bright source. The continuum level and tilt of the 100% transmission level is fitted using a weighted combination of the first two Legendre polynomials.

Absorption coefficient for all other trace gases are calculated using a Voigt line shape and spectroscopic parameters from the atm.101 line list (Toon, G. C., 2014a) and solar lines are fitted using the solar line list (Toon, G. C., 2014b) and the TCCON standard.

Figure 5 shows the spectral fit to a solar absorption spectrum recorded at Eureka on March 27, 2015, at a solar zenith angle (SZA) of 81.32\(^o\) (airmass of 6.3). This spectrum is an average of 5 Eureka scans. The TCCON standard is single scan but 5 scans were averaged to decrease the noise. The measured spectrum (red circles), calculated spectrum (black circles) and transitions from all gases in the window (colored lines, refer to the legend for different gases) are shown in Figure 5b. The residual obtained using a Voigt line shape to calculate the discrete lines of the O\(_2\)
1.27 µm band is shown in red in Figure 5a. The blue residual is the result of using a speed-dependent Voigt line shape with the spectroscopic parameters retrieved from fitting the absorption coefficients in Section 3. To decrease the amount of time it takes to calculate the absorption coefficients, the quadratic-Speed Dependent Voigt (qSDV) computational approach of Ngo et al. (2013) and Tran et al. (2013) was used instead of Eq. (4) since it requires the Voigt calculation only twice, while Eq. (4) requires numerical integration scheme with 33 iterations. 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 γ_L(T). There was only a slight improvement in the fit residuals with the new absorption coefficients (using the qSDV), as seen in Figure 5a.

Absorption coefficients calculated with the qSDV were used to retrieve total columns of O₂ from solar spectra recorded over a one year period at TCCON sites in Eureka (eu) (Nunavut, Canada) (Batchelor et al., 2009; Strong et al., 2017), Park Falls (pa) (Wisconsin, U.S.A) (Washenfelder et al., 2006; Wennberg et al., 2017), Lamont (oc) (Oklahoma, U.S.A) (Wennberg et al., 2017b), and Darwin (db) (Australia) (Deutscher et al., 2010; Griffith et al., 2017) (Deutscher et al., 2010). In total 131 124 spectra were fit using the qSDV and the average root mean square (RMS) residual of the fit only decreased by 0.5%.

5. Impact of O₂ Columns on XCO₂ Measurements

The O₂ column retrieved from the 1.27 µm band with a Voigt line shape and spectroscopic parameters from the atm.101 line list (Toon, G. C., 2014a) (Wunch, D. et al., 2015) has an airmass dependence such that the O₂ column retrieved increases as a function of solar zenith angle (or airmass). Using spectra recorded from Eureka, Park Falls, Lamont, and Darwin over one-year periods, total columns of O₂ were retrieved using (1) a Voigt spectral line shape with spectroscopic parameters from the atm.101 line list and (2) the qSDV with the spectroscopic parameters determined in Section 3. Figure 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 solar zenith angle (SZA). At the smallest SZA, the qSDV retrieves 0.75% less O₂ than the Voigt, with the difference increasing to approximately 1.8% as the SZA approaches 90°. Figure 7 shows XAIR from Park Falls on June 18, 2013. XAIR is the column of air (determined using surface pressure recorded at the site) divided by the column of O₂ retrieved from the spectra and multiplied by 0.2095, which is the dry air mole fraction of O₂ in Earth’s atmosphere. Ideally XAIR should be 1 but when using O₂ retrieved with a Voigt line shape (red points) it is closer to 0.98 near noon (small SZA) and lower near the start and end of the day (large SZA). When using O₂ retrieved with the qSDV, XAIR is closer to 0.988 near noon and a bit higher near the start and end of the day. This means the O₂ column, retrieved with the qSDV, decreases as a function of SZA, while previously the column increased as a function of SZA when the Voigt line shape is used.

5.1 Airmass Dependence of XCO₂

Since the standard TCCON XCO₂ (and all other XGas) is calculated using the column of O₂ instead of the surface pressure, errors associated with the retrieval of O₂, such as the airmass dependence of the O₂ column, will affect XCO₂. Figure 8 is XCO₂ calculated for four different combinations pertaining to the two CO₂ column retrievals and...
the O$_2$ column retrievals. The CO$_2$ columns were retrieved with either a Voigt line shape (the standard GGG2014 approach) or the qSDV with line mixing as done in Mendonca et al. (2016) while the O$_2$ columns were retrieved with either a Voigt (the standard GGG2014 approach) or the new qSDV approach developed here. Figure 8 shows a spurious symmetric component to XCO$_2$ when the total column of O$_2$ is retrieved with the Voigt line shape, regardless of line shape used to retrieve CO$_2$. When the qSDV is used to retrieve total columns of O$_2$, the symmetric component of XCO$_2$ is dismissed regardless of line shape used to retrieve CO$_2$. This is because the airmass dependence of the column of O$_2$ retrieved using the qSDV is more consistent with the airmass dependence of the column of CO$_2$ (for both line shapes used to retrieve CO$_2$). Mendonca et al. (2016) showed that using the qSDV with line mixing results in better fits to the CO$_2$ windows and impacts the airmass dependence of the retrieved column of CO$_2$. When using a Voigt line shape the retrieved column amount of CO$_2$ decreases as airmass increases until the airmass is large (SZA of about 82\(^\circ\)) at which point the retrieved column of CO$_2$ increases as the airmass increases, changing the shape of the airmass dependence of the CO$_2$ column. When the qSDV with line mixing is used, the retrieved column of CO$_2$ decreases as a function of airmass (up until the sun is above the horizon).

In order to correct for this, an empirical correction is applied to all TCCON XCO$_2$ (and XGas). The empirical correction determines the antisymmetrical component of the day’s XCO$_2$, which is assumed to be the true variation of XCO$_2$ throughout the day, as well as the symmetrical component, which is caused by the airmass dependence of the retrieved column of the gas of interest and O$_2$. We can, therefore, represent a measurement as (Wunch et al., 2011):

\[
\gamma_i = \hat{\gamma}_i [1 + \alpha S(\theta_i) + \beta A(t_i)]
\]  

(5)

where $\hat{\gamma}_i$ is the mean value of XCO$_2$ measured that day, $\beta$ is the fitted coefficient of the antisymmetric function $A(t_i)$ and $\alpha$ is the fitted coefficient of the symmetric function $S(\theta_i)$. The antisymmetric function is calculated by (Wunch et al., 2011):

\[
A(t_i) = \sin(2\pi(t_i - t_{noon}))
\]

(6)

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

\[
S(\theta_i) = \left(\frac{\theta_i + 13^\circ}{90^\circ + 13^\circ}\right)^3 - \left(\frac{\theta_i + 45^\circ + 13^\circ}{90^\circ + 13^\circ}\right)^3
\]

(7)

where $\theta_i$ is the SZA in degrees. To determine $\alpha$ for the different line shapes, total columns of CO$_2$ were retrieved using the Voigt line shape (Wunch, D. et al., 2015) and the qSDV with line mixing (Mendonca et al., 2016).

Henceforth, we will refer to XCO$_2$ calculated from O$_2$ and CO$_2$ using the Voigt line shape as XCO$_2$ Voigt and the qSDV line shape as XCO$_2$ qSDV.

Figure 9 shows the average $\alpha$ calculated for each season at Darwin, Lamont, and Park Falls. Eureka XCO$_2$ cannot be used to determine $\alpha$ because Eureka measurements do not go through the same range of SZAs as the other three
sites due to its geolocation. The average \( \alpha \) XCO\(_2\) Voigt are represented by stars in Figure 9, while the squares indicate XCO\(_2\) qSDV. At all three sites, \( \alpha \) 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 \( \alpha \) for XCO\(_2\) Voigt calculated from a year of measurements from Darwin, Park Falls, and Lamont is -0.0071±0.0057 and that for XCO\(_2\) qSDV is -0.0012±0.0054.

For all four sites, \( \alpha = -0.0071 \) is used to correct XCO\(_2\) Voigt measurements. Figure 10a shows the XCO\(_2\) Voigt anomalies plotted as a function of SZA. The data is expressed as the daily XCO\(_2\) anomaly, which is the difference between the XCO\(_2\) value and the daily median value, in order to remove the seasonal cycle. When XCO\(_2\) is left uncorrected for airmass dependencies, there is a clear airmass dependence where the amount of XCO\(_2\) decreases as a function of SZA up to a SZA of approximately 82°, at which point XCO\(_2\) increases as a function of SZA at angles greater than 82°. Figure 10b shows XCO\(_2\) Voigt corrected for the airmass dependence. This airmass correction works well only up to a SZA of approximately 82°, after which the correction only serves to increase the airmass dependence. Figure 10c is the same as 10a but for the uncorrected XCO\(_2\) qSDV measurements, while Figure 10d is the same as 10b but for the corrected XCO\(_2\) qSDV measurements. When the airmass correction is applied to XCO\(_2\) qSDV there is a small difference between the corrected and uncorrected XCO\(_2\) qSDV measurements, 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.

5.2 Accuracy of XCO\(_2\)

To assess the accuracy of TCCON XCO\(_2\) measurements, they are compared to aircraft XCO\(_2\) profile measurements using the method described in Wunch et al. (2010). Figure 11a shows the comparison between the aircraft XCO\(_2\) measurements (legend on the top details the different aircraft) and TCCON XCO\(_2\) Voigt measurements for 13 TCCON sites (given by the color-coded legend on at 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 11a, for the XCO\(_2\) Voigt measurements. Figure 11b is the same as 11a but for the XCO\(_2\) qSDV measurements. The bias between the aircraft XCO\(_2\) measurements and the XCO\(_2\) qSDV measurements is 1.0041±0.0005 as given by the slope of the line of best fit in Figure 11b. This increase in the slope can be explained by an increase in the retrieved column of CO\(_2\) when using the qSDV with line mixing as shown in Mendonca et al. (2016) as well as combined with a decrease in the retrieved O\(_2\) column due to using the qSDV. As discussed previously (section 5) the decrease in the retrieved O\(_2\) column is an improvement but the expected column of O\(_2\) is still approximately 1.2% higher (at the smallest SZA) than it should be. Therefore, the retrieved column of CO\(_2\) is higher than it should be, and the slope would be greater if the retrieved column of O\(_2\) was 1.2% lower. Never the less using the qSDV to retrieve total columns of CO\(_2\) and O\(_2\) thus reduces the difference between TCCON XCO\(_2\) and aircraft XCO\(_2\) measurements by 0.62%.

TCCON XCO\(_2\) measurements are divided by the scale factors (or bias determined in Figure 11a) to calibrate to the WMO scale. For all TCCON XCO\(_2\) measurements retrieved with a Voigt line shape, the airmass correction is first applied to the data and the result is divided by the determined bias factor, 0.9897. Figure 12a to 12d shows
XCO\textsubscript{2} Voigt (for Eureka, Park Falls, Lamont, and Darwin respectively) indicated by red square boxes in the plots. XCO\textsubscript{2} Voigt measurements made at SZA > 82° have been filtered out because they cannot be corrected for the airmass dependence. The blue boxes are XCO\textsubscript{2} qSDV corrected for airmass dependence and scaled by 1.0041. No filter was applied to the XCO\textsubscript{2} qSDV measurements for SZA since the airmass dependence correction works at all SZA. Figure 12\textsuperscript{10}o to 12\textsuperscript{10}h shows the difference between XCO\textsubscript{2} Voigt and XCO\textsubscript{2} qSDV for Eureka, Park Falls, Lamont, and Darwin respectively. The mean differences for the data shown in Figures 12\textsuperscript{10}o to 12\textsuperscript{10}h are 0.113±0.082, -0.102±0.223, -0.132±0.241, and -0.059±0.231 μmol/mol (ppm) for Eureka, Park Falls, Lamont, and Darwin respectively. The difference throughout the day at Park Falls, Lamont, and Darwin varies between -0.6 to 0.2 μmol/mol and is SZA dependent.

Figure 13\textsuperscript{11}a shows XCO\textsubscript{2} Voigt corrected for the airmass dependence, as well as XCO\textsubscript{2} qSDV, uncorrected and corrected for the airmass dependence. These XCO\textsubscript{2} measurements were retrieved from Park Falls spectra recorded on June 18, 2013. For all three XCO\textsubscript{2} measurements, the amount of XCO\textsubscript{2} decreases throughout the day. Figure 13\textsuperscript{11}b shows the difference between the corrected Voigt XCO\textsubscript{2} and the uncorrected qSDV XCO\textsubscript{2}, as well as the difference between the corrected Voigt XCO\textsubscript{2} and the corrected qSDV XCO\textsubscript{2}. The difference between the Voigt and the qSDV (corrected and uncorrected) shows that at the start and end of the day, more XCO\textsubscript{2} is retrieved with the qSDV, while at midday less is retrieved with the qSDV. The range in the differences seen in Figure 12\textsuperscript{10}o to 12\textsuperscript{10}h varies with SZA throughout the day as shown in Figure 13\textsuperscript{11}b.

**6. Discussion and Conclusions**

Using cavity ring-down spectra measured in the lab, we have shown that the Voigt line shape is insufficient to model the line shape of O\textsubscript{2} for the 1.27 μm band, consistent with the results of Hartmann et al. (2013) and Lamouroux et al. (2014). By using the speed-dependent Voigt line shape 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 1 and 2. This is partly due to the blending of spectral lines (i.e., line mixing) and the inability to retrieve the spectroscopic parameters for weak O\textsubscript{2} transitions. Fitting low-pressure spectra would help with isolating spectral lines and decreasing the uncertainty on the retrieved spectroscopic parameters for the Q branch lines.

Accurate measurements of the pressure shifts in the 1.27 μm band have been hard to obtain as shown in Newman et al. (1999) and Hill et al., (2003). While the retrieved pressure shifts show a dependence on quantum number \( m \) (Figure 3c) as one would expect, this dependence is not as strong as the \( m \) dependence of the Lorentz widths (Figure 3b). This can be explained by the fact that line mixing, which is shown to be important for the O\textsubscript{2} A-band, was not considered when fitting the cavity-ringdown spectra. Neglecting line mixing usually produces an asymmetric residual in the discrete lines as well as a broad residual feature associated with the fact that collisions are transferring intensity from one part of the spectrum to another. By fitting a set of Legendre polynomials for CIA we could be simultaneously fitting the broader band feature associated with line mixing while the retrieved pressure shifts, and speed-dependent pressure shifts could be compensating for the asymmetric structure one would see in the discrete
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. However, when dealing with both speed dependence and Dicke narrowing are present, a multi-spectrum fit needs to be used due to the correlation between the parameters (Bui et al., 2014). Domyssawska et al. (2016) recommend using the qSDV to model the line shape of O₂ based on multiple line shape studies of the O₂ B-band. In these studies, a multi-spectrum fit to low pressure (0.27-5.87 kPa) cavity-ring down spectra was preformed testing multiple line shapes that took speed-dependence and Dicke narrowing into account both separately and simultaneously. They found that the line shapes that only used Dicke narrowing were not good enough to model the line shape of the O₂ B-band lines, but a line shape that included either speed-dependence or both speed-dependence and Dicke narrowing produced similar quality fits, ultimately concluding that speed-dependence has a larger effect than Dicke narrowing. It was noted in the study by Wójtewicz et al. (2014) that both Dicke narrowing and speed-dependent effects might simultaneously play an important role in modeling the line shape of the O₂ B-band lines. However, the speed-dependent and Dicke narrowing parameters are highly correlated at low pressures. To reduce the correlation requires either a multi-spectrum fit of spectra at low pressures with high enough signal to noise ratio or spectra that cover a wide range of pressure (Wójtewicz et al., 2014). So, by combining the high-pressure spectra used in this study with low pressure spectra in a multipispectrum fit both the speed-dependence and Dicke narrowing parameters could be retrieved. 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 cavity-ring-down absorption coefficient measurements with those for low pressures and different temperatures as done in Devi et al. (2015 and 2016) for CH₄ in would lead to more accurate line shape parameters for O₂.

By taking speed dependence into account for both CO₂ (in the work of Mendonca et al., 2016) and O₂ (the work presented here), 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 discarded, 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 effects XCO₂ but all trace gases measured by TCCON and in the future the airmass dependence of all XGAs will be determined with these new O₂ columns.

Acknowledgements

This work was primarily supported by the Canadian Space Agency (CSA) through the GOSAT and CAFTON projects and the Natural Sciences and Engineering Research Council of Canada (NSERC). The Eureka
measurements were made at the Polar Environment Atmospheric Research Laboratory (PEARL) by the Canadian
Network for the Detection of Atmospheric Change (CANDAC), which has been supported by the AIF/NSRIT, CFI,
CFCAS, CSA, Environment Canada (EC), Government of Canada IPY funding, NSERC, OIT, ORF, PCSP, and
FQRNT. The authors wish to thank the staff at EC’s Eureka Weather Station and CANDAC for the logistical and
on-site support provided. Thanks to CANDAC Principal Investigator James R. Drummond, PEARL Site Manager
Pierre Fogal, and CANDAC/PEARL operators Mike Maurice and Peter McGovern, for their invaluable assistance in
maintaining and operating the Bruker 125HR. The research at the Jet Propulsion Laboratory (JPL), and California
Institute of Technology was performed under contracts and cooperative agreements with the National Aeronautics
and Space Administration (NASA). Geoff Toon and Debra Wunch acknowledge support from NASA for
the development of TCCON via grant number NNX17AE15G. Darwin TCCON measurements are possible thanks
to support from NASA grants NAG5-12247 and NNG05-GD07G, the Australian Research Council grants
DP140101552, DP110103118, DP0879468 and LP0562346, and the DOE ARM program for technical support. The
research at the National Institute of Standards and Technology was performed with the support of the NIST
Greenhouse Gas Measurements and Climate Research Program. Certain commercial equipment, instruments, or
materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is
not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is
it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.
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https://doi.org/10.1016/j.jqsrt.2013.07.002


https://doi.org/10.1016/j.jqsrt.2014.02.013


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Figure 1: (a) Cavity-ring-down absorption coefficients for O$_2$ measured at the three pressures indicated in the legend at approximately room temperature and a volume mixing ratio of 0.20720(43) for O$_2$. The difference between measured absorption coefficients and those calculated using (b) a Voigt line shape and (c) the speed-dependent Voigt line shape. Note the difference in scale between panels (b) and (c).
Figure 2: The same as Figure 1 but zoomed in to expanded to show four spectral lines in the P branch of the O2 1.27 μm band.
Figure 3: The averaged measured (a) intensity, (b) Lorentz line width, (c) pressure shift, and (d) speed-dependent pressure shift retrieved from the three cavity ring-down spectra of the 1.27 μm band of O₂. All data are plotted as a function of lower state rotational quantum number \( J \) in which \( m = -J \) for the P-branch lines, \( m = J \) for the Q-branch, and \( m = J+1 \) for the R-branch (where \( J \) is the lower state rotational quantum number) and the uncertainties shown are 2\( \sigma \).
Figure 4: (a) The averaged measured speed-dependent width parameter of the 1.27 μm band of O₂ plotted as a function of \( m \), 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 \( m \), lower state rotational quantum number \( J'' \).
Figure 5: (a) The residuals (measured minus calculated) for a spectrum measured at Eureka on March 27, 2015 at a SZA of 81.32°. 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.
Figure 6: The percent difference between the O₂ column retrieved with the Voigt and qSDV line shapes for a year of measurements from Eureka (eu), Park Falls (pa), Lamont (oc), and Darwin (db).
Figure 7: XAIR from Park Falls retrieved from spectra recorded on June 18, 2013. XAIR is calculated using $O_2$ columns retrieved using a Voigt (red) and qSDV (green) line shapes.
Figure 8: XCO$_2$ calculated from the CO$_2$ and O$_2$ columns retrieved from Park Falls spectra recorded on June 18, 2013. The CO$_2$ columns were retrieved using either the Voigt line shape or the qSDV with line mixing, while the O$_2$ columns were retrieved using either the Voigt or qSDV line shapes. XCO$_2$ was calculated in four ways: 1) Both CO$_2$ and O$_2$ columns retrieved using the Voigt line shape (red), 2) CO$_2$ columns retrieved with the Voigt and O$_2$ columns retrieved with the qSDV (green), 3) CO$_2$ columns retrieved with the qSDV and line mixing and O$_2$ columns retrieved with the Voigt (cyan), and 4) CO$_2$ columns retrieved with the qSDV and line mixing and O$_2$ columns retrieved with the qSDV (blue).
Figure 9: The average airmass-dependent correction factor for XCO$_2$ derived from a year of spectra measured at Darwin, Lamont, and Park Falls for different seasons. The dashed lines with stars are the $\alpha$ for XCO$_2$ retrieved using a Voigt line shape for both CO$_2$ and O$_2$ columns. The solid lines with squares are from XCO$_2$ retrieved using the qSDV for both CO$_2$ and O$_2$ columns.
Figure 10: (a) XCO₂ Voigt anomaly for a year of measurements from the four TCCON sites. 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.
Figure 11.9: (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.
Figure 12: (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. The red boxes are XCO$_2$ calculated from using a Voigt line shape in the retrieval and the blue boxes are from using the qSDV. (e) to (h) the difference between XCO$_2$ Voigt and XCO$_2$ qSDV.
Figure 13-1: (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 and 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).