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

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Abstract

A quadratic-speed-dependent Voigt line shape (qSDV) with line mixing (qSDV+LM), together with spectroscopic line parameters from Devi et al. [1,2] for the 2v₃ band of CH₄, was used to retrieve total columns of CH₄ from atmospheric solar absorption spectra. The qSDV line shape [3] with line mixing [4] was implemented into the forward model of GFIT (the retrieval algorithm that is at the heart of the GGG software [5]) to calculate CH₄ absorption coefficients. High-resolution laboratory spectra of CH₄ were used to assess absorption coefficients calculated using a Voigt line shape and spectroscopic parameters from the atm line list [6]. The same laboratory spectra were used to test absorption coefficients calculated using the qSDV+LM line shape with spectroscopic line parameters from Devi et al. [1,2] for the 2v₃ band of CH₄ and a Voigt line shape for lines that don't belong to the 2v₃ band. The spectral line list for lines that don't belong to the 2v₃ band is an amalgamation of multiple spectral line lists. We found that for the P, Q, and R branches of the 2v₃ band, the qSDV+LM simulated the laboratory spectra better than the Voigt line shape. The qSDV+LM was also used in the spectral fitting of high-resolution solar absorption spectra from four ground-based remote sensing sites and compared to spectra fitted with a Voigt line shape. The average root mean square (RMS) residual for 131,124 solar

absorption spectra fitted with absorption coefficients calculated using the qSDV+LM for the $2\nu_3$ band of CH_4 and the new spectral line list for lines that don't belong to the $2\nu_3$ band, was reduced in the P, Q, and R branches by 5%, 13%, and 3%, respectively when compared with spectra fitted using a Voigt line shape and the atm line list. We found that the average total column of CH_4 retrieved from these 131,124 spectra, with the qSDV+LM was $1.1 \pm 0.3\%$ higher than the retrievals performed using a Voigt and the atm line list. The airmass dependence of the retrieved total columns was found to change depending on the choice of spectral line shape. With the Voigt line shape, we found a minimum in CH_4 total columns at a solar zenith angle (SZA) of about 70° . With the qSDV+LM, the retrieved total column of CH_4 decreased monotonically as a function of SZA.

Introduction

The global mean atmospheric concentration of CH_4 reached 150% of its pre-industrial level in 2011. After CO_2 , CH_4 has the highest radiative forcing of well-mixed anthropogenic greenhouse gases (GHGs) and is a driver of global warming and climate change [7]. From 1999 to 2006, the global mean concentration of CH_4 increased at a rate of 0.5 ppb/yr. However, since then the concentration has been increasing at a rate of approximately 6 ppb/yr [7]. About 50-65% of CH_4 emissions come from anthropogenic sources (e.g., fossil fuels, rice fields, landfills, ruminants, and biomass burning) while the remainder comes from natural sources (mostly wetlands). The major sink of CH_4 in the atmosphere is oxidation by OH. As the surface temperature increases in the Arctic, previously frozen land will thaw, potentially resulting in an increased contribution to the atmospheric concentration of CH_4 [8]. Measurements of the atmospheric concentration of CH_4 are thus needed to identify source and sink regions and to assess future changes.

Measurements of CH_4 from ground-based observation networks are sufficient to constrain global emission rates of CH_4 but do not provide enough information to properly assess regional scale

emissions [7]. This is because these observation networks have good coverage in some regions and poor coverage in others, notably the Arctic. Satellite measurements of CH₄ can provide data for regions that are not covered by the ground-based networks. The global distribution of CH₄ total columns has been measured by SCIAMACHY (2002-2012) [9] and GOSAT (2009-present) [10], using the 2v₃ band of CH₄ (spectral range 5800-6400 cm⁻¹) since it provides high sensitivity for CH₄ columns from nadir-viewing platforms. Future satellite missions, such as the Methane Remote Sensing Lidar Mission (MERLIN) [11] plan to measure CH₄ with high accuracy (2%) using the R(6) manifold of the 2v₃ band. This band is also used to retrieve total columns of CH₄ from ground-based high-resolution solar absorption spectra recorded by the Total Carbon Column Observing Network (TCCON) [12].

Frankenberg et al. [13] 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 does not properly describe the spectral line shape of CH₄. Tran et al. [14] 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 2v₃ band) when fitting laboratory and solar spectra performed as well as the Voigt line shape with the spectroscopic line parameters of Frankenberg et al. [13]. This also resulted in a decrease in the airmass dependence of CH₄ total columns retrieved from ground-based solar absorption spectra.

Since then, there have been significant improvements 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. [13]) in studies such as Campargue et al. [15] and Nikitin et al. [16]. The most recent study by Nikitin et al. [17] has further improved on the work done in Nikitin et al. [16]

by including six new spectra in the retrieval of spectroscopic line parameters during the multi-spectral fitting process. Nikitin et al. [17] 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 and R branches [1] as well as the Q branch manifolds of the 2v₃ band [2] were recently performed by Devi et al. Both Devi et al. studies used an interactive multi-spectrum fitting process to retrieve line shape parameters with a speed-dependent Voigt line shape with 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.

Here, we incorporate a speed-dependent Voigt line shape with line mixing (qSDV+LM) with spectroscopic parameters from Devi et al. [1,2] in the forward model of our spectral fitting algorithm (GFIT; [5,11]) to evaluate the impact of speed dependence and line mixing on the retrieval of total columns of CH₄ from the 2v₃ band. Section 2 details the formulas used to calculate absorption coefficients using different spectral line shapes. In Section 3, high-resolution laboratory spectra are used to test the different spectral line shapes. In Section 4, high-resolution ground-based solar absorption spectra are fitted using the qSDV+LM and spectroscopic line parameters from Devi et al. [1,2] for the P, Q and R branches of the 2v₃ band for the first time. The quality of the spectral fits of the P, Q, and R branches of the 2v₃ band is compared to that of spectra fitted using the Voigt line shape and spectral line parameters from atm line list that comes with the GGG software [5]. The difference in the total columns retrieved using the two spectral line shapes is assessed and the implications for atmospheric measurements are discussed.

2. Absorption Coefficient Calculations

2.1 Voigt Line Shape with Line Mixing

The Voigt line shape is the convolution of the Doppler line shape and the Lorentz line shape.

When taking line mixing into account, the absorption coefficient, k , at a given wavenumber ν becomes [18]:

$$k(\nu) = \frac{1}{\pi} \sum_i S_i \left(\frac{1}{\gamma_{D_i}} \right) \left(\frac{\ln(2)}{\pi} \right)^{1/2} (Re[c(\nu, x_i, y_i)] + Y_i Im[c(\nu, x_i, y_i)]) \quad (1)$$

where S_i is the line strength of spectral line i , γ_{D_i} is the Doppler half-width (HWHM), Y_i is the line mixing coefficient [19], c is the complex error function, and

$$x_i = \frac{(\nu - \nu_i^0 - P\delta_i^0)}{\gamma_{D_i}} (\ln(2))^{1/2}, \quad y_i = \frac{\gamma_{L_i}}{\gamma_{D_i}} (\ln(2))^{1/2}. \quad (2)$$

Here, ν_i^0 is the position of the spectral line, P is the pressure, and δ_i^0 is the pressure-shift coefficient.

The Lorentz half-width, γ_{L_i} , is calculated using:

$$\gamma_{L_i}(T) = P \gamma_{L_i}^0 \left(\frac{296}{T} \right)^n \quad (3)$$

where $\gamma_{L_i}^0$ is the Lorentz half-width coefficient ($\text{atm}^{-1} \text{cm}^{-1}$ at reference temperature 296 K) and n is the exponent of temperature dependence. The result is a Voigt line shape with line mixing, which reduces to the regular Voigt line shape when Y_i is equal to zero.

2.2 Speed-Dependent Voigt with Line Mixing

To take into account different speeds at the time of the collision, the Lorentz contribution to the spectral line shape has to be refined for different speeds. The Lorentz half-width coefficient then becomes a function of speed and can be modeled using the following expression given in Rohart et al. [20]:

$$\gamma_{L_i}(V_a) = \gamma_{L_i}(1 + a_{\gamma_{L_i}}((V)^2 - 1.5)) \quad (4)$$

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, and $a_{\gamma_{L_i}}$ is the speed-dependent Lorentz width parameter (unitless) for line i . The absorption coefficient for the speed-dependent Voigt line shape with line mixing becomes:

$$k(v) = \left(\frac{2}{\pi^{3/2}}\right) \sum_i S_i \int_{-\infty}^{\infty} e^{-v^2 V} \left(\tan^{-1} \left[\frac{x_i + V}{y_i} \right] + Y_i \frac{1}{2} \ln \left[\left(\frac{x_i + V}{y_i} \right)^2 + 1 \right] \right) dV \quad (5)$$

with γ_{L_i} replaced with $\gamma_{L_i}(V)$ in y_i , and all other terms as defined above. To enhance computational efficiency, the quadratic-speed-dependent Voigt line shape with line mixing (qSDV+LM) from [3] was used to calculate these absorption coefficients.

3. 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 [5,11] is used to simulate laboratory spectra. The laboratory spectra were recorded at the Jet Propulsion Laboratory (JPL), California Institute of Technology, using a Bruker IFS 125HR Fourier transform infrared (FTIR) spectrometer at a resolution of 0.0056 cm⁻¹. All three spectra were obtained using dilute mixtures of methane in air (with commercially available dry air from Airgas) using a 20.941 m coolable multi-pass Herriot cell [21]. Each spectrum was recorded with 99.999% ¹²C-enriched CH₄ to minimize interferences from other isotopologues. Table 1 lists the laboratory conditions for each spectrum.

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 1a, 2a, and 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. 1) without line mixing ($Y_i = 0$) and using

spectroscopic line parameters from the GGG spectral line list called atm [6]. For the spectral region 5880-6145 cm^{-1} , the spectroscopic line parameters for CH_4 are from HITRAN 2008 [22], with the parameters for the $2\nu_3$ band based on the study by Frankenberg et al. [13], with n in Eq. 3 set to 0.85 in HITRAN 2008, which was not measured in Frankenberg et al. [13]. Additionally, the air-broadened widths for all CH_4 spectral lines in the interval of 5800 - 6000 cm^{-1} are slightly adjusted by subtracting $0.002-0.01(E''/800)^2$ (where E'' is the lower state energy) from the original value found in HITRAN2008. This was done to improve the consistency of CH_4 retrievals from the three windows. Since the work by Frankenberg et al., the spectroscopic parameters for CH_4 in this region have been updated (as previously mentioned) with the recent measurements of Nikitin et al. [17] 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 [6] and GOSAT 2014 CH_4 spectral line lists [17].

In these windows, the most intense CH_4 transitions (HITRAN intensity $> 7.5 \times 10^{-23} \text{ cm}^{-1} / (\text{molecule cm}^{-2})$) belong to the $2\nu_3$ band. However, weak CH_4 transitions (HITRAN intensity $< 7.5 \times 10^{-23} \text{ cm}^{-1} / (\text{molecule cm}^{-2})$) are visible in the laboratory spectra and should be included in the simulation. When we simulated the laboratory spectra using the GOSAT 2014 CH_4 spectral line list [17], we found that the root mean square (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 CH_4 transitions better than the GOSAT 2014 CH_4 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 CH_4 line list. As for the Q branch, we found using a Voigt line shape with the original GOSAT 2014 CH_4 spectral line list simulated the weak CH_4 transitions better than the atm line list (not shown).

Figures 1b, 2b, and 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 $2\nu_3$ CH₄ band (as summarized in Table 2). For all three branches, we find that the Voigt line shape cannot properly model most of the manifolds, as shown by the residual structure in Figures 1b, 2b, and 3b, which corresponds to transitions in the $2\nu_3$ band. This is because $2\nu_3$ band spectroscopic parameters are based on Frankenberg et al. [13], who retrieved these parameters from room temperature laboratory spectra.

In Figures 3 to 5 of Frankenberg et al. [13], 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. [13] to calculate absorption coefficients. Figure 6 of Frankenberg et al. [13] 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 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. [13]. Figure 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 instrument line shape (ILS). When Devi et al. [1] 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 1b and 2b) don't have the temperature dependence seen in the R branch (Figure 3b). However, the cause of the systematic residuals for the R(9) and R(10) manifolds (Figure 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. [13].

We also used the GOSAT 2014 CH₄ spectral line list with a Voigt line shape to simulate the transitions from the 2v₃ band (not shown) but found no difference in the performance between the atm line list [6] and GOSAT 2014 CH₄ spectral line list [17] for the P and R branches. The residual structure was worse for most of the Q branch manifolds when using the GOSAT 2014 CH₄ spectral line list.

Devi et al. [1,2] 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 [1,2]. The temperature dependence of off-diagonal element coefficients were also taken into account using the temperature-dependent parameters in Devi et al. [1,2]. To calculate the rates of upward transfer (W_{ij}) we use the following formula:

$$W_{ij} = -P \left(\chi^{air} \epsilon_{ij}^{air} \left(\frac{296}{T} \right)^{n_{ij}^{air}} + \chi^{self} \epsilon_{ij}^{self} \left(\frac{296}{T} \right)^{n_{ij}^{self}} \right) \quad (6)$$

where n_{ij} is the temperature-dependence exponent of the off-diagonal relaxation matrix element coefficient ϵ_{ij} , χ is the volume mixing ratio, *air* refers to collisions with air, and *self* refers to collisions with CH₄. In order to satisfy the detailed balance relationship [4], we use the following formula:

$$W_{ji} = \left(\frac{\rho_j}{\rho_i} \right) W_{ij} \quad (7)$$

where ρ_j is the population of line j and ρ_i is the population of line i. The diagonal elements of $\mathbf{W}$ are the Lorentz widths given by Eq. 3. Following the method described in [4] we diagonalize the matrix $(\mathbf{v}_o + i\mathbf{W})$, where $\mathbf{v}_o$ is the diagonal matrix of unperturbed v_i^o , using:

$$\mathbf{A}^{-1}(\mathbf{v}_o + i\mathbf{W})\mathbf{A} = \mathbf{\Lambda} \quad (8)$$

where $\mathbf{A}$ is the matrix of eigenvectors whose eigenvalues are diagonal elements $\mathbf{\Lambda}$. The real values of $\mathbf{\Lambda}$ are the effective line center frequencies, $v_i^{effective}$ of spectral line i , which is substituted into Eq. 2 for v_i^o , when calculating x_i . The column vector of effective line strengths, $\vec{S}^{effective}$, is calculated by:

$$\vec{S}^{effective} = Re[(\vec{\mu}^T \mathbf{A})(\mathbf{A}^{-1} \boldsymbol{\rho} \vec{\mu})] \quad (9)$$

where $\boldsymbol{\rho}$ 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 number density ρ_i . $\vec{S}^{effective}$ contains the effective line strength for each spectral line $S_i^{effective}$ that is substituted into Eq. 5 for S_i . The column vector $\vec{Y}$ contains the line mixing parameter for each line (Y_i) and is calculated using the formula:

$$\vec{Y} = Im[(\vec{\mu}^T \mathbf{A})(\mathbf{A}^{-1} \boldsymbol{\rho} \vec{\mu})]_i / S_i^{effective}. \quad (10)$$

It should be noted that Y_i calculated using Eq. 10 is not the first order line mixing approximation as calculated in Rosenkranz et al. [19]. When following Levy et al. [4] the parameter ζ_i is calculated using Eq. 10 without dividing by $S_i^{effective}$. In order to use Eq. 1 and 5 we require Y_i not ζ_i , and since ζ_i is Y_i multiplied by $S_i^{effective}$, we can then get Y_i from ζ_i using Eq. 10.

When taking full line mixing into account, the relaxation matrix was calculated assuming a speed-independent relaxation matrix. This means that $v_i^{effective}$, $S_i^{effective}$, and Y_i were not calculated at different speeds by replacing the diagonal elements of $\mathbf{W}$ by the Lorentz width at a given speed (given by Eq. 4). This is because inversion of $\mathbf{W}$ at every speed is computationally time-consuming

and since the GGG software is designed to calculate absorption coefficients on the fly [5], using a speed-dependent relaxation matrix is impractical [23]. In our approach we follow what was done in Pine and Gabard [24] (for the ν_3 band of CH_4) and use the speed-independent relaxation matrix.

Devi et al. [1,2] also measured the temperature dependence of the pressure shift coefficients for the $2\nu_3$ transitions with the pressure-shift coefficient calculated as [1,2]:

$$\delta_i = \delta_i^o + \delta_i' \times (T - 296) \quad (11)$$

where δ_i will replace δ_i^o (which was defined before) in Eq 2, and δ_i' is the temperature dependence of the pressure-shift coefficient (in units of $\text{cm}^{-1} \text{atm}^{-1} \text{K}^{-1}$). Figures 1c, 2c, and 3c show the residuals using the qSDV+LM line shape when calculating the absorption coefficients for the $2\nu_3$ transitions (as summarized in Table 3). When first simulating the laboratory spectra we found that there was residual structure in some of the $2\nu_3$ manifolds. On closer inspection of the structure, it was realized that some of the structure was not due to the spectral lines of the $2\nu_3$ band rather they were 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 [1,2] were substituted for the GOSAT 2014 CH_4 spectral line list. All manifolds of the $2\nu_3$ band were better simulated with the qSDV+LM when compared to the Voigt, with some small residuals (less than ± 0.01 difference) remaining in some manifolds.

4. Fitting Solar Spectra

To further evaluate the new CH_4 absorption coefficients, ground-based high-resolution solar absorption spectra were fitted. These spectra were recorded using Bruker IFS 125HR FTIR spectrometers with room temperature InGaAs detectors at four TCCON stations. All spectra were recorded with a 45 cm maximum optical path difference (spectral resolution of 0.02 cm^{-1}). All raw interferograms were processed with the I2S software package [5] that corrects them for solar intensity variations [25], phase

errors [26], and laser sampling errors [5] and fast Fourier transforms the interferograms into spectra [27]. The GGG software package [5,11] is used to retrieve total columns of atmospheric trace gases. This is done by the GFIT code, which calculates a solar absorption spectrum using a line-by-line radiative transfer model. The program uses an iterative non-linear least squares fitting scheme to scale the a priori CH_4 profile to obtain the best fit to the measured spectrum. A priori profiles for GHGs such as CH_4 , CO_2 , and N_2O , are created by an empirical model in GGG that is based on measurements from the JPL MkIV Fourier Transform Spectrometer (FTS) balloon flights [28], the Atmospheric Chemistry Experiment (ACE) FTS instrument aboard SCISAT [29], and in situ GLOBALVIEW data [12]. Temperature, pressure, and H_2O a priori profiles are generated from the National Centers for Environmental Prediction (NCEP) data [30]. The calculations are performed for 71 atmospheric layers (0 to 70 km), so all a priori profiles are generated with a vertical grid of 1 km [12].

Figures 4, 5, and 6 show spectral fits for the P, Q and R branches of the $2\nu_3$ band of CH_4 . This spectrum was recorded at Eureka on March 31, 2015, at a solar zenith angle (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 (colored 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 [6] for all CH_4 lines, as summarized in Table 2 (henceforth referred to as Voigt absorption coefficients), and (ii) in blue, the qSDV+LM with spectroscopic parameters from Devi et al. [1,2] for transitions that belong to the $2\nu_3$ band. The weak CH_4 lines ($\text{HITRAN intensity} < 7.5 \times 10^{-23} \text{ cm}^{-1}/(\text{molecules cm}^{-2})$), in the blue residual, were calculated using the Voigt line shape with a combination of spectroscopic line parameters from the GOSAT 2014 CH_4 [17], atm [6] and Devi et al. [1,2] line lists, as summarized in Table 3. For both the blue and red residuals, all other spectral lines (except solar lines) were fitted with a Voigt line shape and spectroscopic line parameters from the GGG2014 telluric line list [6]. Solar lines were fitted using the

GGG2014 solar line list [31]. 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 3 (henceforth referred 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 4, 5, and 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). For individual manifolds of the P and R branches please refer to Figures 3-13 in the supplementary figures.

Frankenberg et al. [13] tested the Voigt parameters (measured in [13]) 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. [13] 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 $2\nu_3$ band (0.85 for all lines in the $2\nu_3$ band). So the red residual in Figures 4-6 is obtained using the Voigt line shape calculated using the spectroscopic parameters of [13] but with the temperature dependence of the Lorentz width set to 0.85 for all lines in the $2\nu_3$ band. When one compares the red residual in Figures 5 and 6 (Voigt with temperature dependence) to the black residual of [13] (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 [2]. The inclusion of temperature dependence for the Voigt parameters does not impact the residual structure of the R branch (when comparing Figure 8 of [13] to Figure 6 in this study). However, with the qSDV+LM line shape and the spectroscopic parameters from [1], 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 (eu) [32], Park Falls (pa) [33], Lamont (oc), and Darwin (db) [34] were used to retrieve total columns of CH₄. Measurements at all sites were filtered for Fractional Variation in Solar Intensity (FVSI), a proxy for variable cloud during a measurement. If the FVSI during the measurement is greater than 5%, this measurement is flagged and not used. Measurements made at Eureka were additionally filtered for XHF (X denotes the column-averaged dry-air mole fraction) measurements of greater than 150 ppt. XHF is used as a dynamic tracer to indicate polar vortex conditions, as the standard TCCON a priori profiles are not representative of measurements made during polar vortex conditions.

Figure 7a, 7b, and 7c show the percent difference of the RMS residual (qSDV+LM minus Voigt, divided by 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 ± 0.160 , 0.563 ± 0.182 , and 0.435 ± 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 1σ . With the qSDV+LM absorption coefficients, the average RMS residuals are 0.434 ± 0.153 , 0.491 ± 0.177 , and 0.422 ± 0.165 , for the P, Q, and R branches, respectively.

Each CH₄ window, corresponding to one of the branches of the 2v₃ band, is used to retrieve a volume scale factor (VSF) that is applied to the *a priori* profile to calculate the total column of CH₄. Figure 8 shows the correlations between the VSF's retrieved in the three spectral fitting windows. Figures 8a, 8b, and 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 8d, 8e, and 8f are the same as Figures 8a, 8b, and 8c respectively, but the retrievals were done using the

qSDV+LM absorption coefficients for transitions in the $2\nu_3$ band. The correlation between each pair of windows using the Voigt absorption coefficients is very good as indicated by the line of best fit and the correlation coefficient (r) shown in the plots. With the qSDV+LM absorption coefficients, we find that the correlation between each pair of windows is also very good, indicating that regardless of the choice of spectral line shape, the VSFs retrieved from the different windows are similar.

The average ratio of total column CH_4 retrieved from all spectra using the qSDV+LM absorption coefficients is 1.011 ± 0.003 relative to the Voigt absorption coefficients. Figure 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 one standard deviation. Figure 9 shows that at very low SZA (i.e., $1\text{--}10^\circ$), 1.2% more CH_4 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 low SZA (as given by the percent difference in RMS residual shown in Figure 7), the spectroscopic parameters used to calculate the absorption coefficients are different. Chesnokova et al. [35] showed that the total column of CH_4 retrieved using a Voigt line shape will differ with the choice of spectral line list used to calculate the absorption coefficients. Since the intensities differ between the two spectral line lists, the total column of CH_4 retrieved will also differ regardless of spectral line shape.

Figure 10 shows the column-averaged dry-air mole fraction of CH_4 (XCH_4) plotted as a function of SZA for solar absorption spectra recorded at Park Falls on June 30, 2013 for the entire day. XCH_4 is calculated by dividing the total column of CH_4 by the total column of O_2 (from the O_2 band centered at 7885 cm^{-1} [36]) and multiplying by 0.2095 [12], which is the dry-air mole fraction of O_2 in Earth's atmosphere. Figure 10a shows XCH_4 for the column of CH_4 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. This is why in Figure 9 the ratio of the total column between the two retrievals goes to 1 as SZA increases. To examine just the shape of the airmass dependence, we have adjusted the total columns retrieved using the Voigt line shape (red crosses in Figure 10b) 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 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 9) while the retrieved O₂ column increases as a function of SZA, so when taking the ratio of CH₄ to O₂, XCH₄ further decreases as a function of SZA.

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. [1,2] and different line shape configurations. Figure 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. 1) with no line mixing ($Y_l=0$) and no temperature dependence ($n=0$ in Eq. 3 and $\delta'_l=0$ in Eq. 11). (ii) The red squares indicate the columns retrieved with the qSDV (Eq. 5) 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 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, $n_{ij}^{air}=0$ 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 XCH_4 , which consistent with what was shown in Tran et al. [14] (Figure 11). 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 CH_4 retrieved (compared to disregarding temperature dependence) for $\text{SZA} < 70^\circ$, and more for $\text{SZA} > 70^\circ$. Therefore, line mixing has the greatest impact on the retrieval of CH_4 from the $2\nu_3$ band, with speed dependence and temperature dependence affecting measurements made at SZA greater than approximately 60° and 70° , degrees respectively.

5. Discussion and Conclusions

A speed-dependent Voigt line shape with full line mixing was implemented into GFIT to calculate CH_4 absorption coefficients that can be used to retrieve total columns of CH_4 . We tested absorption coefficients calculated using the qSDV+LM and the Voigt line shape using high-resolution laboratory and solar spectra in the $2\nu_3$ band of CH_4 . The spectra calculated using the qSDV+LM and spectroscopic line parameters from Devi et al. [1,2] reproduced the laboratory spectra better than the Voigt with spectroscopic line parameters from [6] for the P, Q, and R branches. 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 study by Devi et al. [1,2]. 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 [5] software.

In the study by Devi et al. [1,2], residual differences of less than ± 0.005 between the measured and calculated laboratory spectra were achieved. In this study, we were able to simulate the manifolds

of the P, Q, and R branches 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. [1,2] can be attributed to the differences between GGG [5] and the spectral fitting software used in Devi et al. [1,2]. Although there are many differences between the two spectral fitting routines, we note two major differences between them. First of all, in the multi-spectrum fitting procedure used in Devi et al. [1,2] the instrument line shape (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, we have combined three spectral line lists (as detailed in Table 3), while the Devi et al. [1,2], 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. [1,2] does not include some weak CH₄ lines in the spectral range of the TCCON windows. As shown in Figures 4 to 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 as well, which is due to the inclusion of the GOSAT 2014 CH₄ spectral line list [17].

The use of TCCON spectra to retrieve vertical profiles of CO₂ is currently in development [37]. In the future, TCCON spectra may also be used for profile retrievals of CH₄. Sussmann et al. [38] showed that the choice of spectroscopic parameters effects the quality of the profile retrieval of CH₄ (from the mid-infrared), and adopting spectroscopic parameters that decreased the fit residual led to greater precision of the integrated column of CH₄ from the profile retrieval. However, in [38] Tikhonov regularization was used to constrain the retrieved profile shape. This was done because a Voigt line shape was used to calculate the absorption coefficients. Since profile retrievals are sensitive to the choice of spectral line shape [13], using the qSDV+LM should result in more accurate profile retrievals without the need for Tikhonov regularization.

We have shown that there is an airmass dependence for the retrieved total column of CH_4 regardless of choice of spectral line shape. If left uncorrected, this airmass dependence artifact would lead to unrealistic differences in the seasonal cycle of XCH_4 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 [12], 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 CH_4 changes (goes 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 a 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 CH_4 in the polar regions. With the qSDV+LM, the airmass dependence of XCH_4 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 O_2 column used to calculate XCH_4 . We note that studies [35,36] have shown that the Voigt line shape is insufficient to describe the spectral line shape of O_2 in this band. Since the choice of spectral line shape effects the airmass dependence of O_2 as shown in Tran et al. [41] for the O_2 A-band, the inclusion of a better spectral line shape for the O_2 band centered at 7885 cm^{-1} could decrease the airmass dependence of XCH_4 retrieved with the qSDV+LM.

TCCON measurements of XCH_4 have been compared to aircraft profile measurements of XCH_4 made with instruments calibrated to meet World Metrological Organization (WMO) standards as detailed in Wunch et al. [42]. When comparing TCCON measurements of XCH_4 to aircraft profiles Wunch et al. [42] 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.

In conclusion, we have tested the qSDV+LM on high-resolution laboratory and solar spectra and found that it improves the retrievals of total columns of CH₄ in three ways: (1) by reducing the RMS fitting residuals and hence the derived uncertainties, (2) by simplifying the airmass dependence of the total column for SZA > 82°, and (3) by improving the consistency of retrieved gas amounts from the P, Q, and R branches. We found that the biggest improvement was for the P and Q branches of the 2v₃ band of CH₄. Fitting high-resolution solar absorption spectra confirmed that using the qSDV+LM improves the fits to transitions that belong to the 2v₃ band, and that on average it results in retrievals of 1.1% more CH₄ than the Voigt line shape. We showed that taking line mixing into account had the greatest impact on the airmass dependence of the retrieved CH₄ column, with speed-dependence and the temperature dependence of the spectroscopic parameters influencing the airmass dependence when measurements were made at SZA > 60° and 70°, degrees respectively. We therefore, recommend that the qSDV+LM be used with the spectroscopic line parameters from Devi et al. [1,2] when retrieving total columns of CH₄ from solar absorption spectra.

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Tables

Table 1: Summary of the experimental conditions for the air-broadened CH₄ laboratory spectra recorded with the Bruker IFS 125HR FTIR at JPL.

Spectrum name ^a	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

^a All spectra were obtained using a coolable multi-pass Herriott cell with a path length of 20.941 m [21].

Table 2: Summary of spectral line shapes and spectroscopic line lists used to calculate CH₄ absorption coefficients as shown in Figures 1b, 2b, 3b for the laboratory spectra and the red residuals in Figures 4a, 5a, and 6a.

Spectral range (cm ⁻¹)	Spectral line shape	Spectral line list parameters	HITRAN intensity cut-off cm ⁻¹ / (molecule cm ⁻²)
5880-5995	Voigt	atm [6]	>1.0x10 ⁻²⁹
5996-6008	Voigt	atm [6]	>1.0x10 ⁻²⁹
6010-6145	Voigt	atm [6]	>1.0x10 ⁻²⁹

Table 3: Summary of new spectral line shapes and spectroscopic parameters used to calculate CH₄ absorption coefficients as shown in Figures 1c, 2c, 3c for the laboratory spectra and the blue residuals in Figures 4a, 5a, and 6a.

Spectral range (cm ⁻¹)	Spectral line shape	Spectral line list parameters	HITRAN intensity cut-off cm ⁻¹ / (molecule cm ⁻²)
5880-5995	qSDV+LM	Devi et al. [1]	>7.5x10 ⁻²³ (i.e. 2v ₃ P branch transitions)
	Voigt	Combination of GOSAT 2014 CH ₄ spectral line list [17], atm [6], and Devi et al. [1].	<7.5x10 ⁻²³
5996-6008	qSDV+LM	Devi et al. [2]	>7.5x10 ⁻²³ (i.e. 2v ₃ Q branch transitions)
	Voigt	GOSAT 2014 CH ₄ spectral line list [17], and Devi et al. [2].	<7.5x10 ⁻²³
6010-6145	qSDV+LM	Devi et al. [1]	>7.5x10 ⁻²³ (i.e. 2v ₃ R branch transitions)
	Voigt	Combination of GOSAT 2014 CH ₄ spectral line list [17], atm [6], and Devi et al. [1]	<7.5x10 ⁻²³

621 **Figures**

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 623 Figure 1: (a) Laboratory spectra for the P branch of the 2v₃ band of CH₄ with the colour for each
 624 spectrum indicated in the legend. (b) Residual (measured minus calculated spectra) using the Voigt line
 625 shape with spectroscopic line parameters from atm line list [6] for all CH₄ lines. (c) Residual for the
 626 qSDV+LM and spectroscopic line parameters from Devi et al. [1,2] for lines belonging to the 2v₃ CH₄
 627 band. For CH₄ transitions that do not belong to the 2v₃ band, a combination of parameters from the
 628 GOSAT 2014 [17], atm line list [6], and Devi et al. [1] line lists with a Voigt line shape was used to
 629 calculate absorption coefficients as described in the text.

Figure 2: The same as Figure 1 but for the Q branch of the $2\nu_3$ band of CH_4 .

Figure 3: The same as Figure 1 but for the R branch of the $2\nu_3$ band of CH_4 .

Figure 4: Spectral fits to the P branch of the $2\nu_3$ band of CH_4 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 2 (in red, RMS1) and the qSDV+LM with line parameters as given in Table 3 (in blue, RMS2). (b) The measured (red circles, T_m) and calculated using the qSDV+LM (black circles, T_c) spectra, along with the gases included in the fit (refer to the legend to the right) in the spectral window.

Figure 5: Same as Figure 4 but for the Q branch of the $2\nu_3$ band of CH_4 .

Figure 6: Same as Figure 4 but for the R branch of the $2\nu_3$ band of CH_4 .

Figure 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 from Eureka (eu), Park Falls (pa), Lamont (oc), and Darwin (db).

Figure 8: Correlations between CH₄ 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.

Figure 9: Ratio of total column CH_4 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 10: Example of the airmass dependence of XCH_4 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 XCH_4 from retrievals with the Voigt line shape and the qSDV+LM. (b) is the same as (a) but XCH_4 retrieved with the Voigt line shape are multiplied by 1.012.

Figure 11: The air mass dependence of XCH_4 from one day of Park Falls solar absorption spectra recorded on June 30, 2013 using spectroscopic parameters from Devi et al. [1,2] with a Voigt, Voigt with line mixing, Voigt with line mixing and temperature dependence, qSDV, qSDV+LM and no temperature dependence, and qSDV+LM with temperature dependence.