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Interactive comment on "Improving the Retrieval of XCO_2 from Total Carbon Column Network Solar Spectra" *by* Joseph Mendonca et al.

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Response to Referee 2

We thank the reviewer for the comments on our manuscript. Attached is the updated manuscript with all changes. In the manuscript highlighted text is the added text and red crossed out text is deleted text. Please see below for our response to the comments.

Comment 1 - The paper is very theoretical. Line 92 starts with: to take speed dependence into account ... Here it would be nice to explain what is meant by speed dependence. It should be mentioned that the assumed basis for the Lorentz portion of the Voigt profile is, that for all collisions between the molecules the statistical average velocity is taken. However, in reality this is not true, the molecules have a distribution

of speeds, which requires the qSDV.

To address this, we have added the following:

Lines 104-105: "The Voigt line shape is the convolution of the Lorentz and the Gaussian profiles, which model pressure and doppler broadening of the spectral line respectively."

Lines 112-113: "The Voigt line shape assumes that pressure broadening is accurately represented by a Lorentz profile calculated for the stastical average velocity at the time of collission."

Lines 115-118: "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."

Comment 2 - The same holds for the Dicke narrowing, mentioned in line 59. What is the Dicke narrowing? It should be mentioned that when the mean free path of an atom is much smaller than the wavelength of the radiative transition, the atom changes velocity and direction many times during the emission or absorption of a photon. This causes an averaging over different Doppler states and results in an atomic linewidth that is narrower than the Doppler width (I have taken this from Wikipedia).

To address this comment we have added the following:

Lines 71-74: "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)."

Comment 3 - The O2 concentration in the atmosphere is very stable and well known.

I would be interested to see the difference between the known O2 concentration and the O2 from the TCCON spectra as a function of the SZA. These results are somehow hidden in the paper (Figure 6), but since the qSDV is applied to CO2 and O2 it would be good to see where the differences mentioned (0.004) are coming from, from CO2 or O2.

To address this comment we have added another figure (Figure 7) which shows XAIR calculated using the column of O2 retrieved with the Voigt and the qSDV. Ideally XAIR should be 1 since the column of O2 is being used as a proxy for the dry column of air when calculating XCO2. However as shown in Figure 7 it is not. When using a Voigt lie shape to retrieve the O2 column, XAIR is 2% lower than it should be (at the smallest SZA) and has an airmass dependence that decreases as SZA increases (so the retrieved O2 column increases as SZA increases). By using the qSDV to retrieve the O2 column, less O2 is retrieved which results in the O2 column decreasing by 0.8% at the smallest SZA and up to 1.8% at the highest SZA as shown in Figure 6. Thus when the qSDV is used to retrieve O2 XAIR is closer to 1.The airmass dependence of XAIR changes when O2 is retrieved with the qSDV, causing XAIR to now increase as the airmass increases. The airmass dependence of the O2 column is thus similar to the airmass dependence of the CO2 column, so when calculating XCO2 with the column of O2 retrieved using the qSDV, the airmass dependence of XCO2 is minimized as shown in the new Figure 8.

We have added the following on lines 254-261: “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.”

We address the comment about the 0.004 change in comment 4.

Comment 4 - I found it a bit disappointing that the airmass dependance is now + 0.004 instead of - 0.013. This is a large reduction, but the results show that still something is wrong in the measurements/retrieval. The authors might discuss this in more detail. See above at 3.

The positive bias that now exists with the new spectroscopy is because the retrieved columns of CO2 have increased when retrieved using the qSDV with line mixing while the retrieved columns of O2 have decreased with the qSDV. This combination of an increase in the CO2 column with a decrease in the O2 column results in an increase in XCO2. The decrease in retrieved O2 column is good as noted in comment 3 but still needs to decrease further to match the column of dry air calculated from surface pressure measured at the TCCON stations. So if the retrieved O2 column decreased further the positive bias between TCCON and the aircraft measurements would increase. This means that the retrieved columns of CO2 are too high but for now compensate for the fact that the retrieved O2 columns are still larger than they should be.

We have added the following to discuss this point on lines 319-324: “This increase in the slope can be explained by an increase in the retrieved column of CO2 when using the qSDV with line mixing as shown in Mendonca et al. (2016) as well as combined with a decrease in the retrieved O2 column due to using the qSDV. As discussed previously (section 5) the decrease in the retrieved O2 column is an improvement but the expected column of O2 is still approximately 1.2% higher (at the smallest SZA) than it should be. Therefore, the retrieved column of CO2 is higher than it should be, and the slope would be greater if the retrieved column of O2 was 1.2% lower.”

Comment 5 - For me the fact that the airmass dependence is nearly gone when applying qSDV (Figure 8) very important. This should be more highlighted as main result.

Figure 8 c and d look very similar. For me an airmass correction is not necessary, or is this a mistake in the panels?

Figures 8c and 8d are now Figures 10c and 10d. Figures 10c and 10d do look very similar but there is still an airmass dependence given by the fact that the correction term is not 0. It is now -0.0012, which is smaller than with a Voigt, but we still need to apply the correction to the data to account for this small airmass dependence. Since the airmass dependence has been significantly decreased Figures 10c and d look similar but are not the same.

Comment 6 - May be a Figure showing XCO2/O2 as a function of SZA for i) XCO2/O2, ii) XCO2(sQDV)/O2 ii) XCO2/O2(sQDV), iii) XCO2 (qSDV)/O2(qSDV) would be interesting to see where the improvement is coming from. For me a few other Figures of 1-5 could be deleted or put in the supplement.

We have added Figure 8 to show how the changes to the retrieved CO2 or O2 affect their airmass dependence. Figure 8 shows that the improvement of the retrieved column of O2 has a greater impact than the improvements made to the retrieval of CO2. However, the improvement made to the retrieval of CO2 are more critical at large SZA because it makes the airmass dependence of the column of CO2 for large SZA consistent with that for small SZA, allowing the SZA restriction on measurements at large SZA to be removed.

We have added the following lines 265-278: “Figure 8 is XCO2 calculated for four different combinations pertaining to the two CO2 column retrievals and the O2 column retrievals. The CO2 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 O2 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 XCO2 when the total column of O2 is retrieved with the Voigt line shape, regardless of line shape used to retrieve CO2. When the

qSDV is used to retrieve total columns of O2, the symmetric component of XCO2 is diminished regardless of line shape used to retrieve CO2. This is because the airmass dependence of the column of O2 retrieved using the qSDV is more consistent with the airmass dependence of the column of CO2 (for both line shapes used to retrieve CO2). Mendonca et al. (2016) showed that using the qSDV with line mixing results in better fits to the CO2 windows and impacts the airmass dependence of the retrieved column of CO2. When using a Voigt line shape the retrieved column amount of CO2 decreases as airmass increases until the airmass is large (SZA of about 82o) at which point the retrieved column of CO2 increases as the airmass increases, changing the shape of the airmass dependence of the CO2 column. When the qSDV with line mixing is used, the retrieved column of CO2 decreases as a function of airmass (up until the sun is above the horizon).”

It is important that the Figures 1-5 remain since they show that the retrieved spectroscopic parameters have a dependence on quantum number m which has been shown to be the case in other studies of the discrete lines of the O2 1.27 μm electronic transitions.

Comment 7 – The main part of the paper deals with the speed-dependent Voigt line shape. I would suggest to include this in the title, may by: Improving the Retrieval of XCO2 from Total Carbon Column Network Solar Spectra by inclusion of the speed-dependent Voigt line shape.

Changed the title to: “Using a Speed-Dependent Voigt Line Shape to Retrieve O2 from Total Carbon Column Observing Network Solar Spectra to Improve Measurements of XCO2”

Comment 8 - In the conclusions the authors write: 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 O2 for the 1.27 μm band, ... As far as I see, the improvement might also results because the qSDV is applied also the CO2.

The improvement made to the retrieval of O2 has had an impact on the airmass dependence of XCO2 at all SZA while the improvements to the retrieval of CO2 has mainly impacted the airmass dependence at high SZA. As shown in Figure 8 using the O2 columns retrieved with the qSDV decreased the airmass dependence of XCO2 regardless of the line shape used to retrieve the CO2 columns. However, improvements made to the CO2 retrievals results in better measurements of XCO2 at high SZA. See comment 6 for discussion on this.

Please also note the supplement to this comment:
https://www.atmos-meas-tech-discuss.net/amt-2018-62/amt-2018-62-AC2-supplement.pdf

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