Fitting CO_2 Lab Spectra to Improve TCCON Airmass Dependence

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Introduction

Carbon dioxide (CO_2) is a small constituent of the Earth's atmosphere but a big component of the greenhouse effect. Currently the global averaged concentration of CO_2 in the atmosphere is over 400 ppm, the highest its been in the past 500,000 years, due to human activities.

The Total Carbon Column Observing Network (TCCON) is a network of ground-based Fourier transform spectrometers (FTS) that record solar absorption spectra. The goal of TCCON is to validate space based measurements of CO_2 (and other greenhouses gases) and help understand how carbon is exchanged between the atmosphere, biosphere and ocean.

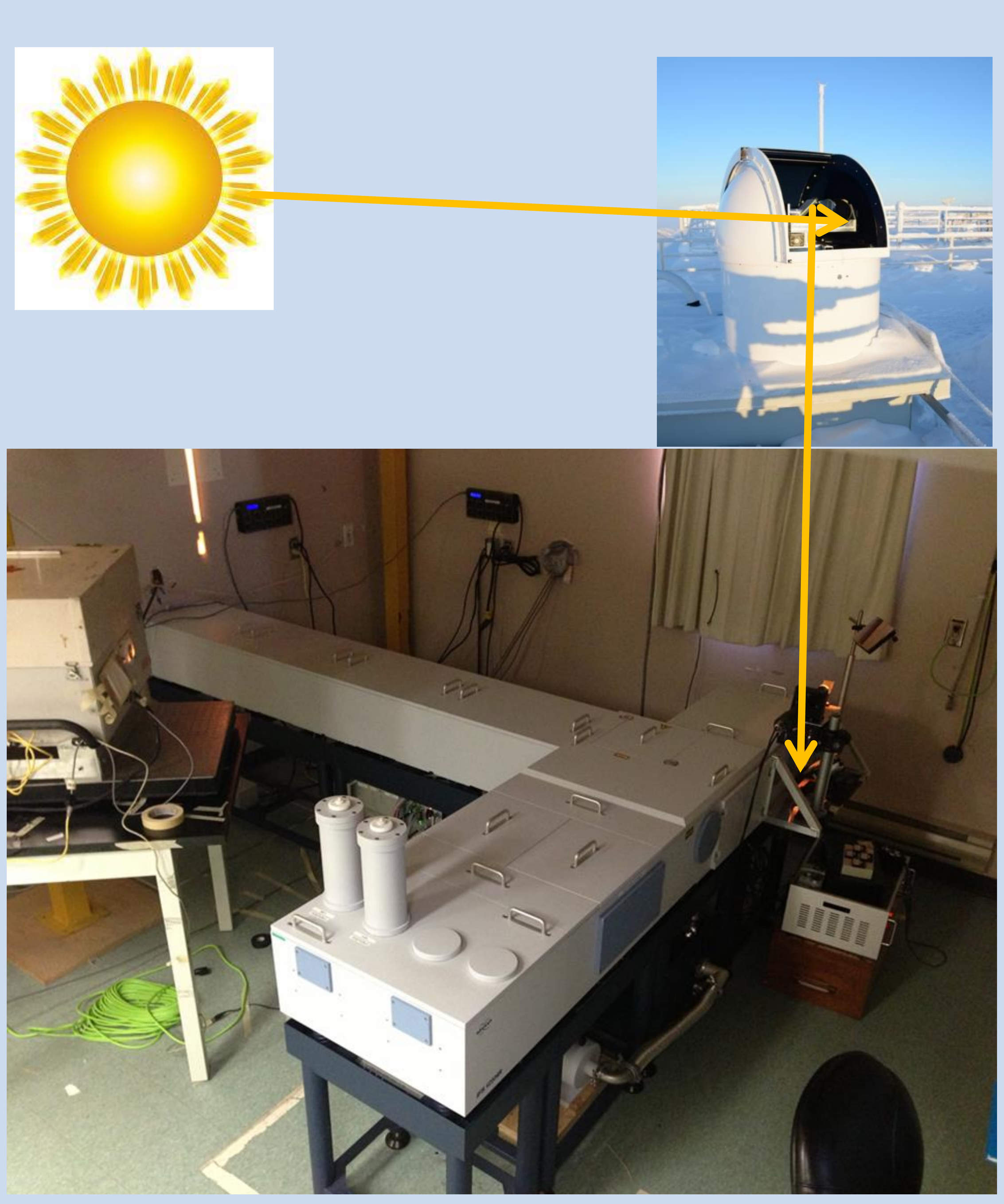
Therefore both a high precision measurements and a good forward model (used to calculate a spectrum) are needed to retrieve XCO_2.

To calculate the absorption coefficients our forward model uses a Voigt line shape. The spectral line shape describes the shape of the structure associated with the molecular transition between energy levels.

By fitting Lab spectra I will show that Voigt line shape isn't good enough to model the line shape of CO_2.

Instrumentation

- The PEARL FTS (Bruker 125HR Fourier Transform Infrared Spectrometer) is located at the Polar Environmental Atmospheric Research Laboratory (PEARL) in Eureka, Nunavut.
- Total Columns of CO_2 are retrieved from spectra recorded in the near-infrared region.
- The optical layout of the instrument is based on a modified Michelson interferometer.



Spectral Line Shape Model

The Voigt line shape is the convolution of Gaussian, from Doppler broadening, and Lorentz, from pressure broadening, profiles.

Line mixing (LM) occurs when collisions transfer intensity from one line to another. This happens if the difference between the 2 rotational energy levels is less than the thermal energy.

Speed dependence (SD) takes into account variable speed at the time of collision.

The SD Voigt with LM (SDV+LM) line shape takes into account Doppler broadening, pressure broadening, LM and SD.

$$k(v) = \sum_i S_i \int_{-\infty}^{\infty} \frac{v e^{v^2}}{\pi^{3/2}\alpha_D}\left[2arctan\left(\frac{(v - v_o^i - P\delta_o^i + v\alpha_D)}{\alpha(v)}\right) + Y_o^i \ln\left(\frac{(v - v_o^i - P\delta_o^i + v\alpha_D)}{\alpha(v)}\right)\right] dv$$

where S_i =line strength, v = speed, $\alpha(v)$=speed dependent Lorentz width, P=pressure, α_D=Doppler width, δ_o^i =pressure shift, v_o^i =center line frequency, and Y_o^i =line mixing coefficient

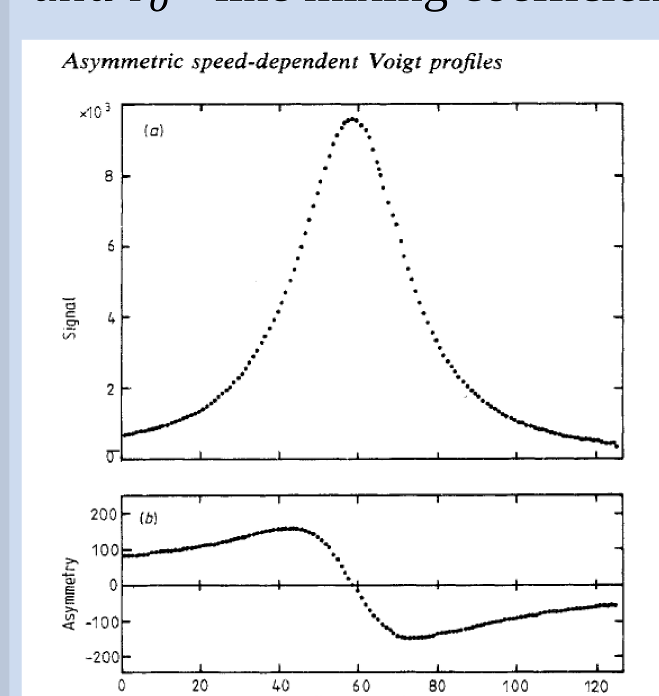


Figure 1. Shows the SDV+LM line shape. In the top panel is the profile given by the arctan term. In the bottom panel is the profile given by the ln term.

Figure from: Shannon et al. (1985)

Results

Lab spectrum was recorded by Bruker 125HR at JPL (by Linda Brown, Keeyoon Sung, and given to Geoff Toon and I), With Resolution: 0.00444 cm^{-1}, total gas pressure :599.8 Torr @ 296.1 K, with 4.95% ^{12}C-enriched $^{16}O^{12}C^{16}O$.

- Fit shows systematic residual when using a Voigt line shape Figure 2.

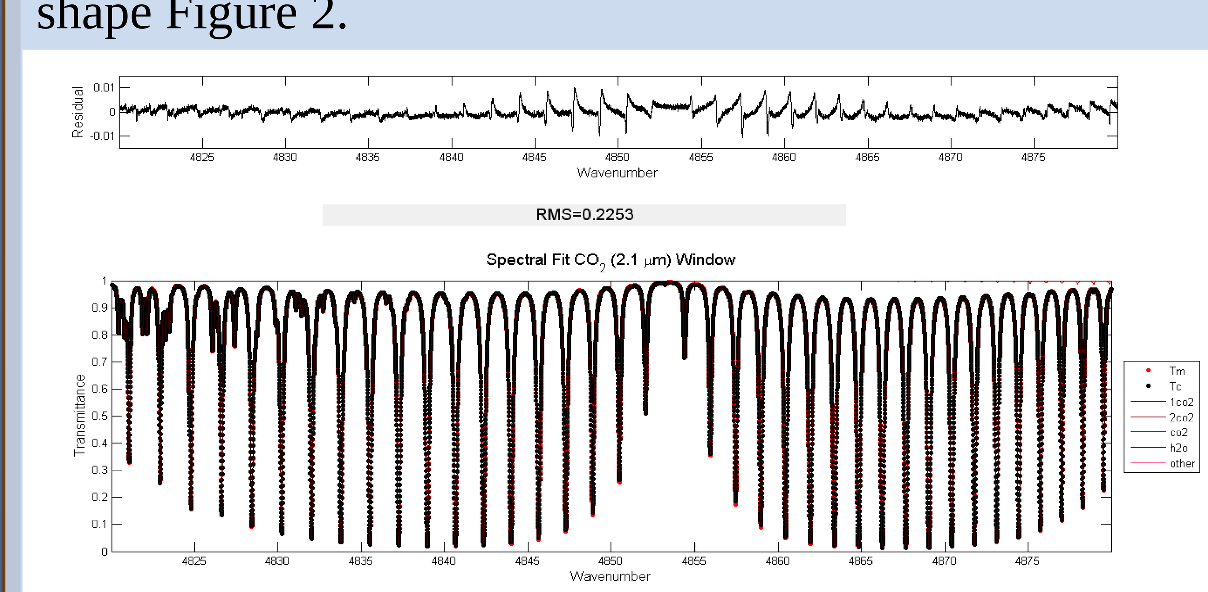


Figure 2. Spectral fit using the Voigt line shape and HITRAN 2012 spectroscopic parameters.

- Systematic residual reduced when using a SDV+LM line shape Figure 3.

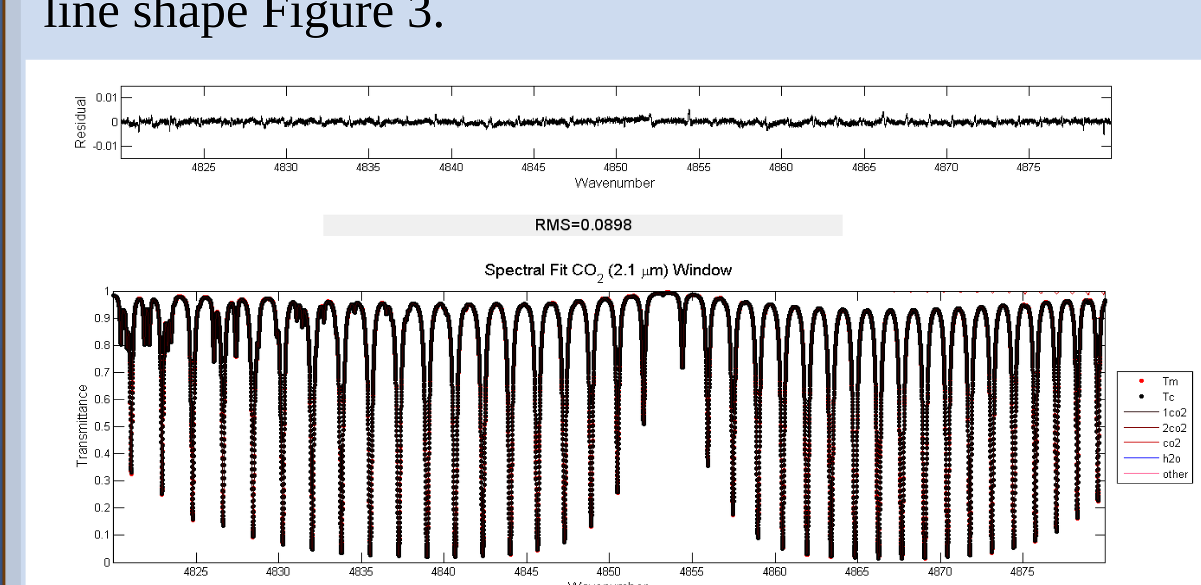


Figure 3. Spectral fit using the SDV+LM line shape and HITRAN 2012 spectroscopic parameters.

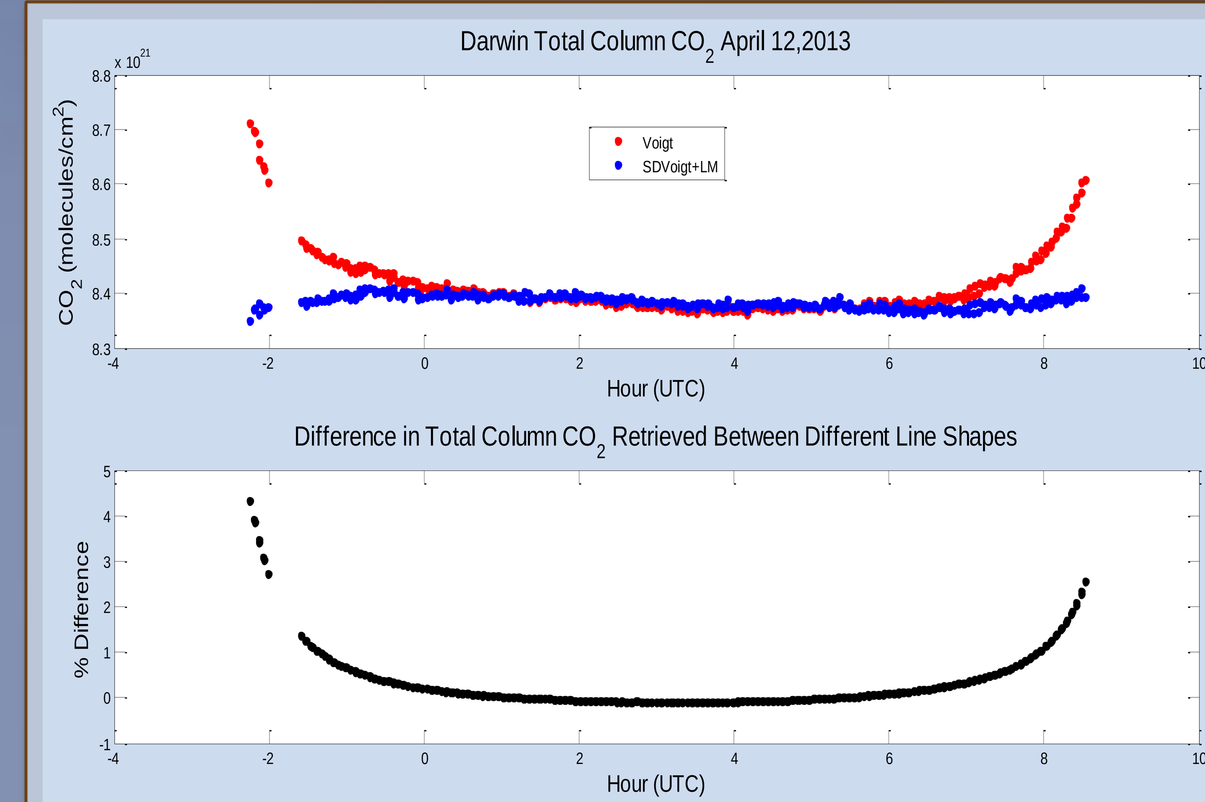


Figure 4. The top panel shows column of CO_2 from Darwin retrieved using a Voigt profile (red) and the SDV+LM (blue). The bottom panel shows the difference between CO_2 retrieved using the different line shapes.

- The SDV+LM decreases the dependence CO_2 column has on airmass.

Conclusion

- Spectral fits of lab spectrum improve when SDV+LM line shape is used
  - But some systematic residuals still remain for solar spectra.
- CO_2 column airmass-dependence improves when SDV+LM is used.
  - But symmetrical component still has some curvature.

Future Work

- Stream line SDV+LM line shape in GFIT.
- Investigate airmass dependence of O_2 column.

References

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