ACOS/OCO-2 Spectroscopy Activities at NASA JPL

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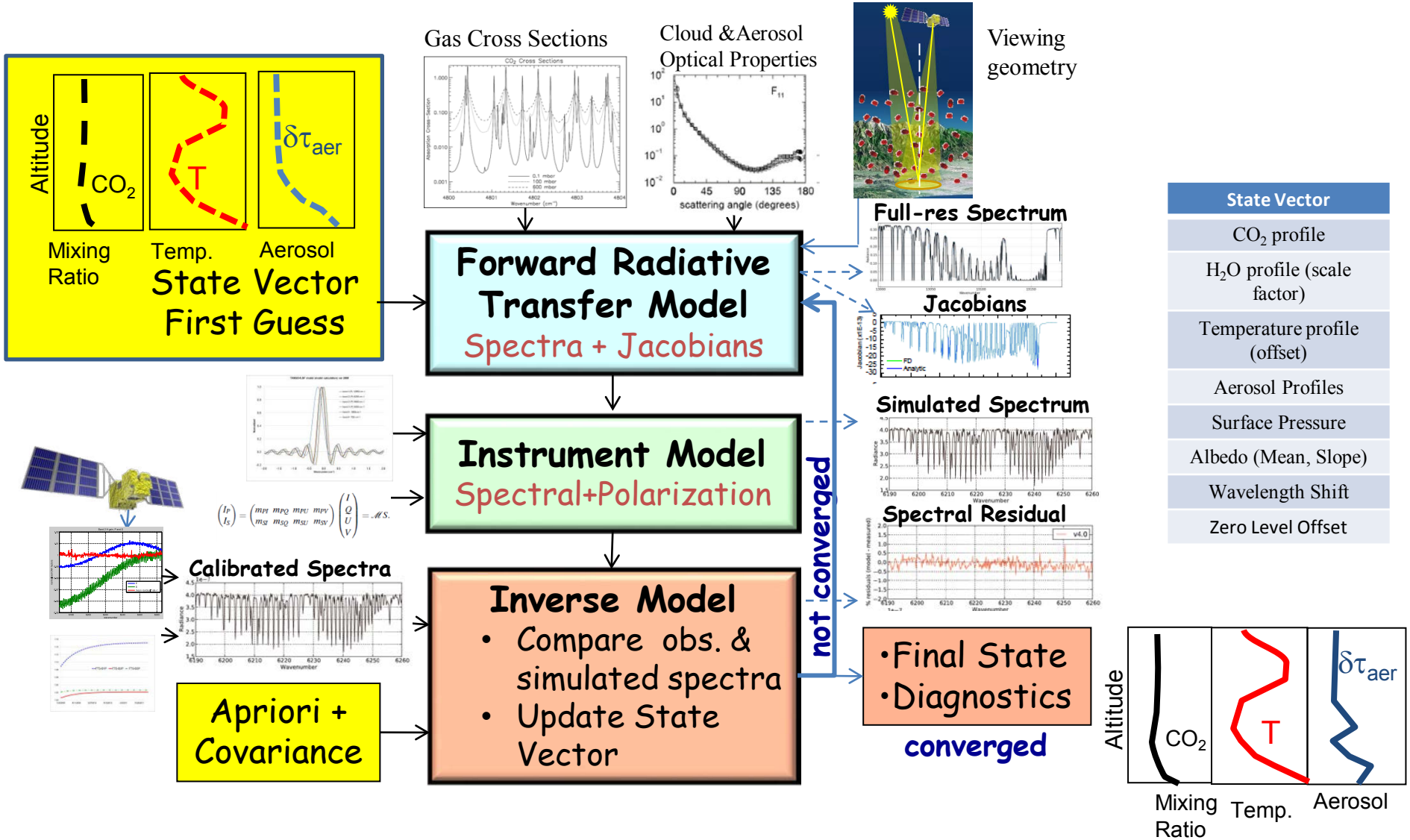
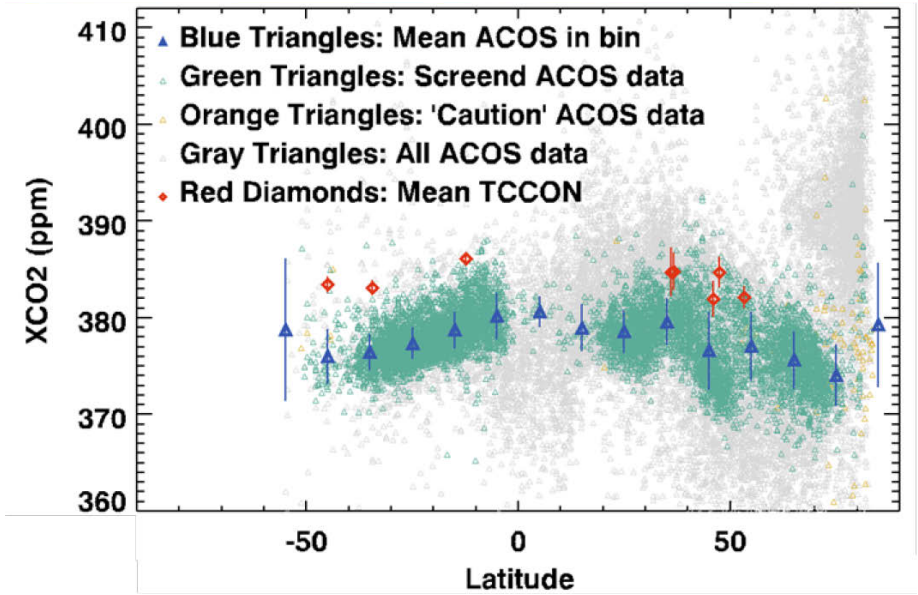
Government sponsorship acknowledged.

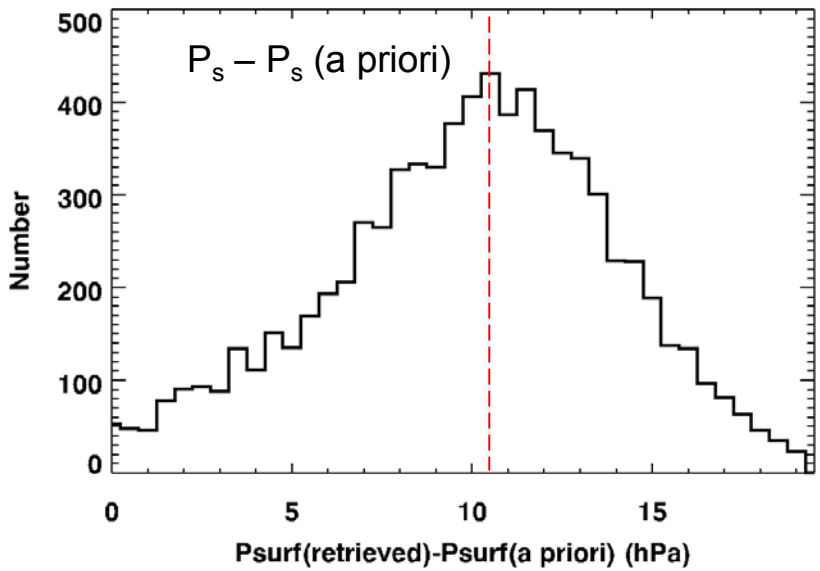
The ACOS "Full Physics" X_{CO2} Retrieval Algorithm



Biases in Early ACOS X_{CO2} Products



ACOS GOSAT X_{CO2} estimates (green and grey triangles) and their zonal averages (blue triangles with 1σ errors) are compared to TCCON X_{CO2} estimates (red diamonds).

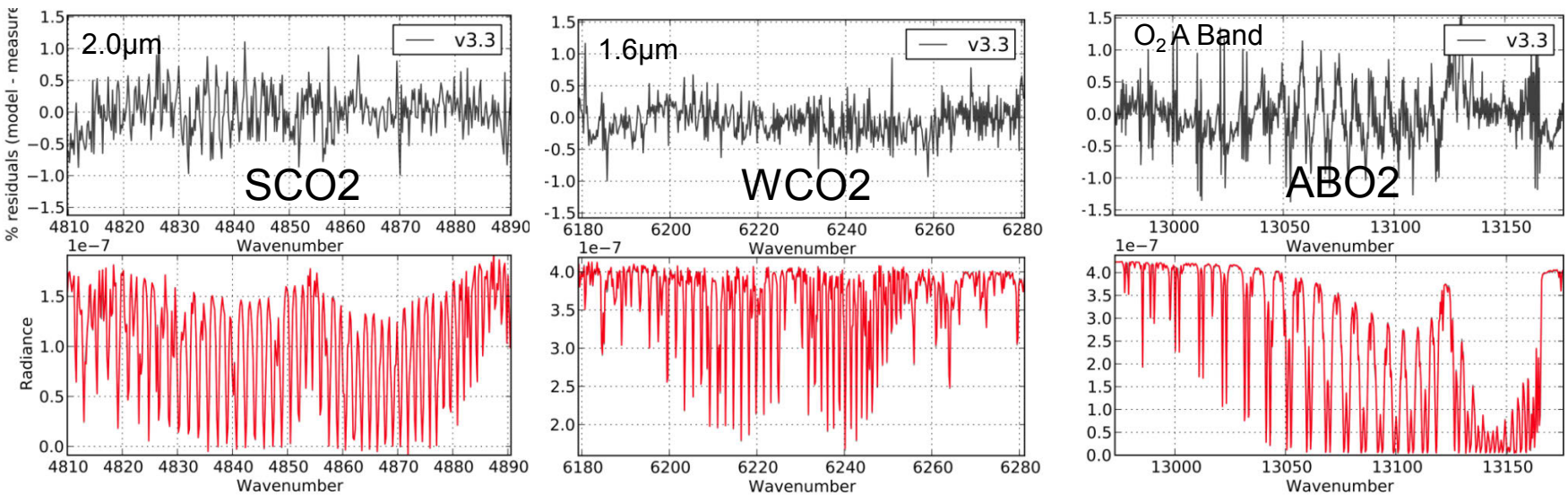


Global histogram of differences between retrieved surface pressures and a priori (ECMWF) surface pressures show a ~10 hPa bias.

- Initial comparisons of ACOS GOSAT and TCCON retrievals showed a consistent global bias of ~2% (7 ppm) in X_{CO2} when compared with TCCON and aircraft measurements.
- About 2/3 of this bias is associated with a ~10 hPa (1%) high surface pressure bias, that was traced to limitations in the Oxygen A-band spectroscopy.
- Much of the remaining bias is associated with uncertainties in CO_2 spectroscopy

Evidence of Shortcomings in Gas Absorption Coefficients

- Persistent spectrally-dependent residuals in ensembles of GOSAT and TCCON retrievals provide additional evidence of shortcomings gas absorption cross sections
  - Residuals correlated with spectral features limit the retrieval algorithm's ability to exploit the full information content of the spectra, and converge to a unique, best estimate of X_{CO2}

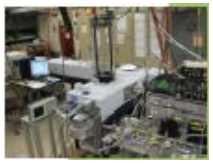


Persistent spectral residuals are seen in all 3 bands used to retrieve X_{CO2} from GOSAT spectra. Those in the SCO2 and ABO2 are most strongly correlated with the band structure. These issues do not impair TCCON X_{CO2} retrievals, because TCCON uses the WCO2 and O2 $^1\Delta_g$ band instead of the A-band in these retrievals.

Improved Gas Absorption Cross Sections

The ACOS ABSCO team embarked on a three-element approach to improve our understanding the CO_2 and O_2 absorption bands needed to retrieve X_{CO2}, including:

- New laboratory measurements (Long path FTS, Cavity Ring-down, Photoacoustic)
- Ground-based direct solar observations from TCCON
- GOSAT measurements



GOSAT soundings

- 1-3 bands, multiple absorbers
- Low spectral resolution
- Unconstrained atmosphere, aerosols, surface albedo

TCCON spectra

- 1-3 bands, multiple absorbers
- High spectral resolution
- Full atmospheric column
- Atmosphere conditions constrained at surface

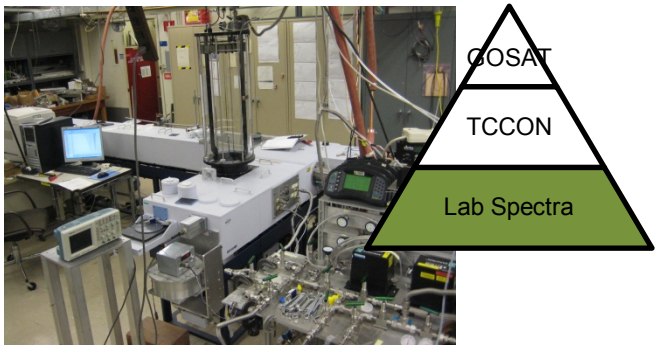
Laboratory spectra

- 1 band, one absorber
- High spectral resolution
- Known laboratory conditions
- Mostly room temperature, low optical depth

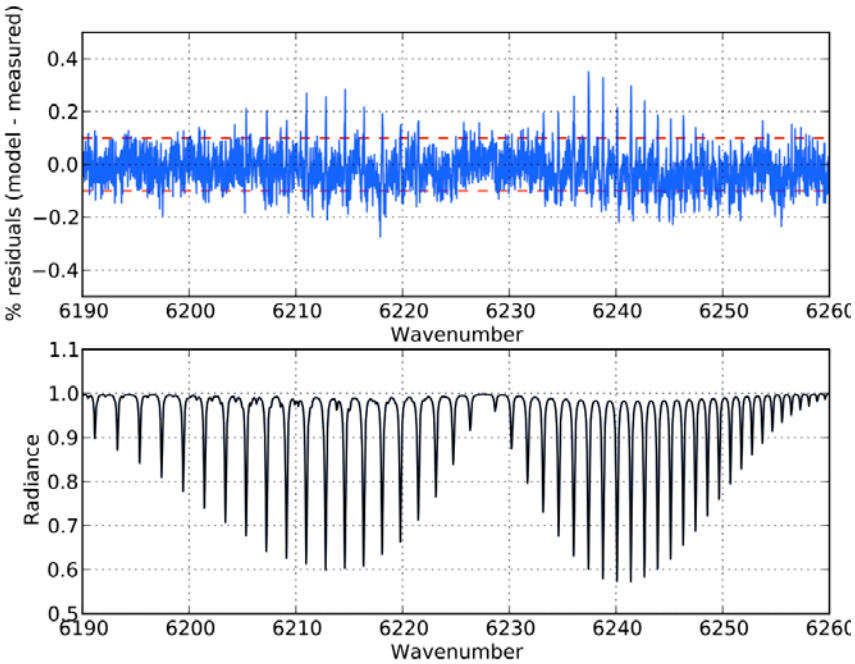
Advances in Laboratory Measurements

- The initial focus was on the CO_2 bands at 1.61 and 2.06 microns
  - Exploiting available measurement capabilities and recent advances in instrumentation and measurement techniques
    - Improved characterization of trace gas composition, temperature, and optical path length in convention, long-path absorption cells
    - New methods, including Frequency Stabilized Cavity Ring-Down (FS-CRDS) and Photoacoustic methods, that provide high signal-to-noise ratios over a wide dynamic range, facilitating measurements of weak absorption
    - Advanced, multi-spectral fitting techniques, that derive spectral line parameters (positions, strengths, widths, pressure shifts) from ensembles of spectra collected for a range of optical paths, pressures, temperatures, and absorbing gas concentrations
    - Self-consistent treatment of line mixing and line shapes that include speed-dependence and collisional narrowing as well as pressure and Doppler broadening effects
  - This investigation has yielded dramatic improvements in our ability to fit laboratory measurements of CO_2

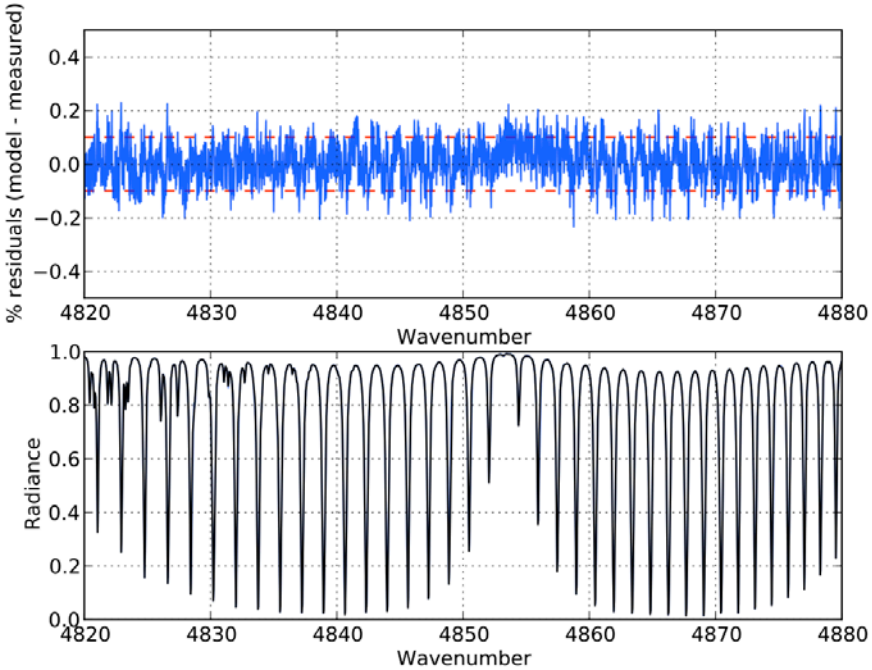
Evaluation with lab spectra



JPL FTS

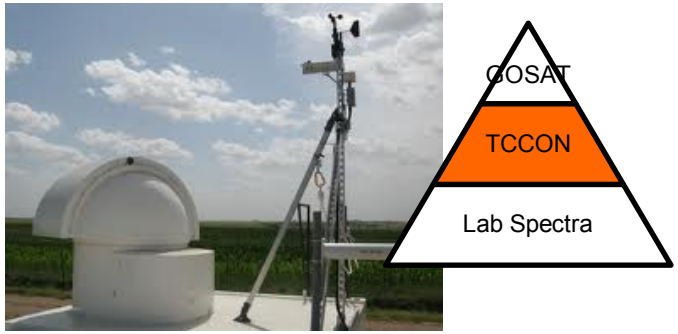


1.6 μm band, path length 32.54m
optical path difference 75cm
Total cell pressure is 742 Torr
Sample is 9.03% air-broadened $^{16}O^{12}C^{16}O$



2 μm band, path length 29.3m
Optical path difference 112.5 cm
Total pressure 599.8 Torr
Sample: 4.95% air-broadened $^{16}O^{12}C^{16}O$

Evaluation with TCCON network data

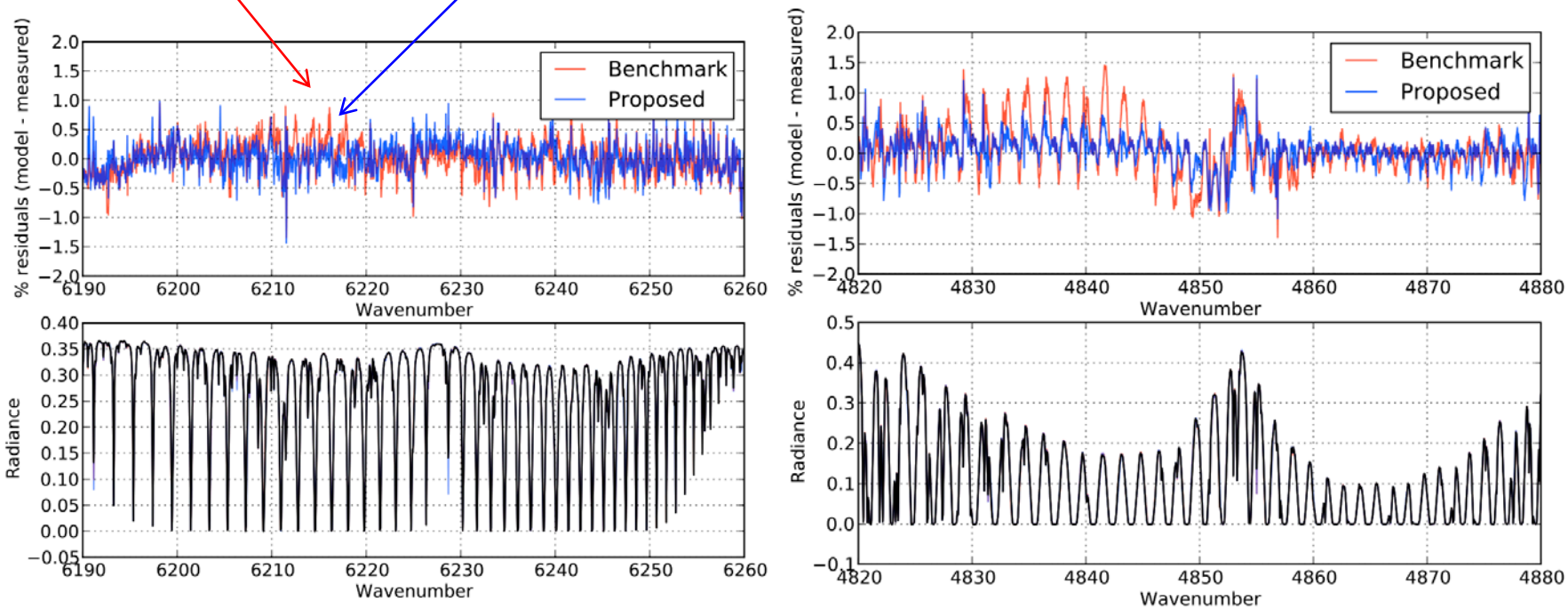


TCCON retrieval for Park Falls 22 Dec. 2004
~12 airmasses

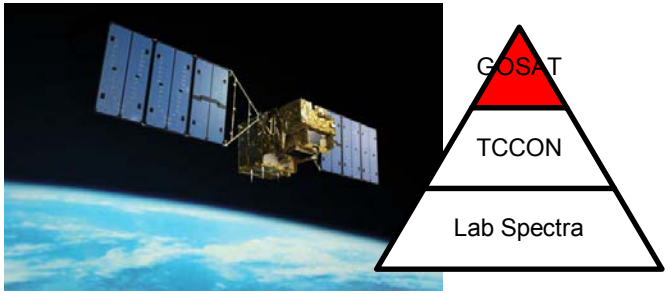
State of the art
First-order line mixing, Voigt shapes

"Ongoing" model
Nearest-neighbor line mixing
Speed dependent profile

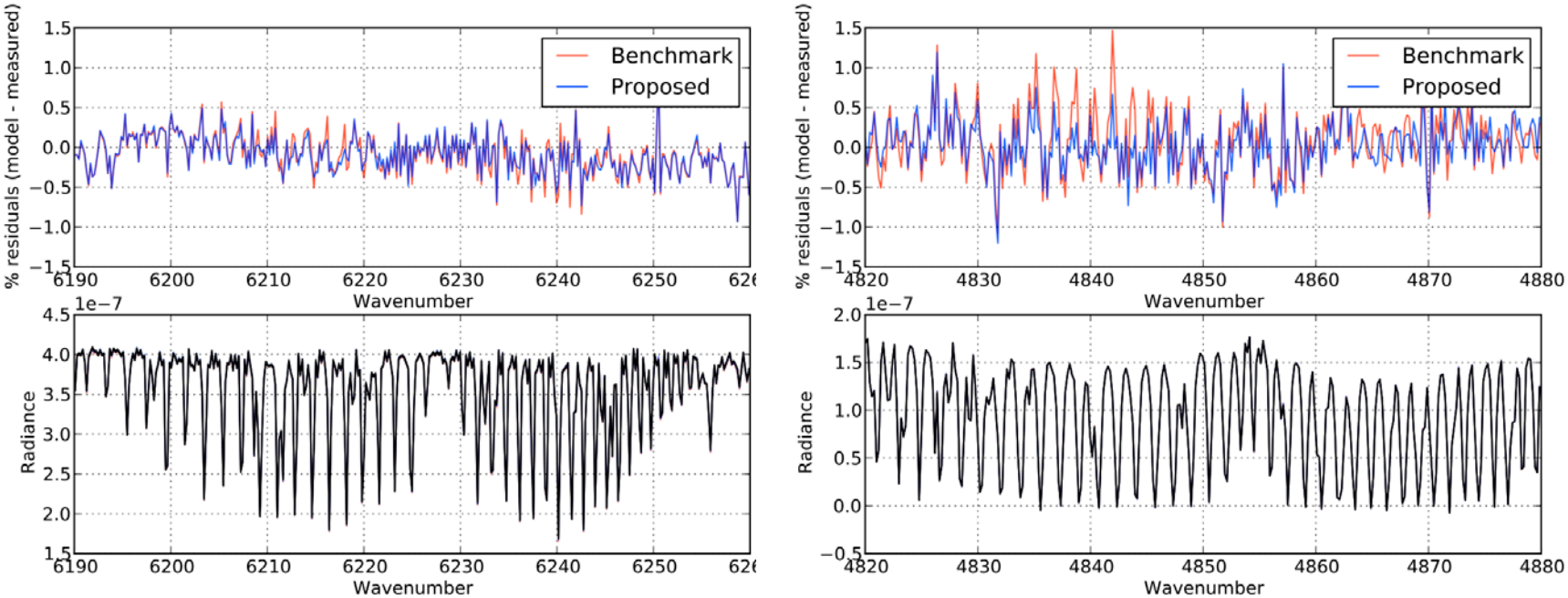
Thompson et al., *JQRST* [2012]
Results shown here do not include H_2O broadening of CO_2.



Evaluation with GOSAT data



- Mean of soundings over TCCON stations
- Three-band retrieval using surface pressure to estimate Column-averaged dry mole fraction $\mathbf{X_{co2}}$

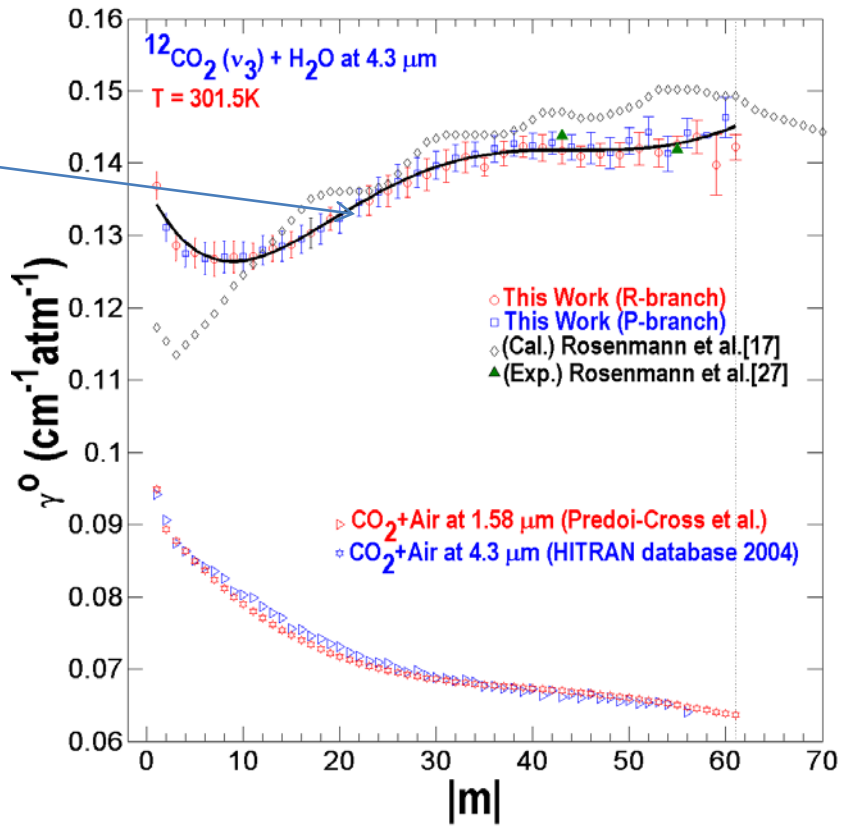


CO_2 lines broadening by H_2O

- Two recent publications suggest that water vapor broadens CO2 lines much more effectively than air (~1.8x).
- Consistent results now available from 2 different experiments

	Sung et al. (4.3 μm) half widths (cm^{-1})	Wallace et al. (1.6 μm) halfwidth (cm^{-1})
R14	0.1287 (±1.4 %)	0.136 (±19.8 %)
R16	0.1303 (±1.6 %)	0.134 (±17.9 %)
R18	0.1323 (±1.2 %)	0.133 (±20.3 %)

- Unlike air broadening and self broadening, which decrease with increasing rotational quantum number |m|, water broadening of CO_2 increases with increasing |m|.
- New measurements are being conducted to confirm these results and assess their impact on XCO2 retrievals from TCCON and GOSAT.



Water broadened half-widths of CO_2 (top) is compared to air broadened half widths (bottom) as function of rotational transition, |m|.

* K. Sung, L. Brown, RA Toth, T. J. Crawford, *Can J. Phys*, **87**, 469-484 (2009)

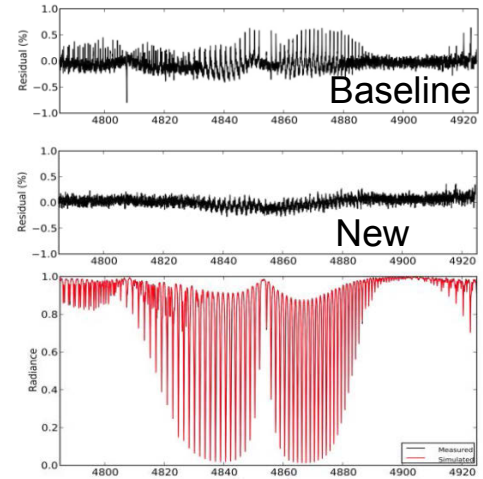
* K. Sung, L. Brown, RA Toth, TJ Crawford, *Can J. Phys*, **87**, 469-484 (2009)

Measurements of CO_2 Spectra

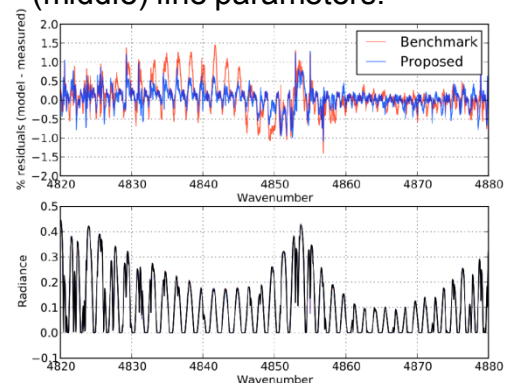
- The new, self-consistent line parameters yielded substantial improvements in fits to laboratory measurements of CO_2
  - Typical peak-to-peak residuals were reduced from 0.5% to 0.1%

- The use of these new line parameters in X_{CO2} retrievals from TCCON and GOSAT spectra also yielded reductions in both bias and spectrally-dependent residuals, but these reductions were more modest than those seen in the lab.

- These differences in performance may be associated with the physical conditions (e.g. vertical variations in p, T, or gas amount) or absorbers (e.g. water vapor line and continuum absorption) that were not included in the lab measurements.



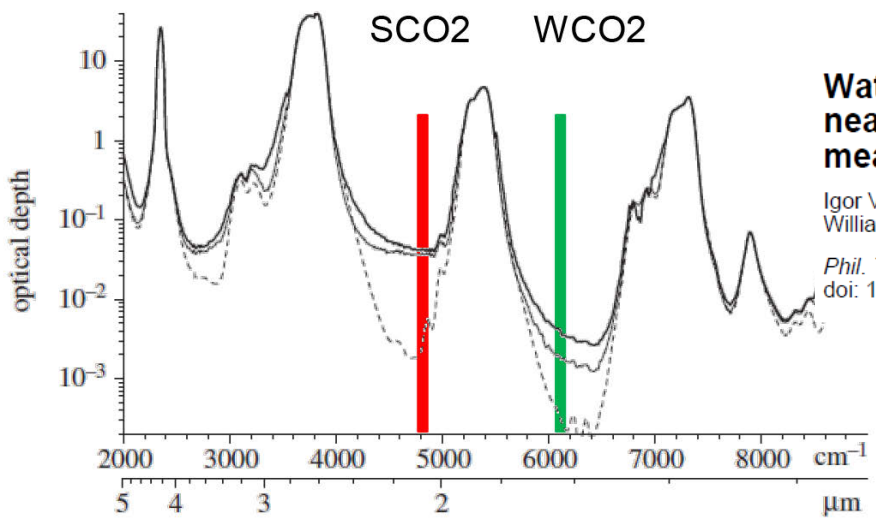
Lab measurements of the SCO2 band (bottom) shown with residuals for baseline (top) and revised (middle) line parameters.



TCCON measurements of the SCO2 band (bottom) shown with residuals for baseline (red) and revised (blue) line parameters.

Other Spectroscopy Issues

- Recent laboratory measurements indicate that the self- and air-broadened water continua absorption in the SCO2 (and WCO2) band may be much stronger than previously assumed.
- This continuum absorption could contribute to both the spectrally-dependent residuals, and observed biases between X_{CO2} retrievals using the SCO2 and WCO2 bands



Water vapour foreign-continuum absorption in near-infrared windows from laboratory measurements

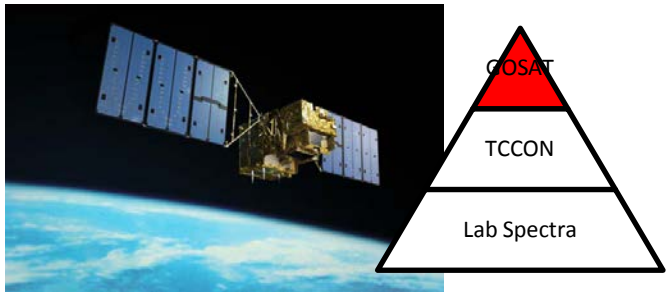
Igor V. Ptashnik, Robert A. McPheat, Keith P. Shine, Kevin M. Smith and R. Gary Williams

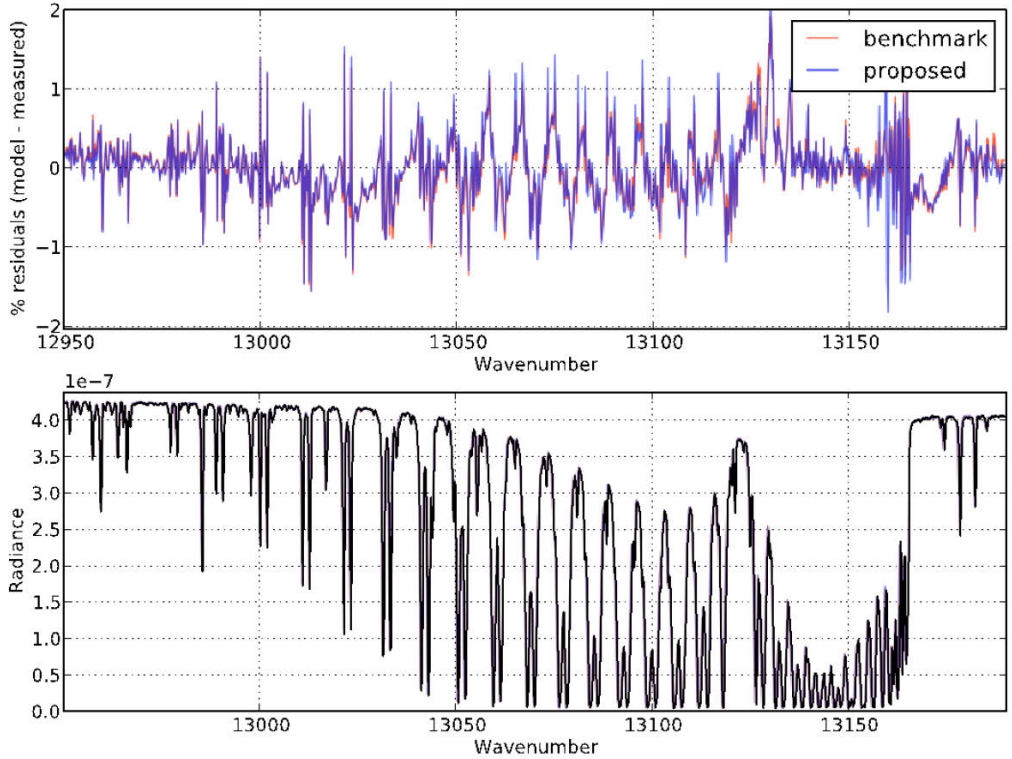
Phil. Trans. R. Soc. A 2012 **370**, 2557-2577
doi: 10.1098/rsta.2011.0218

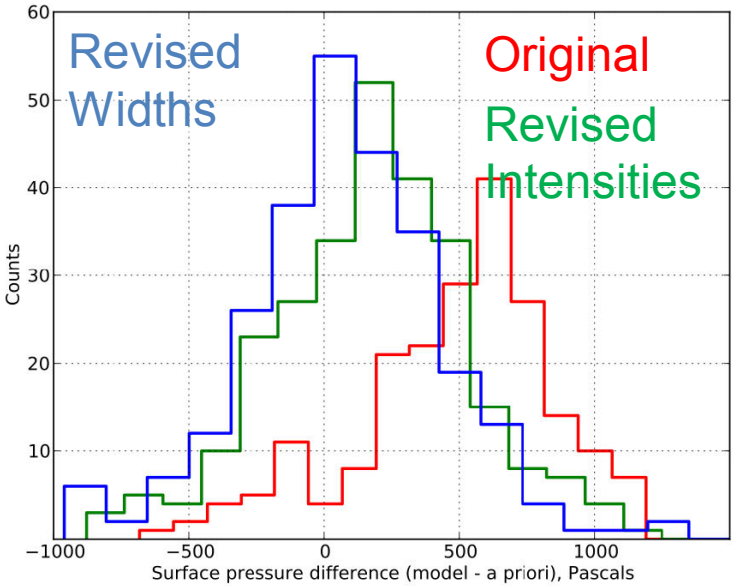
Simulated water vapor continuum optical depth in the short wave infrared region for a mid-latitude summer atmosphere by models that use the MTCKD-2.5 continuum (dashed line), which is currently implemented in ACOS algorithm, and for models that use new measurements (Ptashnik et al. 2011) for self- (light grey solid line) and self + foreign (dark solid line) continuum absorption.

Evaluation of O_2 with GOSAT data

- Estimation of Xco_2 requires surface pressure information.
- O_2 A band is used for surface pressure information (among other things).



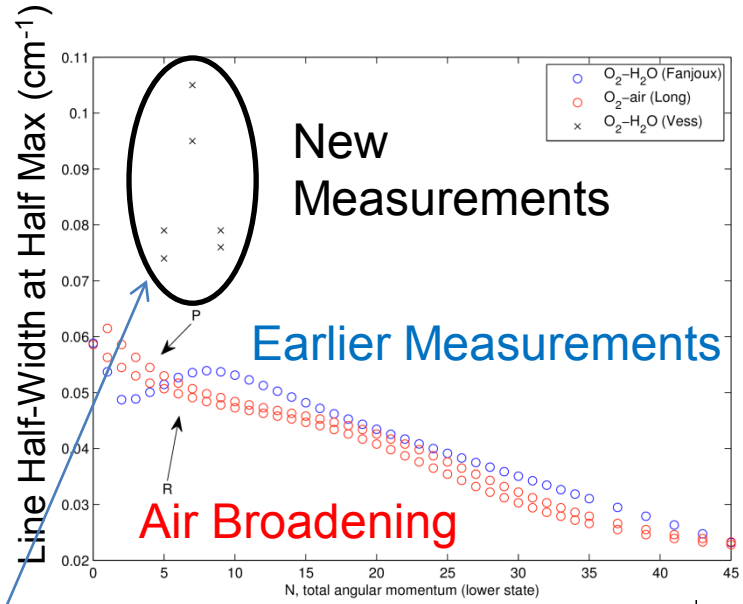


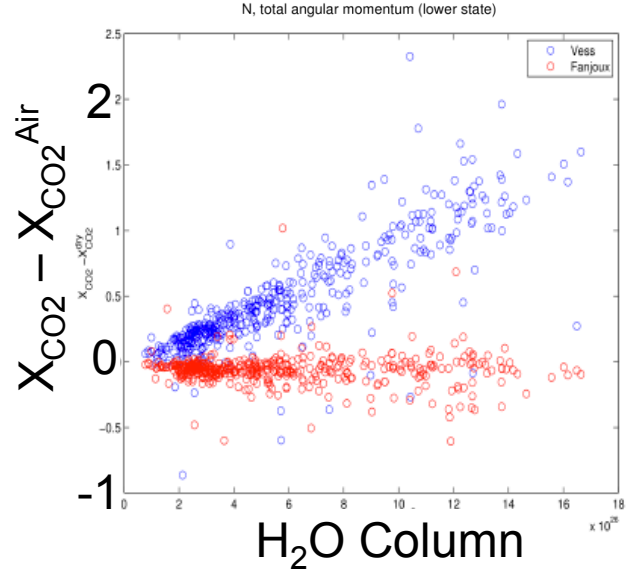


Surface pressure biases due to uncertainties in line strengths and widths.

Causes and Impacts of Column O_2 Biases

- O_2 A-Band cross sections have been scaled by 1.025 to correct 10 hPa surface pressure bias
  - This is a temporary fix!
- Known errors in the details of O_2 spectroscopy are contributing some of this bias
  - Errors in intensity and pressure shifts
  - Oversimplifications in line shape
  - Uncertainties in Line Mixing
  - Uncertainties in collision-induced absorption
  - O_2 lines broadened by water vapor
    - New measurements indicate a much larger effect than older measurements
    - TCCON observations processed with the air broadened and new water-broadened cross sections show large (2 ppm) X_{CO2} differences
- New laboratory studies are under way to address these issues.





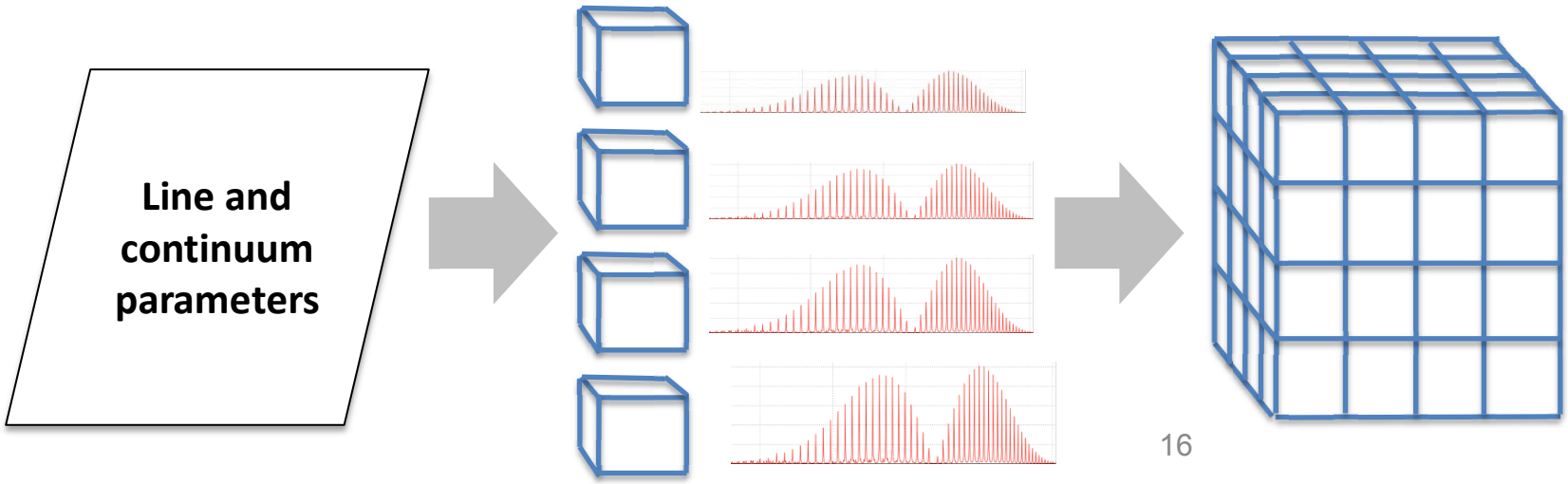
Summary of ACOS Gas Absorption Line Lists

	0.76µm O_2	1.61µm CO_2	2.06µm CO_2	H_2O
Spectral range	12745-13245 cm^{-1}	4700-6500cm^{-1}	4700-6500cm^{-1}	**12745-13245 cm^{-1}** 4700-6500cm^{-1}
Spectral resolution	0.01cm^{-1} or 0.002cm^{-1}	0.01 cm^{-1} or 0.002cm^{-1}	0.01 cm^{-1} or 0.002cm^{-1}	0.01 cm^{-1} or 0.002cm^{-1}
Position	**Long (2010), Long (2011)**	Devi (2007)[1]	Benner/Devi (2011)[1]	**Gordon (2012), Rothman (2010)**
Intensities	**“**	“	“	**“**
Air-widths	Tran (2008)	Predoi-Cross (2009)[1]	“	**“**
Air-shifts	Brown (2009) Robichaud (2008a) Predoi-Cross (2008)	Devi (2007b)[1]	“	**“**
Temp. dep.	Brown (2000)[1,2]	Predoi-Cross (2009)[1]	“	**“**
Line shapes	Voigt / **Galatry**	Speed-dependent Voigt	Speed-dependent Voigt	Voigt
Isotopologue abundance	Rothman (2009)[1]	Rothman (2009)	**Rothman (2009)**	Rothman (2009)
H_2O broadening	**Vess (2012)**	**Sung (2009)**	**Sung (2009)**	-
Air-Line mixing	Tran (2008)	Devi (2007)	Benner/Devi (2011)	-
“ Temp. dep.	Tran (2008)	-	-	-
Speed dep.	-	Devi (2007)[1]	Benner/Devi (2011)[1]	-
Continuum	CIA via Tran (2008)	-	*	**Mlawer (2012)**

Absorption coefficient (ABSCO) Tables

❑Pre-computed ABSCO look-up tables

- **Problem:** Advanced spectroscopic models too slow for online use
- **Solution:** pre-computed lookup table for linear interpolation
- 71 Pressure levels, 17 Temperature
- Recently expanded from 3-dimensions (wavenumber, pressure, temperature) to add a 4th dimension, to accommodate water variable amounts of water vapor broadening



Gas Absorption Line List References (1 of 2)

Brown, L. R., Plymate, C. Experimental line parameters of the oxygen A band at 760nm. J Mol Spectrosc 2000; 199:166–79.
Line list is available in the acos/absco repository at the following location:
acos/level_2/exe/absco/input/line_mixing/o2/lm_o2_inputs_20091026/SDF.dat

Devi, V. M., D. C. Benner, L. R. Brown, C. E. Miller, and R. A. Toth (2007), Line mixing and speed dependence in CO2 at 6227.9 cm-1: Constrained multispectrum analysis of intensities and line shapes in the 30013 ← 00001 band, J. Mol. Spectrosc. 245, 52-80.

Anu Dudhia, RFM Software package and user guide available at http://www.atm.ox.ac.uk/RFM/.

I.E. Gordon, L. Lodi, G.C. Toon, J. Tennyson, L.R. Brown, L.S. Rothman. "Evaluation of the experimental and theoretical spectral parameters of water vapor lines in the 2-μm region using Solar-pointing FTS spectra," (2012) in preparation.

J.-M. Hartmann, H. Tran, and G. C. Toon, *Influence of line mixing on the retrievals of atmospheric CO2 from spectra in the 1.6 and 2.1 μm regions,* Atmos. Chem. Phys. Discuss., 9, 1–26, 2009

J. Lamouroux, H. Tran, A.L. Laraia, R.R. Gamache, L.S. Rothman, I.E. Gordon, and J.-M. Hartmann, J. Updated database plus software for line-mixing in CO2 infrared spectra and their test using laboratory spectra in the 1.5-2.3 μm region, Quant. Spectrosc. and Rad. Transfer 111, 2321-2331 (2010).

D.A. Long, D.K. Havey, M. Okumura, C.E. Miller, J.T. Hodges, O2 A-band line parameters to support atmospheric remote sensing, Journal of Quantitative Spectroscopy and Radiative Transfer, Volume 111, Issue 14, September 2010, Pages 2021-2036, ISSN 0022-4073, 10.1016/j.jqsrt.2010.05.011.

Mlawer, E.J., V.H. Payne, J.-L. Moncet, J.S. Delamere, M.J. Alvarado, D.D. Tobin, Development and recent evaluation of the MT_CKD model of continuum absorption, submitted to *Phil. Trans. Roy. Soc.A*, une 13, 2012 370 1968 2520-2556.

Niro, F., Boulet, C., and Hartmann, J. M.: Spectra calculations in central and wing regions of CO2 IR bands between 10 and 20 μm. I: Model and laboratory measurements, J. Quant. Spectrosc. Radiat. Transfer 88, 483–498, 2004.

F. Niro, T. von Clarmann, K. Jucks, and J.-M. Hartmann (2005), Spectra calculations in central and wing regions of CO2 IR bands between 10 and 20 m. III: atmospheric emission Spectra, J. Quant. Spectrosc. Radiat. Transfer 90, 61–76.

Predoi-Cross, A., C. Holladay, H. Heung, J.-P. Bouanich, G. Ch. Mellau, R. Keller, and D. R. Hurtmans (2008), Nitrogen-broadened lineshapes in the oxygen A-band: Experimental results and theoretical calculations, J. Mol. Spectrosc. 251, 159–175.

Predoi-Cross, A., A. R. W. McKellar, D. Chris Benner, V. Malathy Devi , R. R. Gamache, C. E. Miller, R. A. Toth, and L. R. Brown (2009), Temperature dependences for air-broadened Lorentz half width and pressure-shift coefficients in the 30013←00001 and 30012←00001 bands of CO2 near 1600 nm, Can. J. Phys. (in press).

Ptashnik et al. *Journal of Geophysical Research*, vol. 116, D16305, doi:10.1029/2011JD015603, 2011.

Robichaud, D. J., Hodges, J. T., Maslowski, P., Yeung, L.Y., Okumura, M., Miller, C. E.,et al. High-accuracy transition frequencies for the O2 A-band. J Mol Spectrosc 2008;251:27–37.

Gas Absorption Line List References (2 of 2)

Robichaud, D. J., Hodges, J. T., Brown, L. R., Lisak, D., Maslowski, P., Yeung, L. Y., et al. Experimental intensity and line shape parameters of the oxygen A-band using frequency-stabilized cavity ring-down spectroscopy. J Mol Spectrosc. 2008; 248:1–13.

Robichaud D. J., Hodges, J. T., Lisak, D., Miller, C. E., Okumura, M. High-precision pressure shifting measurement technique using frequency-stabilized cavity ring-down spectroscopy. JQSRT 2008;109:435–44.

Rothman, L. S., et al. (2005), The HITRAN molecular spectroscopic database: Edition of 2004, J. Quant. Spectrosc. Radiat. Transfer, 96, 139 – 204.

Rothman, L. S. et al. *The HITRAN 2008 molecular spectroscopic database.* Journal of Quantitative Spectroscopy and Radiative Transfer, 110 (2009) 533–572.

Rothman, L. S., I. E. Gordon, R. J. Barber, H. Dothe, R. R. Gamache, A. Goldman, V. I. Perevalov, S. A. Tashkun, J. Tennyson (2010). HITEMP, the high-temperature molecular spectroscopic database. *Journal of Quantitative Spectroscopy and Radiative Transfer*. 111:15, p. 2139-2150.

Keeyoon Sung; L. R. Brown, R. A. Toth, T. J. Crawford. Fourier transform infrared spectroscopy measurements of H_20-broadened half-widths of CO_2 at 4.3 um. *Canadian Journal of Physics*; May 2009, Vol. 87 Issue 5, p. 469.

Thompson, D. R., D.. C. Benner, L. R. Brown, D. Crisp, V. Malathy Devi, Y. Jiang, V. Natraj, F. Oyafuso, K. Sung, D. Wunch, R. Castaño a, C. E. Miller Atmospheric validation of high accuracy CO_2 absorption coefficients for the OCO-2 mission. *Journal of Quantitative Spectroscopy and Radiative Transfer* (2012), http://dx.doi.org/10.1016/j.jqsrt.2012.05.021.

Tran, H, Boulet, C, and Hartmann, J.-M. Line mixing and collision-induced absorption by oxygen in the A band: Laboratory measurements, model, and tools for atmospheric spectra computations. Journal of Geophysical Research, vol. 111, D15210, doi:10.1029/2005JD006869, 2006.

Tran, H. and Hartmann, J. M. An improved O2 A band absorption model and its consequences for retrievals of photon paths and surface pressures, Journal of Geophysical Research, vol 113, D18104, 2008.

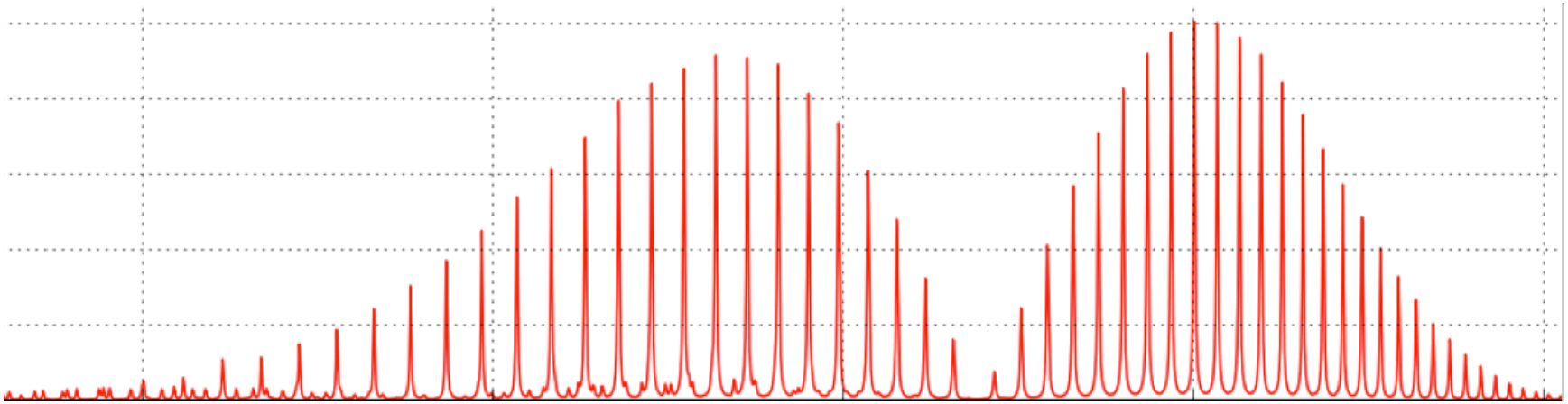
Toth, R. A., C. E. Miller, V. M. Devi, D. C. Benner, and L. R. Brown (2007), Air-broadened width and pressure shift coefficients of 12C16O2: 4700 – 7000 cm-1, J. Mol. Spectrosc. 246, 133-157.

Toth, R. A., Brown, L. R., Miller, C. E., Malathy Devi, V., and Benner, D. C.: Spectroscopic database of CO2 line parameters: 4300–7000 cm−1 , J. Quant. Spectrosc. Radiat. Transfer 109, 906–921, 2008.

Toon, G. Personal Communication.

E. M. Vess, C. J. Wallace, H. M. Campbell, V. E. Awadalla, J. T. Hodges, D. A. Long, and D. K. Havey. Measurement of H2O Broadening of O2 A-Band Transitions and Implications for Atmospheric Remote Sensing. *Journal of Physical Chemistry*. 2012 (in press).

Wunch, D., Toon, G. C., Wennberge, P. O. et al. Calibration of the total carbon column observing network using aircraft profile data. *Atmos Meas. Tech. Discuss., 3*, 2603-2632, 2010. www.atmos-meas-tech-discuss.net/3/2603/2010/ doi:10.5194/amtd-3-2603-2010

Preliminary Conclusions

- The new models seem a step in the right direction
  - Qualitatively similar improvements for three instruments and retrieval codes
- Accuracies are not yet to the desired 0.1% level
  - Some systematic errors remain
- New measurements (CRDS, PAS) may help constrain line shapes
- **Key components of the approach:**
  - **Consistent use of line parameters with line shape used in their determination**
  - **Use of multiple spectra in the fitting of line shape and line parameters**