CO_2 Spectroscopy Evaluation: 670 to 7000 cm^{-1}

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Several CO_2 linelists including HITRAN 2008, 2012, and 2016 (two versions), have been evaluated by fitting laboratory spectra (mainly Kitt Peak) and atmospheric solar absorption spectra (MkIV & TCCON).

The 670-7000 cm^{-1} region of interest was divided into 41 windows, most encompassing at least one complete CO_2 absorption band or sub-branch. Regions with no discernable CO_2 absorption were skipped.

The GFIT spectral fitting algorithm was used in all cases. It assumed a Voigt lineshape and no line-mixing. This evaluation focusses on the RMS residuals that were achieved and the window-to-window consistency of the retrieved CO_2 amounts.

Between evaluations of the different linelists, only the CO_2 linelist was changed. The spectroscopy of the interfering gases (e.g. H_2O, O_3, CH_4, etc.) was unchanged, so any difference in the RMS fitting residuals or the retrieved CO_2 amounts is entirely attributable to the CO_2 linelist under evaluation.

A new "greatest hits" linelist (ATM18) was subsequently developed by "cherry picking" from the best predecessor linelists. Ad hoc manual adjustments were then performed to fix obvious errors (e.g., bad line positions, pressure shifts, inconsistent retrieved CO_2 amounts). To keep this report concise, the ATM18 linelist is presented in parallel with the evaluation of earlier linelists, even though it was developed much later.

This presentation shows highlights from the full 42-page report:
https://mark4sun.jpl.nasa.gov/report/CO2_Spectroscopy_Evaluation-compressed.pdf

Motivation

The main motivation for improving CO_2 spectroscopy is to make more accurate measurements of atmospheric CO_2, the second most important GHG (after H_2O) and the main driver of climate change [CO_2 has increased 60% since pre-industrial times whereas H_2O has increased by only 5-10%].

Being a simple linear molecule, the spectroscopy of CO_2 is already very good, in comparison with H_2O, O_3, CH_4 or even O_2. So the improvements embodied in HITRAN 2016 appear pretty modest in terms of the fitting residuals or the retrieved atmospheric CO_2 amounts. But due to the long lifetime of atmospheric CO_2 a large atmospheric concentration (400 ppm) has accumulated. This means that atmospheric CO_2 has a large DC component, upon which the AC variations of interest are superimposed. So a very high measurement accuracy (0.25%) is required to see ~1 ppm spatio-temporal variations of atmospheric CO_2 caused by source/sink imbalances. This does NOT mean that all spectroscopic line parameters of all CO_2 lines need to be measured to 0.25% accuracy. But certainly further improvements beyond HIT2016 are needed.

CO_2 has a highly predictable atmospheric abundance, founded on many highly accurate in situ measurements (mass spec. and NDIR) made on the surface, on aircraft, and balloons (e.g. aircore) from a wide variety of locations and seasons. CO_2 can be predicted to better than 1 ppm (0.25%) anywhere in the Earth's atmosphere between the PBL and the mesosphere. Its isotopic fractionation is also highly predictable (better than 0.1%). This fact allows the use of CO_2 for remote sensing of temperature, and as a proxy for the number of air molecules encountered along the light path. For example, CO_2 is used to determine the tangent altitude in limb viewing experiments (e.g. solar occultation). Also CO_2 measurements have been used to determine the light path in nadir measurements of reflected sunlight, improving measurements of atmospheric CH_4.

Methodology

Upon receiving a new linelist of a gas, it is used to fit a wide variety of atmospheric spectra, acquired under known atmospheric conditions, over a series of prescribed windows.

These atmospheric spectra include balloon solar occultation spectra covering 10-40 km altitude, and ground based solar absorption spectra measured from 0 to 4 km altitude, at temperature from -40 to +40C, and zenith angles from 0 to 89 deg.

The results are assessed in terms of the fitting residuals and the consistency of the column amounts over the different windows.

If the new linelist produced equal or better fits than any predecessor in a particular region, then don't bother to examine the spectral fits, simply accept the new linelist in this region.

If the new linelist produces poorer fits to atmospheric spectra in a particular window, fit laboratory spectra to see if those fits also worsened (very common).

If the lab spectra also worsened, and there is an obvious cause (e.g. line position error, width error) the the problem is fixed manually, guided by the fits to the lab spectra. If there is no obvious cause, the new linelist is reverted to the best predecessor over the window.

When the fits (atmospheric and laboratory) are satisfactory in every window (better or equal to any predecessor linelist) then the retrieved gas amounts are examined on a window-by-window basis. If the atmospheric and laboratory retrievals are in agreement that a particular window produces erroneous retrieved gas amounts, those line intensities are scaled to bring the retrieved gas amounts into agreement with the other windows.

The CO_2 Linelists Evaluated

HITRAN 2008: 314,919 CO_2 lines

HITRAN 2012: 471,847 CO_2 lines

ATM 2016: 450,493 CO_2 lines
Based mainly HITRAN 2012. Uses Toth (2009) for the 5740-6500 cm^{-1} region because it gave better fits (and still does). Empirical adjustments have been made throughout to fix obvious errors (mainly line position errors).

HITRAN 2016a: 554,183 CO_2 lines
Based on files the linelists that Iouli Gordon sent me June 27, 2017 (O2_hit16_first-9iso) and on June 30, 2017 (hit838corr). Before using, I fixed 19 lines with ABHW=0 and one with an intensity of zero (used HIT 2012 value).

HITRAN 2016b: 554,879 CO_2 lines
Downloaded from HITRAN-Online website on Nov 28, 2017 (5a1de32a.par). Includes isotopologs 11 & 12. A format of "f5.3" had been enforced for SBHW, which changes some lines that were previously "f5.4", e.g.

25   3.681760 1.943E-33 1.457e-12.0865.1155   in HIT16a

became

25   3.681760 1.943E-33 1.457e-12.08650.116   in HIT16b

ATM 2018: 524,724 CO_2 lines (new linelist)
Mostly HIT 2016b, except in regions where ATM 2016 or HIT 2008 were better. Some ad hoc empirical adjustments.

The CO_2 Spectra Analyzed

Kitt Peak lab spectra: 136 from Kitt Peak and 12 from JPL (Keeyoon Sung).
0.1 <Pressure < 700 Torr.
All at room temperature (291-303 K) except for two (268K and 235K)
23 Kitt Peak spectra are enriched in ^{13}C, giving the lab spectra a much higher sensitivity to spectroscopic errors in isotopologs 2, 5, 6, 10, 11, 12, than the other lab spectra (or atmospheric spectra).

Most lab spectra have < 1000 cm^{-1} of useful coverage, which makes it difficult to compare intensities measured at low wavenumbers with those from high wavenumbers because these are seldom in the same spectrum.

MkIV balloon solar occultation spectra: cover 650-5650 cm^{-1} simultaneously at 0.010 cm^{-1} resolution. 19 spectra cover 10-40 km tangent altitude.

MkIV ground-based solar absorption spectra: cover 650-5650 cm^{-1} simultaneously at 0.005 cm^{-1} resolution. A subset of 122 spectra were analyzed.

TCCON ground-based solar absorption spectra: cover 4000-15000 cm^{-1} simultaneously at 0.015 cm^{-1} resolution. A subset of 25 spectra were analyzed.

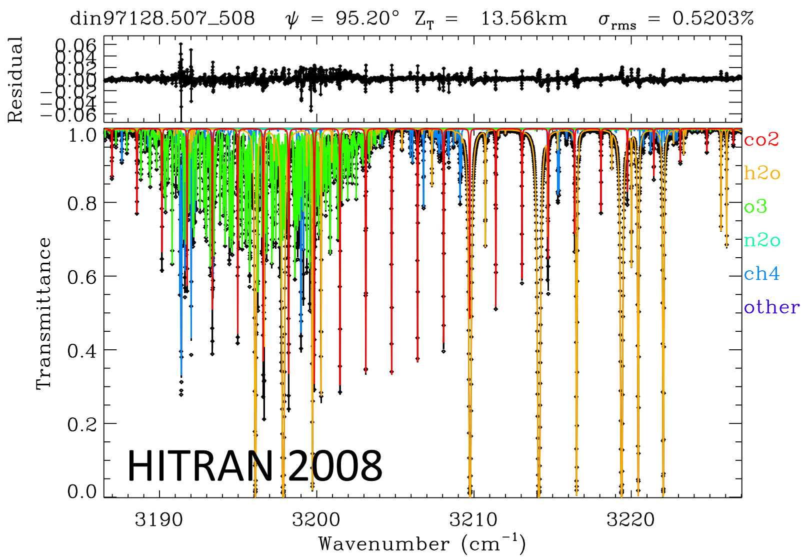
MkIV Balloon Spectra

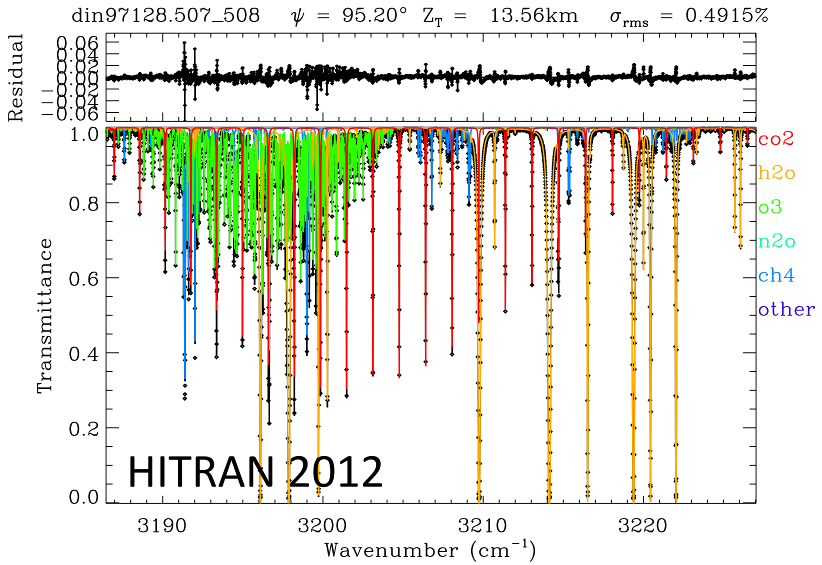
MkIV instrument observes direct sunlight from balloon, covering the entire 650-5650 cm^{-1} region simultaneously at 0.01 cm^{-1} resolution (60 cm OPD). Using the sun as a source allows a broad-bandwidth to be measured at high resolution and SNR. Broad simultaneous coverage is an important attribute when testing the band-to-band consistency of the spectroscopy. [In contrast, the majority of the Kitt Peak lab spectra have less then 1000 cm^{-1} of useful coverage, which means, for example, that the v_2 band is rarely in the same spectrum as the v_3]

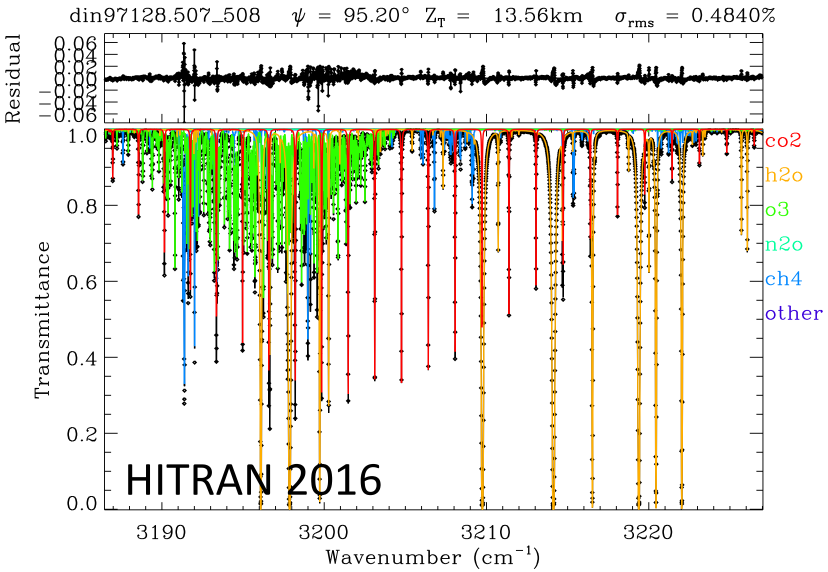
As the sun rises/sets, the ray path through the atmosphere passes through progressively lower/higher pressure. During the course of a 50 minute occultation, the tangent point varies from 10 to 40 km altitude encountering pressures from 3 mbar to 300 mbar and temperatures from 210 to 250K.

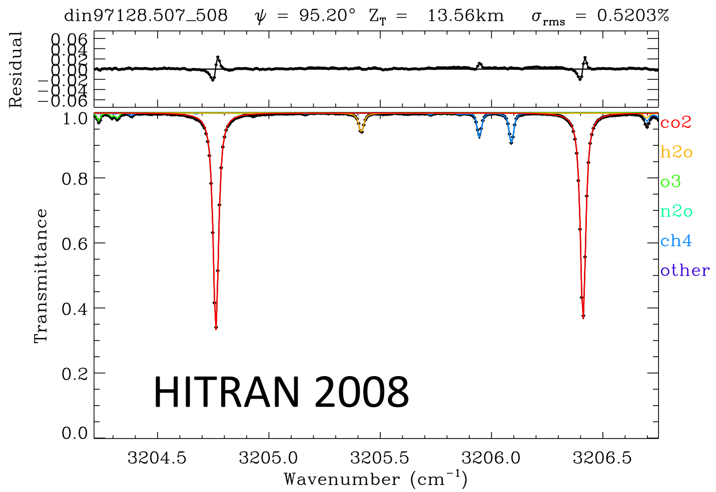
The CO_2 VSF (averaged over several good windows) is used to determine the viewing geometry (tangent altitude). It is therefore going to take an average value close to 1.0, by definition. The balloon spectra are therefore worthless for assessing absolute CO_2 band intensities. But the window-to-window biases are still valid. The average value of the VSF for the windows used in this work is not exactly 1.0 because an older linelist (pre-HITRAN_2K) was used in the determination of the tangent altitudes. Also, the windows used for the tangent point determination were only a small subset of those evaluated here.

MkIV balloon spectral fits at 14 km altitude in the 3200 cm^{-1} region

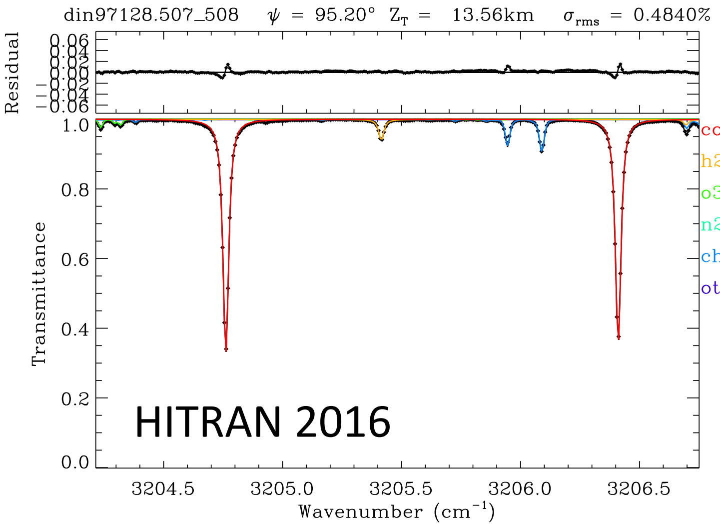




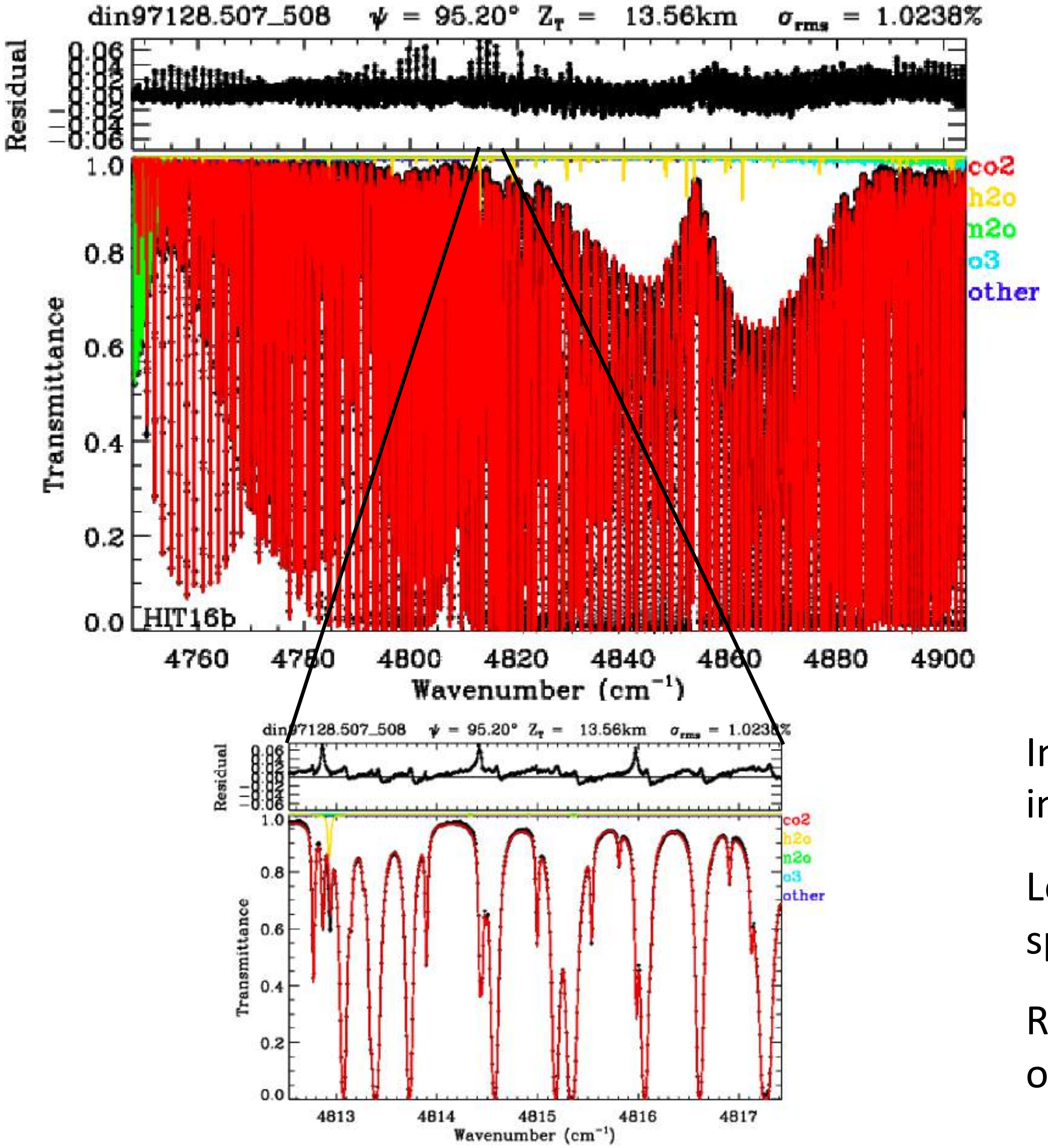


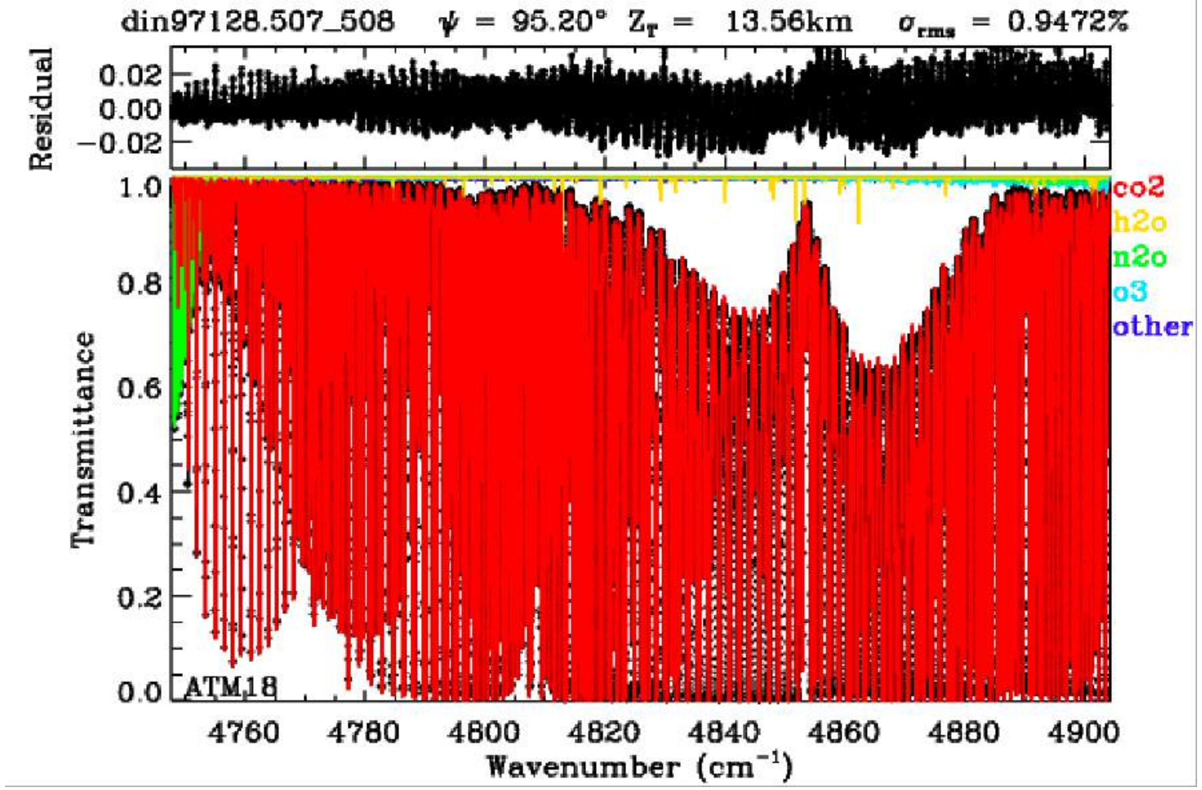


Illustrating the progressive improvement in the spectral fits from HIT08 to HIT16 in the 3205 cm^{-1} window where CO_2 lines are from v_2+v_3 combination band centered at 3182 cm^{-1}. Residuals are mainly due to H_2O, O_3 and CH_4, but these linelists were unchanged in this CO_2 study, so improvement in rms fitting residuals is due solely to CO_2. HIT16 still not perfect, but better than its predecessors.



Example of fits to MKIV balloon spectra





In this region, the spectral fits deteriorated with HIT16 due to an inconsistency in the strengths of the weak and strong lines.

Left panel shows fit obtained using HIT16b, showing regularly spaced spikes in residuals and a peak residual of 7%.

Right panels shows fit obtained using ATM18 with a peak residual of 4%. Fits made with HIT08 & HIT12 look similar.

MkIV Balloon: RMS Spectral Fitting Residuals

Top Panel: Plot of the data tabulated on the previous slide. Shows RMS residuals for 35 windows using 6 different linelists. The absolute fitting residuals are dominated by interfering atmospheric absorptions, especially H_2O.

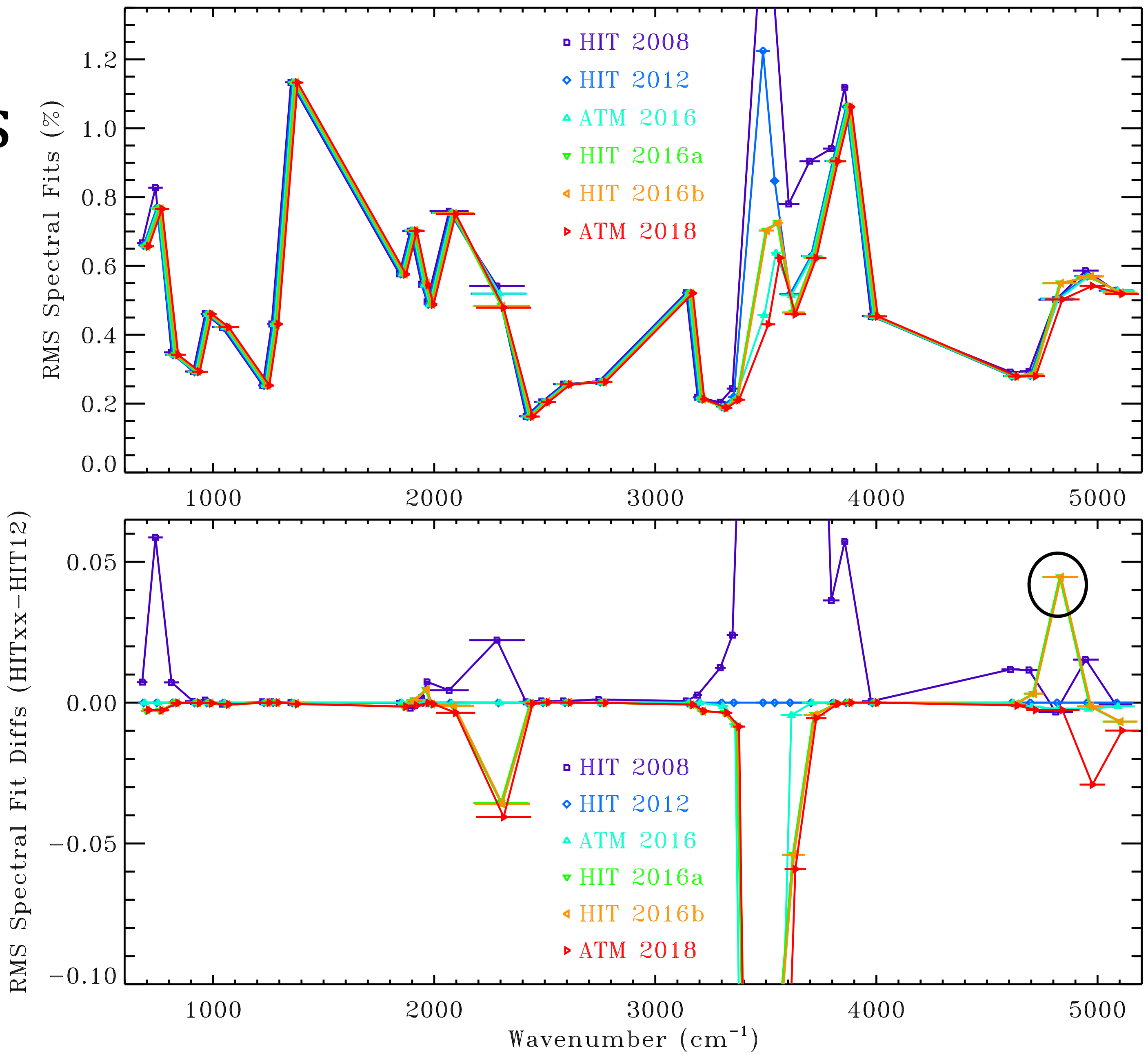
Bottom Panel: Differences from HIT12.

Difference between HIT16a and HIT16b are tiny because isotopologs 11 & 12 are not discernable in atmospheric spectra and because the rounding of the SBHW values doesn't matter in air-broadened spectra.

HIT16 shows improvements over HIT12 below 900 cm^{-1}, and in windows centered at 2290, 3496, 3548, 3623, 4962 and 5096 cm^{-1}.

In the 4825 cm^{-1} window, used by OCO & GOSAT, the HIT16 linelist achieves the worst fits (circled) and HIT08 the best, as for lab spectra.

The ATM18 linelist is always best, or close to.



MkIV Balloon: Retrieved CO_2 VMR Scale Factors

Plotting the VSF values tabulated in the previous slide, along with their error bars.

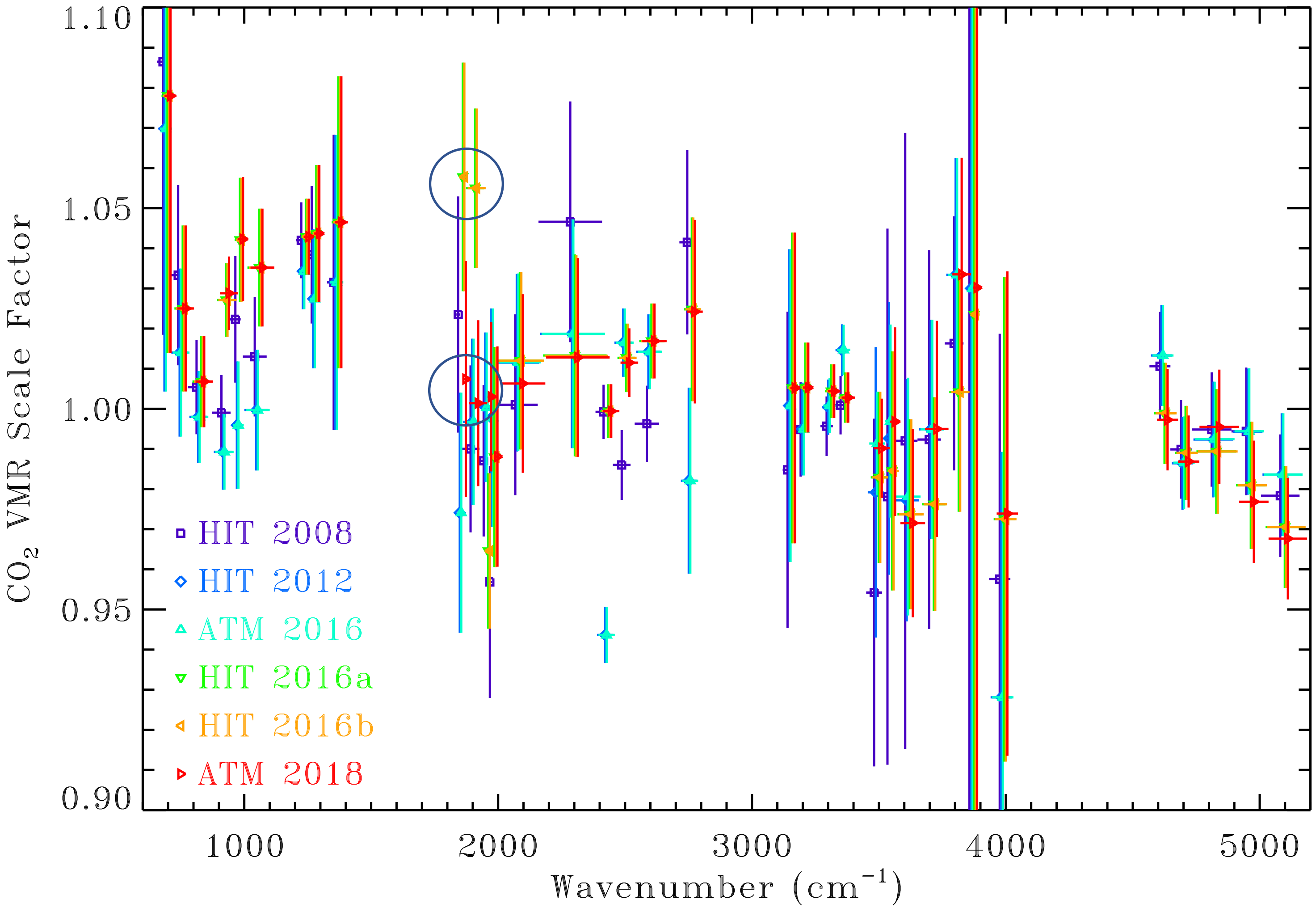
HIT12 points mostly buried under the ATM16 points, except around 3600 cm^{-1}.

HIT16a points mostly buried beneath HIT16b points. X-values offset for clarity.

MkIV instrument records 600-5650 cm^{-1} simultaneously, so derived VSFs should have good window-to-window consistency.

Upper circle indicate anomalously high HIT16 values in the 1800-2000 cm^{-1} region, which were also seen in lab spectra. Lower circle shows pre-2016 HITRAN & ATM18.

Somewhat high (~1.04) VSFs for all linelists are seen in 1200-1400 cm^{-1} region containing the v_1 band (symmetric stretch) of the ^{17}O and ^{18}O isotopologs. These are not definitive enough to warrant fixing.



RMS Residuals from fits to laboratory spectra

Showing the RMS spectral fits for 41 windows, averaged over the 148 lab spectra. This is done for 6 different linelists. These are the same data tabulated on the previous slide.

Upper panel shows absolute RMS residuals. Lower panel shows differences from HIT12.

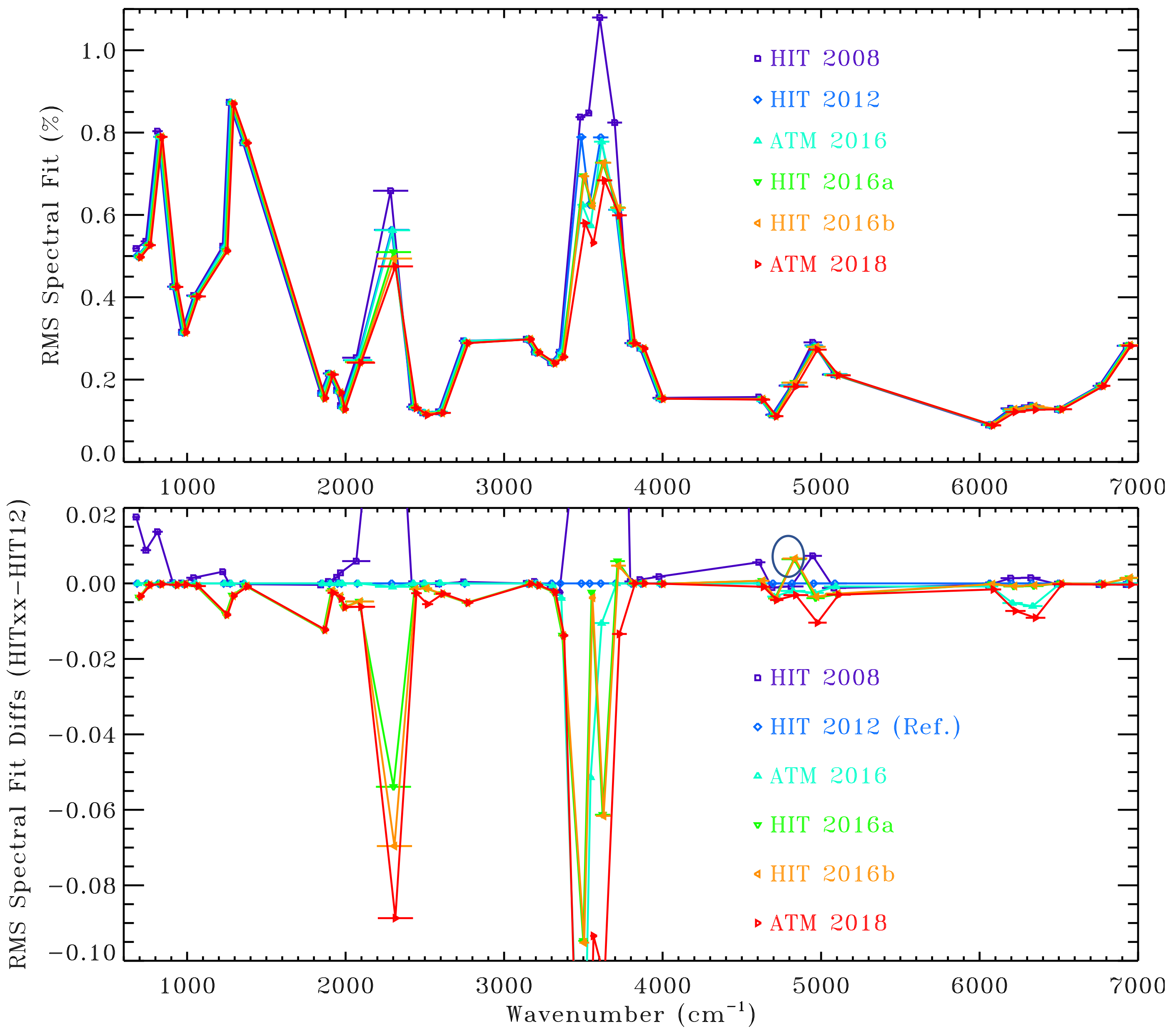
The absolute value of the RMS fit is unimportant. This is generally dominated by instrumental issues and interfering absorptions (e.g. H_2O).

Variation of RMS from linelist to linelist is entirely due to the CO_2 spectroscopy, since nothing else has been changed.

Big improvements are apparent for HIT16a,b in the 2300 cm^{-1} and the 3600 cm^{-1} regions.

HIT16a and HIT16b produce similar results. The largest difference is seen at 2300 cm^{-1} due to inclusion of isotopologs 11 & 12 i9nto HIT16b.

In the 4825 cm^{-1} window, HIT16 produces the worst fits (circled).



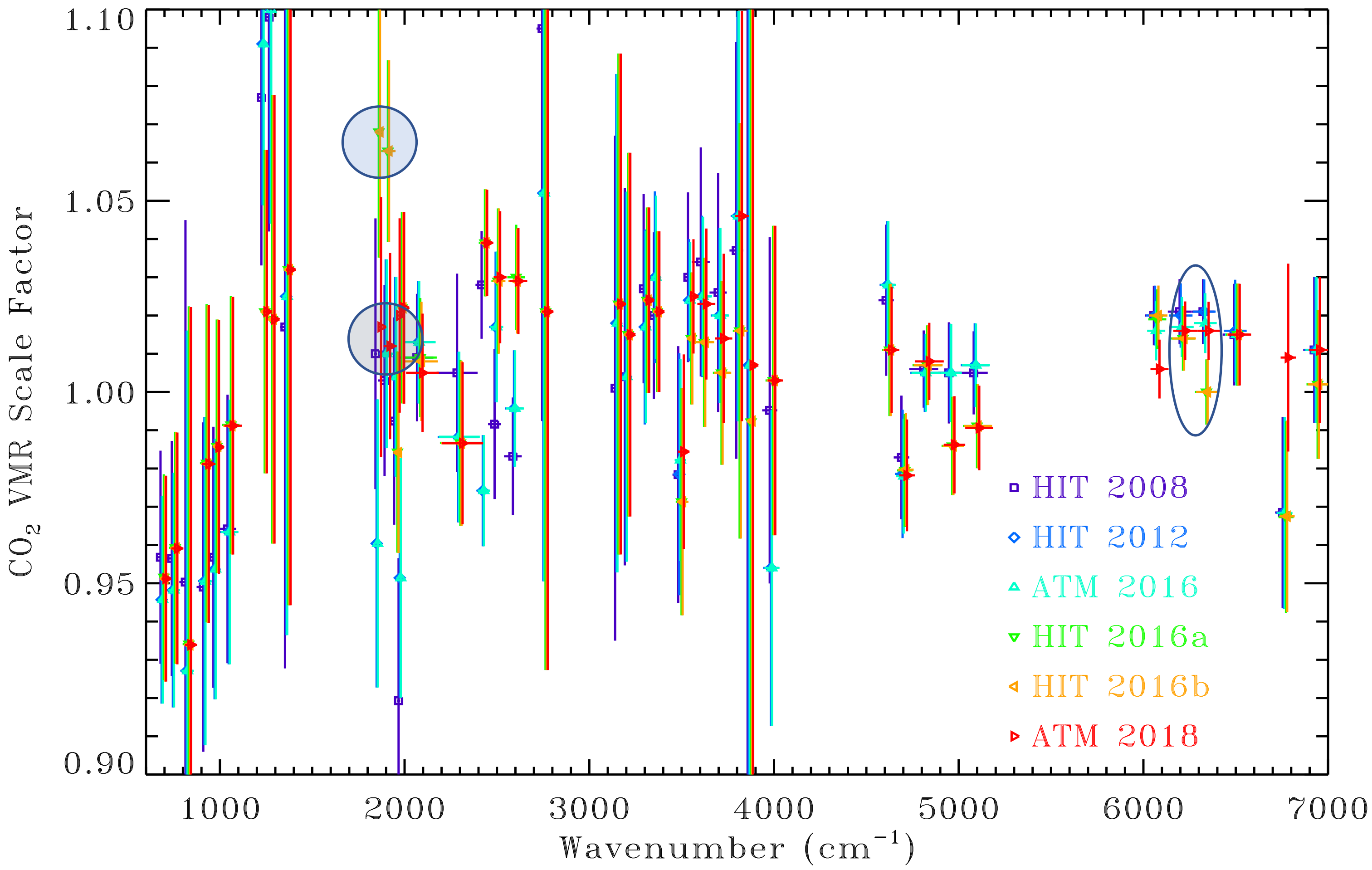
CO_2 VMR Scale Factors retrieved from lab spectra

Comparison of VSF values for all 6 linelists using the data tabulated in the previous slide, together with their untabulated uncertainties. Red points (ATM 2018) are identical to those shown in top panel of slide # 9.

VSF values greater than 1 mean that the line intensities, or the absorber amounts, need to be multiplied by the VSF value.

Width and line position errors can also contribute to an incorrect retrieved CO_2 amount, but in this case the relationship between the VSF value and the width/position error is more complicated.

A discrepancy is apparent between retrievals in the 6220 and 6338 cm^{-1} bands using HIT16



Chris Boone reported 5-10% larger retrieved ACE CO_2 amounts from 1915 cm^{-1} band than from 2050 cm^{-1} band using HIT16 with ACE data. Kitt Peak lab spectra confirm this (upper circle). This bias didn't exist with earlier linelist editions. It was fixed in ATM18 (lower circle). A 4% reduction to ATM18 CO_2 intensities in the 6740 cm^{-1} band is also apparent.

RMS Residuals from fits to lab spectra - Discussion

HITRAN 2008 is clearly the worst overall. But above 6400 cm^{-1}, it is the best.
Of the pre-2018 linelists, HIT16b is the best overall.
ATM18 is of course the best overall, being cherry-picked from the best parts of the earlier linelists.

Comparing HITRAN 2012 with ATM 2016: They produce similar results

- In 14 windows ATM 2016 is better
- In 27 windows they produce equally good fits
- In 0 windows HITRAN 2012 is better

It is no surprise that HITRAN 2012 is nowhere better than ATM 2016. If it had been, I would have replaced the offending lines in ATM 2016 with those from HITRAN 2016. Additionally, empirical adjustments have been performed to the ATM linelist to fix obvious deficiencies (e.g., position errors).

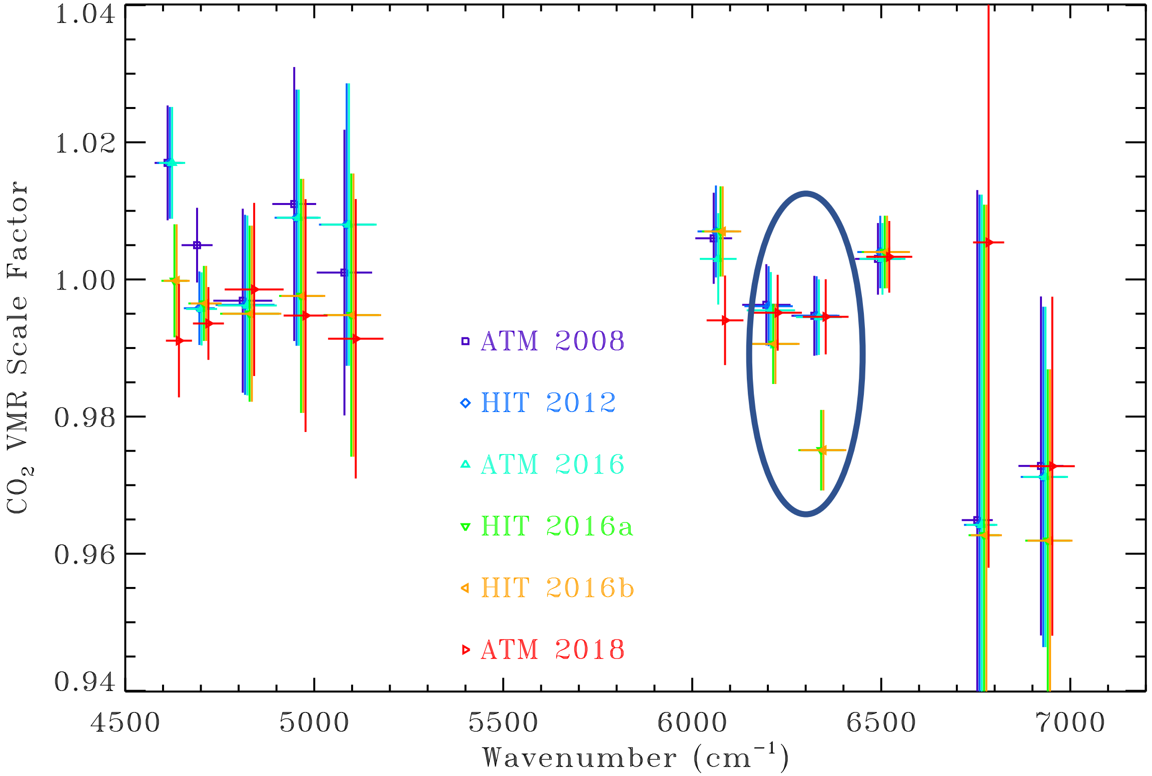
Comparing HITRAN 16a and 16b: They produce very similar results. Small differences in fits to pure CO_2 spectra due to truncation of SBHW to "f5.3" format. Improvements seen in strong bands at 2300 cm^{-1} and ~3600 cm^{-1} in ^{13}C-enriched lab spectra due to addition of isotopologs 11 and 12 to HIT16b

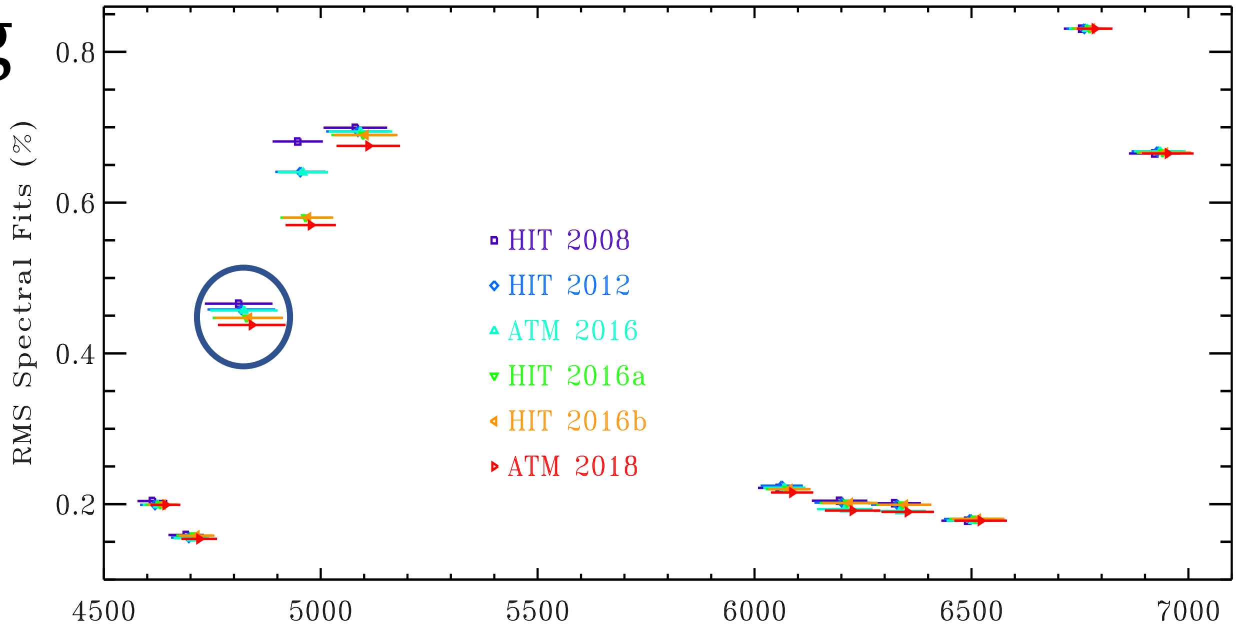
- In 10 windows HIT16a is slightly better
- In 24 windows they produce the same rms fit
- In 7 windows HIT16b is slightly better

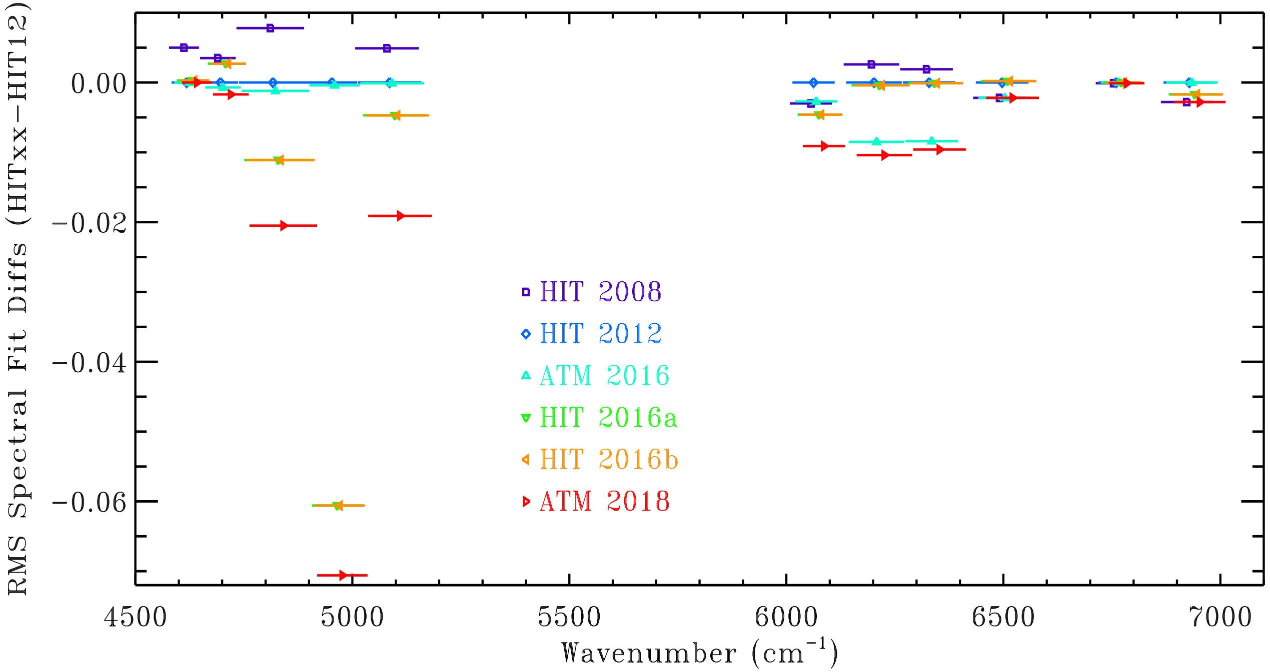
Since only 2/148 lab spectra used here was below 290K, these results don't really validate the T-dependent parameters.
In the 4825 cm^{-1} window the HIT16 linelists produces significantly poorer residuals than any predecessor.

TCCON Ground-Based RMS fitting residuals (right) & VSFs (below)

TCCON CO_2 windows circled below. The HIT16 linelists reduce the CO_2 retrieved from the 6221 and 6338 cm^{-1} windows by 0.5% and 1.5% respectively, as compared with the other linelists, introducing a new 1.5% inconsistency.







Retrieved CO_2 VSFs: All 4 datasets

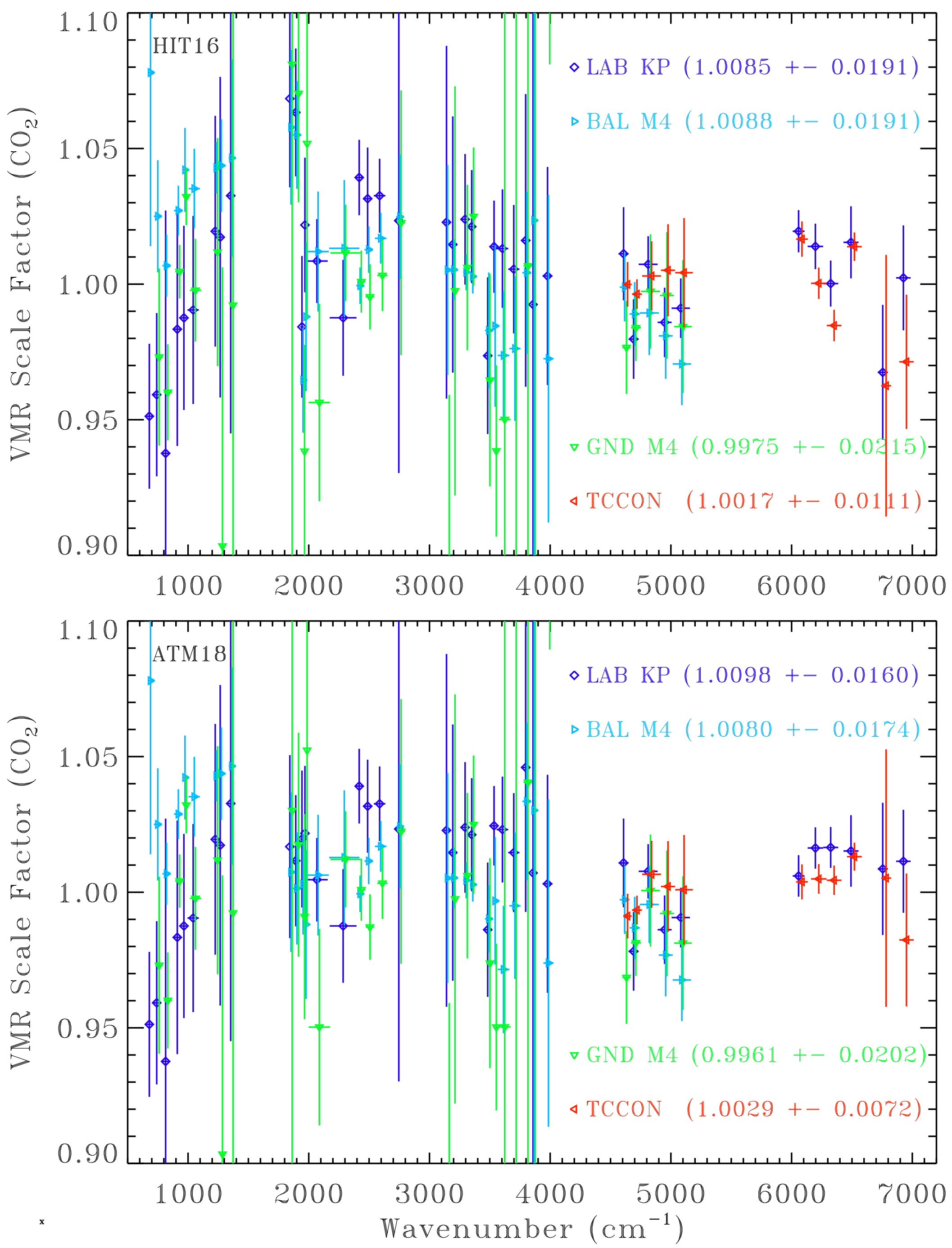
Plot show CO_2 VSFs for the HIT16b linelist (top panel) and the ATM18 linelist (bottom panel). The data are color-coded by the measurement data type (not the linelist). The ATM18 has better window-to-window consistency for all four measurement types, due mainly to the explicit adjustments made in the 1800-1993 cm^{-1} and 6720-6800 cm^{-1} regions.

In general, the error bars overlap between the four different datasets, in terms of the bias in the retrieved CO_2 amounts.

Lab data cover the entire wavenumber range. The GND_M4 and BAL_M4 datasets cover 700-5500 cm^{-1}. The TCCON covers 4000+ cm^{-1}. Only over 4000-5600 cm^{-1} do all four datasets overlap.

GND_M4 VSFs are generally lower than those from the other datasets. Below 1200 cm^{-1} the lab data and GND M4 show VSFs below 1.0, but BAL M4 shows values above 1.0 and with smaller errors.

GND M4 ground also have the worst window-to window consistency (2.02%). TCCON has the best (0.72%) but only covers well-behaved, unsaturated windows.



Summary & Conclusions

Four spectral datasets (Kitt Peak lab, MkIV balloon, MKIV ground, and TCCON ground) have been used to evaluate six different CO_2 linelists (HIT08/12/16a,b and ATM 16/18) over 670 to 7000 cm^{-1}.

Spectral fitting was performed with the GFIT code using a Voigt lineshape. The linelists were evaluated in terms of: the rms fitting residuals; and the window-to-window consistency of the retrieved gas amounts. There was no analysis of separate isotopologs. They were all lumped together as CO_2 which makes it important to know the fractionation. Analyzing the twelve CO_2 isotopologs separately is beyond the scope of this work.

RMS Spectral Fitting Residuals

Results show progressive overall RMS fit improvements in each HITRAN version, but there have been some regions where the HITRAN 2016 fits have regressed. For example, in the 4825 cm^{-1} window used by OCO-2 and GOSAT, HIT16 produces the worst fits to lab and MkIV balloon spectra (low-P) suggesting the positions and/or relative intensities in HIT16 are worse than predecessors, but that the widths/shifts are better.

Window-to-Window Consistency of Retrieved CO_2 Amounts

Retrieved CO_2 in the 1900 cm^{-1} region with HITRAN 2016 is biased 5% larger than in the 2050 cm^{-1} region, as pointed out by Chris Boone from ACE data. In previous HITRAN version the 1900 cm^{-1} window produced no significant bias. This problem was fixed for ATM18.

In the 6200-6400 cm^{-1} region used by TCCON the consistency of the retrievals between the 6220 and 6338 cm^{-1} bands has degraded from better than 0.1% to 1.5%. This is a serious problem because TCCON performs an weighted average of the CO_2 retrieved from these two windows. With the existence of a bias, anything that affects the uncertainties of one window relative to the other will perturb the weighted average.

ATM18 CO_2 Linelist

A new linelist (ATM18) was generated, based primarily on HITRAN 2016b, except for:

- Replacing the 3419 - 3923 cm^{-1} and 5750 - 6598 cm^{-1} sections with ATM16.
- Replacing the 6715 - 7000 cm^{-1} section with HIT08
- For isotopologs 10,11,12, using HIT16b throughout.
- Scaling all CO_2 line intensities in the 1800 to 1993 cm^{-1} interval by 1.05
- Scaling all $^{12}CO_2$ line intensities in the 6720 to 6800 cm^{-1} interval by 0.96
- Scaling all $^{12}CO_2$ line widths by 0.99 over 960 to 1000 cm^{-1}

On top of this, ad hoc corrections (mainly position adjustments) were applied, where beneficial.

There are very few windows where the ATM18 linelist doesn't produce the best (or equal best) RMS fits. In all four datasets, the ATM18 linelist produces the best average rms fits. In 2/4 datasets the ATM18 linelist produces the best window-to-window consistency in retrieved CO_2 amount, the exceptions being that the **HIT08** linelist produces the best consistency for the MkIV balloon and TCCON ground datasets.

The main weakness of this evaluation is that there were very few low-temperature lab measurements. So the selection of predecessors lines for inclusion into ATM18 might be different with more low-T lab spectra. In future, obtain additional low-T lab spectra (air-broadened) to test T-dependence of ABHW.

I recommend the ATM18 linelist for use by the NDACC and TCCON FTIR networks.

Acknowledgements

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