Spectroscopy Evaluation

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It is usually impossible to fit IR solar spectra (high SNR) down to their noise level. Residuals are usually dominated by systematic errors arising from defects in:

- atmospheric T/P/VMR profiles
- instrumental response (e.g. ILS, zero-level-offsets, channel fringes, ghosts)
- spectroscopy

For spectra measured with a well-calibrated FTS under well-known atmospheric conditions, the first two systematic errors can usually be minimized, revealing the underlying spectroscopic problems.

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HITRAN 2012 Linelist Evaluation

Used MkIV balloon spectra to evaluate HITRAN 2012 (released June 2013)

- 10-40 km altitude range analyzed
- Defined 100+ windows covering 700 to 5600 cm^{-1}

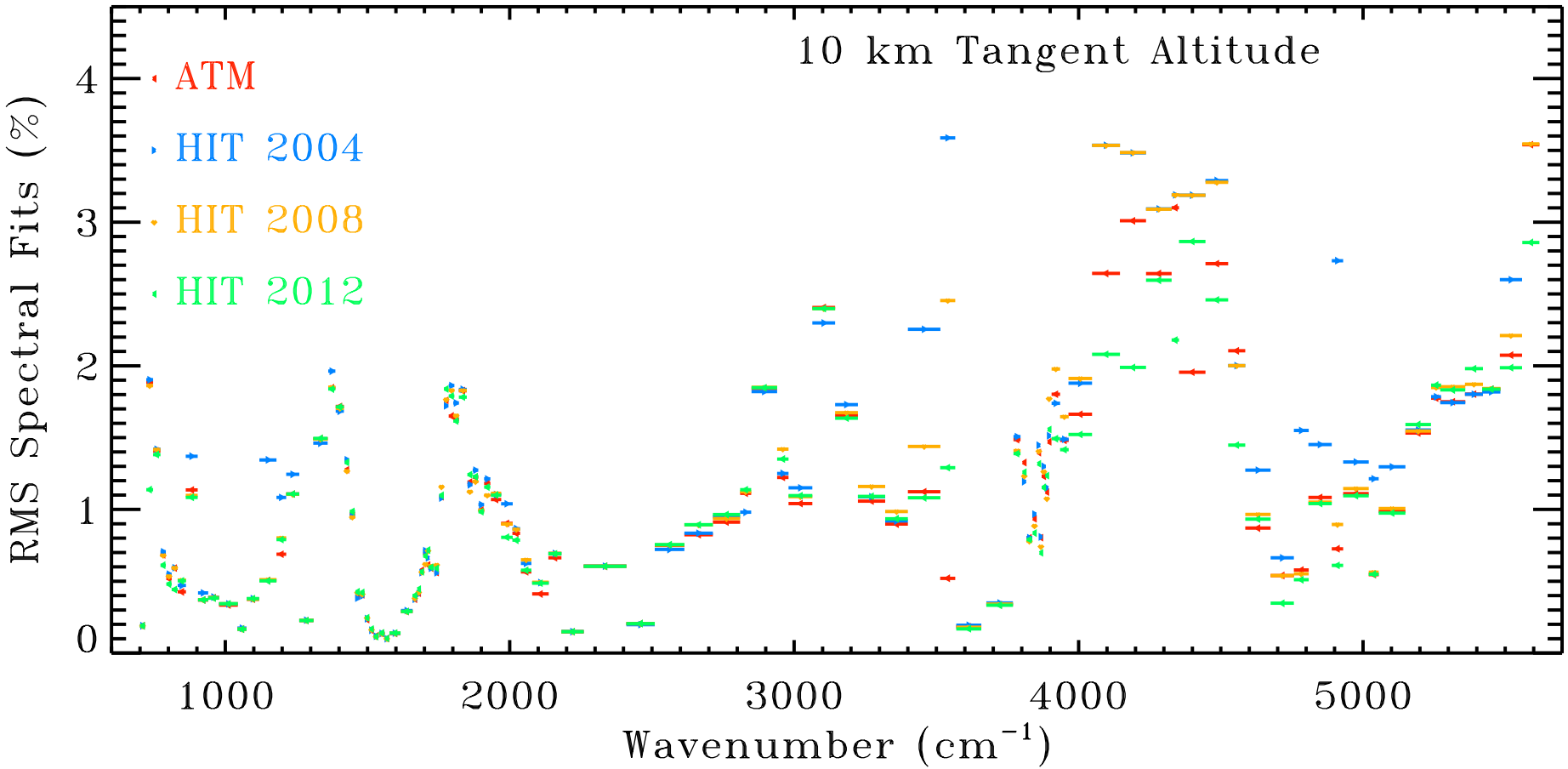
Compared quality of spectra fits with HITRAN 2008, 2004 and ATM13 linelists.

ATM linelist is "greatest hits" compilation that I maintain based originally on ATMOS linelist (Brown, 1996) and used for MkIV, ATMOS and TCCON

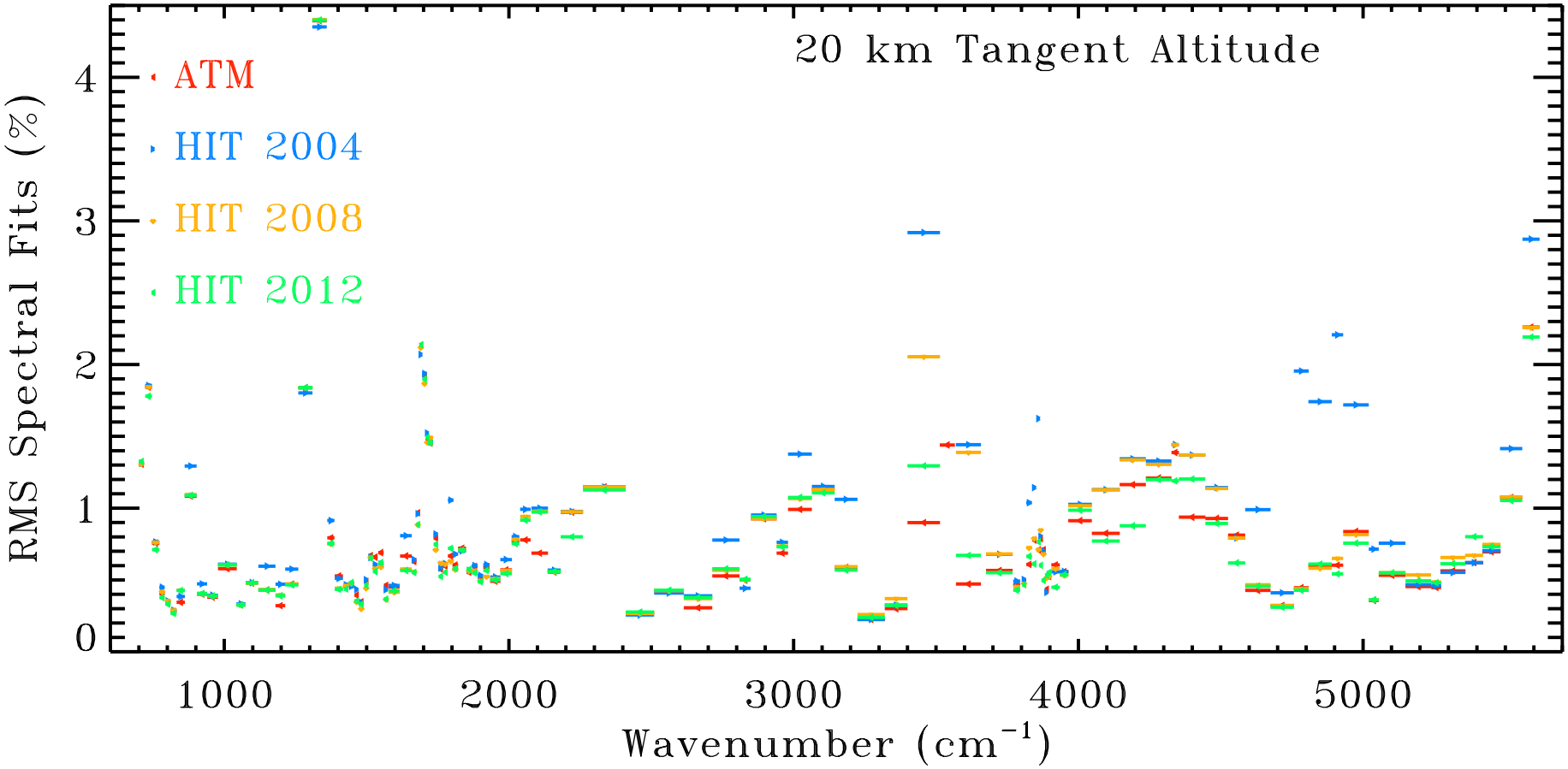
- Updated with new data (.e.g. HITRAN) for specific gases/bands if they represent a significant improvement to atmospheric spectral fits
- Manual adjustments to fix specific problems (guided by lab data)

Why use MkIV balloon spectra and not ACE? 2x higher spectral resolution makes it easier to determine the underlying causes of large fitting residuals.

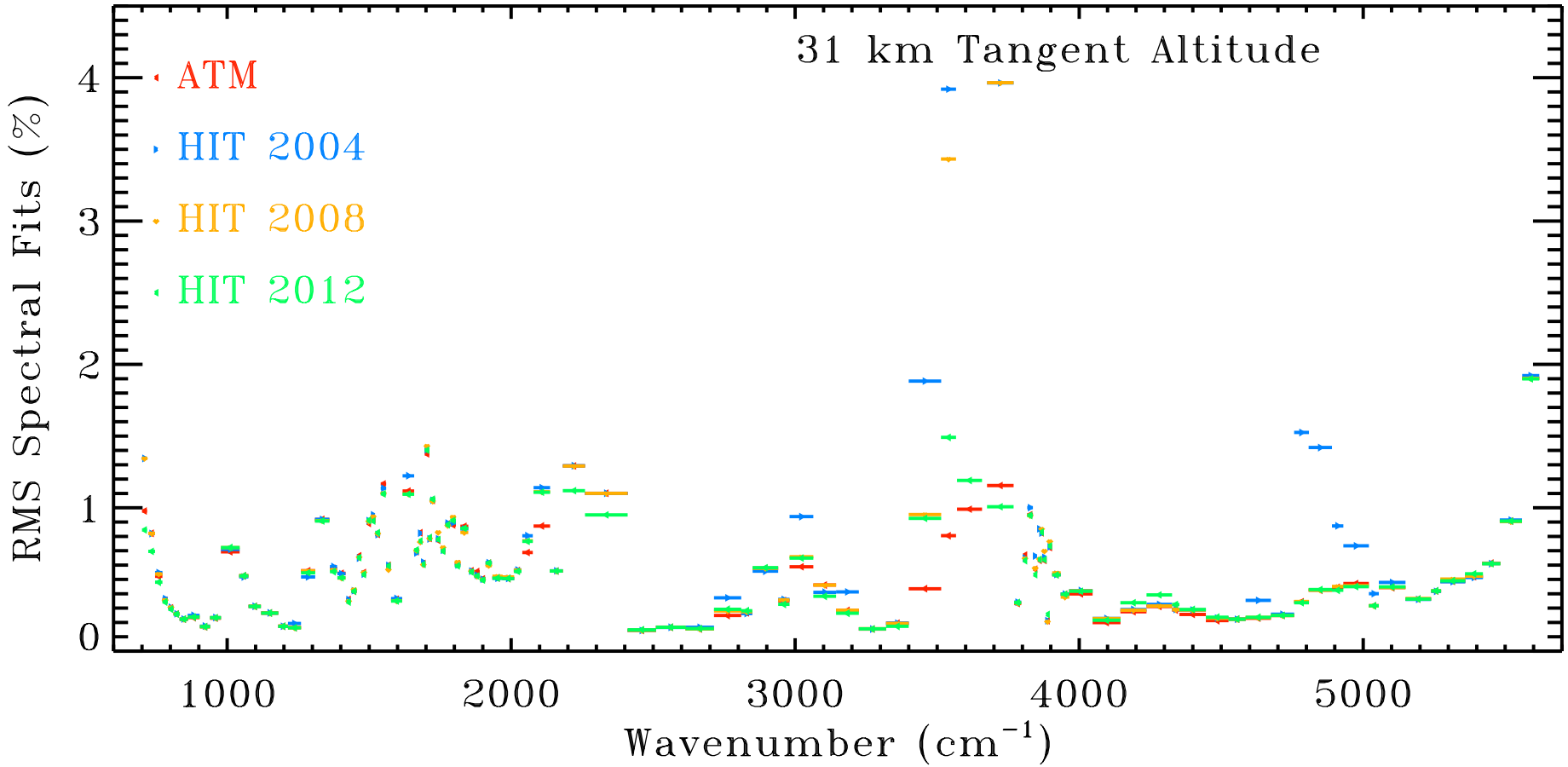
RMS Fitting Residuals at 10 km altitude



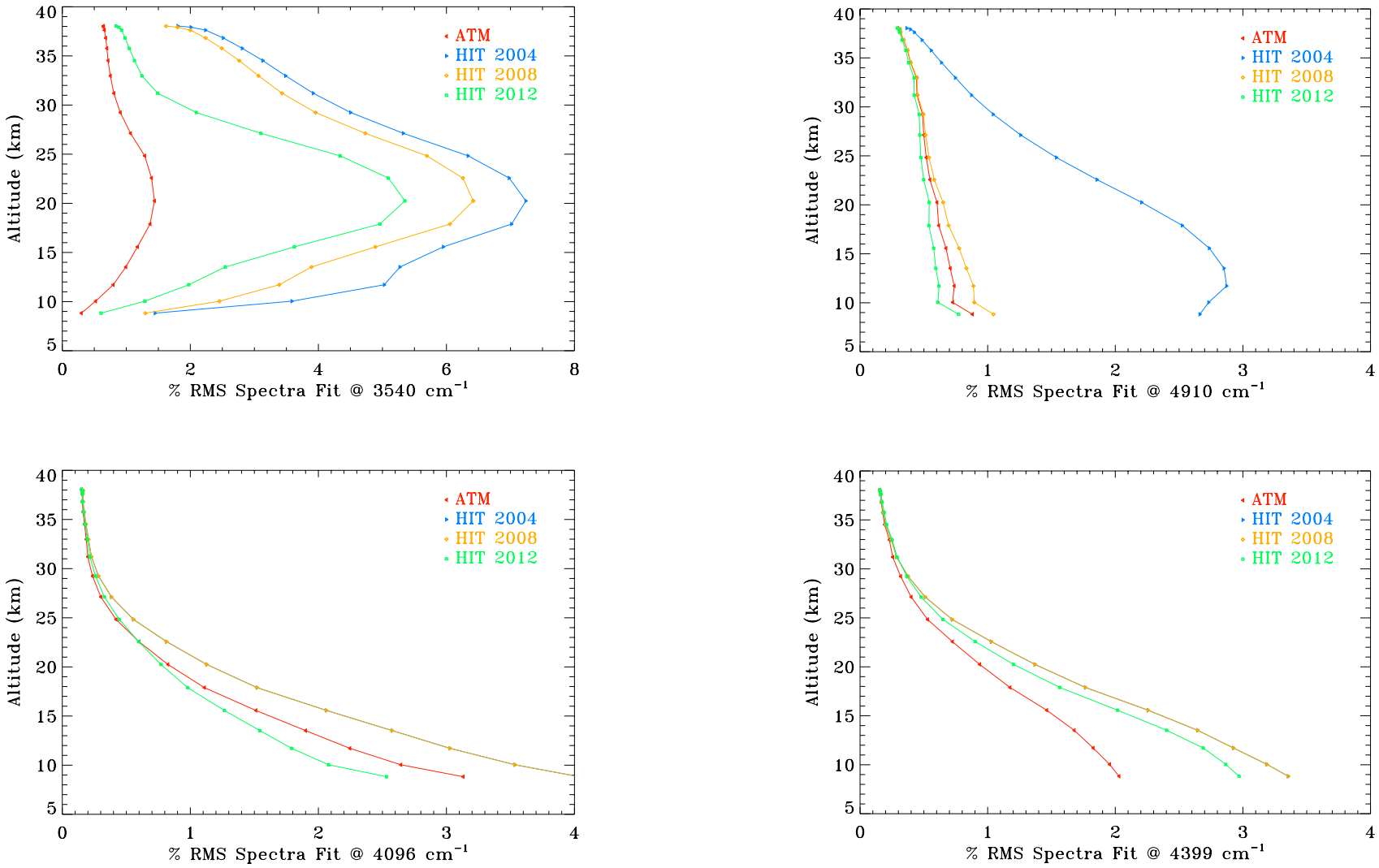
RMS Residuals at 20 km altitude



RMS Residuals at 31 km altitude

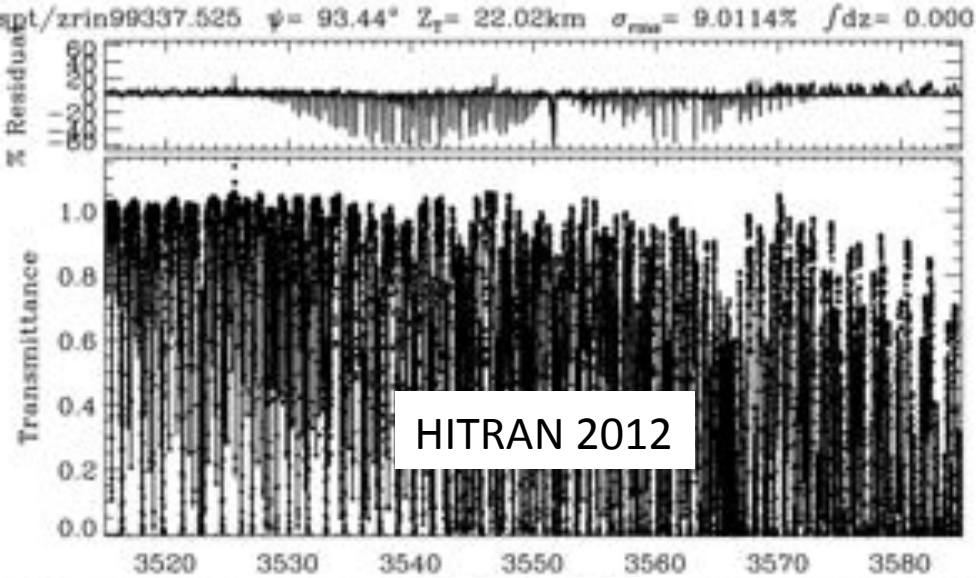


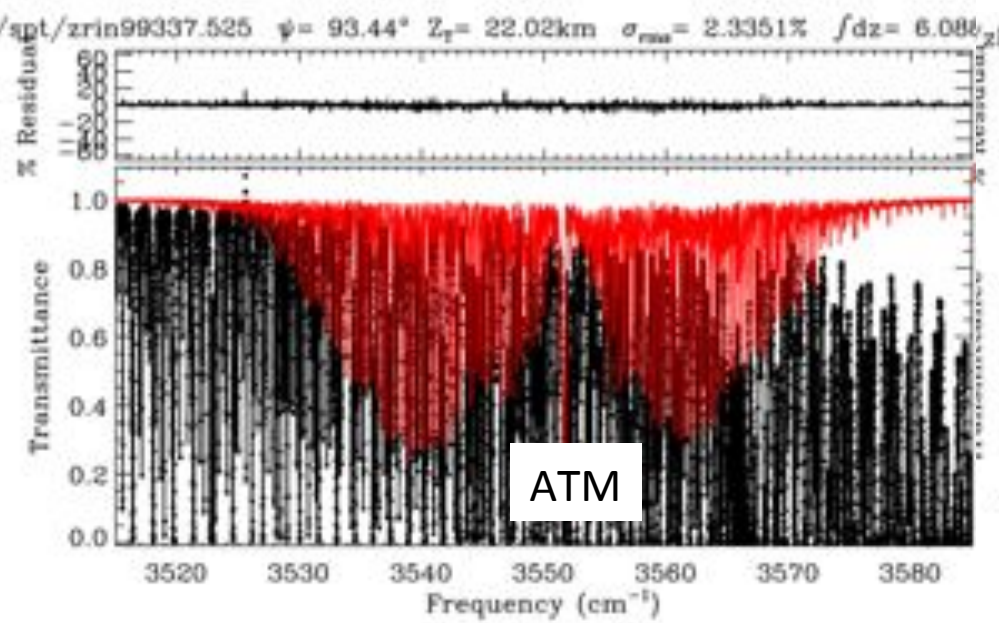
Vertical Behavior of RMS Residuals

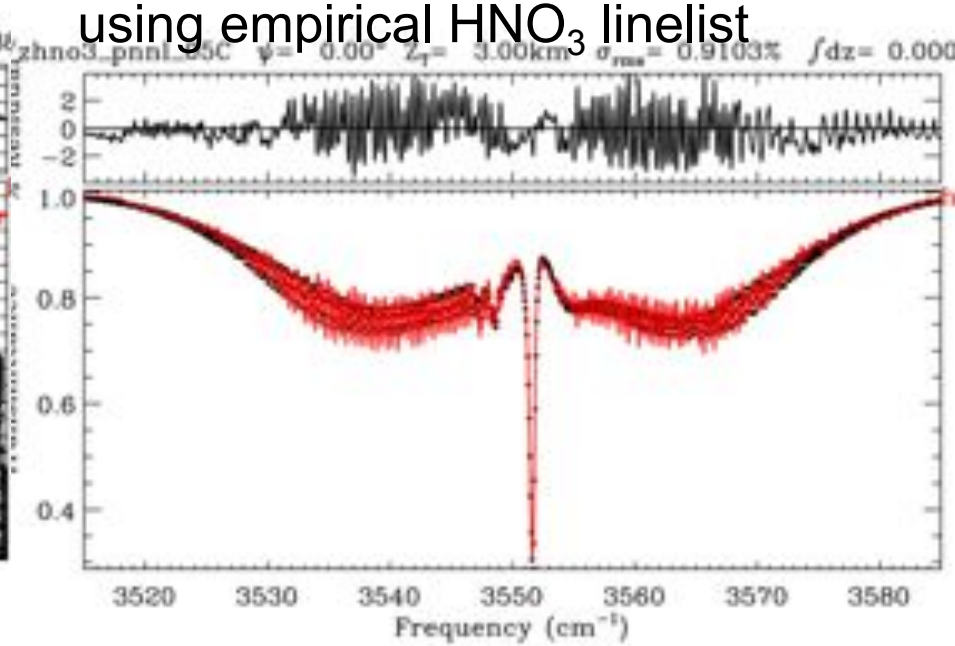


Vertical behavior of RMS residual mirrors vertical profile of gas primarily responsible

Missing 3551 cm^{-1} ν_1 HNO_3 band





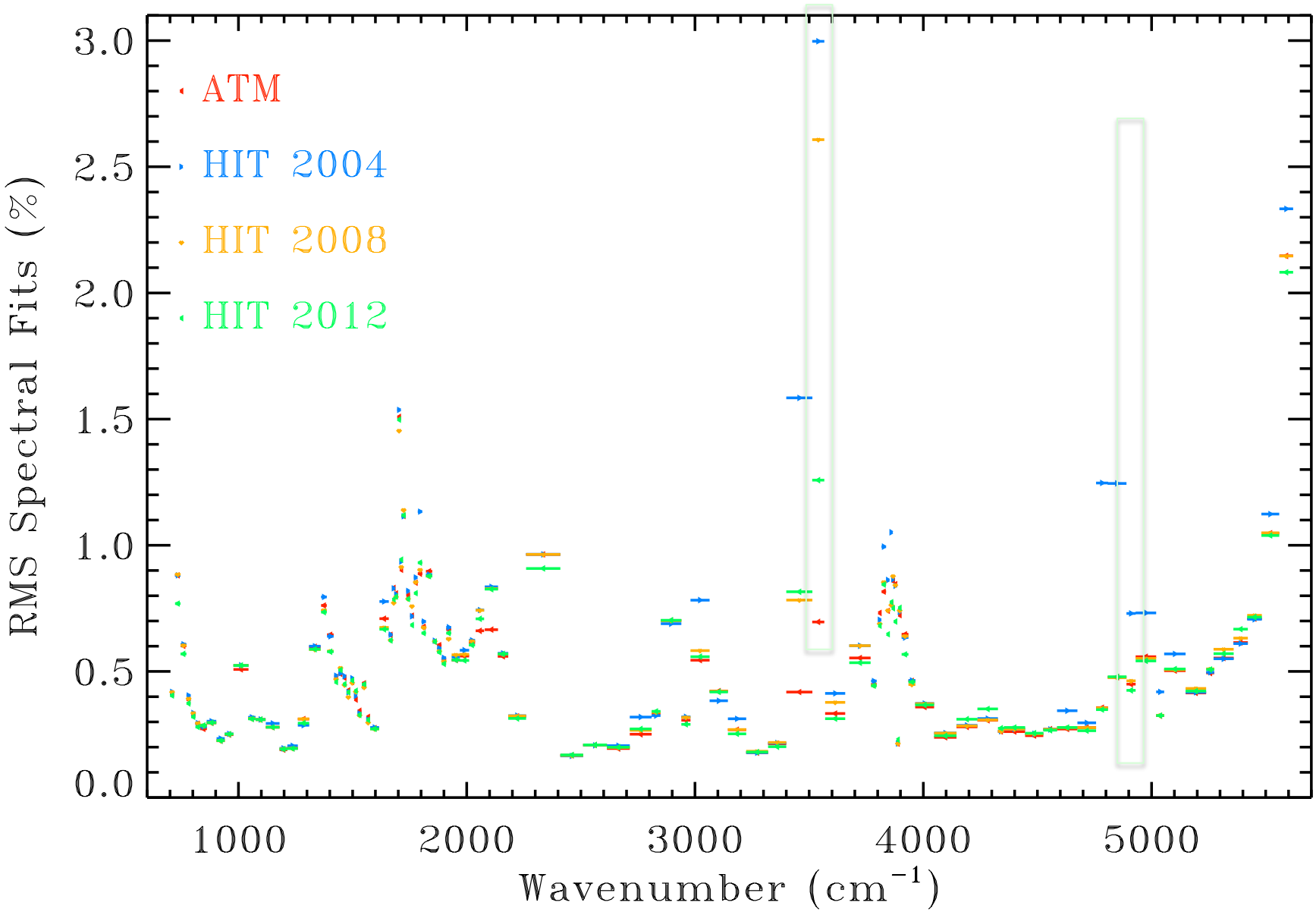


Upper Left: Fit to MkIV balloon spectrum using HITRAN 2012

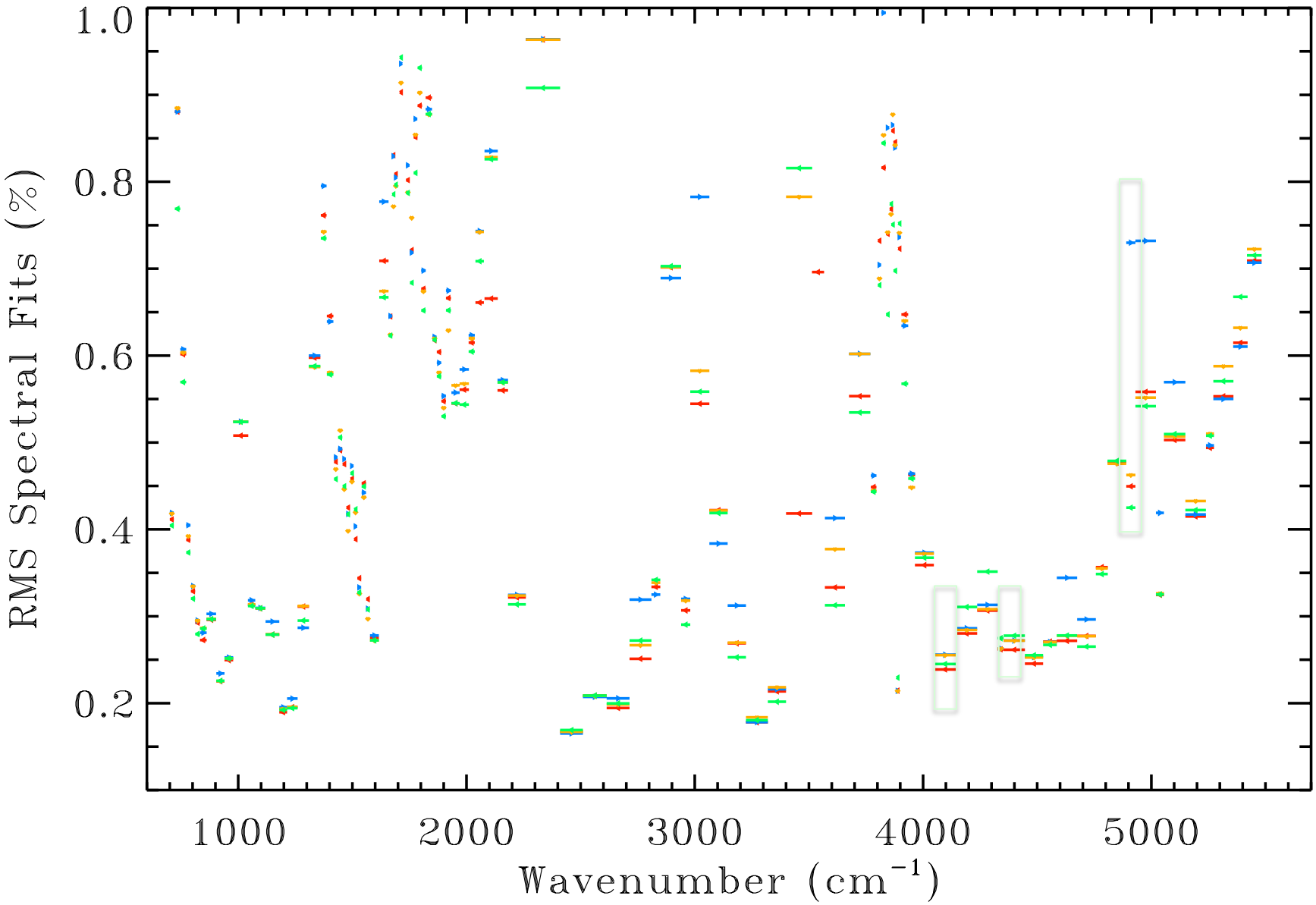
Lower Left: MkIV spectrum fitted using HITRAN 2012 + empirical HNO_3 linelist

Lower Right: PNNL spectral fit using empirical HNO_3 linelist

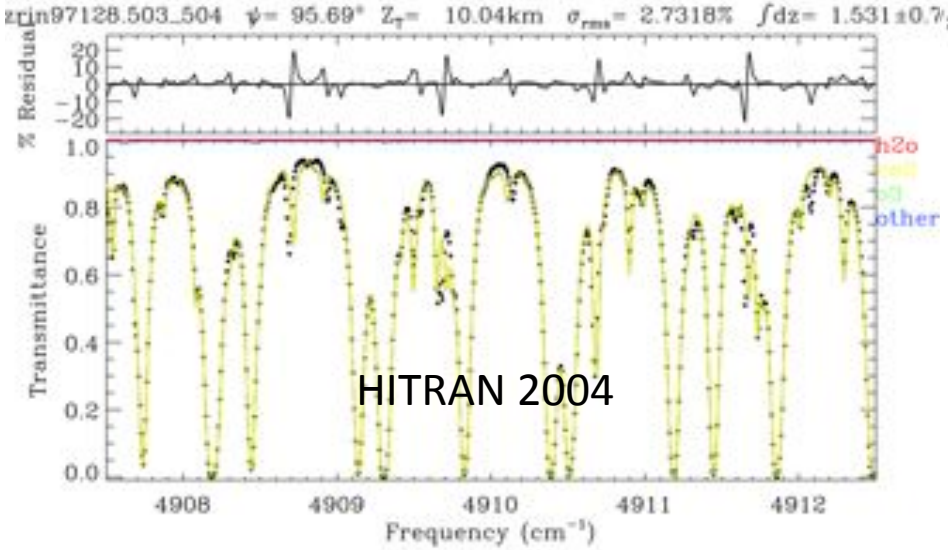
Vertically-averaged RMS fits

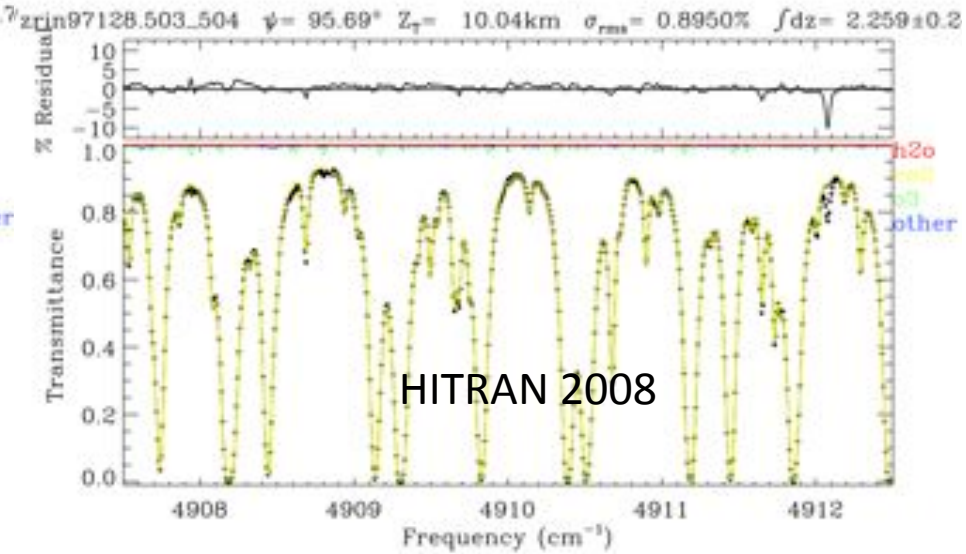


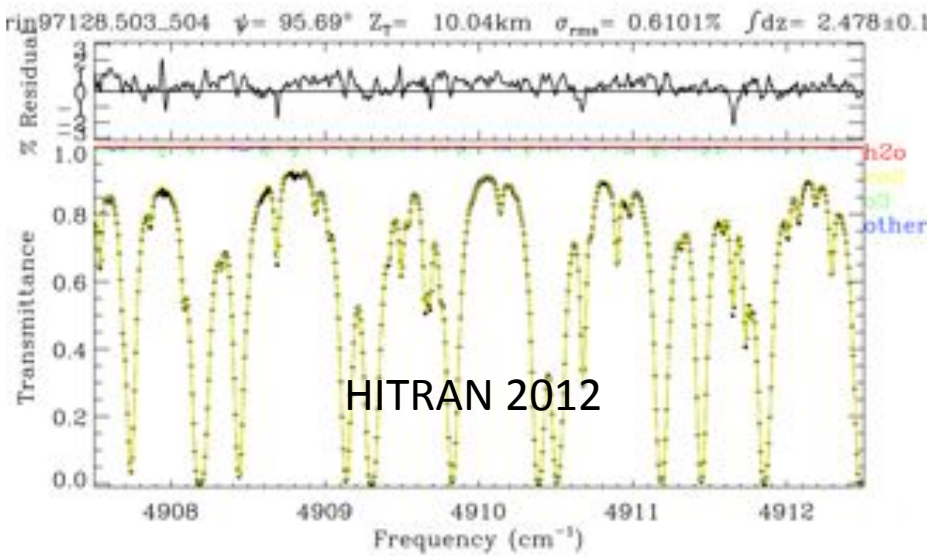
Vertically-averaged RMS fits (zoomed)

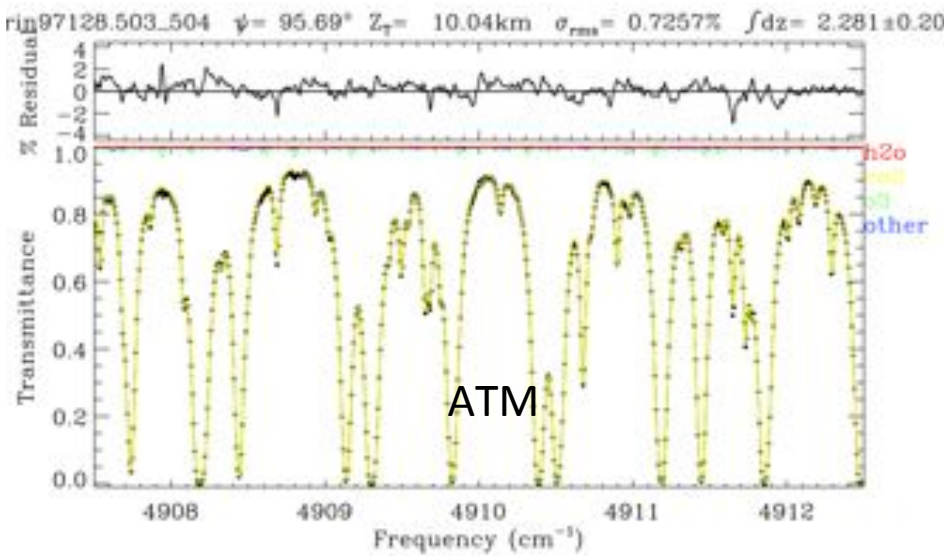


Improved CO_2 at 4910 cm^{-1}

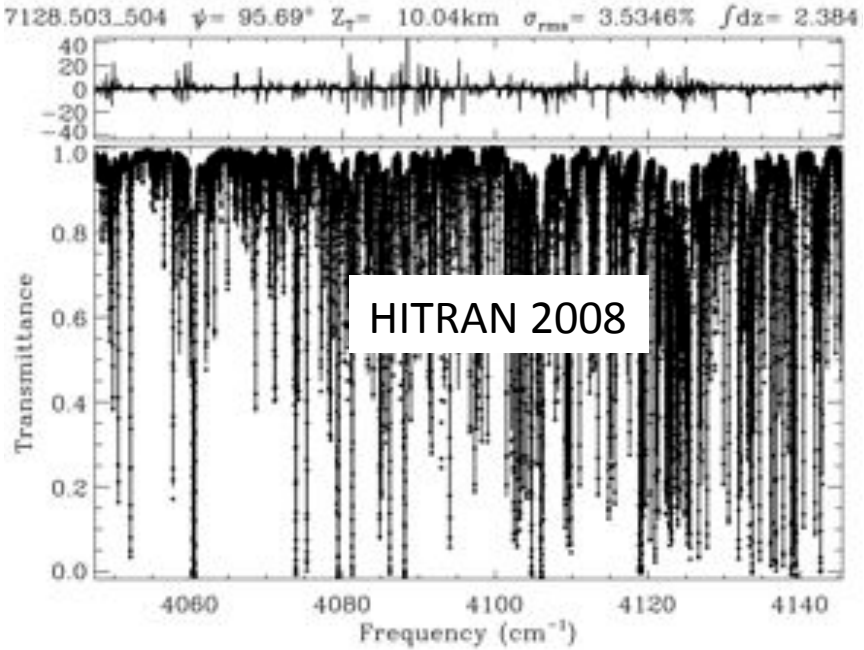








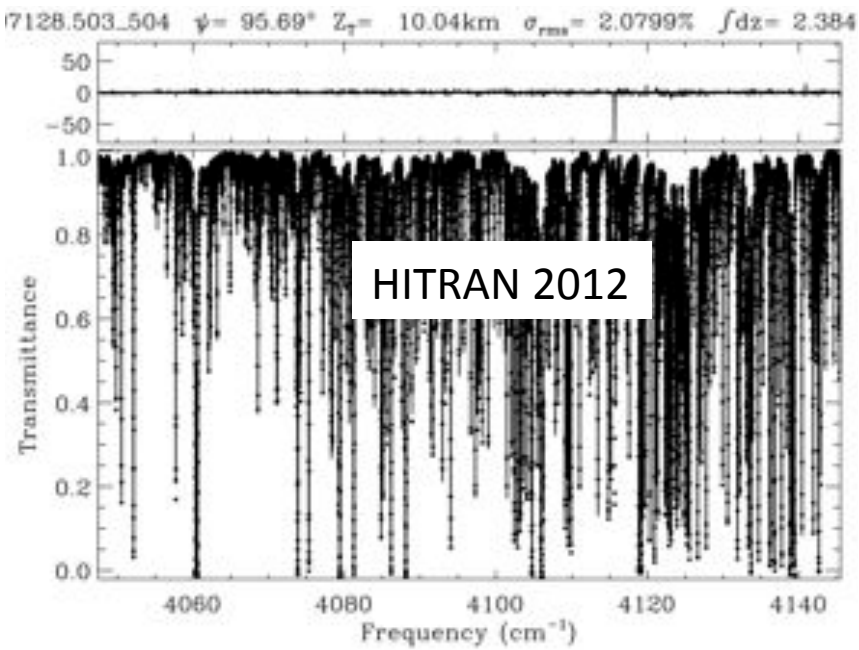
CH_4 Problem

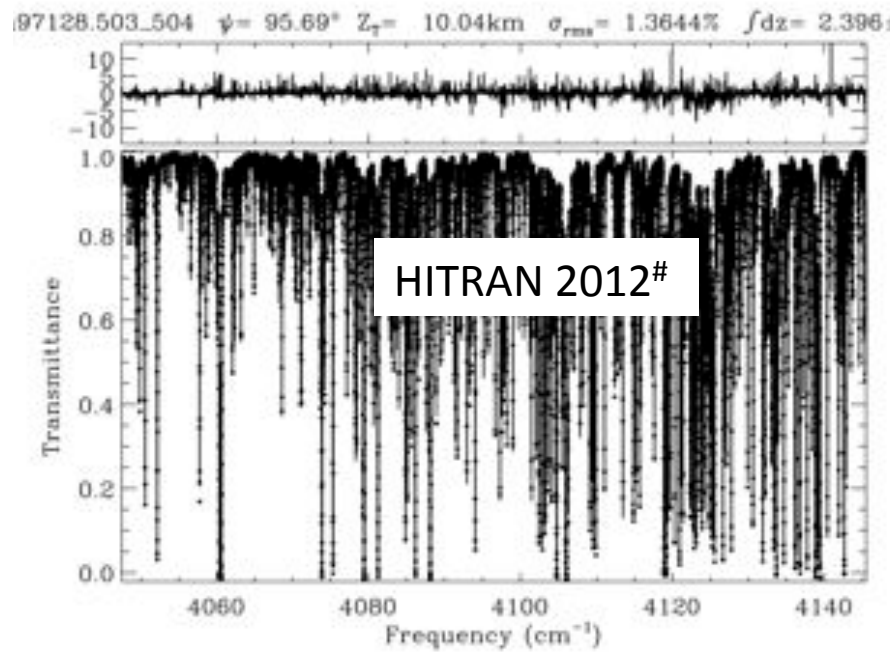


Improvement in HITRAN 2012 CH_4

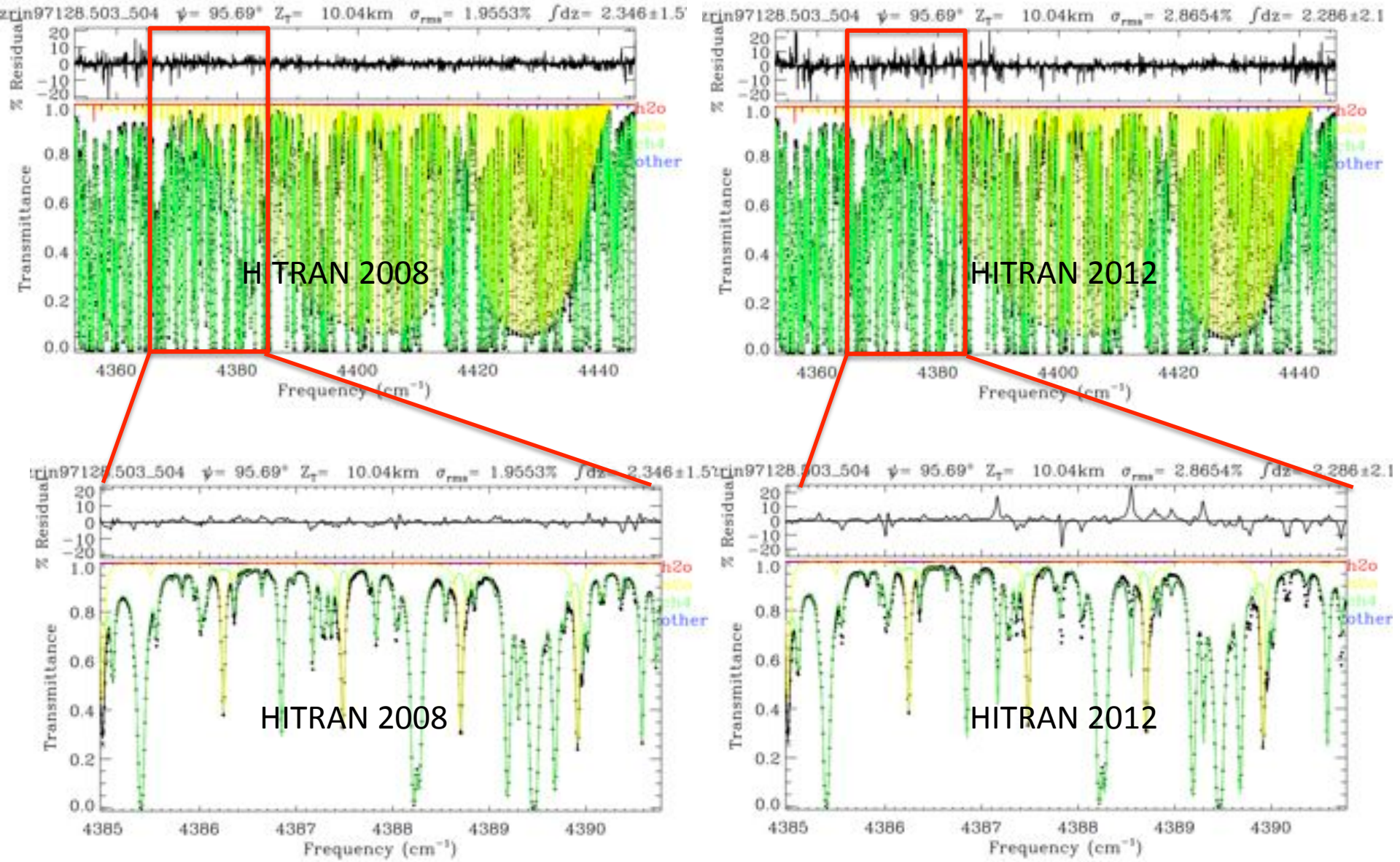
But would be much better if CH_4 line at 4115.6594 cm^{-1} hadn't disappeared

Manually fix this problem by copying missing line from HIT2008 to HIT2012

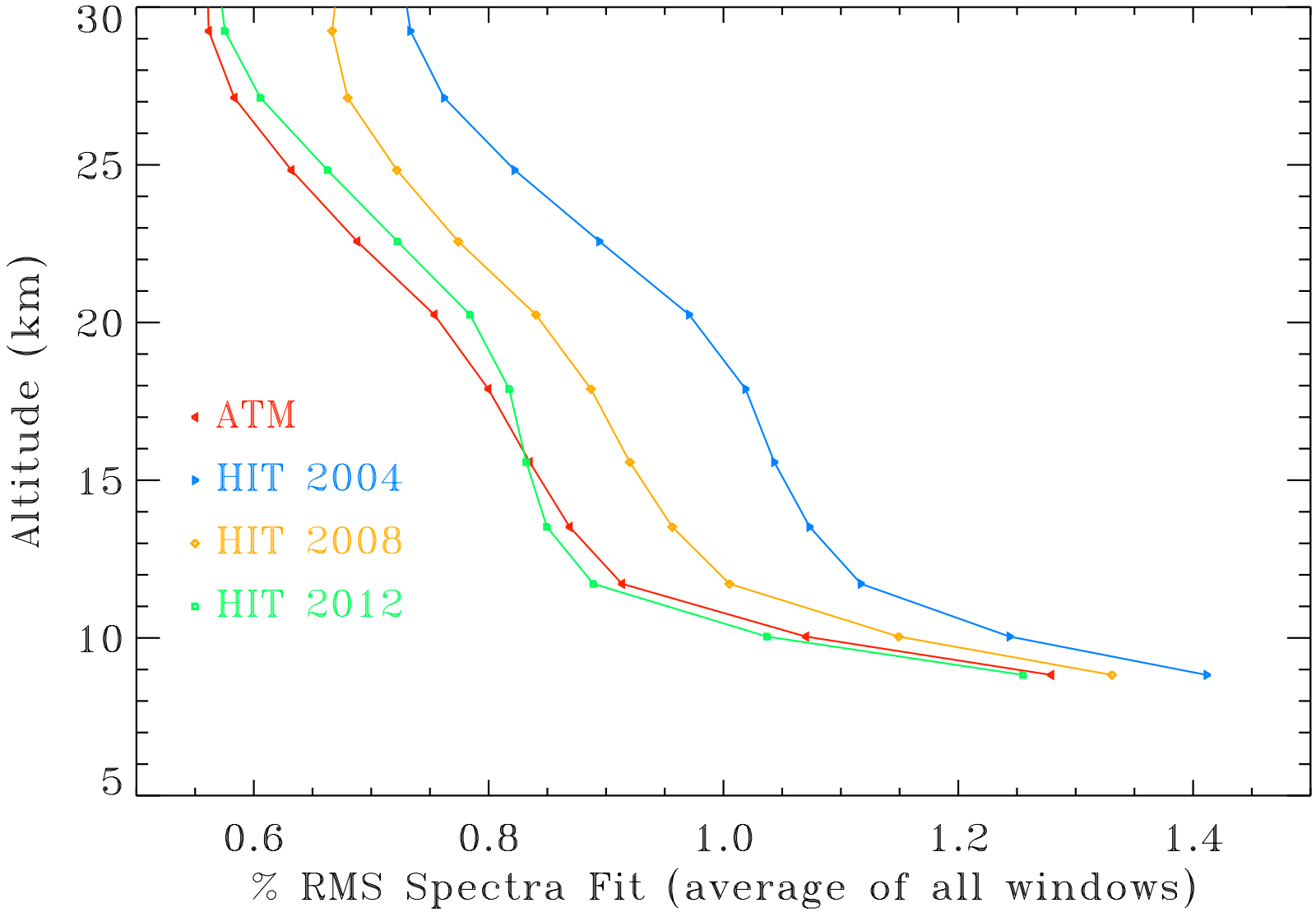




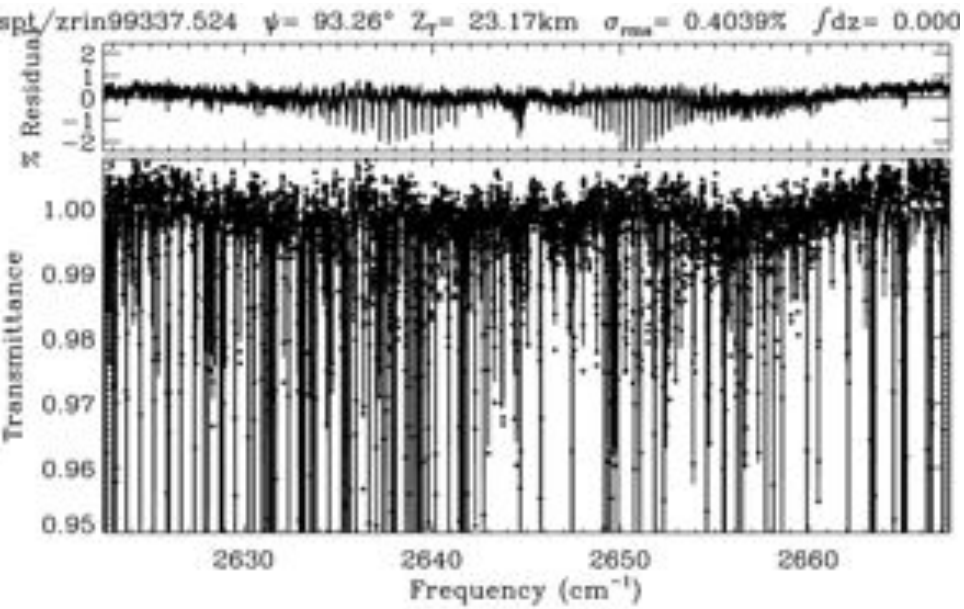
Another CH_4 problem



Spectrally-averaged RMS



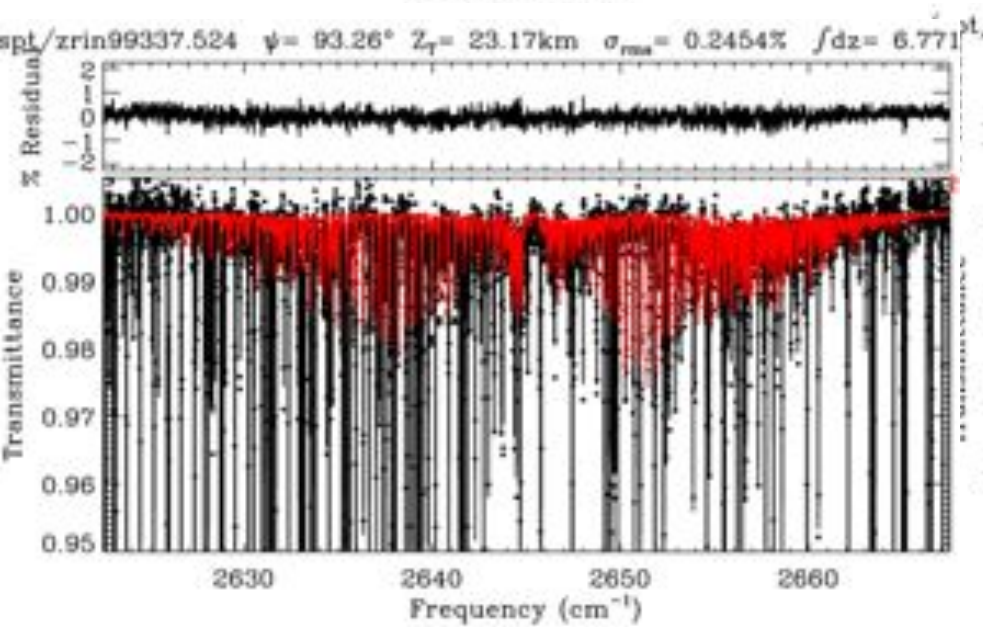
HNO_3 2645 cm^{-1} $2nu_3$ band

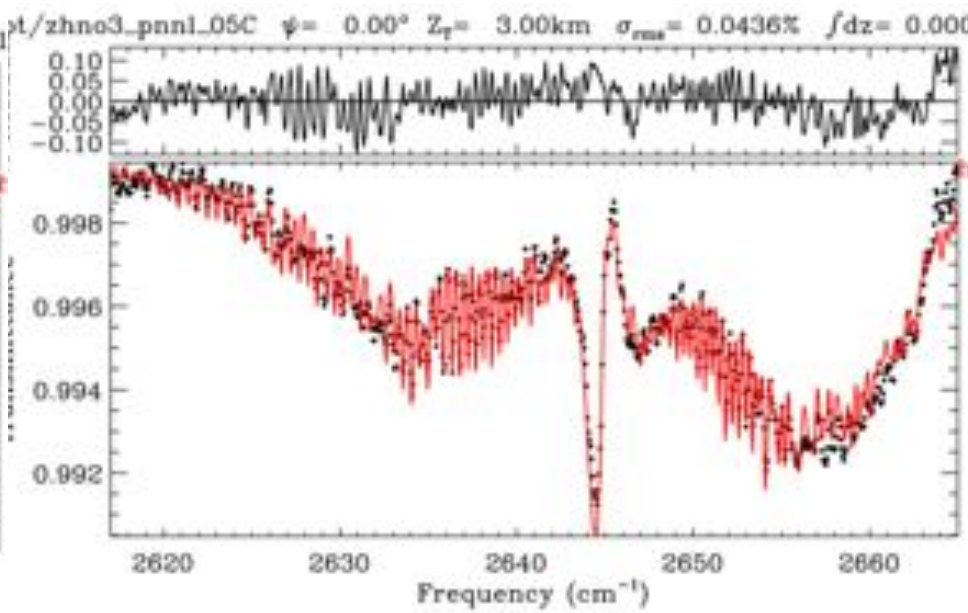


Upper Left: Fit to MkIV balloon spectrum using HITRAN 2012

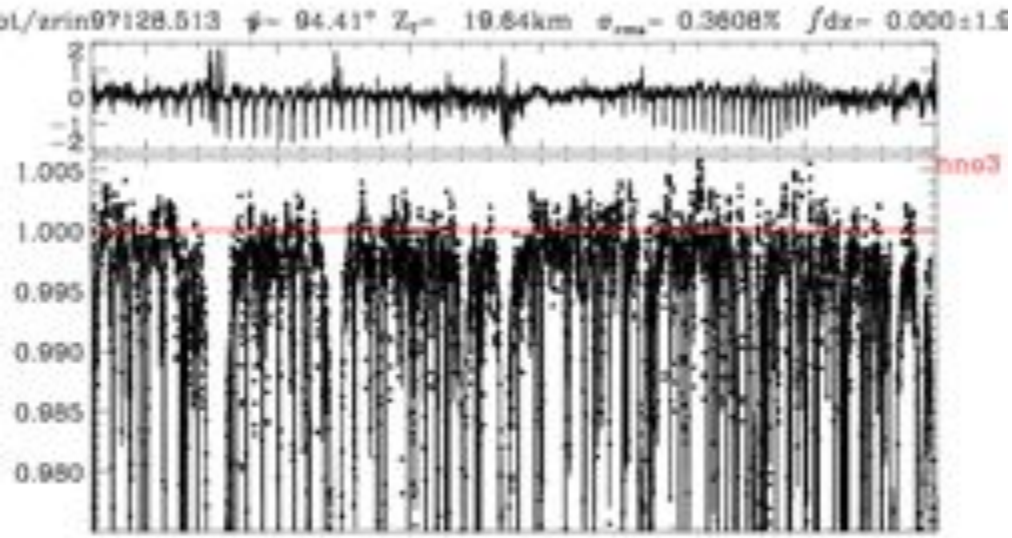
Lower Left: Fit using HITRAN 2012 + empirical HNO_3 linelist

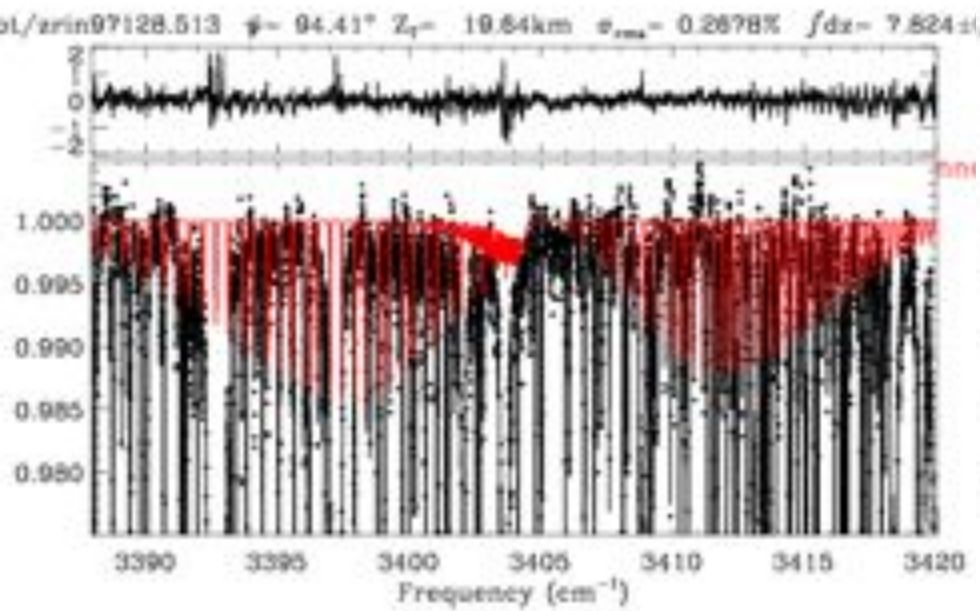
Lower Right: Fit to PNNL spectrum using kludged HNO_3 linelist

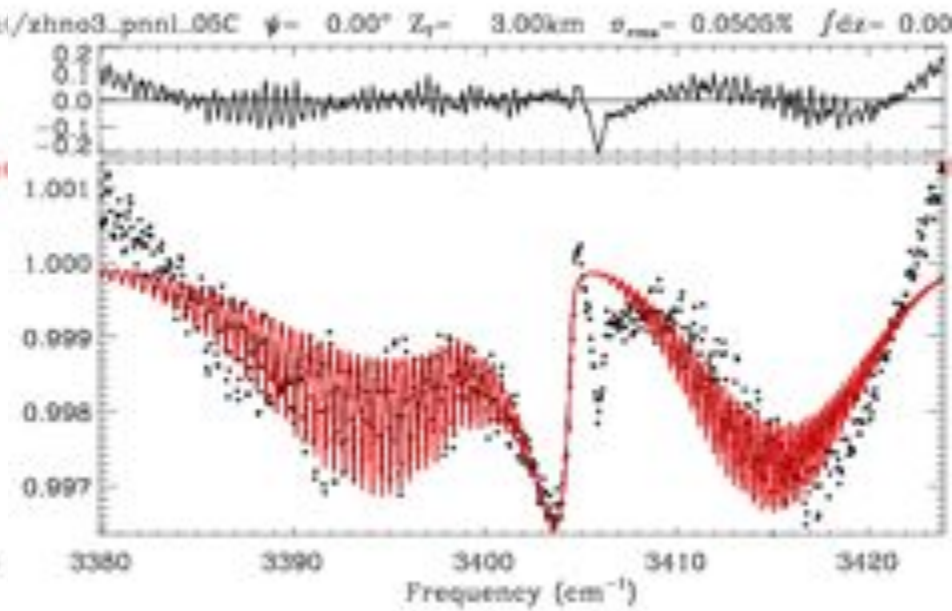




HNO_3 3404 cm^{-1} $2nu_2$ band





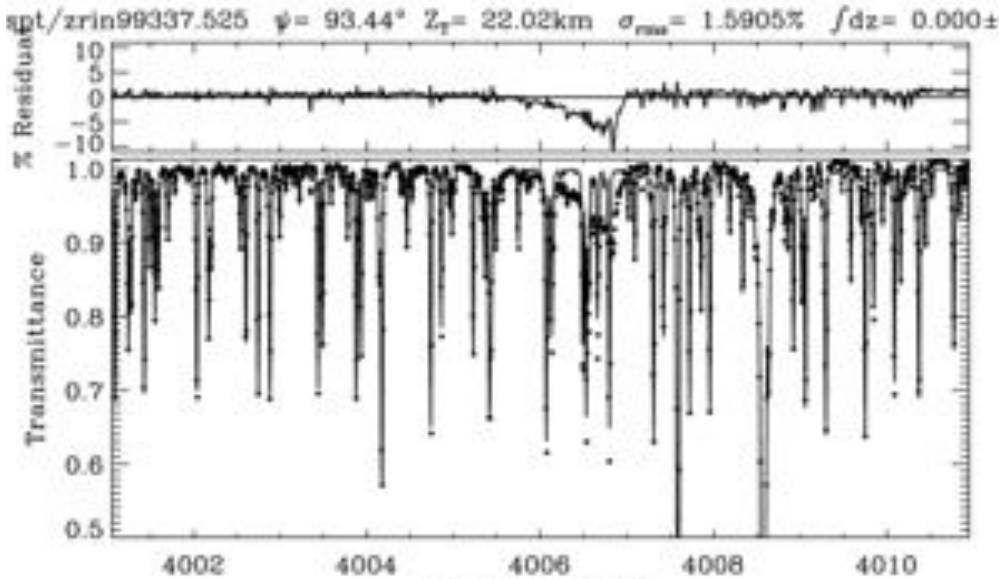


Upper Left: Fit to MkIV balloon spectrum using HITRAN HNO_3

Lower Left: Fit using HITRAN 2012 + empirical HNO_3 linelist

Lower Right: Fit to PNNL spectrum using kludged HNO_3 linelist

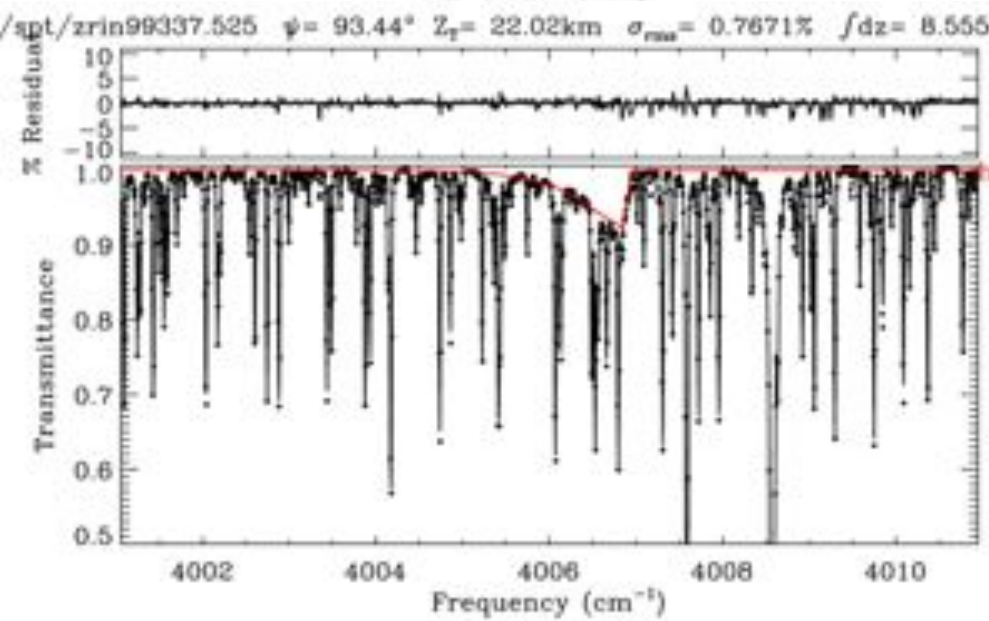
HNO_3 4006 cm^{-1} $\nu_1+\nu_9$ band Q-branch

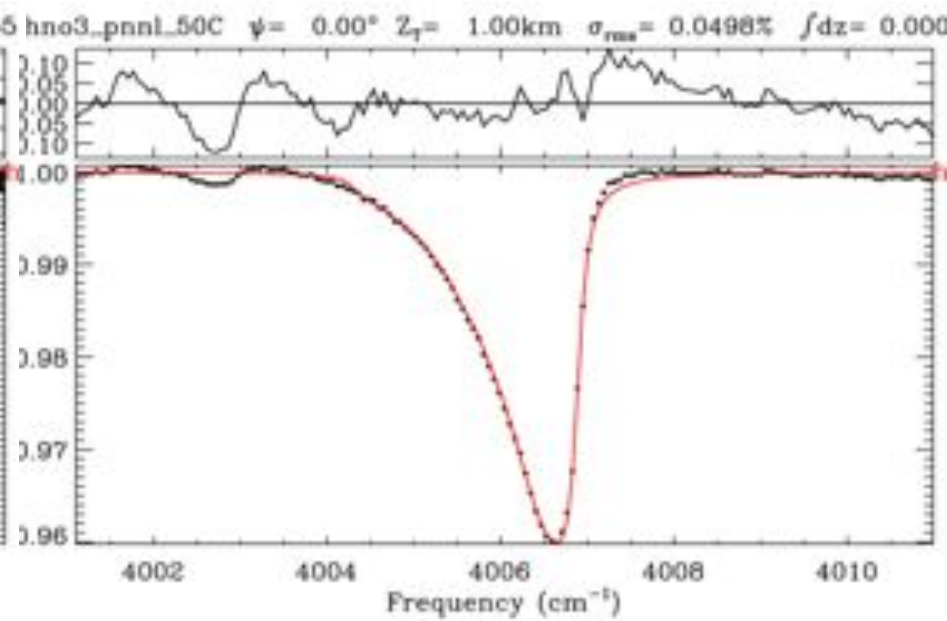


Upper Left: Fit to MkIV balloon spectrum at 22 km tangent altitude

Lower Left: Fit to same spectrum with new kludged HNO_3 linelist

Lower Right: Fit to PNNL spectrum using same kludged HNO_3 linelist





Summary/Conclusions/Plans

Fitted balloon spectra at 17 different altitudes and 108 different spectral windows

HITRAN 2012 is better than HITRAN 2008

HITRAN 2008 is better than HITRAN 2004

HITRAN 2012 is generally better than ATM, except above 16 km in windows with strong missing HNO_3 bands (e.g. the nu_1 centered at 3551 cm^{-1})

Major improvements to the CO_2 spectroscopy in HITRAN 2012, especially at higher frequencies.

CH_4 generally better in HITRAN 2012 but with some exceptions

The 10-40 km altitude range of this study, means H_2O is under-represented. Need to also include ground-based atmospheric spectra for more sensitivity to H2O.

And need to extend study into NIR using ground-based spectra (Kitt Peak, TCCON)

Need to looks at consistency of retrieved gas amounts between different windows

Need better HNO_3 spectroscopy, especially above 1800 cm^{-1}.

Acknowledgements

NASA UARP funding

Larry Rothman and Iouli Gordon who put together the HITRAN 2012 and earlier lists

Plus all the spectroscopists who contributed to HITRAN 2012

Sorry to spend much more time highlighting HITRAN 2012 deficiencies, rather than its (more numerous) successes. But these are more interesting and offer better prospects for improvement.