HITRAN 2012 Water Vapor Spectroscopy validation

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Focus here on the 4000-8000 cm^{-1} and 13000 cm^{-1} spectral regions used for tropospheric measurements of H_2O , HDO, CO, N_2O, CO_2, HF, O_2, and CH_4 by:

- Satellite Instruments (e.g. SCIAMACHY, GOSAT, OCO-2, TROPOMI)
- In situ instruments (TDL)
- Ground-based solar absorption (NDACC, TCCON)

For the more abundant atmospheric gases (e.g. H_2O, CO_2, CH_4, N_2O, CO), whose fundamental bands are saturated, the weaker overtone/combination bands in the NIR region are better for making tropospheric measurements.

*Good H_2O spectroscopy important for retrievals of **all** gases due to the near-ubiquitous H_2O interference.*

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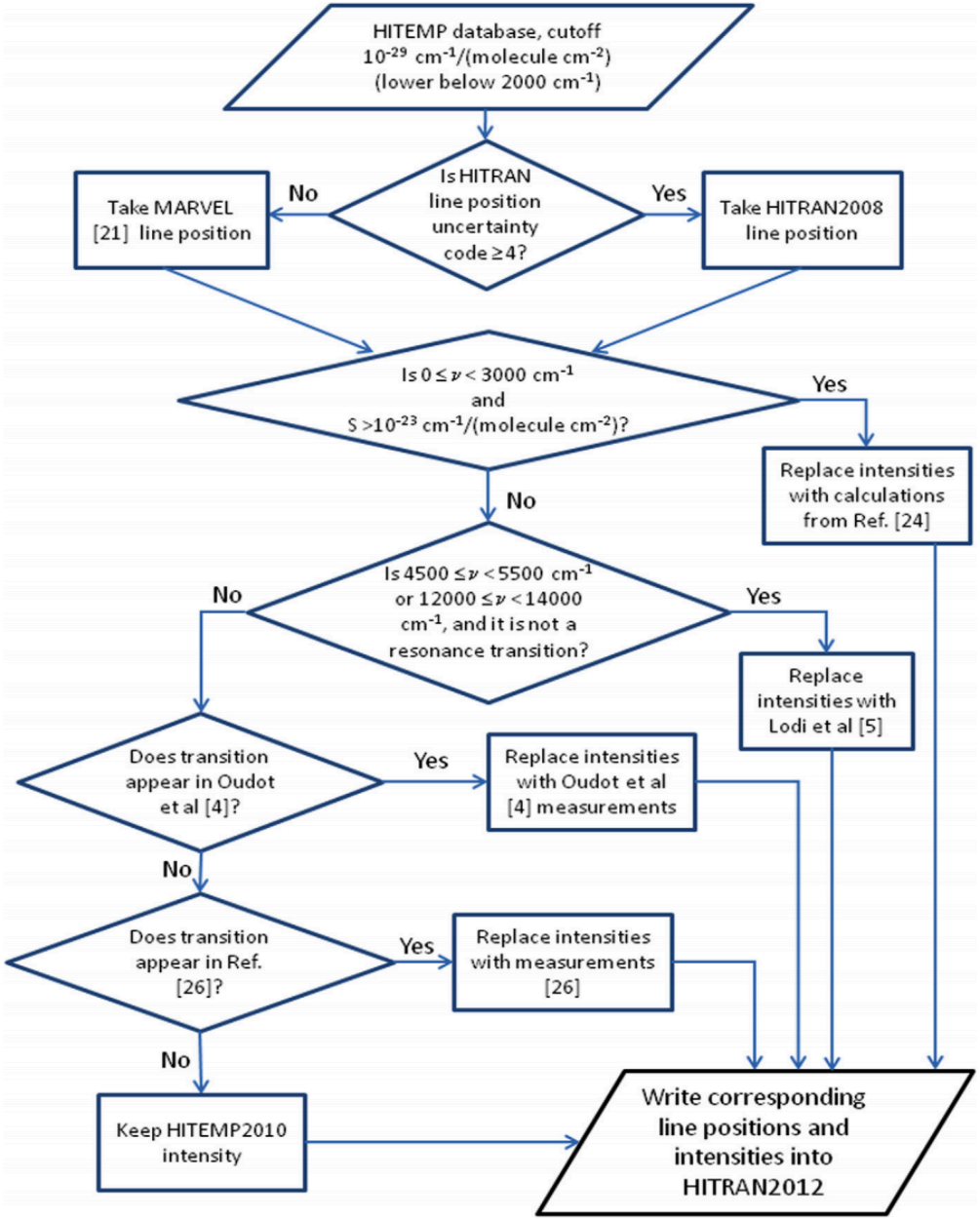


Fig. 2. Flow diagram for the construction of line positions and intensities for the $H_2{}^{16}O$ line list.

HITRAN 2012 H_2O

H_2O linelist construction flowchart, from Rothman et al., 2013

In 4500-5500 & 12000-14000 cm^{-1} regions, positions from empirical energy levels and intensities from the ab initio calculations

[4] Oudot C, Wang L, Thomas X, Von der Heyden P, Daumont L, Régalia L. Intensity measurements of $H_2{}^{16}O$ lines in the spectral region 8000–9350 cm-1 J Mol Spectrosc 2010;262:22–9.

[5] Lodi L, Tennyson J, Polyansky OL. A global, high accuracy ab initio dipole moment surface for the electronic ground state of the water molecule. J Chem Phys 2011;135.

[24] Martin MA, Coudert L, Pirali O, Balcon O. Positions and intensities of water vapor transitions in 0–6000 cm-1 region. J Chem Phys, 2013.

[26] Wagner G, Birk M. Water line intensities in the 1 mm region. J Quant Spectrosc Radiat Transfer 2013.

Laboratory versus Atmospheric Spectra

Atmospheric spectra are great for identifying deficiencies in the linelist, but should not be used to remedy these deficiencies. Laboratory spectra should be used when possible.

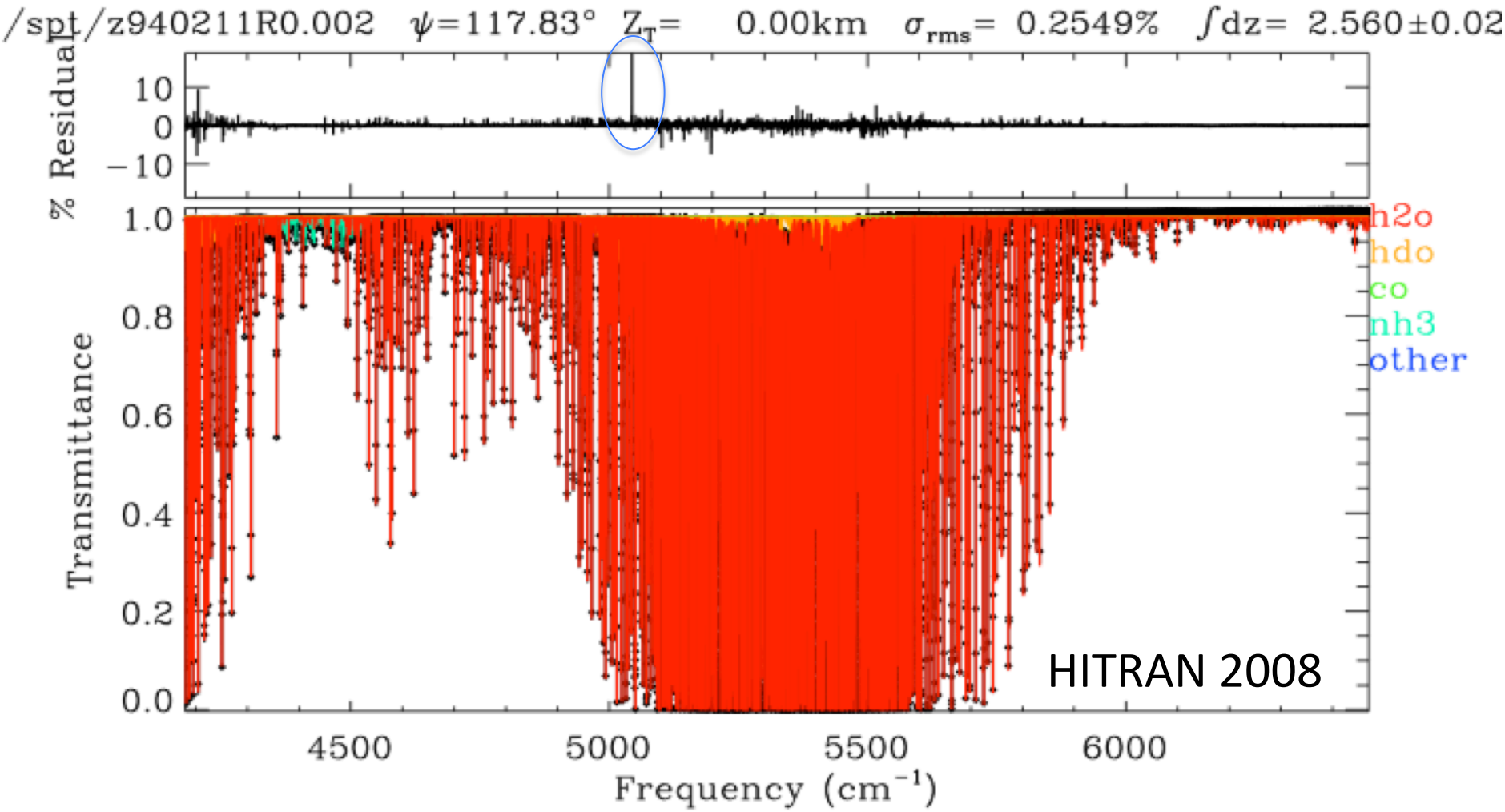
Exceptions to this are H_2O, N_2, O_2 where insufficient gas can be contained in a cell to see all the lines observable in atmospheric spectra.

- In Kitt Peak laboratory spectra, the largest H_2O slant column measured at T<25C is 1E+22 molecules/cm^2 (433m path at 7 Torr)
- TCCON spectra from Darwin at 87° SZA contain 3E+24 molecules/cm^2 of H_2O (equivalent to 40 km path at 20 Torr)

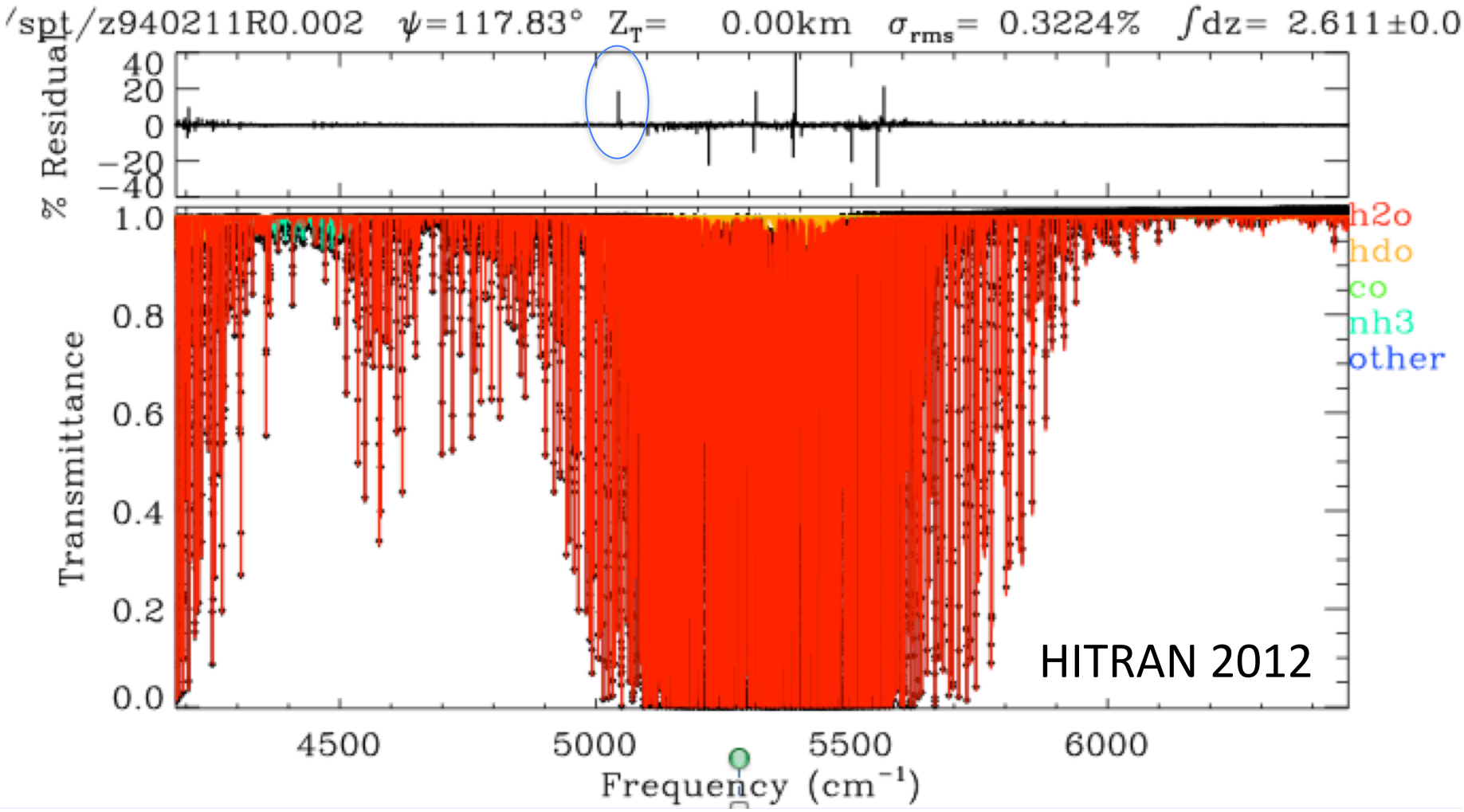
To evaluate the HITRAN 2012 H_2O spectroscopy I fitted:

- Kitt Peak laboratory spectra (helps validate the stronger lines)
- Ground-based TCCON spectra (helps validate the weaker lines)

Fit to Kitt Peak laboratory spectrum (T=20C P=1.85 Torr, Path=433m)

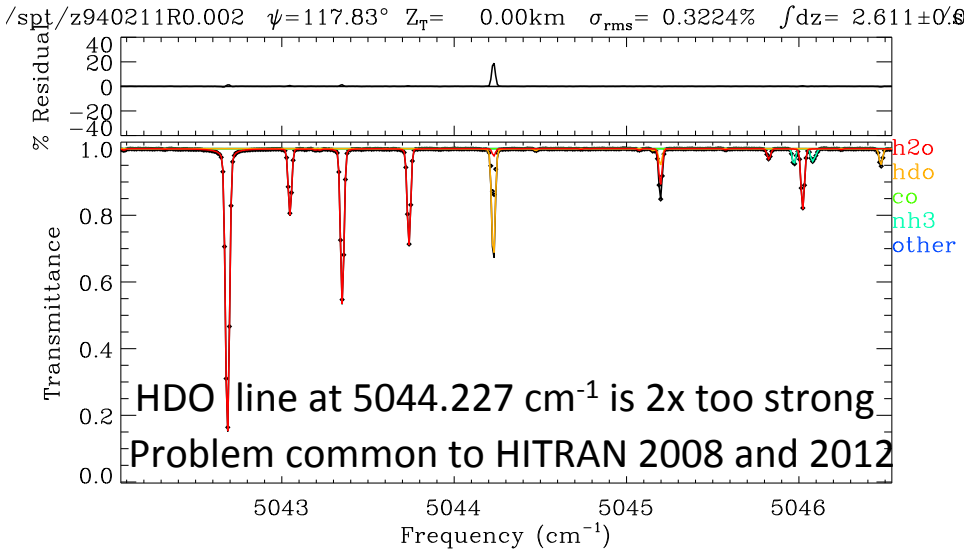


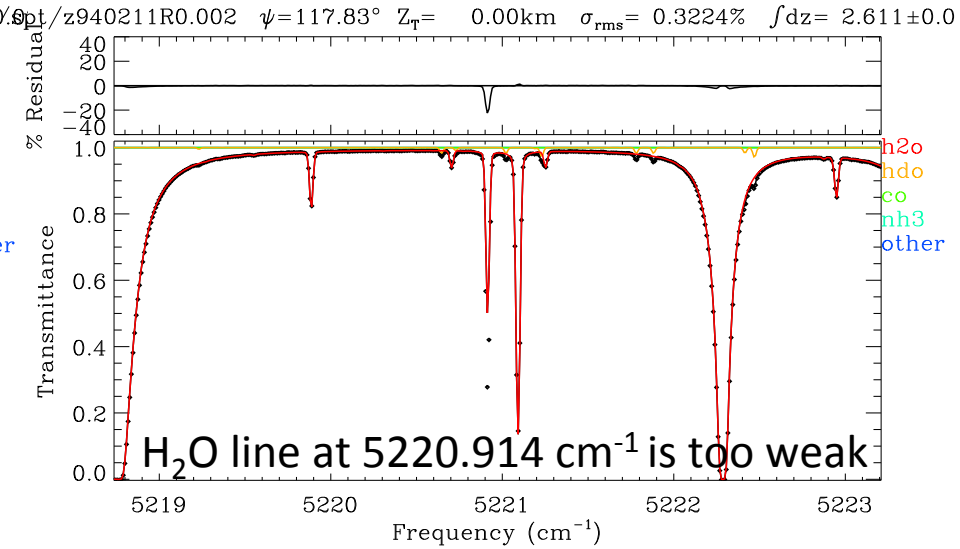
Same Kitt Peak laboratory spectrum

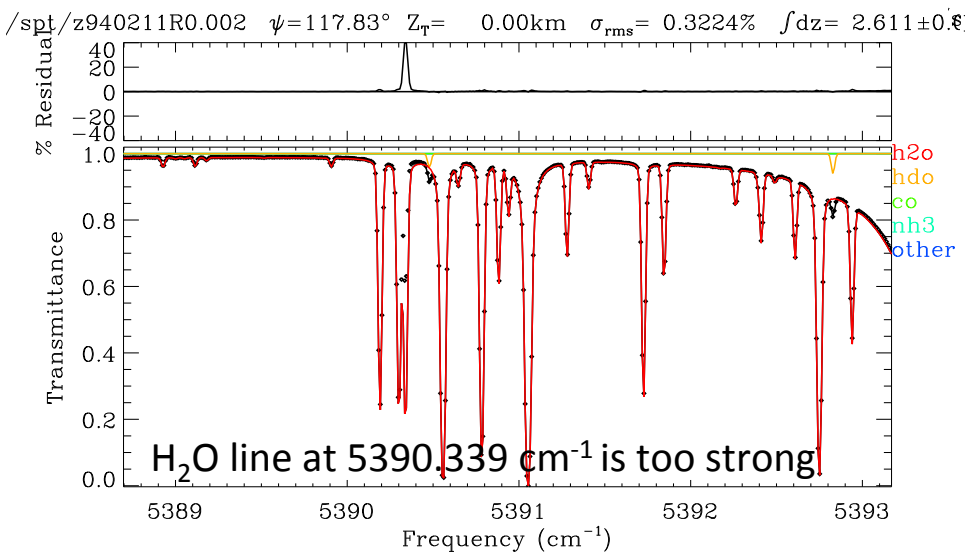


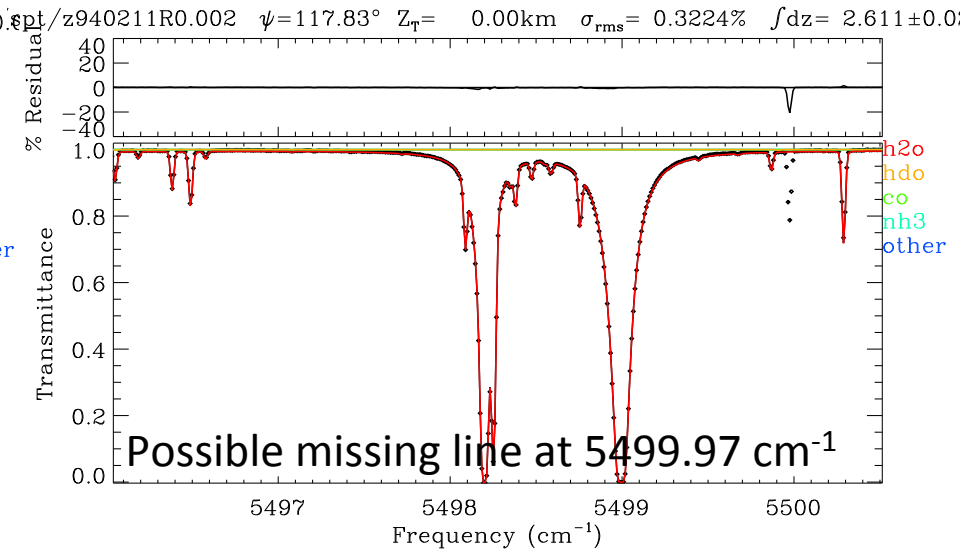
Fits are worse overall due to presence of a few very large residuals in 5000-5600 cm^{-1}

Zoom into large residuals (5000-5600 cm^{-1})

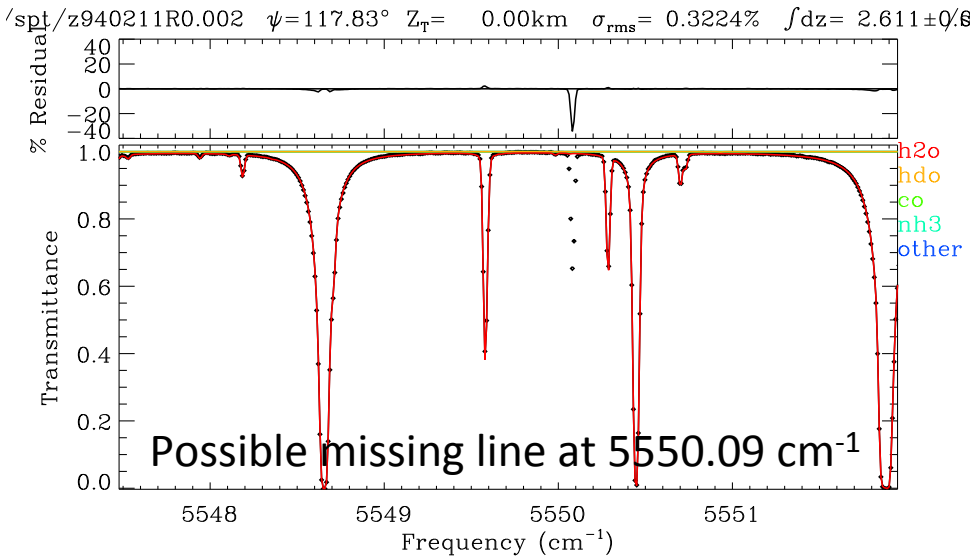


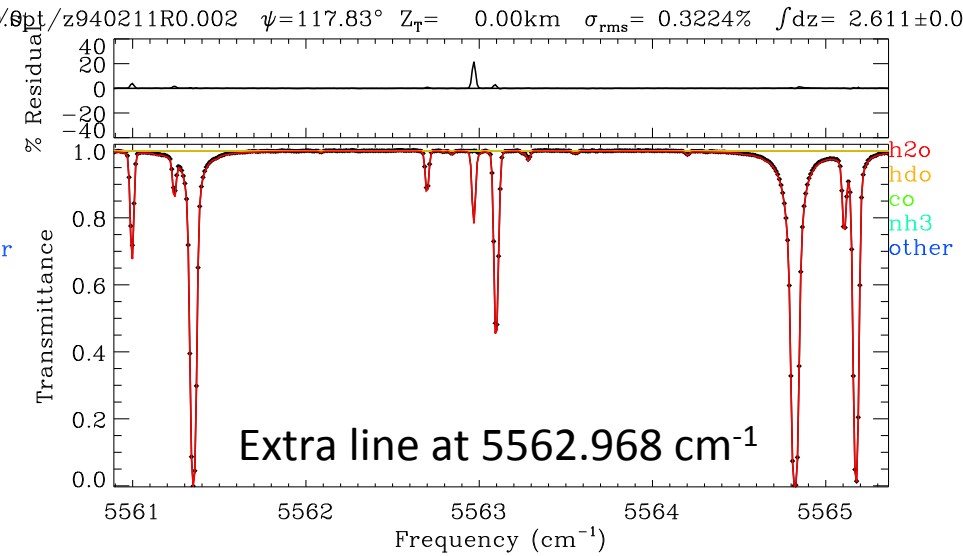






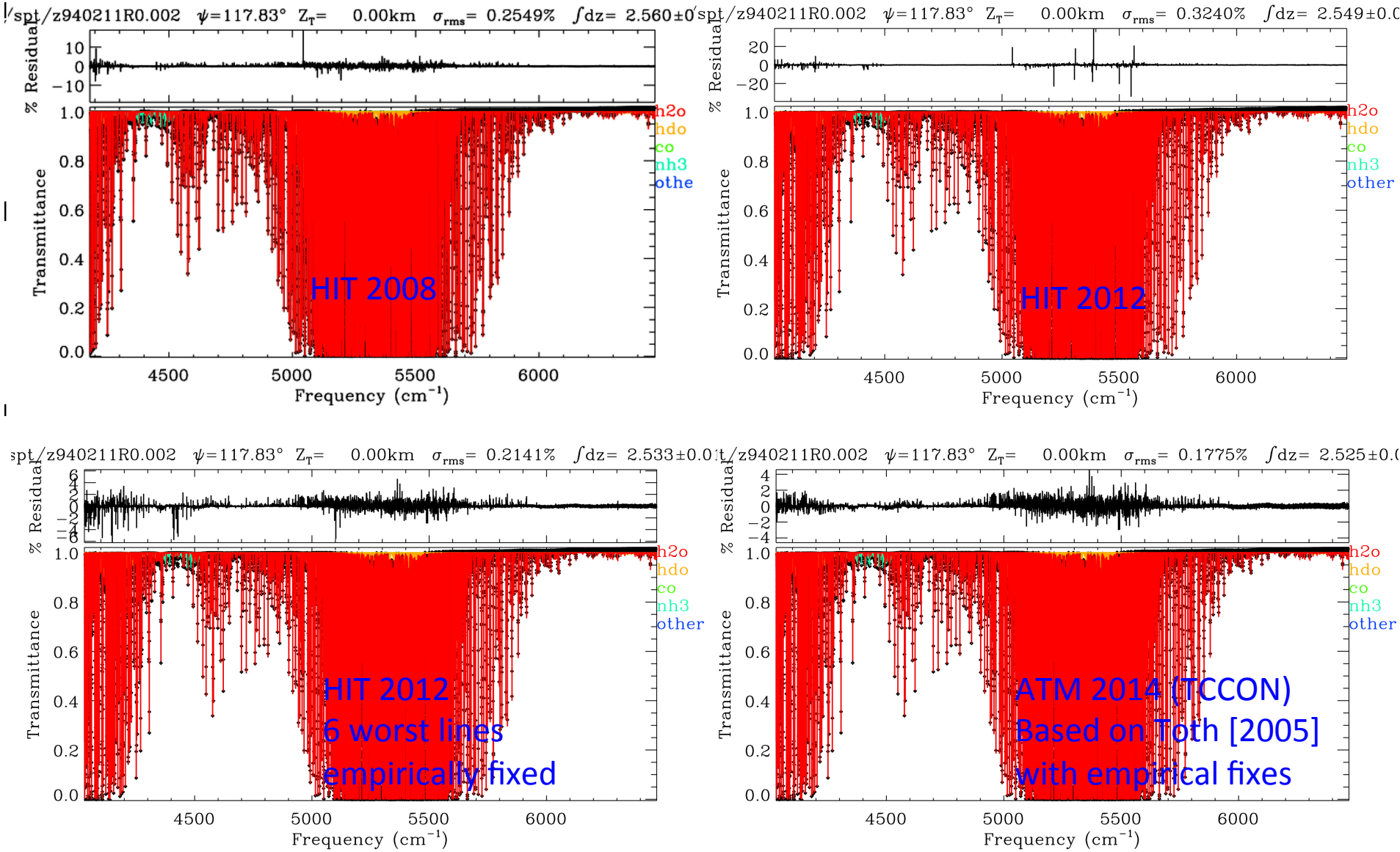
More large Residuals



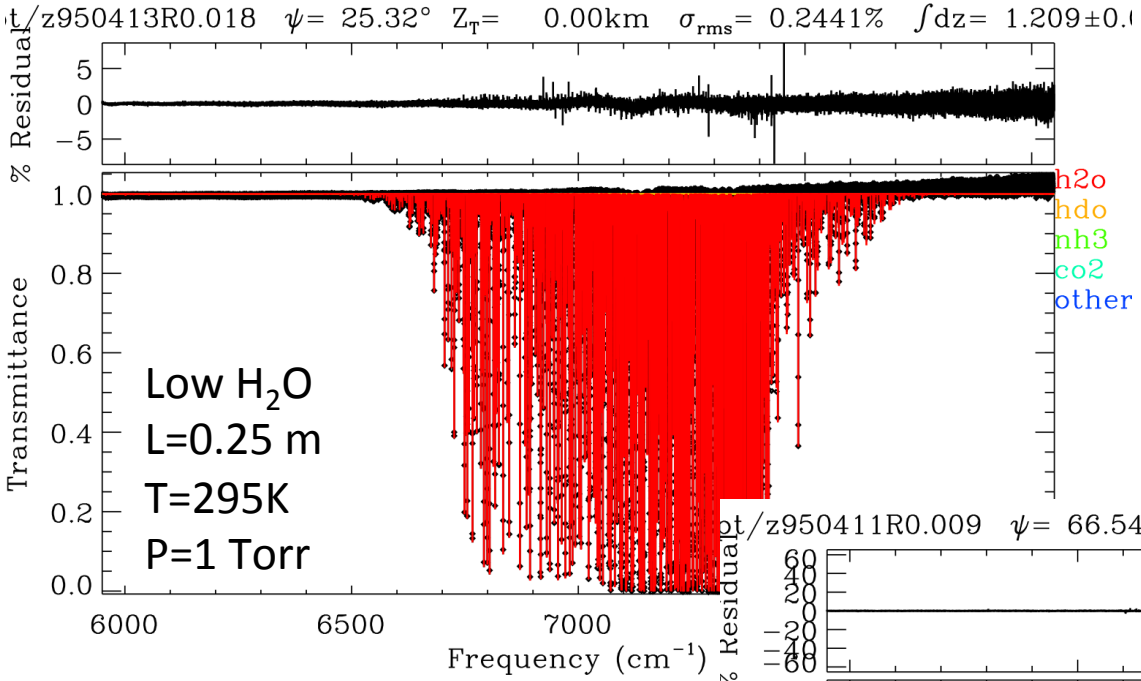


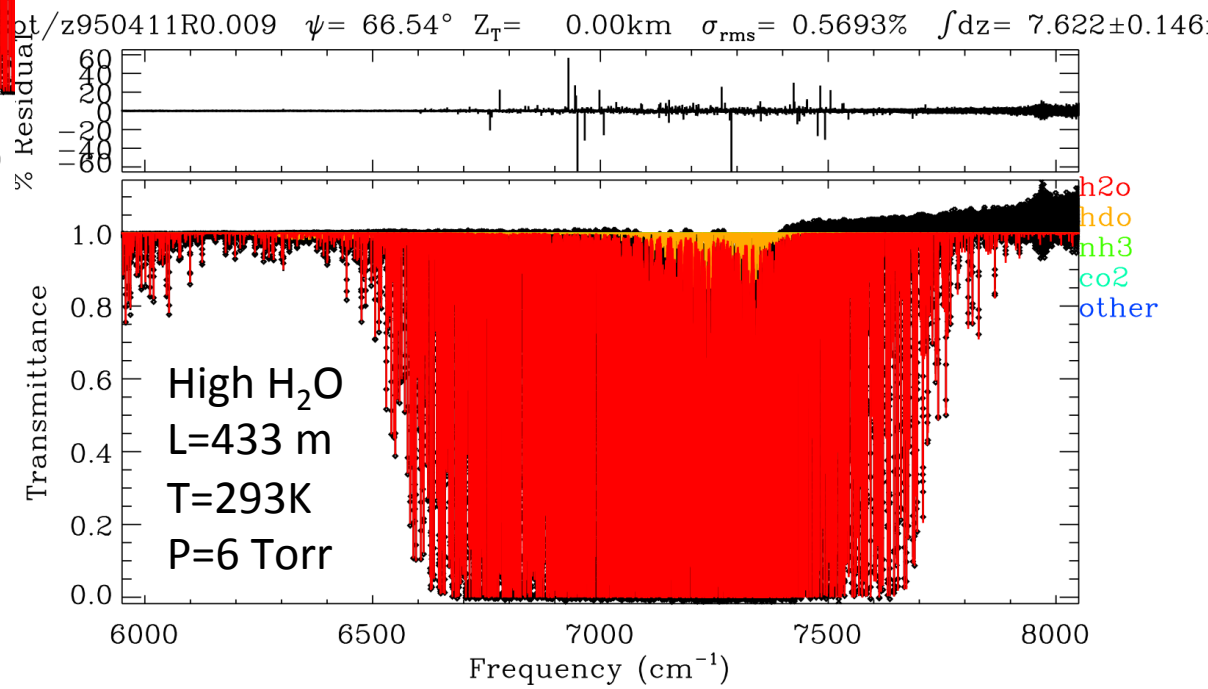
If I manually fixed these large residuals, how much better would the fits be?

H_2O Linelist Comparison



6000-8000 cm^{-1} region HITRAN 2012

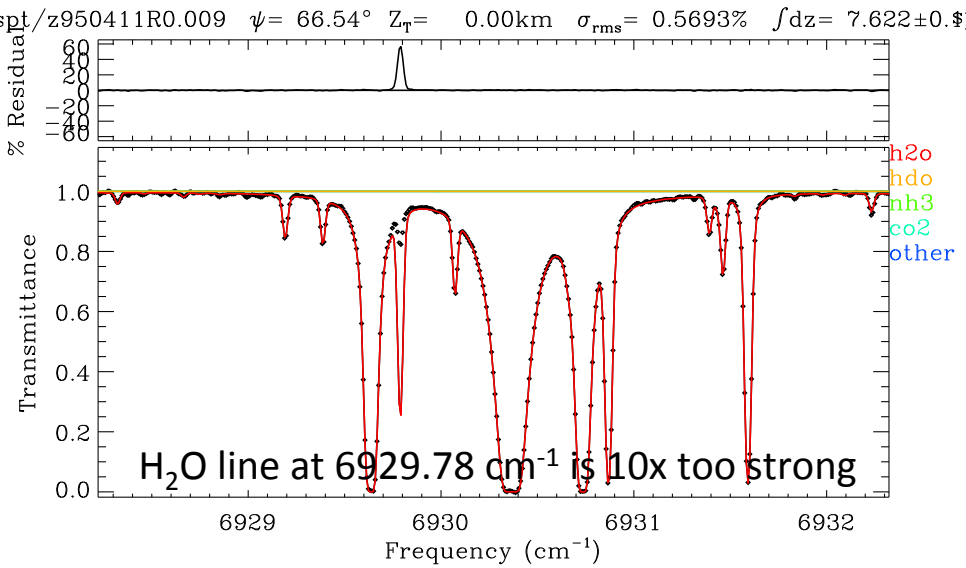


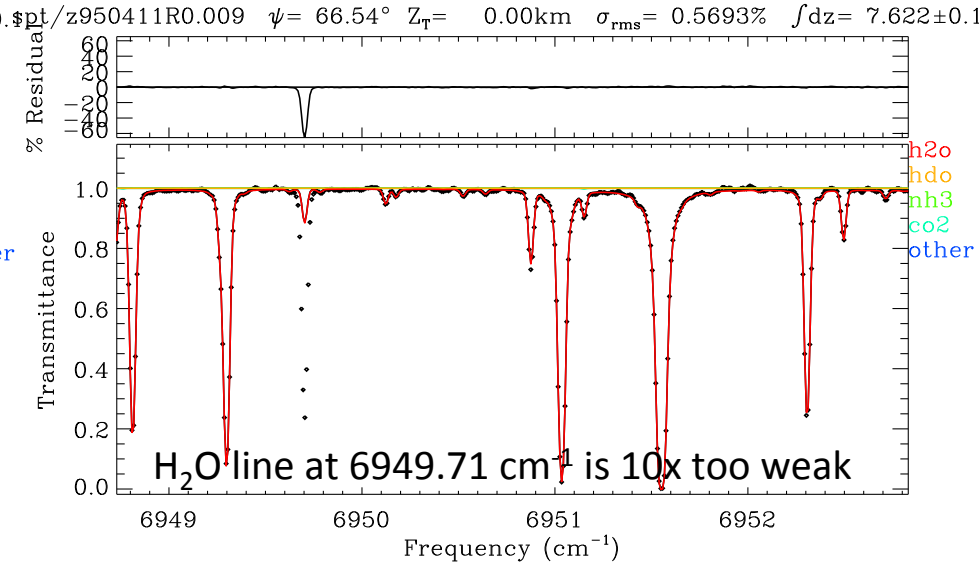


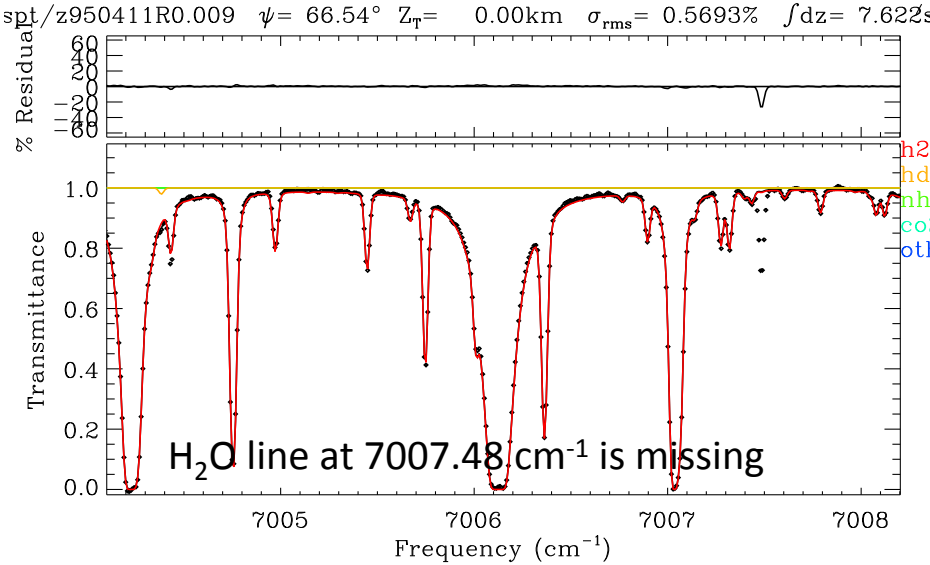
In 5900-6400 cm^{-1} region used by TCCON, GOSAT & OCO-2, H_2O lines are rather weak, Even in High H_2O lab spectrum.

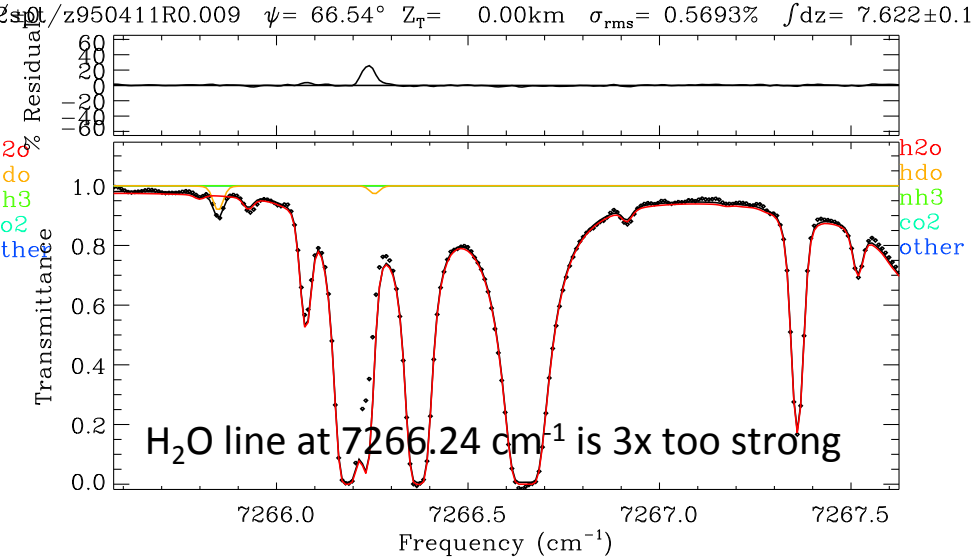
Ditto for 7800-8050 cm^{-1} used By TCCON (1.27 um O_2 band)

Zoom into large residuals (6900-7500 cm^{-1})

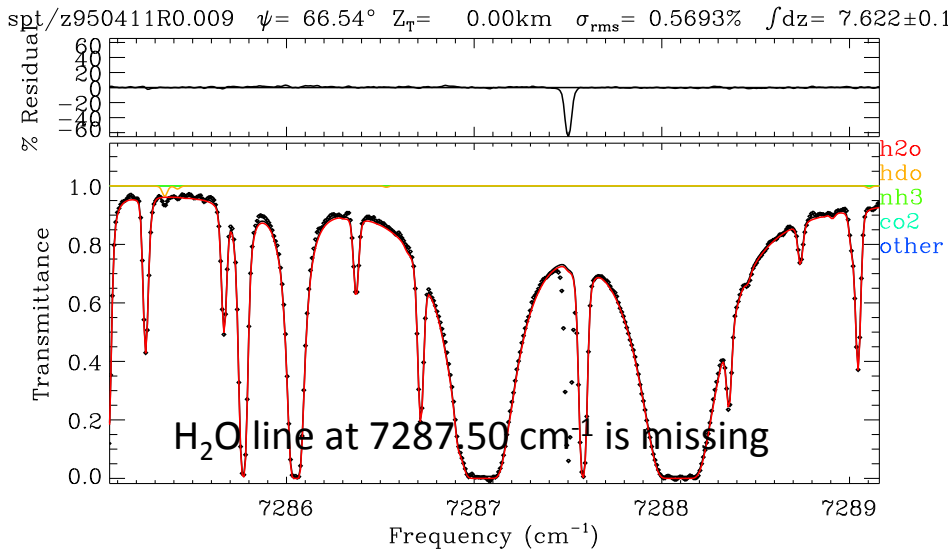


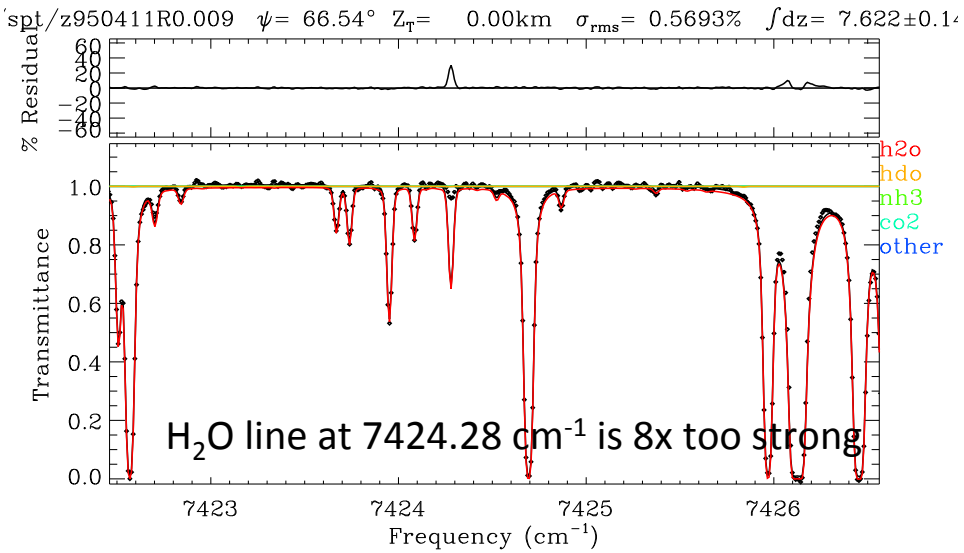


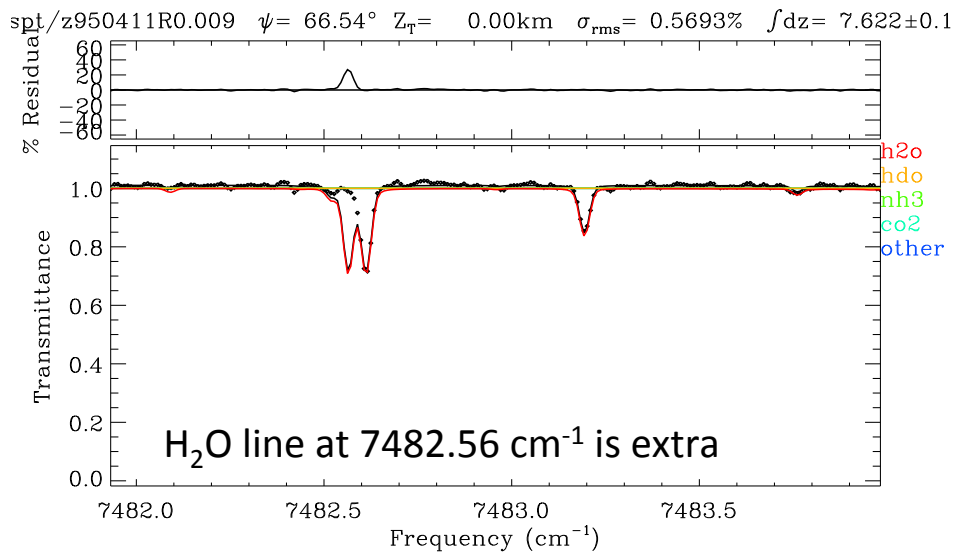


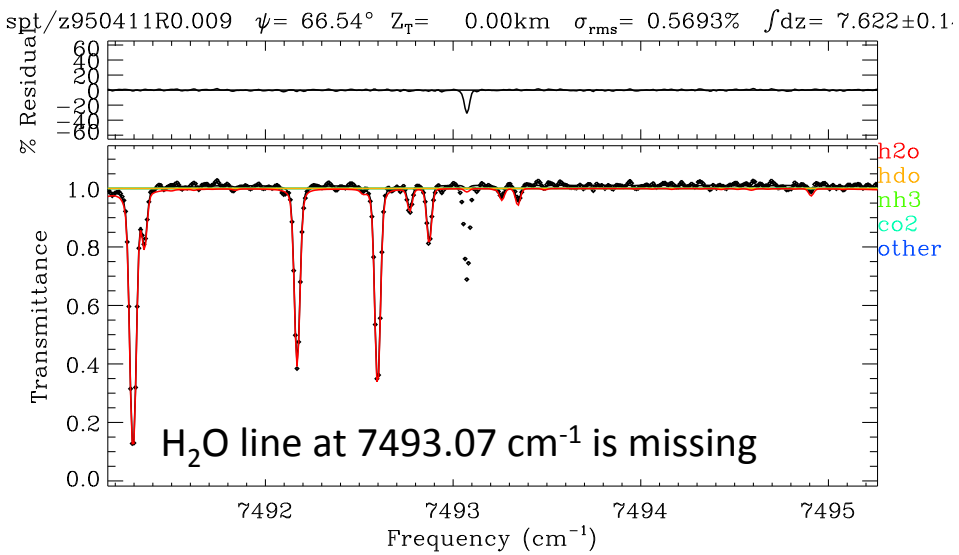


Zoom into large residuals (6900-7500 cm^{-1})



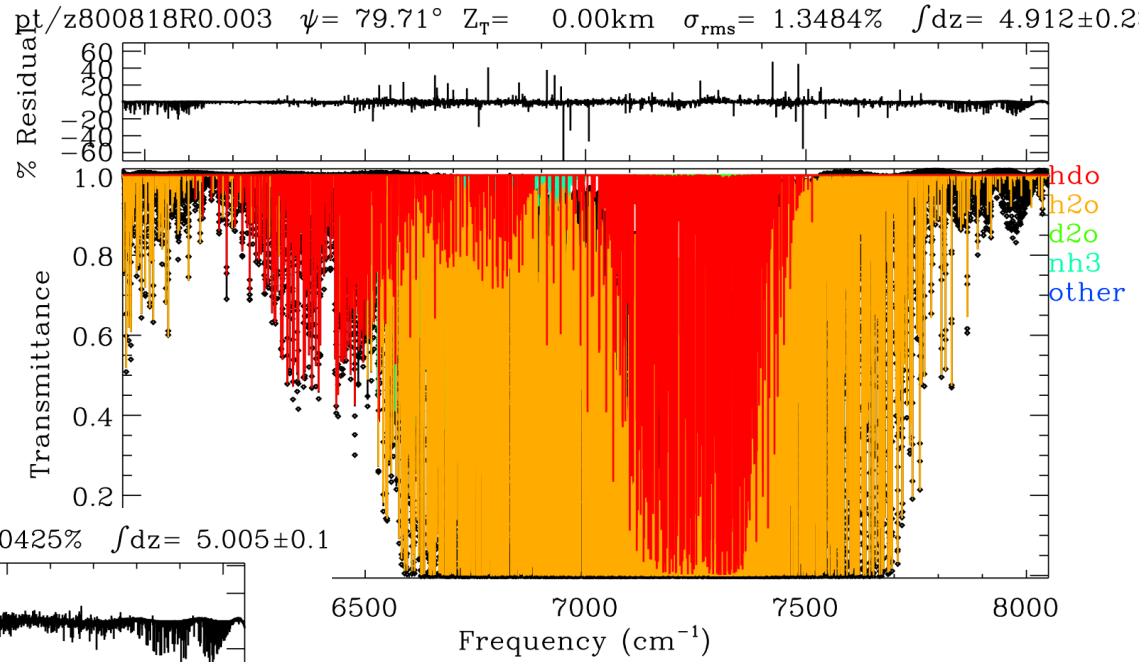


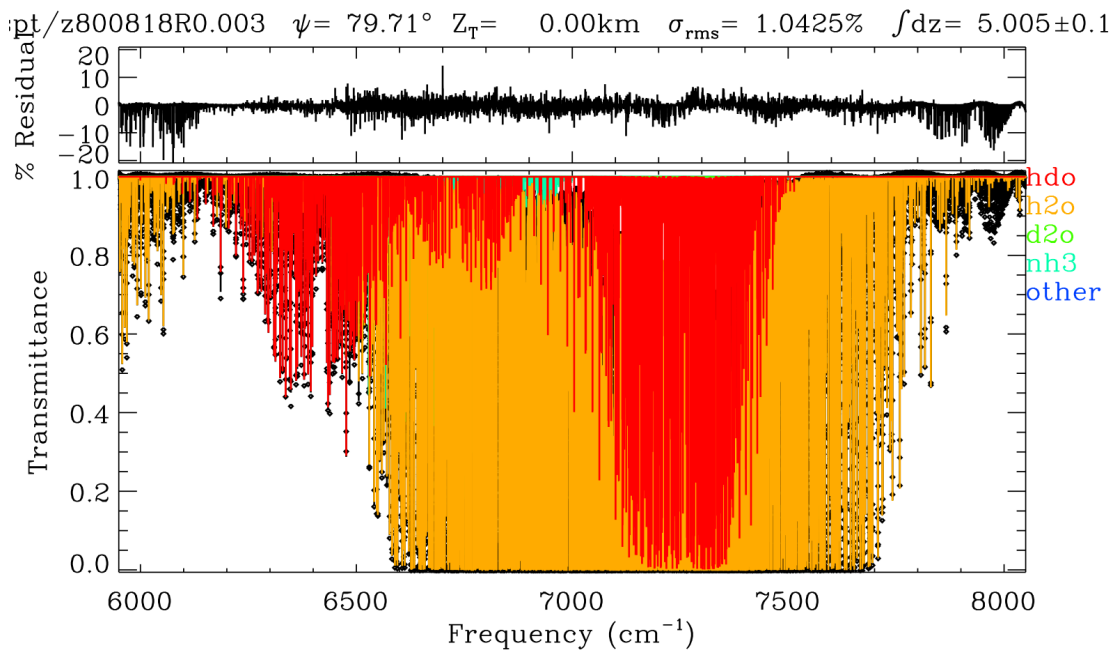




Kitt Peak HDO-enriched H_2O

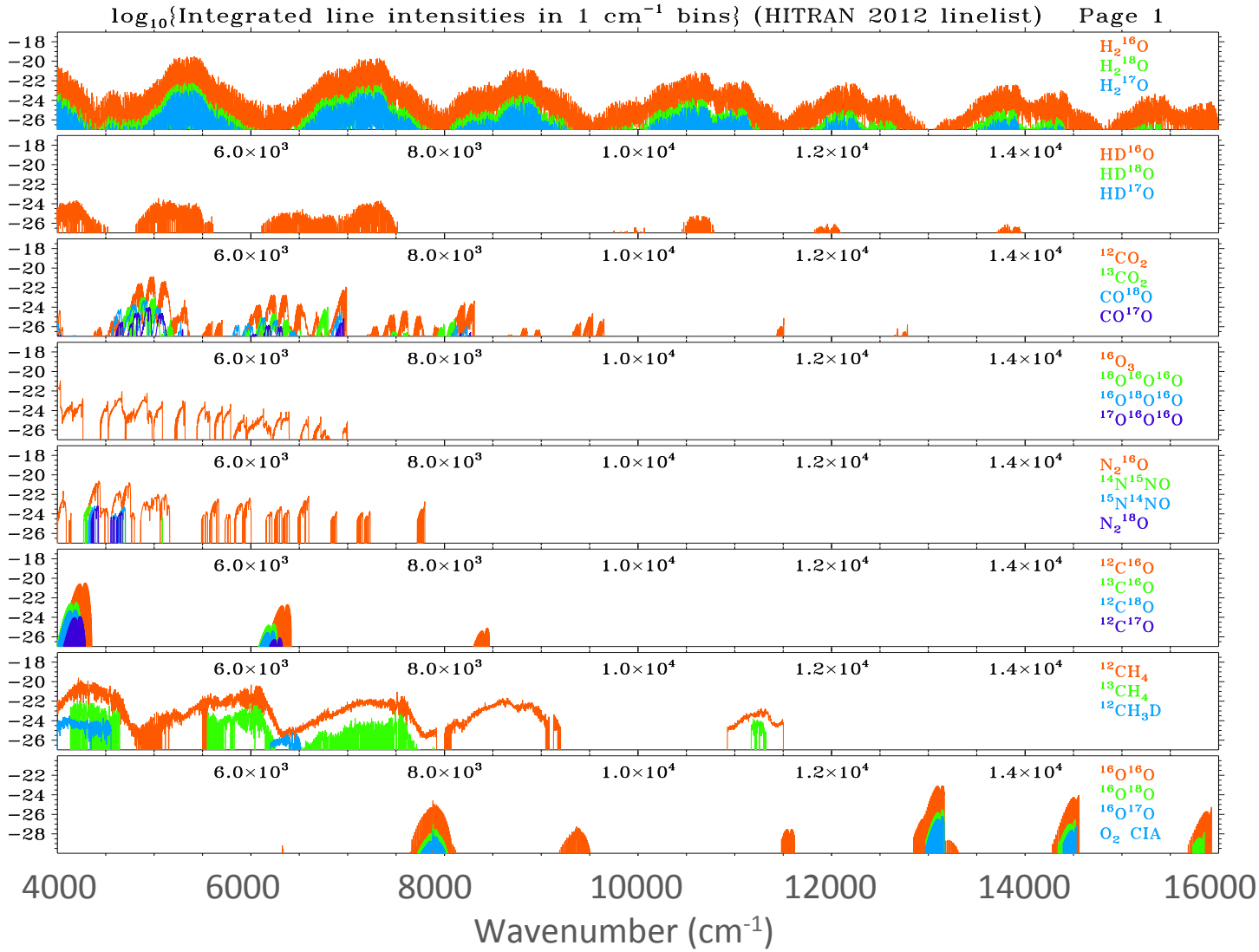
Top: Fitted with HITRAN 2012





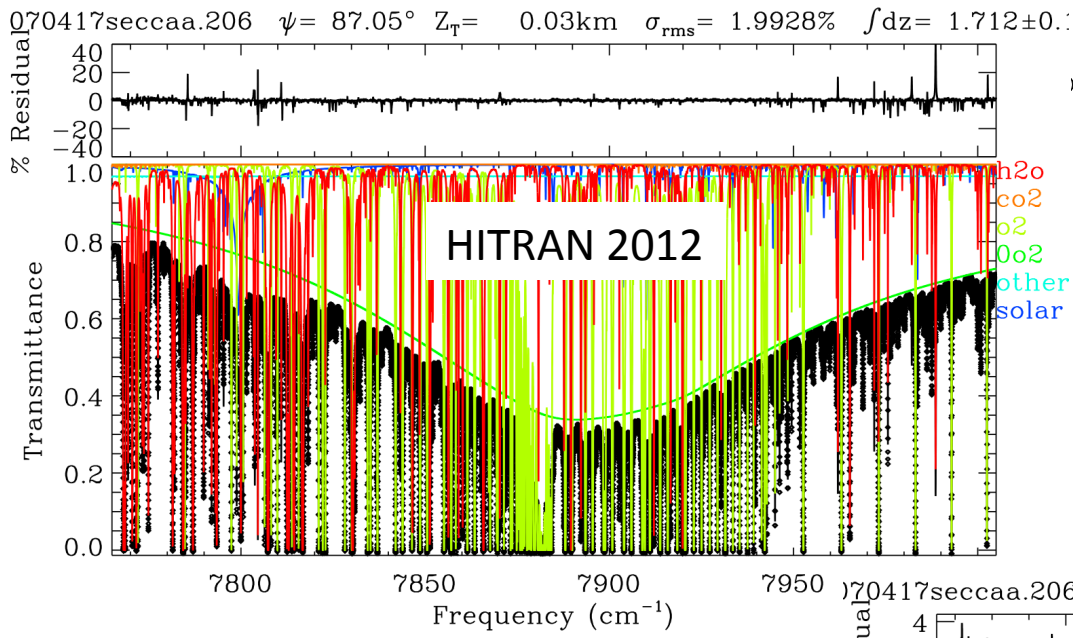
Bottom: Fitted with ATM 2014

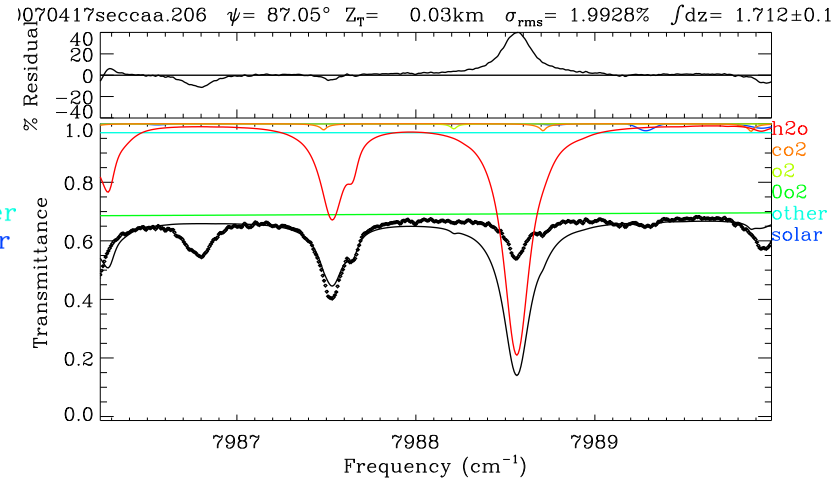
HITRAN 2012 Coverage Summary

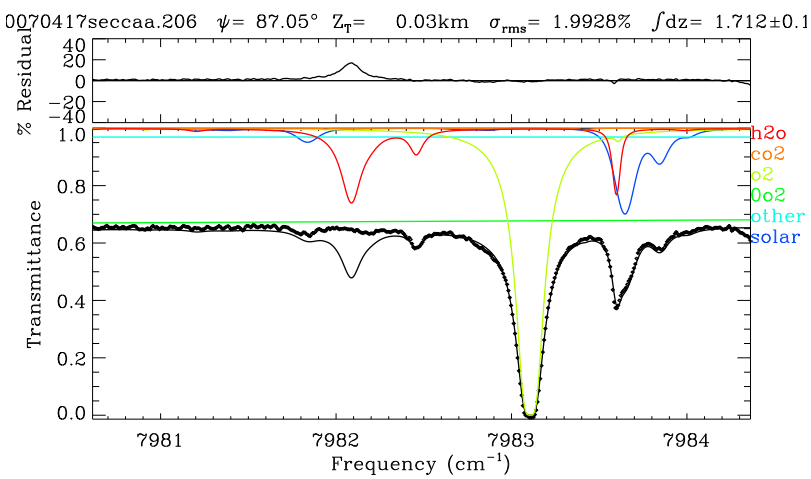


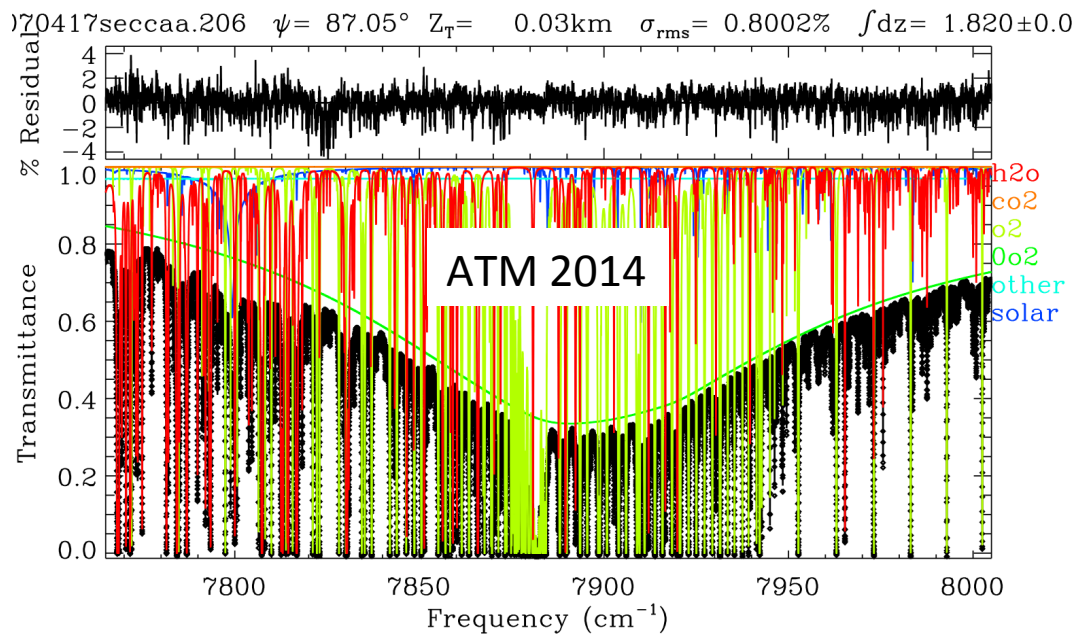
Beyond 7500 cm^{-1}, the H_2O line intensities decrease rapidly and so use atmospheric spectra.

Fit to wet Atmospheric Spectrum

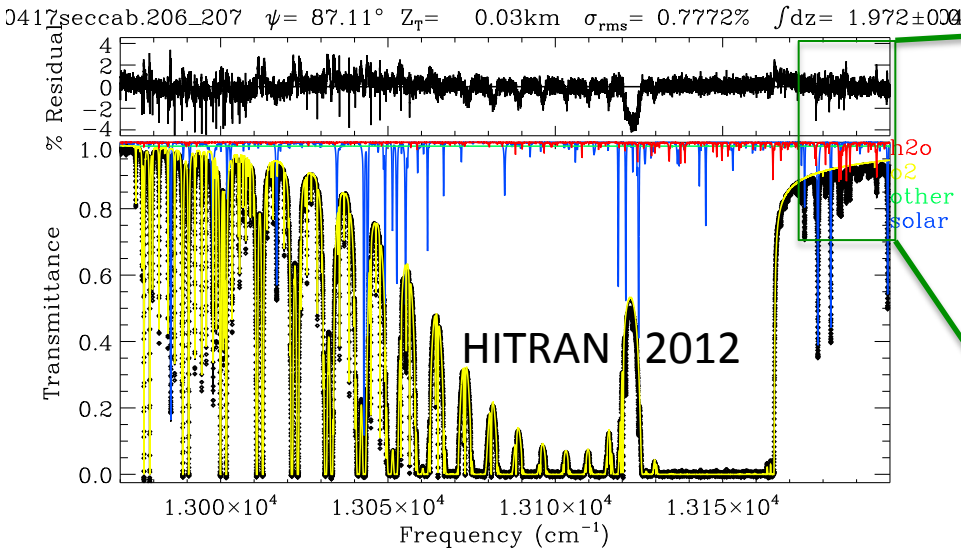


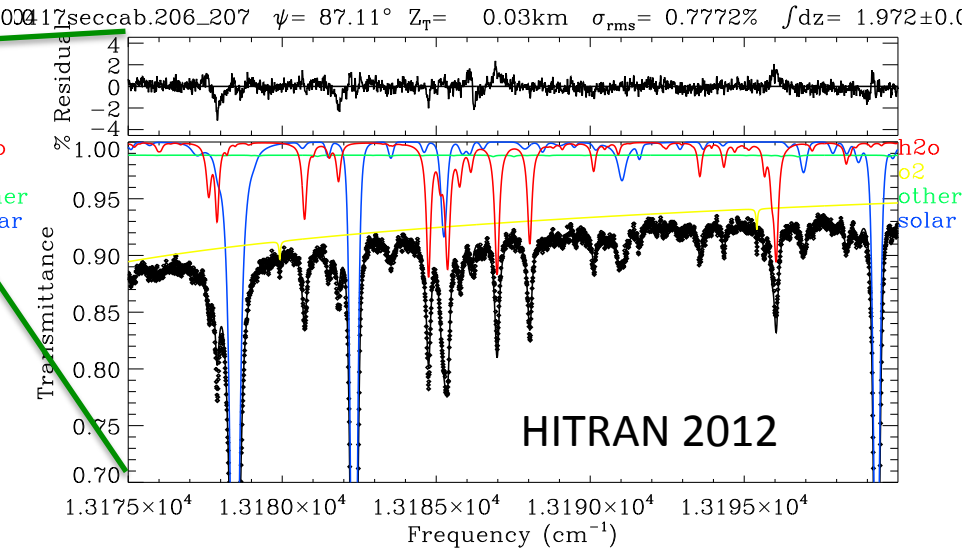






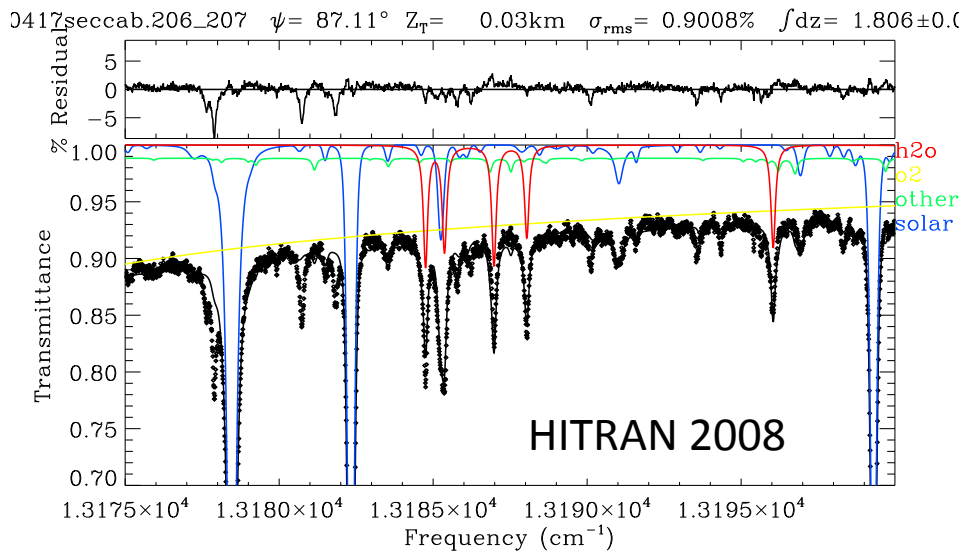
O_2 A-band region in TCCON spectrum





Wet high-airmass Darwin spectra reveal H_2O lines up to 10% deep to the right of the O_2 band-head.

These were poorly represented in HITRAN 2008, much better in HITRAN 2012, but still not perfect.



Summary/Conclusions

General

Laboratory spectra allow validation of the stronger H_2O lines ($S > 10^{-25}$).

Long-path atmospheric spectra allow validation of weaker H_2O lines ($S > 10^{-27}$).

Although the HITRAN 2012 H_2O linelist is generally better than HITRAN 2008, there are places where it is worse, causing large residuals in atmospheric spectral fits

If not fixed, these large H_2O-related spikes/dips in the residuals bias atmospheric retrievals based on least-squares spectral fitting, even if H_2O is not target gas.

Empirically fixing these deficiencies is time consuming (not easily automated) and has to be re-done every time a new theoretical linelist is produced.

Specific

D_2O should be in HITRAN as the 7'th water vapor isotopolog, to facilitate fitting of isotopically-enriched HDO lab spectra.

Need better NH_3 linelist in 4400 cm^{-1} region to fit contamination in KP lab spectra.

Acknowledgements

NASA funding from Upper Atmosphere and Carbon Cycle research programs.

Kitt Peak Observatory and the people who worked there, for recording high quality laboratory & atmospheric spectra, and making them available to the public.

Spectroscopists who contributed to the development of the HITRAN 2012 linelist.

HITRAN Committee for organizing this meeting.