

Spectroscopy Discussion

For most gases, spectroscopy (target & interfering gases) is a major error term
How do we minimize the impact of spectroscopic errors?

Clearly, all sites should be using the same spectroscopy, but different sites are dominated by different spectroscopic errors.

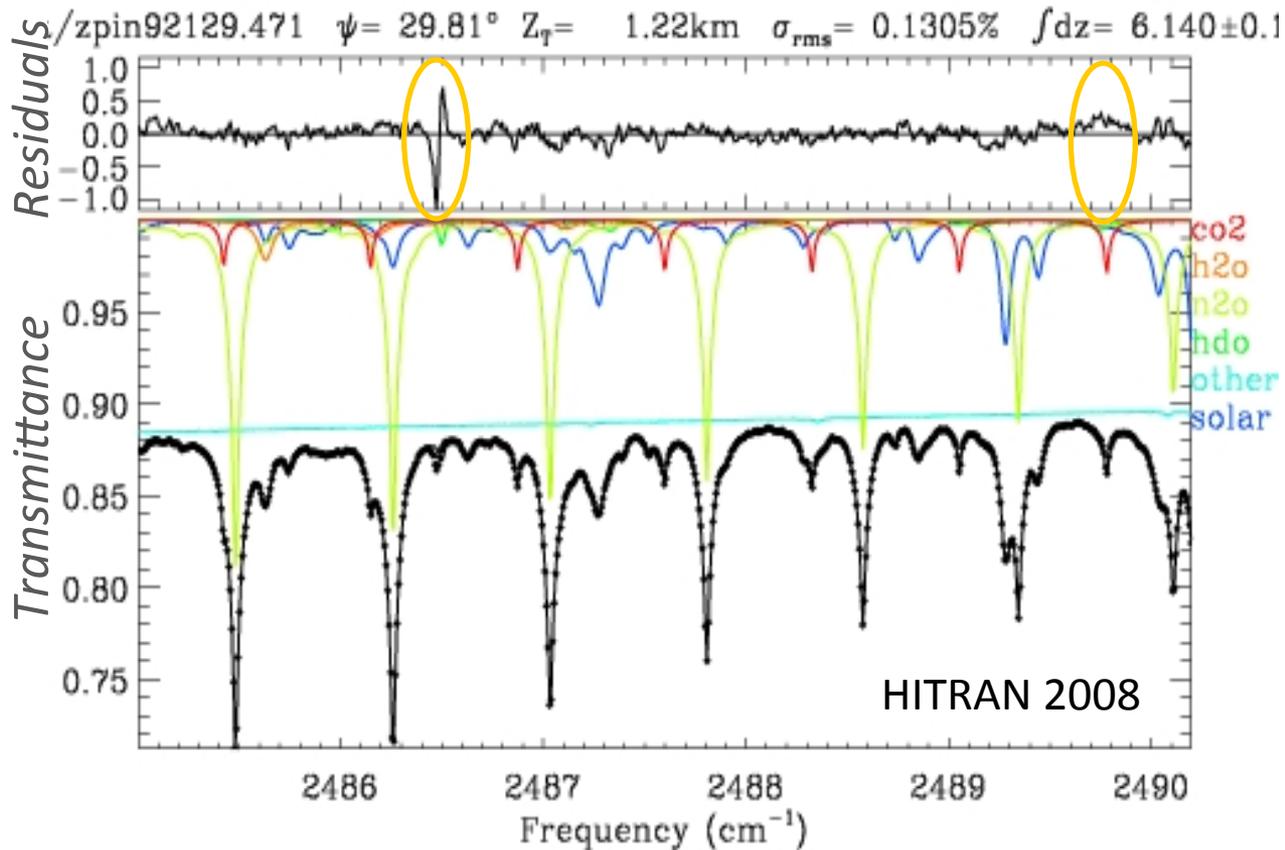
- Tropical sites H₂O & HDO spectroscopy is critical (many missing lines)
- Polar sites O₃ & HNO₃ spectroscopy is relatively more important
- Polar sites → higher airmass → so weaker lines relatively more important
- So consistency of weak/strong lines essential for avoiding latitude biases.

How should we be handling known spectroscopic deficiencies?

- Upgrade to latest HITRAN version (2012) and hope it's better
- “Cherry Pick” from among candidate linelists on gas-by-gas, band-by-band basis
- Attempt empirical corrections to latest HITRAN
- Catalog deficiencies and report them to HITRAN

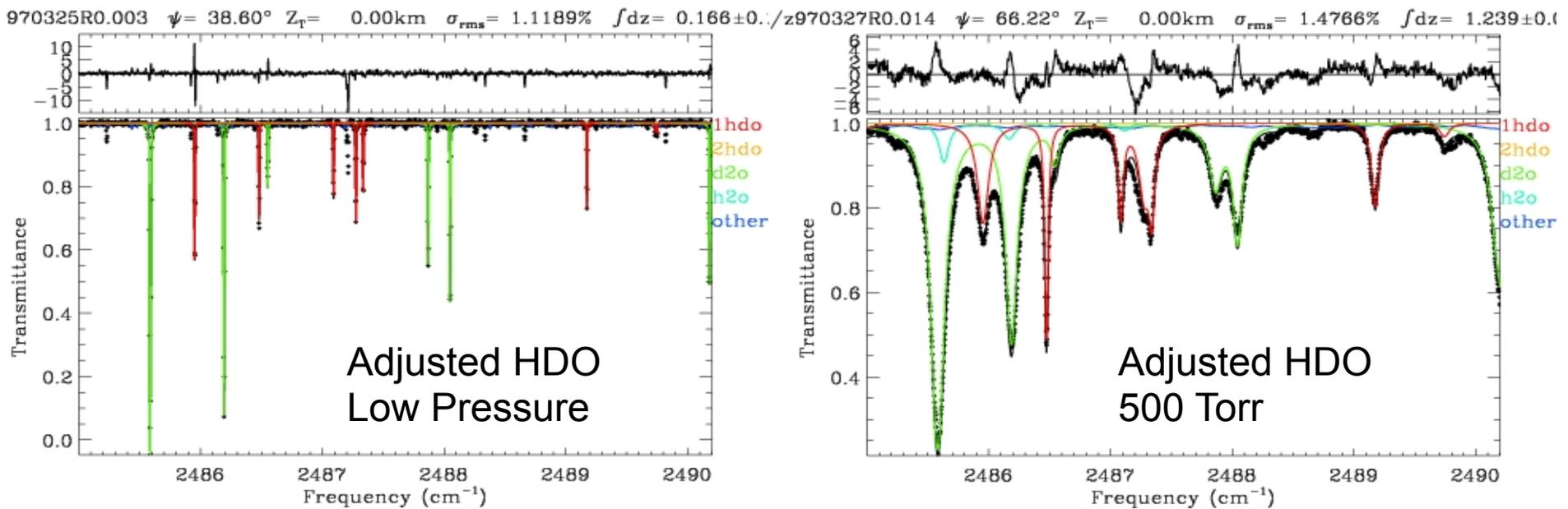
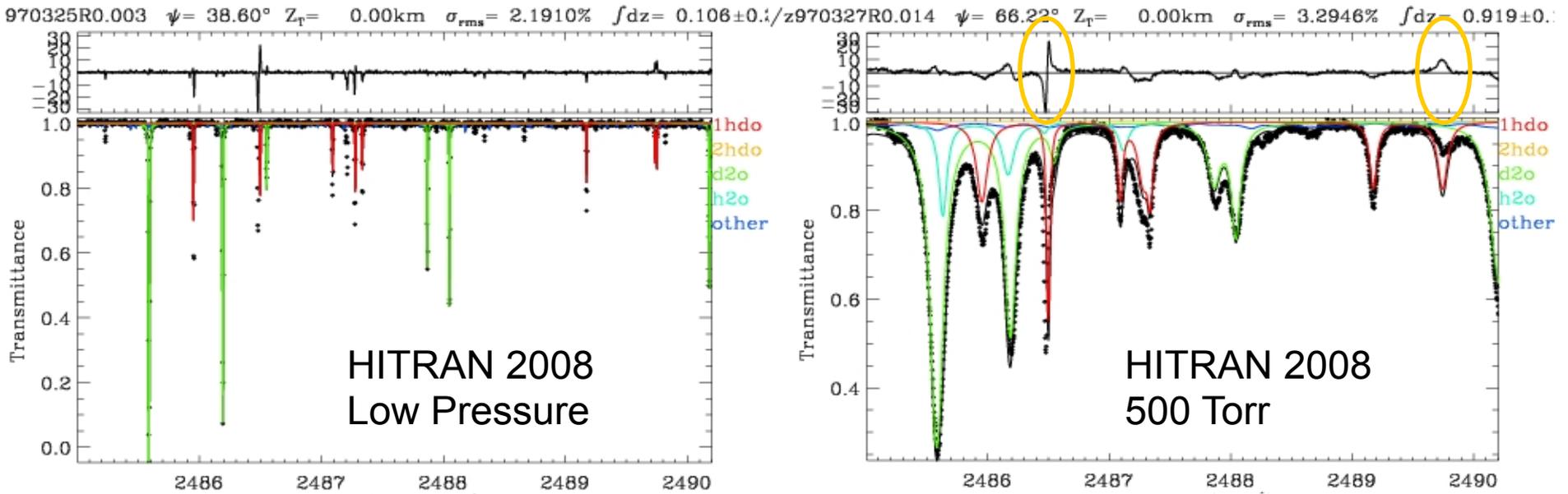
The following slides are intended to stimulate discussion, not provide answers.

Case Study 1: HDO Spectroscopic Deficiency



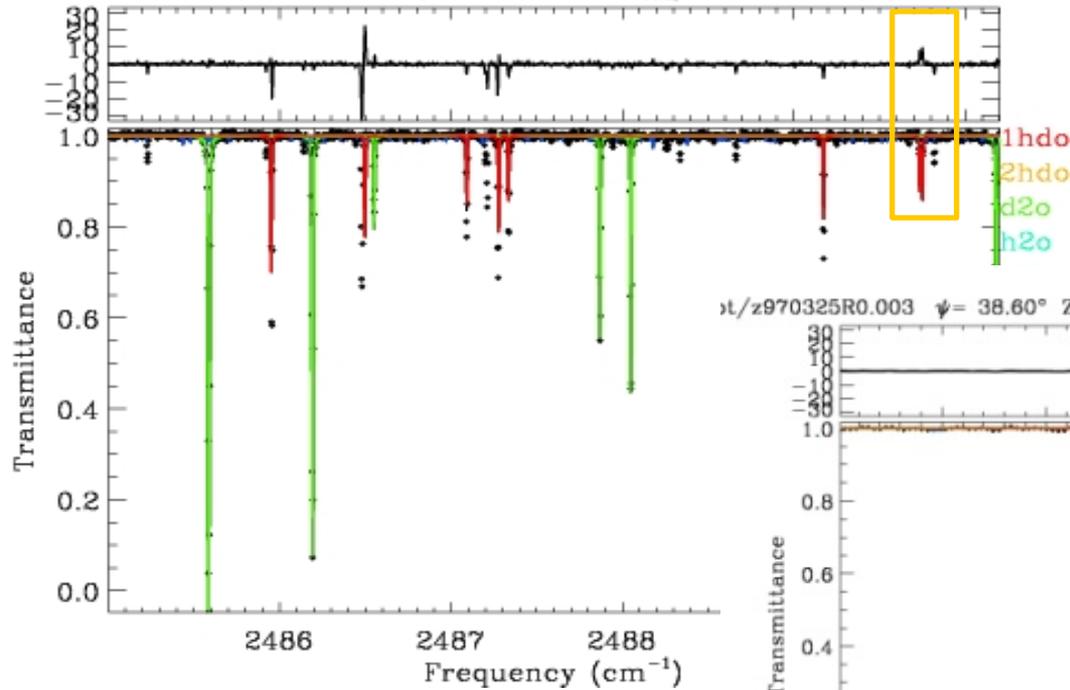
Spectral fits to MkIV ground-based spectra in the $2485\text{-}2490\text{ cm}^{-1}$ region used to retrieve CO_2 and N_2O . Large residuals are associated with HDO.

Fits to Kitt Peak Lab HDO spectra



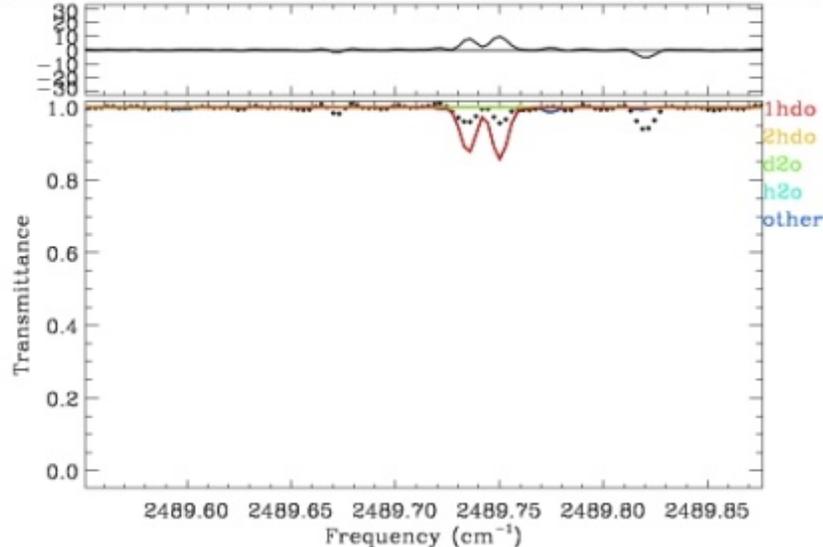
Zoom into low-pressure Kitt Peak Spectra

970325R0.003 $\psi = 38.60^\circ$ $Z_T = 0.00\text{km}$ $\sigma_{\text{rms}} = 2.1910\%$ $\int dz = 0.106 \pm 0.1$



The intensities of these two HDO lines are 6 times too strong.

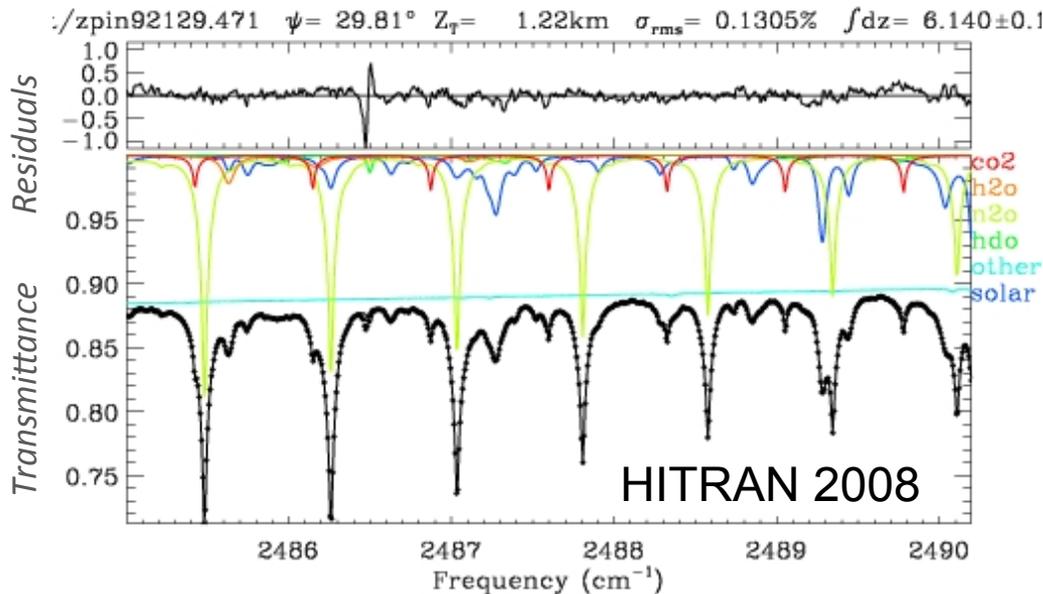
970325R0.003 $\psi = 38.60^\circ$ $Z_T = 0.00\text{km}$ $\sigma_{\text{rms}} = 2.1910\%$ $\int dz = 0.106 \pm 0.1$



Why do HDO lines have such large errors when these lab spectra have been available for over 15 years?

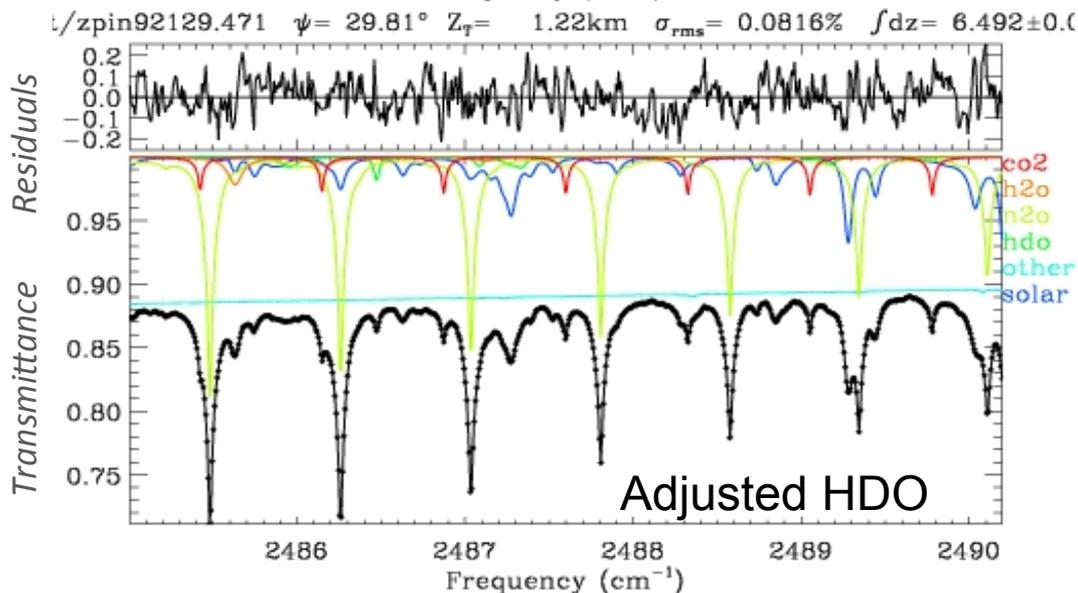
Checking for self-consistency against lab spectra not high priority.

After Fixing HDO lines in this region



Spectral fit using HITRAN 2008 linelist (shown previously)

Large residual due to HDO line having pressure shift = 0.0 and Incorrect position

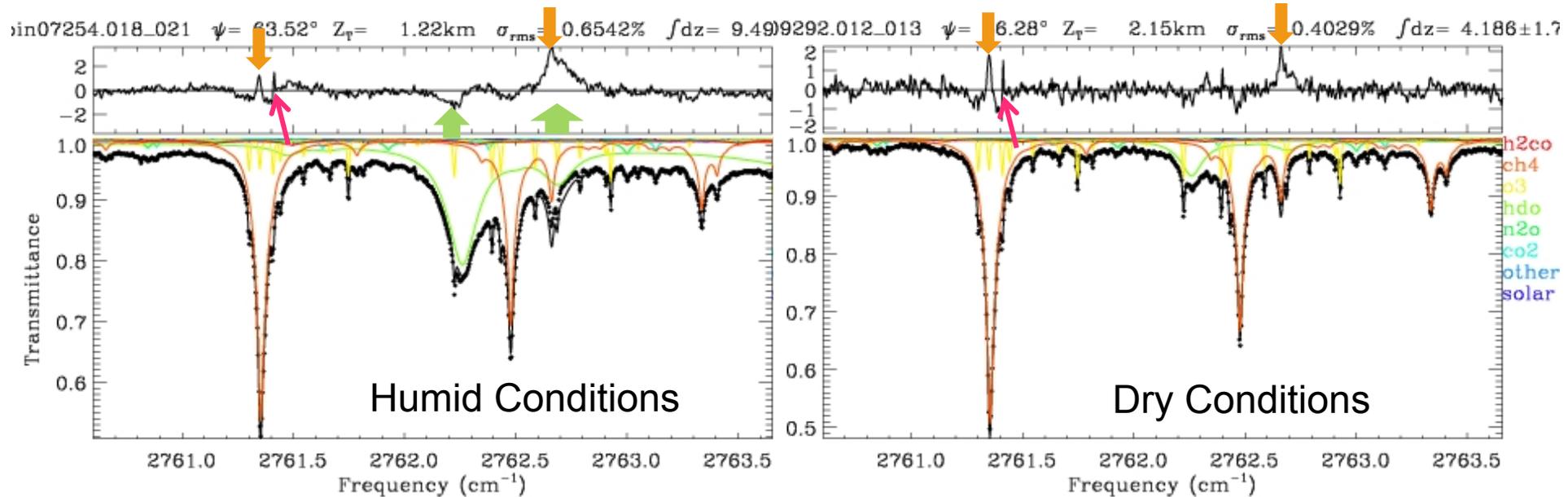


After empirically adjusting HDO lines based on fits to Kitt Peak laboratory spectra.

Retrieved CO_2 increases by $> 5\%$
Retrieved N_2O changes by $> 2\%$

Use of HITRAN 2008 linelist would cause HDO-dependent bias in the retrieved CO_2 and N_2O in this window.

Case Study 2: Ground-based MkIV H₂CO



Fits to ground-based MkIV spectra made using HITRAN 2008 linelist.

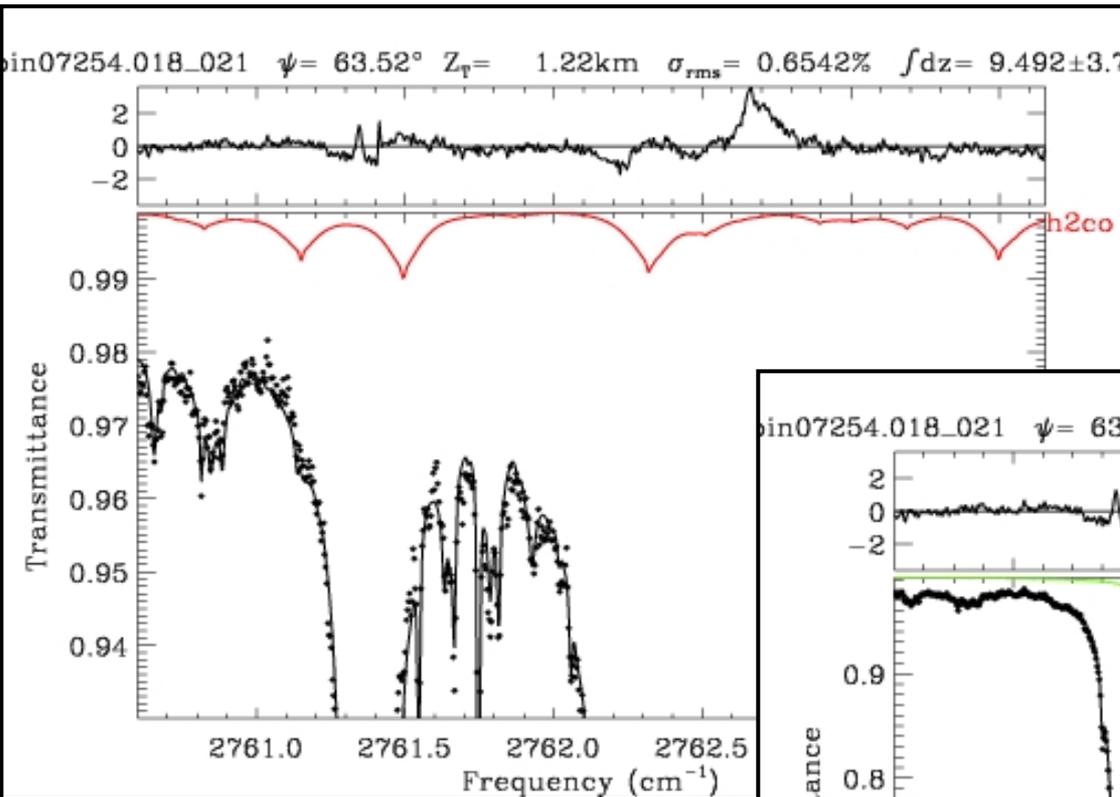
H₂CO absorptions are typically <1% deep, so 2-3% residuals are unacceptable.

Three spectroscopic problems are visible here:

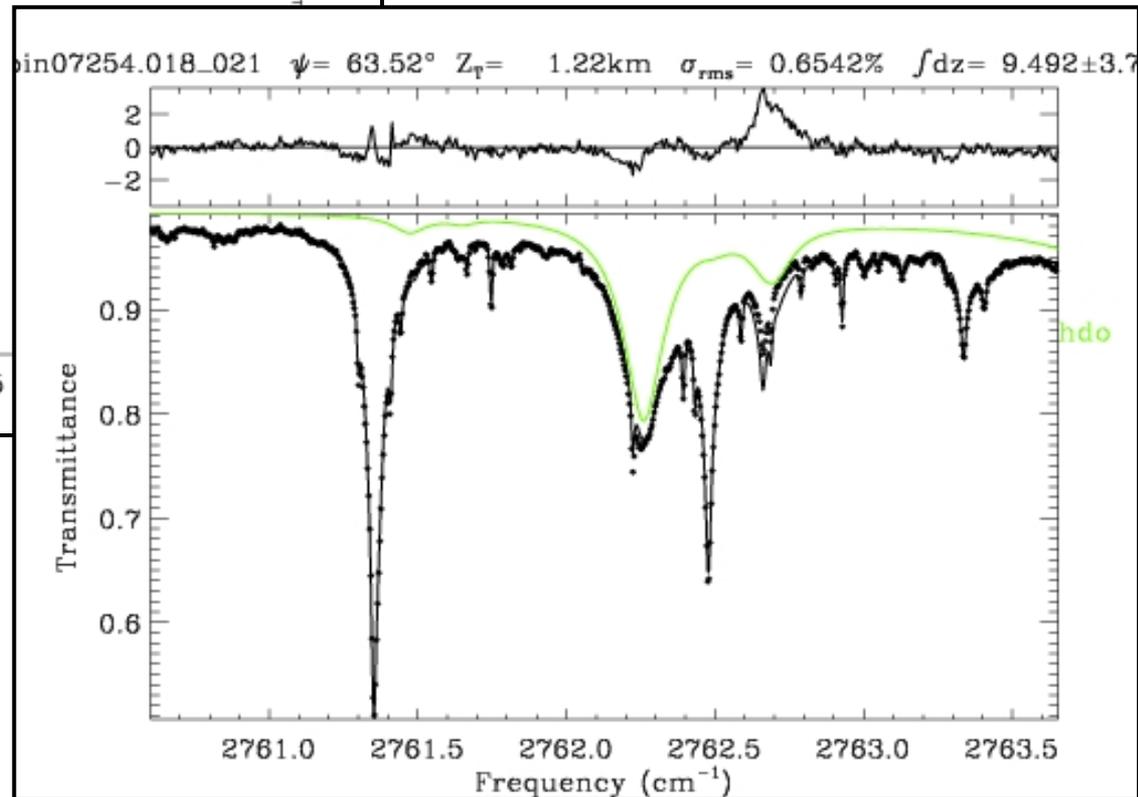
- 1) Broad positive residual around 2762.7 cm⁻¹, observed under humid conditions, due to intensity error in underlying HDO line.
- 2) CH₄ lines at 2761.34 and 2762.66 cm⁻¹ seem too narrow
- 3) O₃ line at 2761.41 cm⁻¹ is in wrong position.

H₂CO and HDO contributions

Left: H₂CO absorptions of primary interest in this window are only ~1% deep. So 3% residuals are unacceptable. Need to improve interfering spectroscopy.



Right: Large residual at ~2762.704 cm⁻¹ seems to be associated with an HDO line.



Toth 2003 Water Vapor Linelist

Available from: http://mark4sun.jpl.nasa.gov/data/spec/H2O/RAToth_H2O.tar

Non-HITRAN format containing calculated and measured intensities

All lines in the 2762 cm⁻¹ region are HDO (gas=49)

Calculated and Measured
Intensities agree well

Gas	I	Freq	Lower			Upper			Calculated Intensity	E"	ABHW	SBHW	SHIFT	?	?	Measured Intensity
49	1	2761.66304	7	5	3	8	5	4	8.33E-08	942.53244	.0608	.303	.00000	25.		2.35E-07
49	1	2762.26020	2	0	2	2	1	1	9.51E-06	66.18451	.1032	.430	.00000	3.	-20.	9.83E-06 2.
49	2	2762.50018	4	1	4	3	1	3	4.38E-07	99.58727	.0920	.496	.00000	6.		
49	1	2762.66663	5	1	4	5	0	5	9.11E-07	221.94609	.0934	.457	.00000	4.		2.22E-06
49	1	2762.70437	3	2	1	3	1	2	1.58E-06	116.46133	.0964	.470	.00000	5.	-7.	7.15E-07 10.
49	1	2764.54270	3	1	3	2	1	2	1.92E-04	58.12689	.0959	.510	.00000	8.	4.	1.91E-04 3.
49	1	2765.11285	1	0	1	1	1	0	7.47E-06	32.49637	.1050	.462	.00000	2.	5.	7.51E-06 3.

Calculated & Measured
Intensities disagree by factor 2.2

HITRAN 2008 WV positions & intensities 800-7900 cm⁻¹ mostly based on Toth's work. **Unfortunately the calculated intensities were adopted, not the measured intensities.** So changed intensity of 2762.704 cm⁻¹ HDO line from calculated to measured value.

From Rothman [JQSRT, 2013]

2.1.1 Deficiencies in the HITRAN2008 H₂O line list

Several deficiencies related to the water-vapor line list were identified and addressed:

(1) Due to the difficulties associated with measurements of water-vapor line intensities, some values given in HITRAN were reported to have problems. For instance, intensities in the 8000-9000 cm⁻¹ spectral region were reported to have been systematically in error (10-15%) by authors of more recent experiments [4], theoretical calculations [5], and atmospheric retrievals [6, 7].

Less dramatic, but still noticeable (5-10%) inconsistencies were identified below 8000 cm⁻¹ (see, for instance Refs. [8-10]) where a majority of intensities down to 1750 cm⁻¹ (for stronger lines) originated from the unpublished SISAM database of Toth [11]. It is worth pointing out that the SISAM database tabulates intensities obtained both experimentally and using a semi-empirical model. However, only the calculated ones were adopted into the HITRAN database, and it was later determined that the experimental values were often superior to the calculated ones. In fact, the water vapor line list used by the **TCCON** (Total Carbon Column Observing Network) community [12] employs the measured values from Toth when the retrievals using HITRAN were not satisfactory.

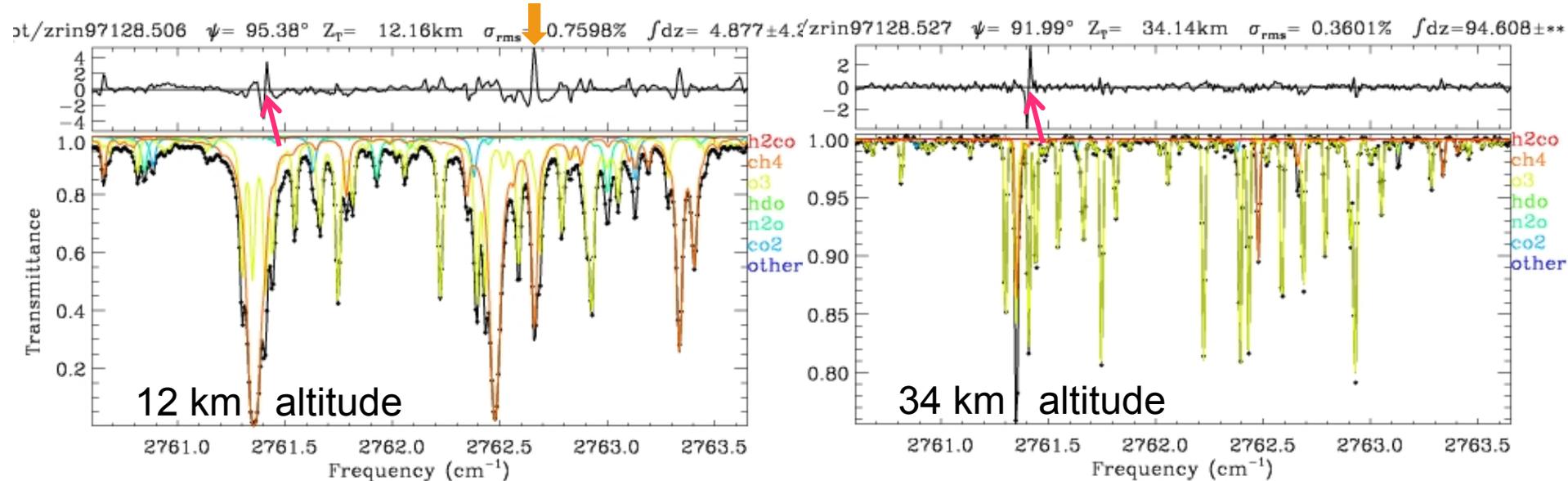
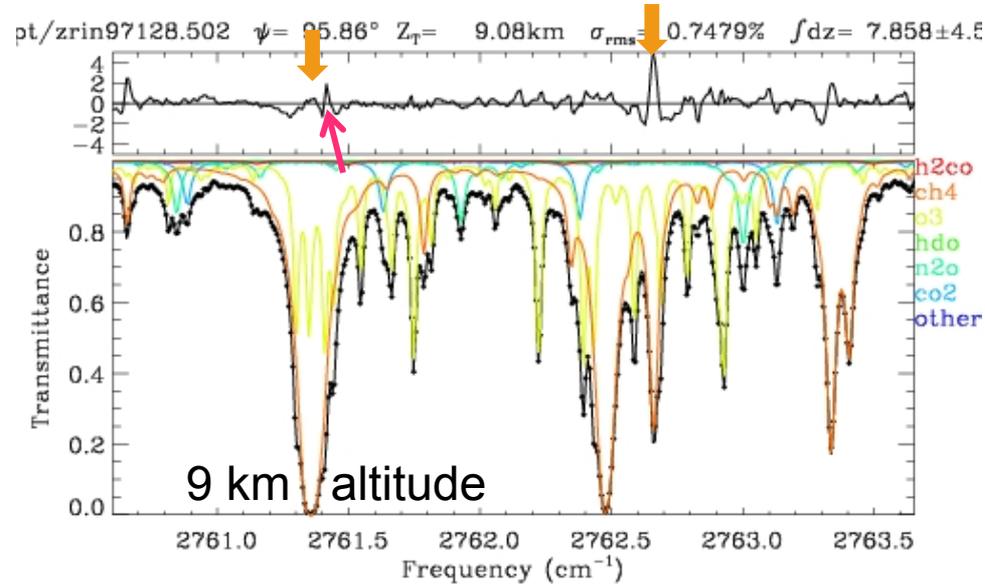
MkIV balloon spectra: 9, 12, 34 km

HITRAN 2008 linelist

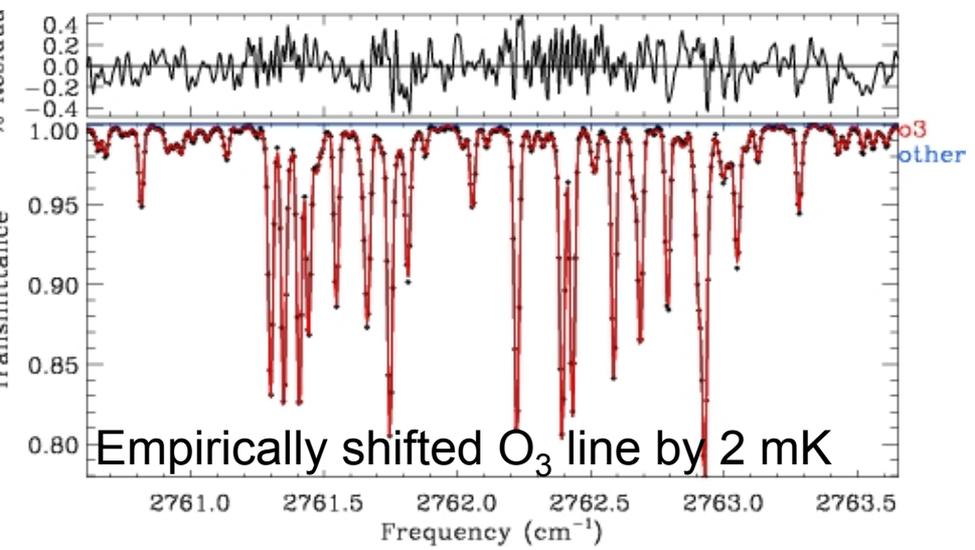
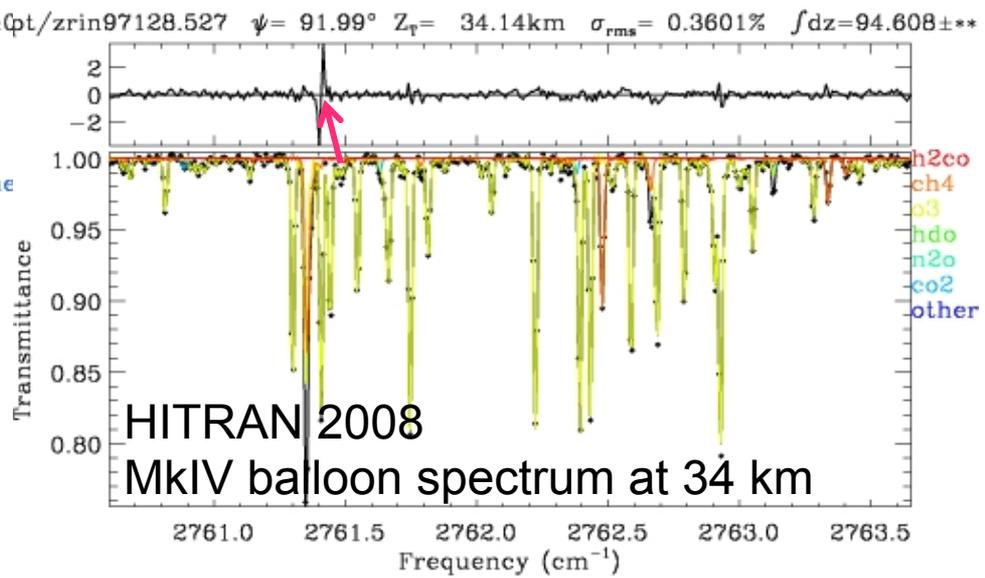
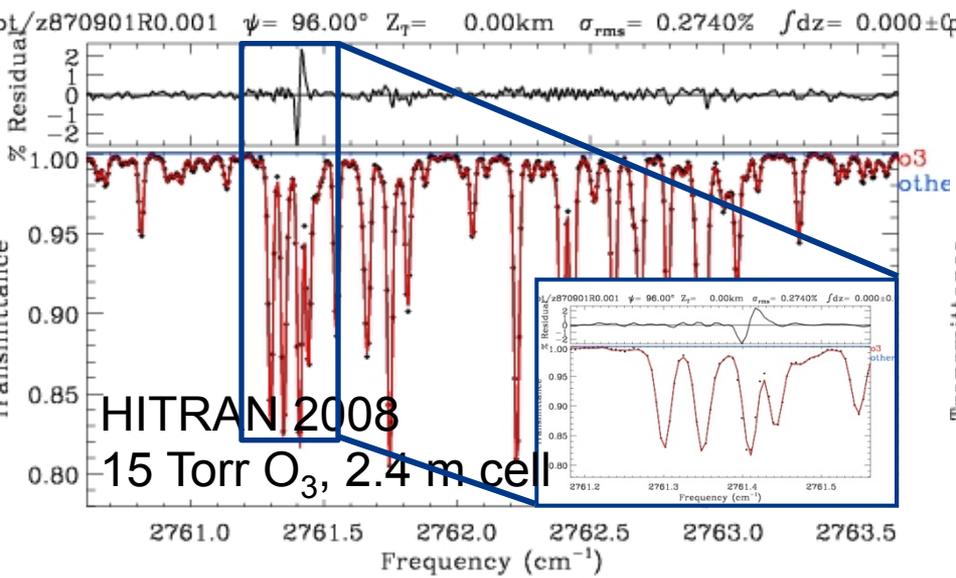
Balloon spectra confirm problems seen in ground-based spectra:

- CH_4 line at 2762.66 cm^{-1} too narrow
- O_3 line at 2761.41 cm^{-1} position error

[HDO lines too weak to be observed above 9 km altitude in this region.]



Fitted Kitt Peak laboratory O₃ spectra

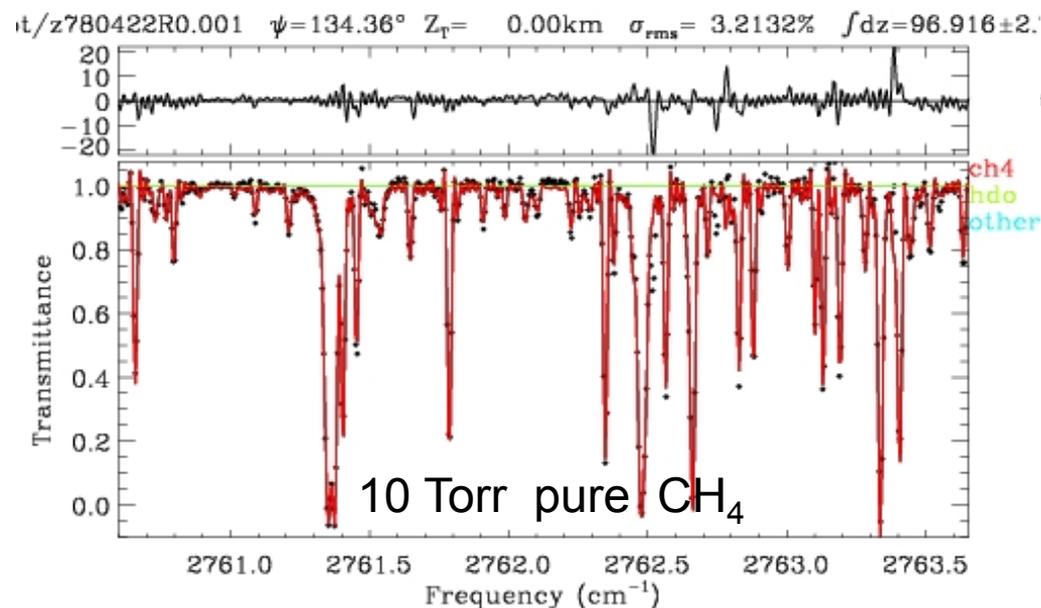
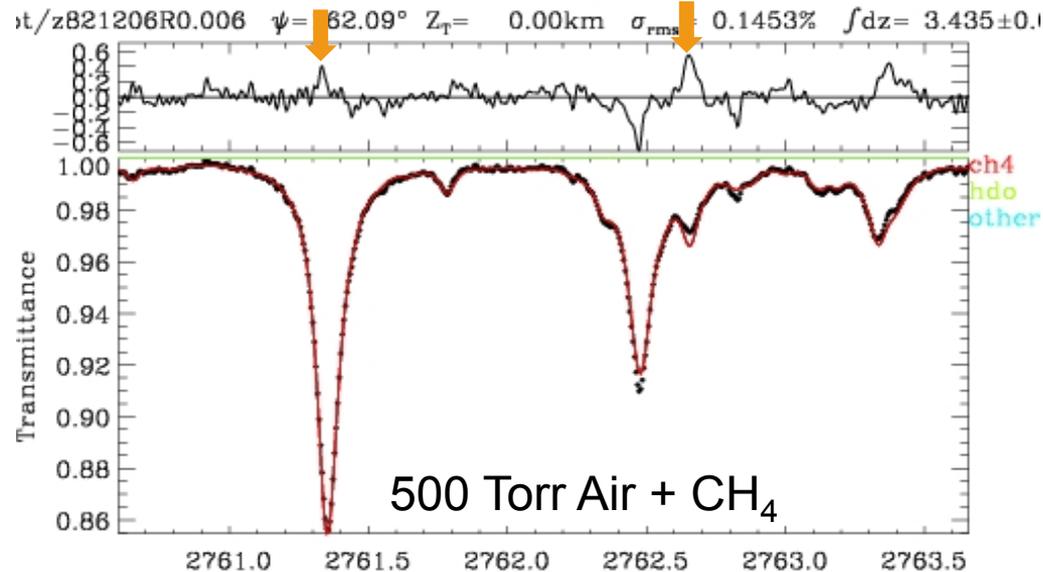


The Kitt Peak O₃ spectral fitting residuals are remarkably similar to those in the 34 km MkIV balloon spectrum.

After empirically correcting the position of the wayward O₃ line at 2761.4 cm⁻¹, the KP fitting residuals improved by a factor 5

How can one line position be so poor, when all the others are so good?

Fits to KP Lab CH₄ Spectra -- HITRAN

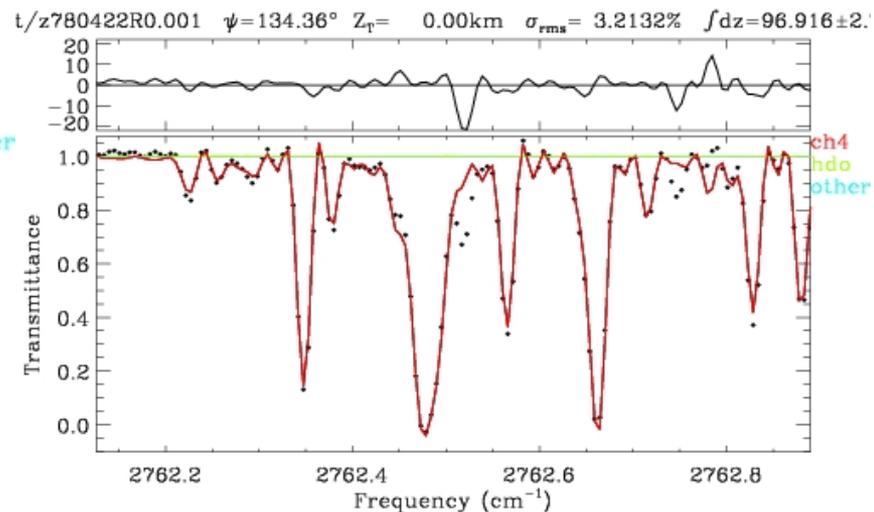


HITRAN 2008 Linelist

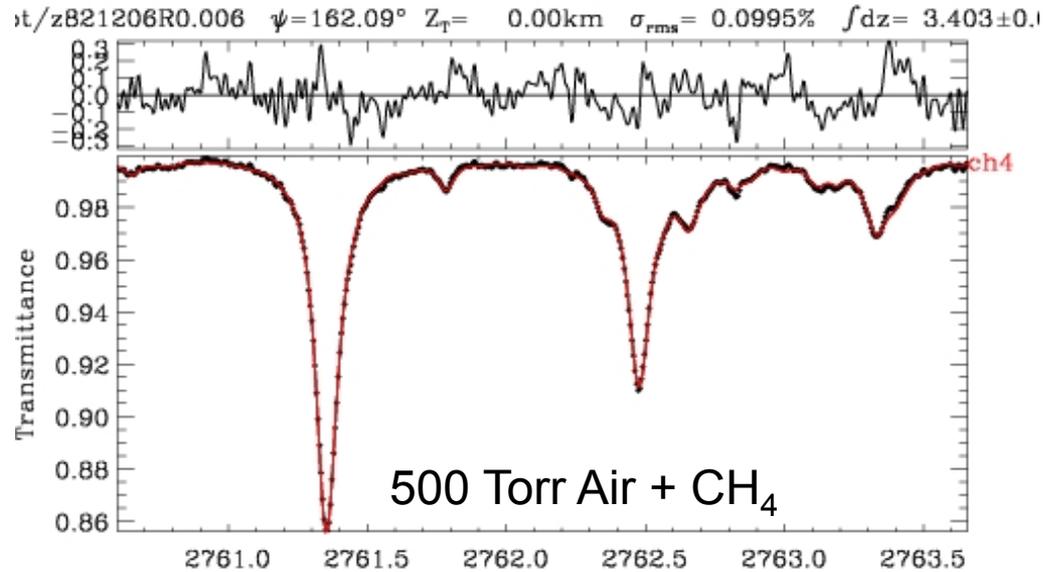
Very similar residuals to those seen in MkIV balloon spectra

Problems seen in high pressure lab spectrum, not low pressure - width.

Also, missing or misplaced line at 2762.521 cm⁻¹

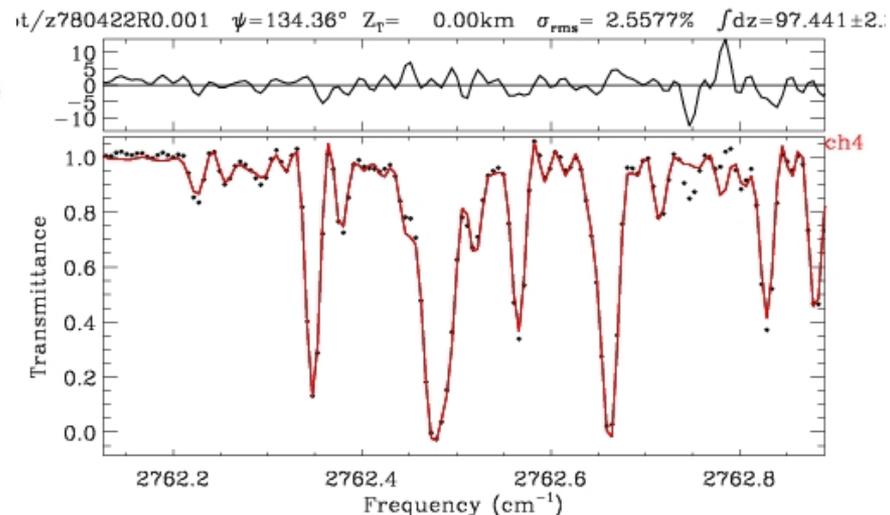
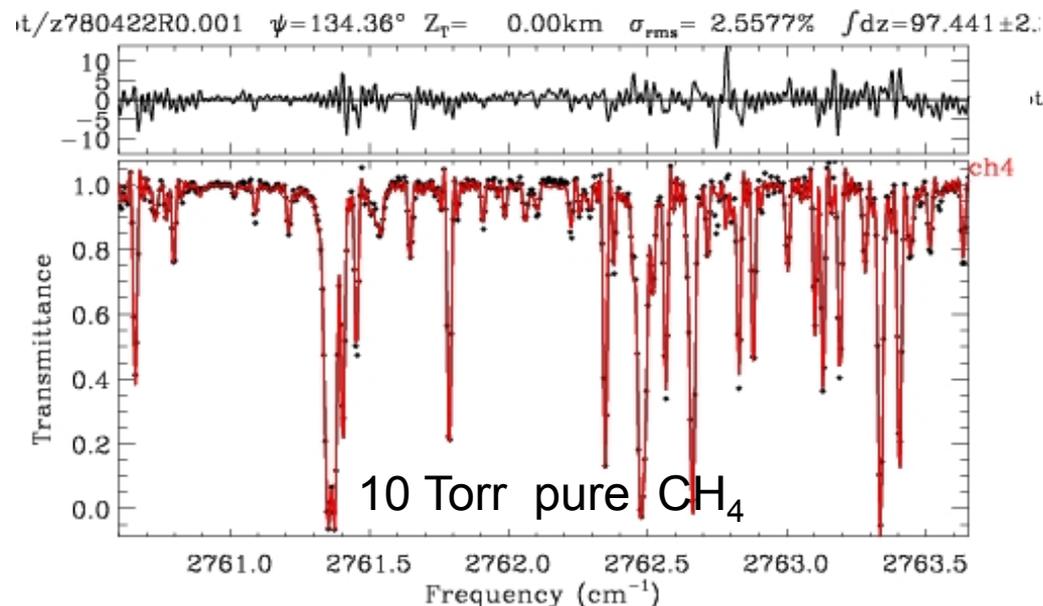


Fits to KP Lab CH₄ Spectra – Adjusted

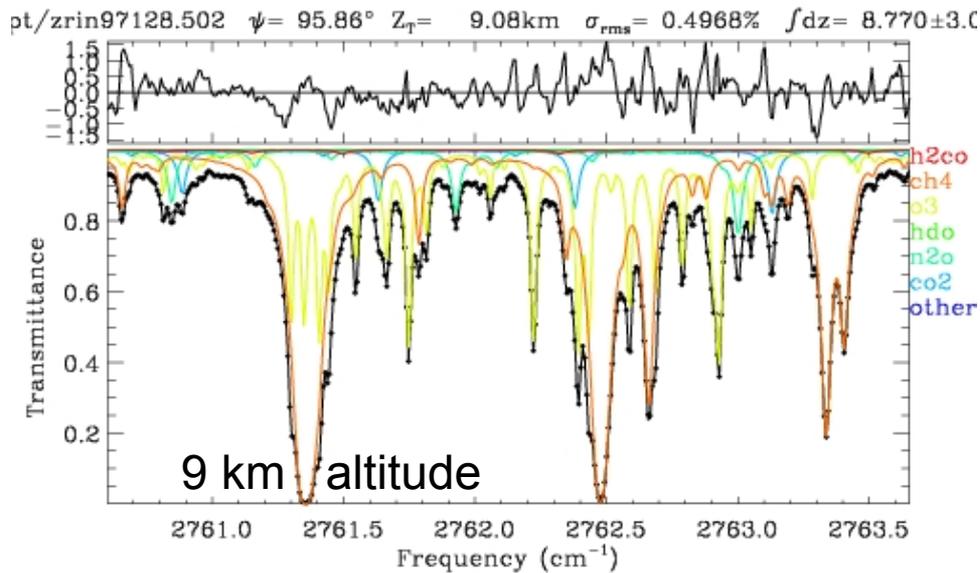


Empirically Adjusted Linelist

After manually adjusting the widths of the stronger CH₄ lines and adding the missing line at 2762.52 cm⁻¹, fits to lab spectra are much improved, both at low and high pressure.



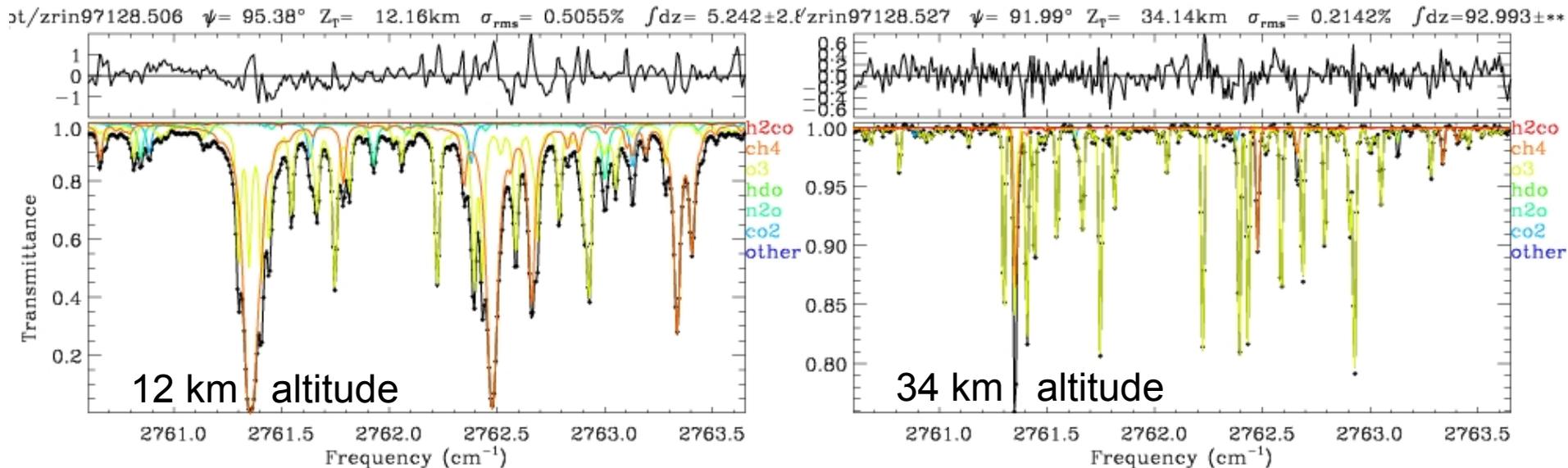
Re-fitted MkIV solar spectra: 9, 12, 34 km



Using Empirically Adjusted Linelists

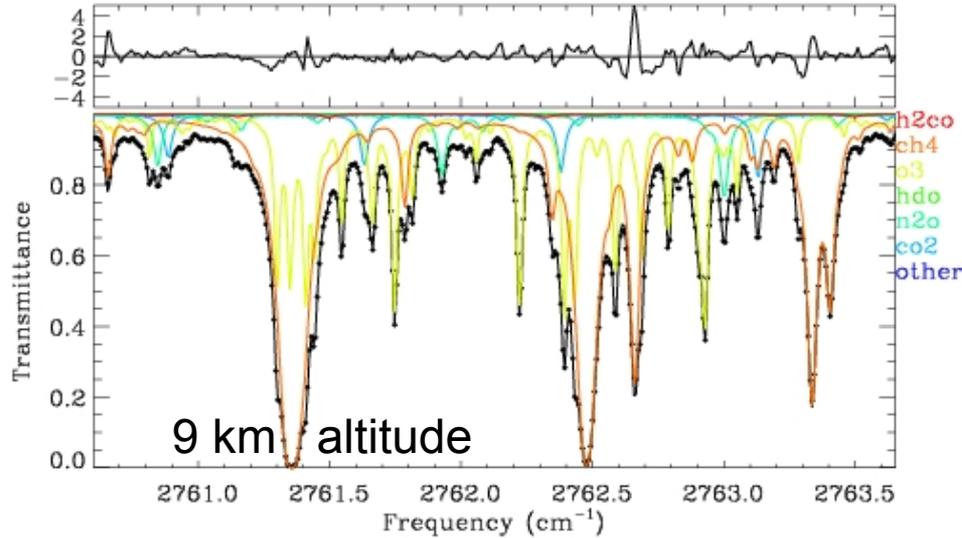
Peak residuals are 2-5 times smaller than using HITRAN 2008

RMS residuals are reduced by 30%



MkIV balloon spectra: 9, 12, 34 km

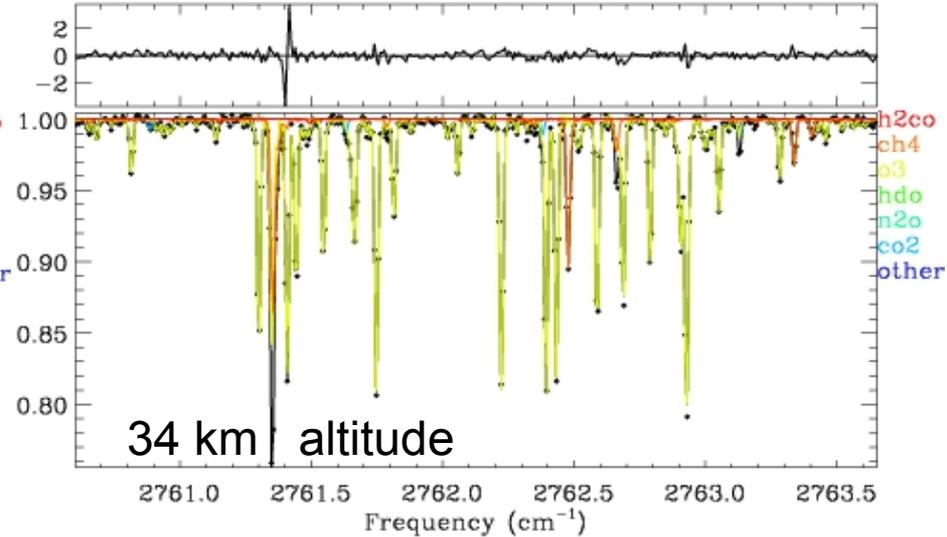
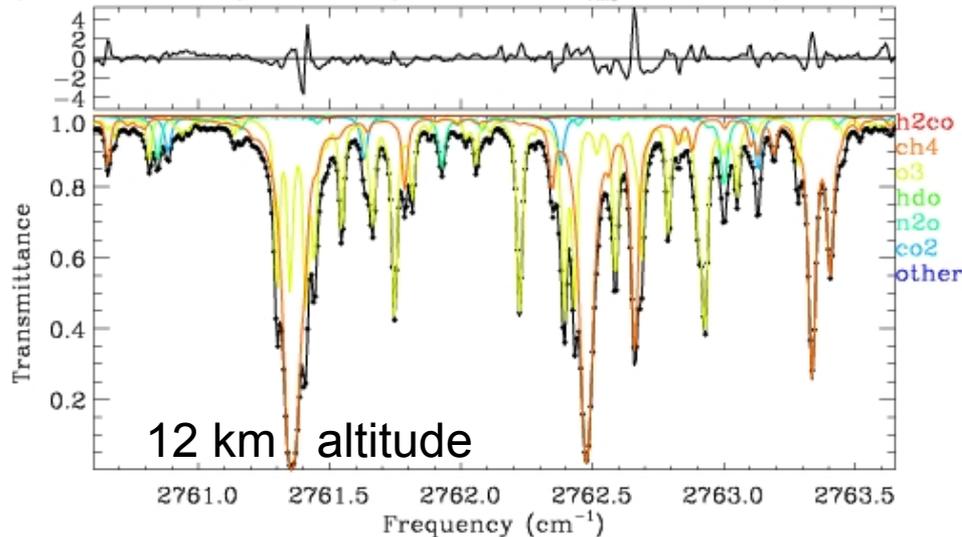
pt/zrin97128.502 $\psi = 95.86^\circ$ $Z_T = 9.08\text{km}$ $\sigma_{\text{rms}} = 0.7479\%$ $\int dz = 7.858 \pm 4.5$



HITRAN 2008 linelist

Reminder of what it looked like
Before empirical adjustments.

pt/zrin97128.506 $\psi = 95.38^\circ$ $Z_T = 12.16\text{km}$ $\sigma_{\text{rms}} = 0.7598\%$ $\int dz = 4.877 \pm 4.2$ / zrin97128.527 $\psi = 91.99^\circ$ $Z_T = 34.14\text{km}$ $\sigma_{\text{rms}} = 0.3601\%$ $\int dz = 94.608 \pm **$



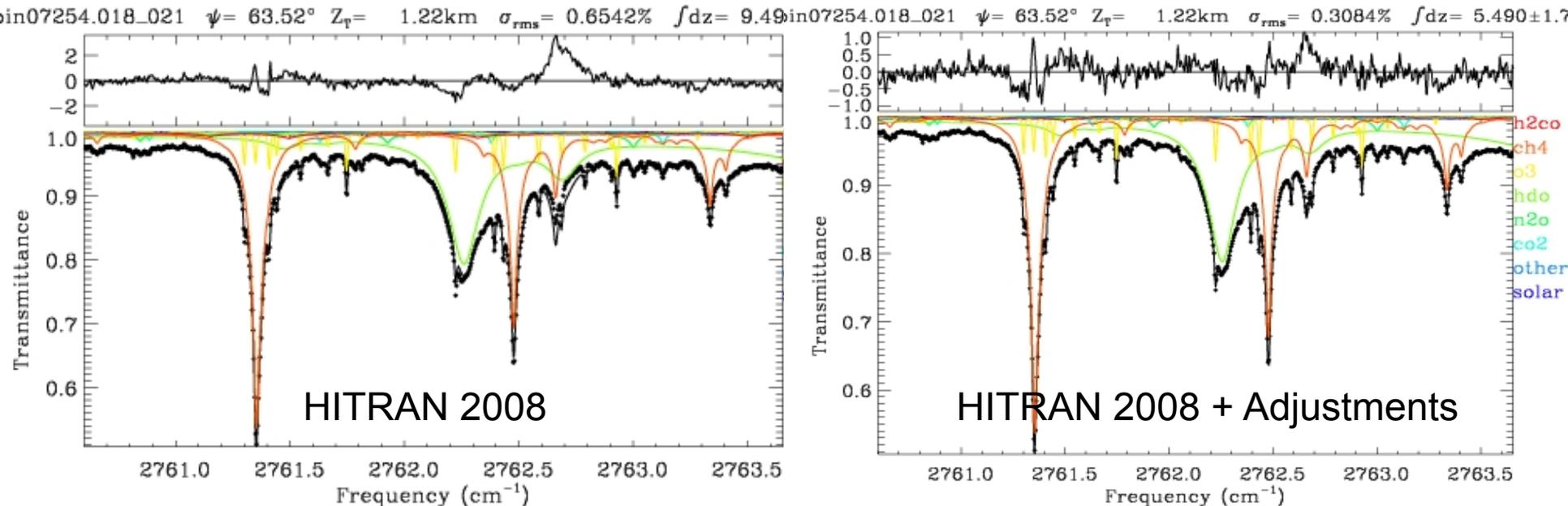
Summary: Ground-based MkIV H₂CO

Main linelist adjustments were:

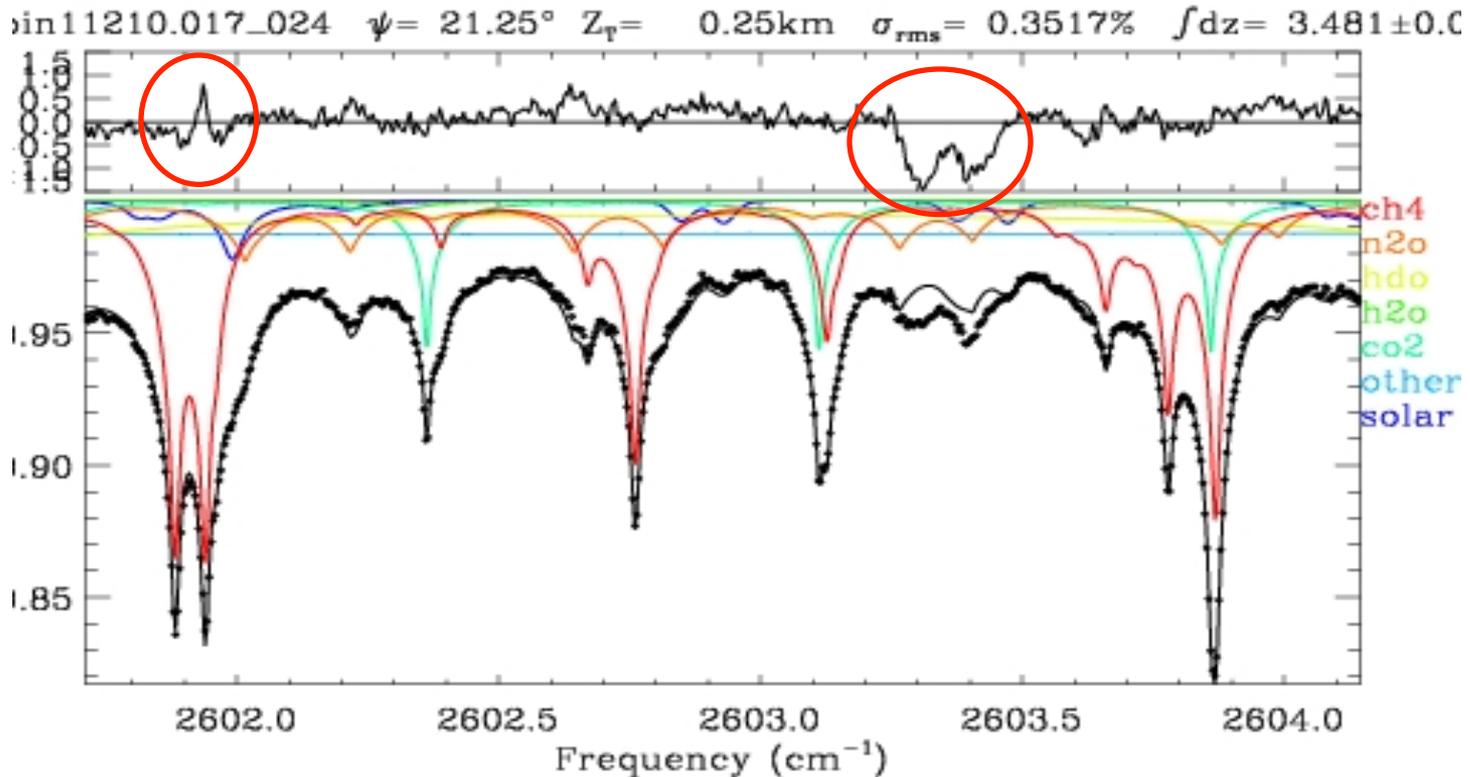
- Factor 2.2 reduction in strength of 2762.70 cm⁻¹ HDO line (Toth's obs)
- Increased width of 2762.662 cm⁻¹ CH₄ line from 0.056 to 0.070 cm⁻¹/atm
- Added missing CH₄ line at 2762.521 cm⁻¹, consistent with KP lab spectra
- Shifted position of the O₃ line at 2761.4095 to 2761.4074 cm⁻¹

Adjustments reduce rms residuals by factor 2 for wet case, and 20% for dry.

For wet spectrum, linelist adjustments reduce retrieved H₂CO by 40%

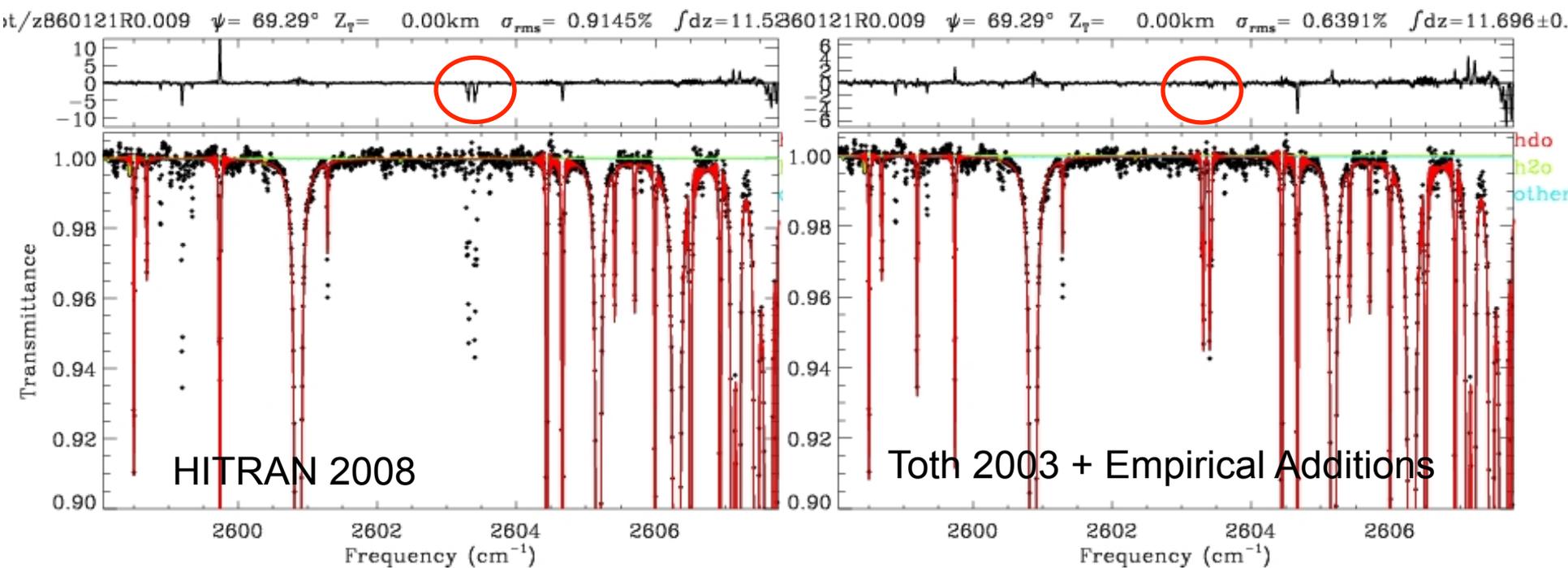


Case Study 3: Ground-based CH₄



One of three mid-IR windows used to retrieve CH₄ from the ground
Large residuals seen at 2603.3 and 2603.4 cm⁻¹ under humid conditions.
Residuals can reach 1.5% at low airmass and 10% at high airmass.
Shape of residuals, and their variability suggest water vapor.
Also, CH₄ line at 2601.93 cm⁻¹ has wrong shape (width problem?)

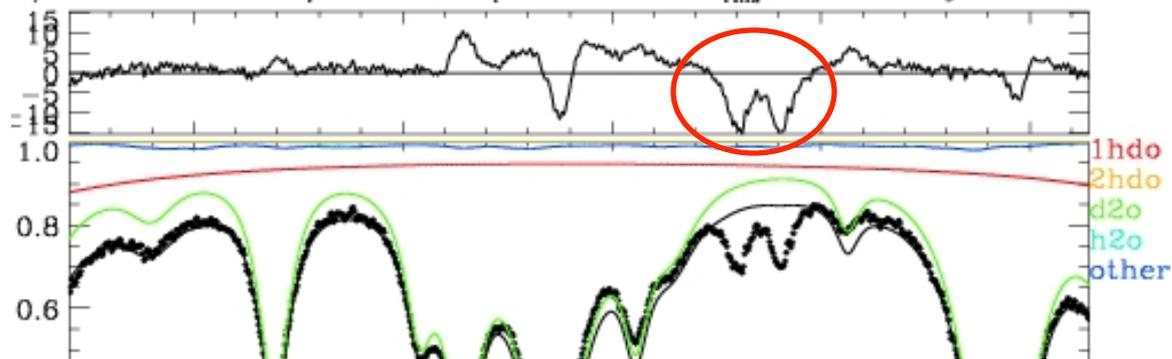
Kitt Peak HDO Laboratory spectrum



Fitted a KP lab H_2O spectrum measured in Jan 1986 at 4 Torr and 24C.
Left panel shows several lines missing from HITRAN 2008 in this region.
Right panel shows fits using HDO linelist empirically adjusted/supplemented with several new lines. Note change in residual scale 12% \rightarrow 6 % peak.

500 Torr KP D-enriched lab spectrum

st/z970327R0.014 $\psi = 66.22^\circ$ $Z_T = 0.00\text{km}$ $\sigma_{\text{rms}} = 3.1120\%$ $\int dz = 1.281 \pm 0.1$



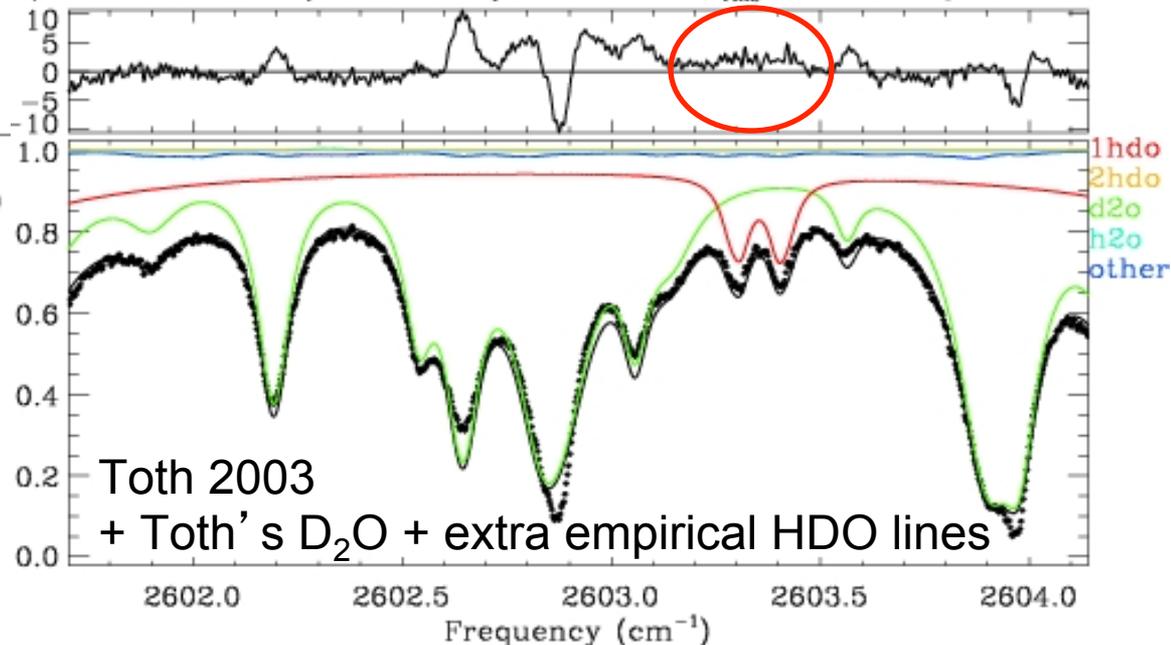
Residuals seen in fits of atmospheric spectra at 2603.3 and 2603.4 cm^{-1} also seen in D-enriched lab spectra, implying that missing lines are HDO.

HITRAN 2008
+ Toth's D₂O

2602.0 2602.5 2603.0
Frequency (cm^{-1})

Adding extra HDO lines fixes the problem. Other large residuals due to D₂O, which are not a problem for atmospheric observations.

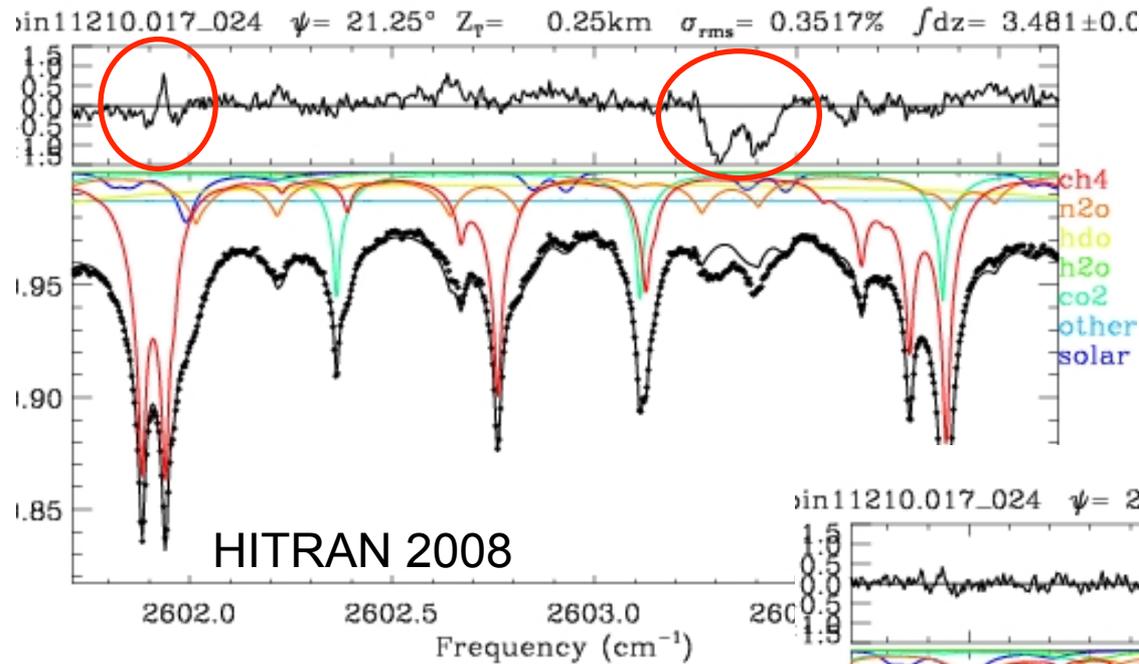
st/z970327R0.014 $\psi = 66.22^\circ$ $Z_T = 0.00\text{km}$ $\sigma_{\text{rms}} = 2.2492\%$ $\int dz = 1.380 \pm 0.1$



Toth 2003
+ Toth's D₂O + extra empirical HDO lines

2602.0 2602.5 2603.0 2603.5 2604.0
Frequency (cm^{-1})

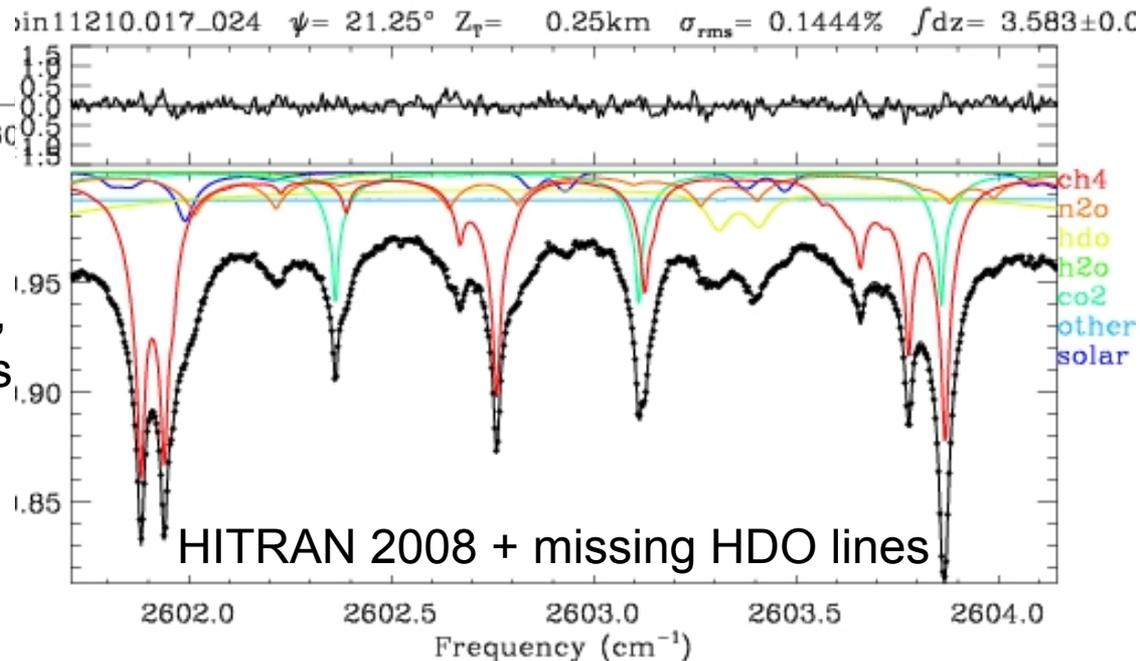
Summary – Ground-based MkIV CH₄



HITRAN 2008

Addition of missing HDO lines improves spectra fits by factor 2.5, under humid conditions & changes retrieved CH₄ by up to 3%. Since atmospheric HDO is highly variable, the missing lines make the retrieved CH₄ seem noisy.

Addition of the missing HDO lines completely fixes residuals in fits to atmospheric solar spectra



HITRAN 2008 + missing HDO lines

Solar Spectra for Spectroscopy Validation

In almost any region in the mid-IR, systematic residuals arising from spectroscopic inadequacies can be seen in solar atmospheric spectra.

Non-linear least-squares spectral fitting techniques, generally used in remote sensing, give undue influence to the largest residuals. So need to fix or avoid them.

In 90% of cases, the pattern of systematic residuals seen in fits to solar spectra are also apparent in fits to lab spectra with similar conditions.

So analysis of relatively few solar spectra measured under a wide, but well known, range of conditions (cold/warm, low/high airmass) can provide a good test of spectroscopy of nearly all gases important for Earth remote sensing, identifying:

- Important missing lines
- Errors in existing lines

Solar spectra also have the benefit of high SNR and broad spectral coverage because the sun is a very bright source. Allows band-to-band consistency checks.

Atmospheric spectra not only allow identification of spectroscopic problems, they also provide diagnostic information, and allow evaluation of proposed solutions

HITRAN 2012 was released June 6

The HITRAN 2012 Molecular Spectroscopic Database

L.S. Rothman^{a,*}, I.E. Gordon^a, Y. Babikov^b, A. Barbe^c, D.Chris Benner^d, P.F. Bernath^e, M. Birk^f, L. Bizzocchi^g, V. Boudon^h, L.R. Brownⁱ, A. Campargue^j, K. Chance^a, E.A. Cohenⁱ, L.H. Coudert^k, V.M. Devi^d, B.J. Drouinⁱ, A. Fayt^l, J.-M. Flaud^k, R.R. Gamache^m, J.J. Harrisonⁿ, J.-M. Hartmann^k, C. Hill^o, J.T. Hodges^p, D. Jacquemart^q, A. Jolly^k, J. Lamouroux^{k,m}, R.J. LeRoy^r, G. Li^a, D.A. Long^p, O.M. Lyulin^b, C.J. Mackie^{a,†}, S.T. Massie^s, S. Mikhailenko^b, H.S.P. Müller^t, O.V. Naumenko^b, A.V. Nikitin^b, J. Orphal^u, V. Perevalov^b, A. Perrin^k, E.R. Polovtseva^b, C. Richard^a, M.A.H. Smith^v, E. Starikova^b, K. Sungⁱ, S. Tashkun^b, J. Tennyson^o, G.C. Toonⁱ, V.I.G. Tyuterev^c, J. Vander Auwera^w, G. Wagner^f

Contains 4.4 million lines in main HITRAN 2012 linelist (HITRAN 2008 had 2.7M)
Plus nearly 3 million lines in supplemental folder (**SF6**, CF4, ClNO3)

New gases: C₄H₂, HC₃N, H₂, CS, SO₃

New isotopologs: C¹⁷O₂, H¹⁵NO₃, DF, DCl, DBr, DI, ¹³COF₂, ¹³C₂H₆, C₂HD, ¹⁵N₂

HITRAN 2012 Evaluation

Have recently been evaluating a beta release of HITRAN 2012 database

I mainly used MkIV balloon occultation transmittance spectra for this:

1. Solar and instrumental features removed by the ratioing
2. Cover wide range of conditions:
 - Temperatures from 200K to 270K
 - Pressures from 3 mbar to 500 mbar
 - Large variation in gas amounts

This methodology is very effective at finding large residuals. These are very important in least-squares fitting.

In subsequent plots, three different linelists are compared:

- HITRAN 2008
- HITRAN 2012
- ATM 2013

ATM 2013 Linelist

ATM 2013 is an empirically adjusted spectroscopic database prepared by me.

Mostly based on HITRAN 2008, but with many exceptions & empirical adjustments. For example, H₂O is still mostly based on original Toth [2003] work, but using measured intensities instead of calculated (as HITRAN had intended for HIT2008)

ATM 2013 is the linelist currently distributed with TCCON.

Upon release of a new linelist update, I test it in the intervals of interest:

- If it is better, I adopt it
- If it is worse I reject it

Most often results are mixed. I adopt new linelist while manually fixing the things that are worse.

MkIV Ground-based

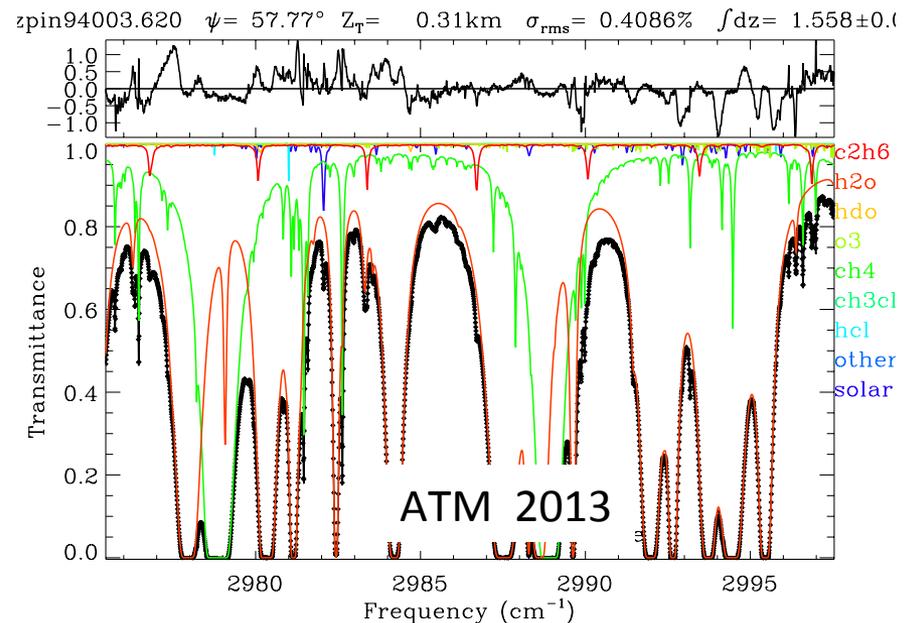
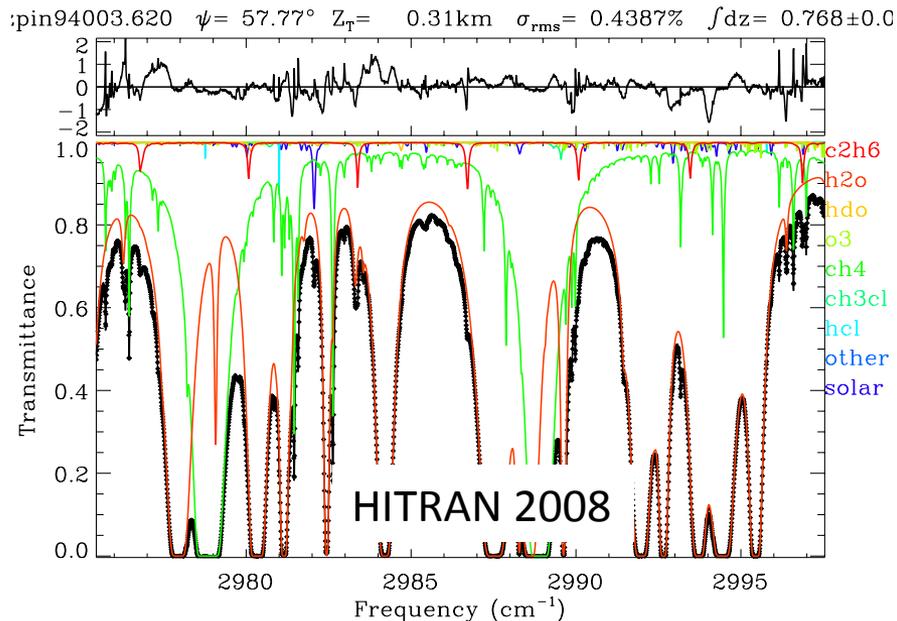
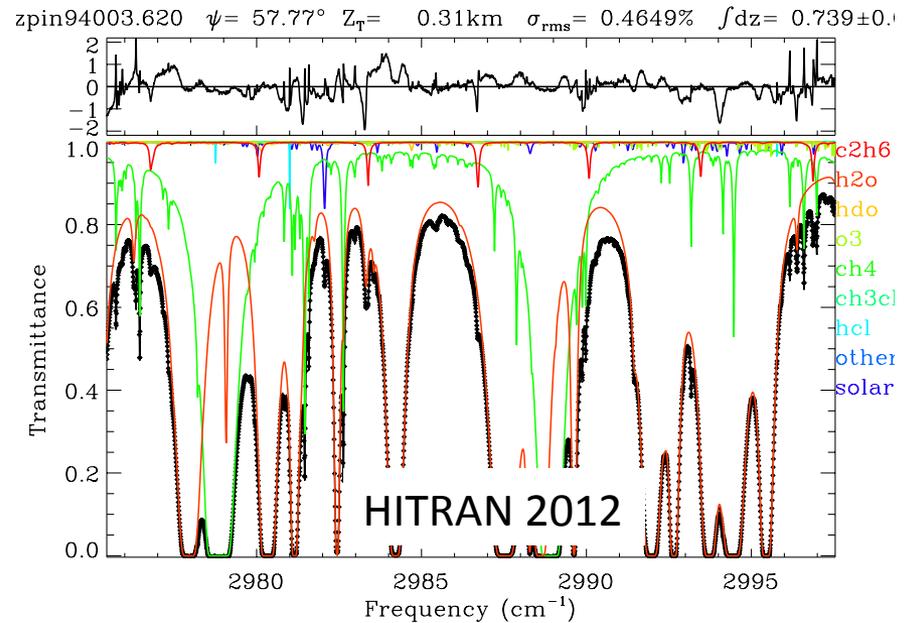
2975 to 3000 cm^{-1} region used for retrieval of C_2H_6

Systematic residuals far exceed noise

Strong interfering CH_4 and H_2O absorption

HITRAN 2012 is worse than HITRAN 2008 !!

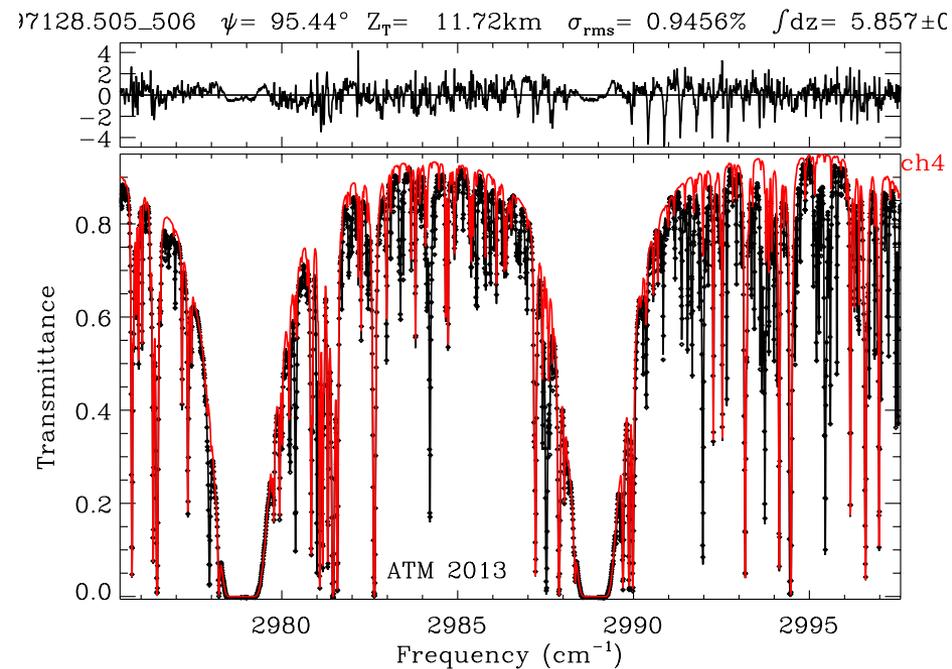
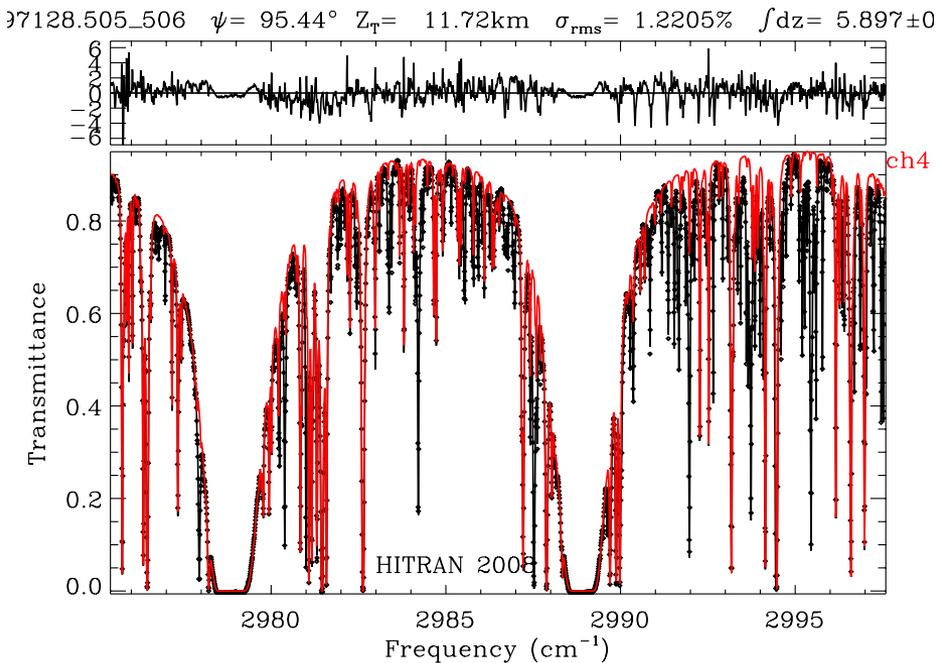
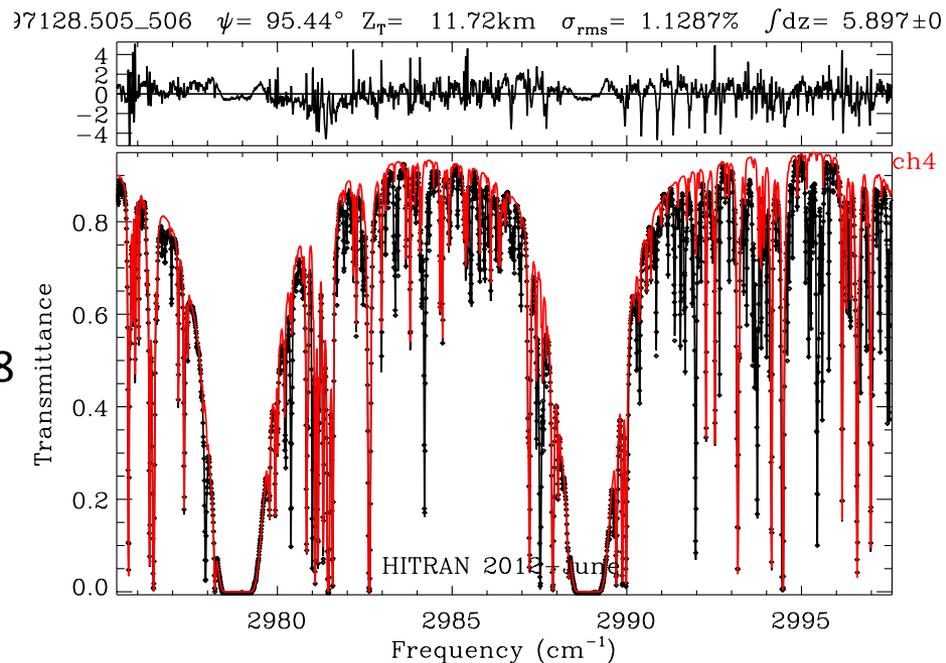
But ATM 2013 is better than either. Why?



MkIV Balloon Spectral Fits 12 km altitude

Here HITRAN 2012 is better than HITRAN 2008
Widths are less important at 12 km altitude

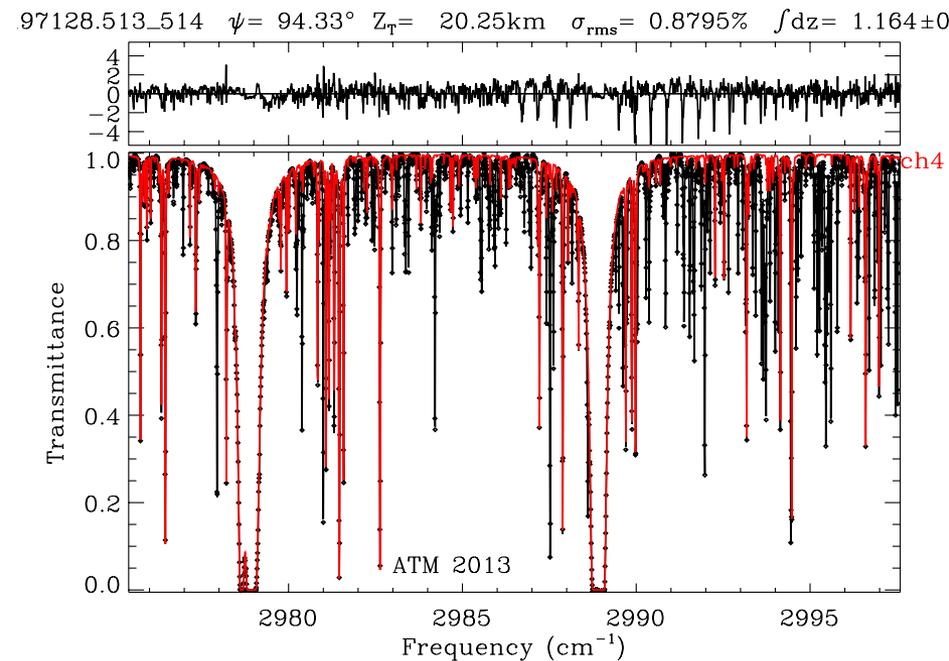
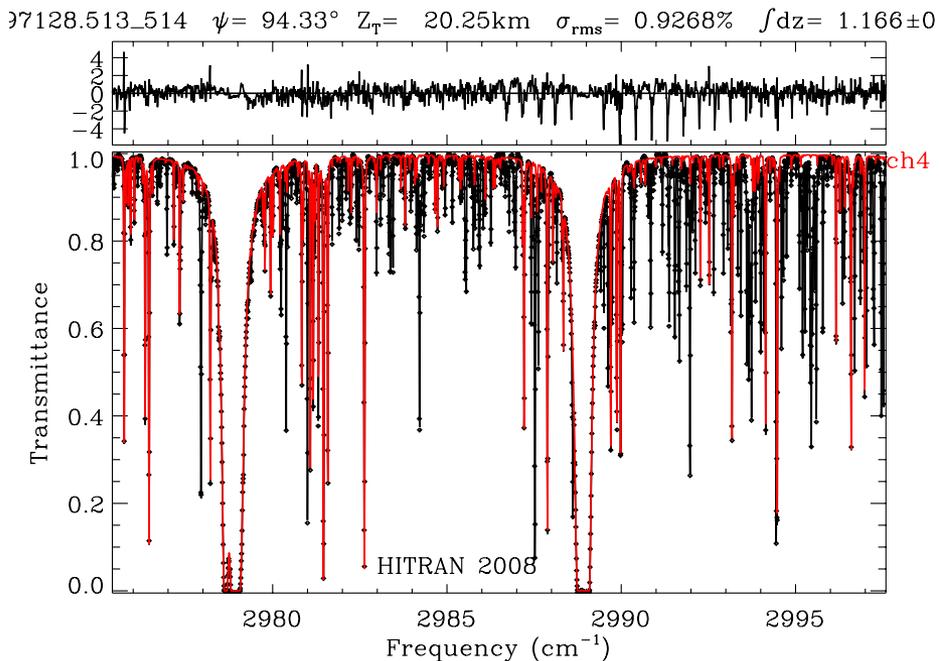
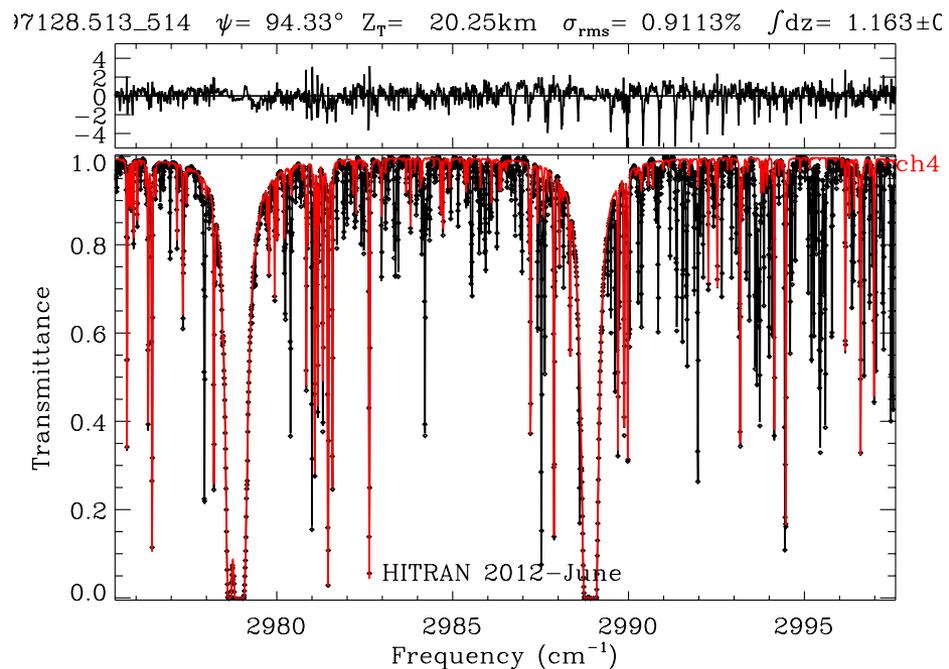
Residuals dominated by missing HNO_3 band



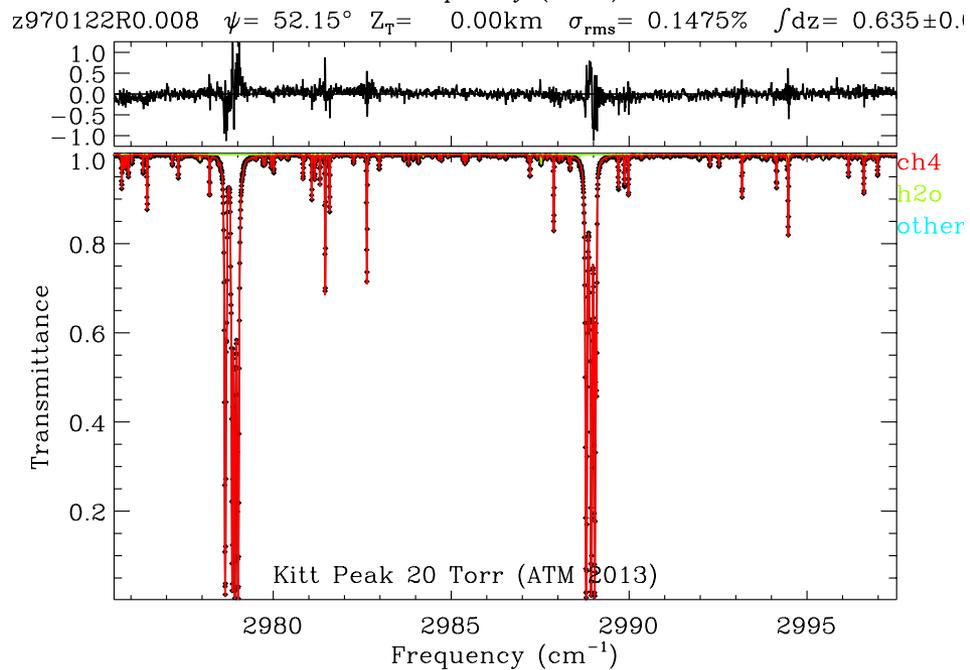
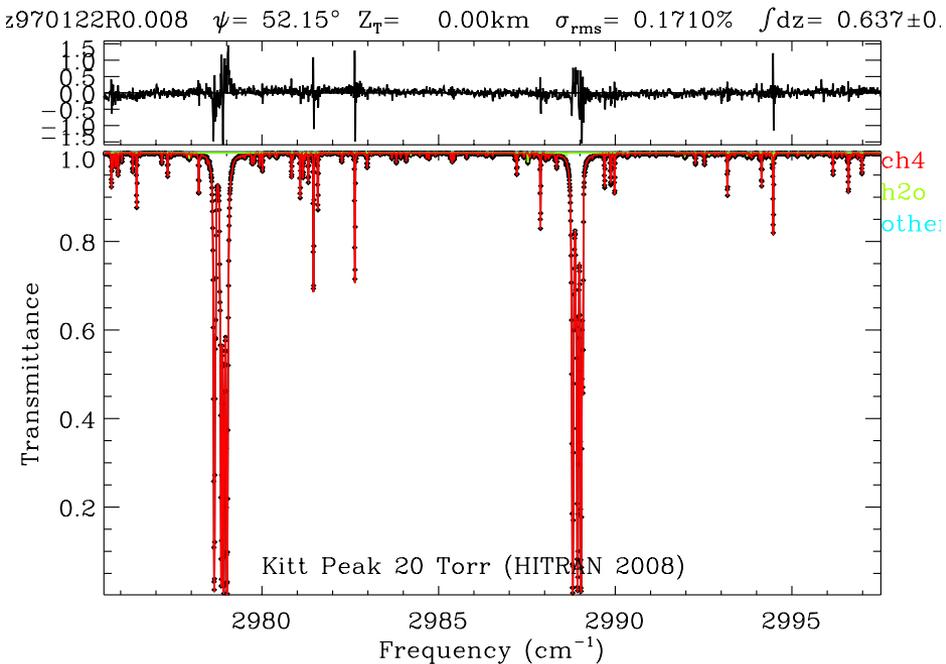
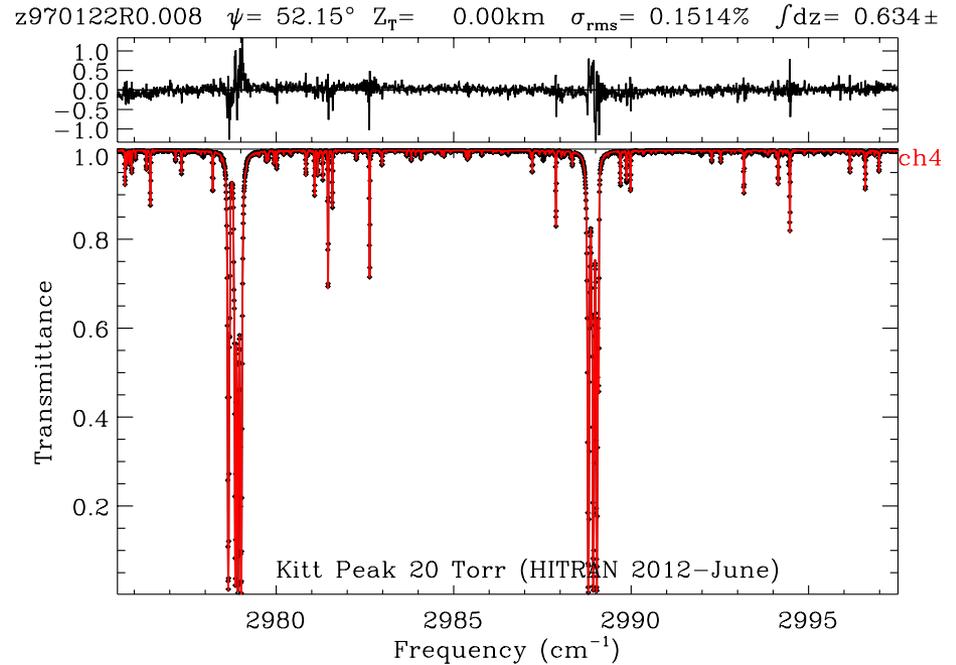
MkIV Balloon 20 km altitude

HNO₃ residuals are more apparent

All three linelists are missing HNO₃

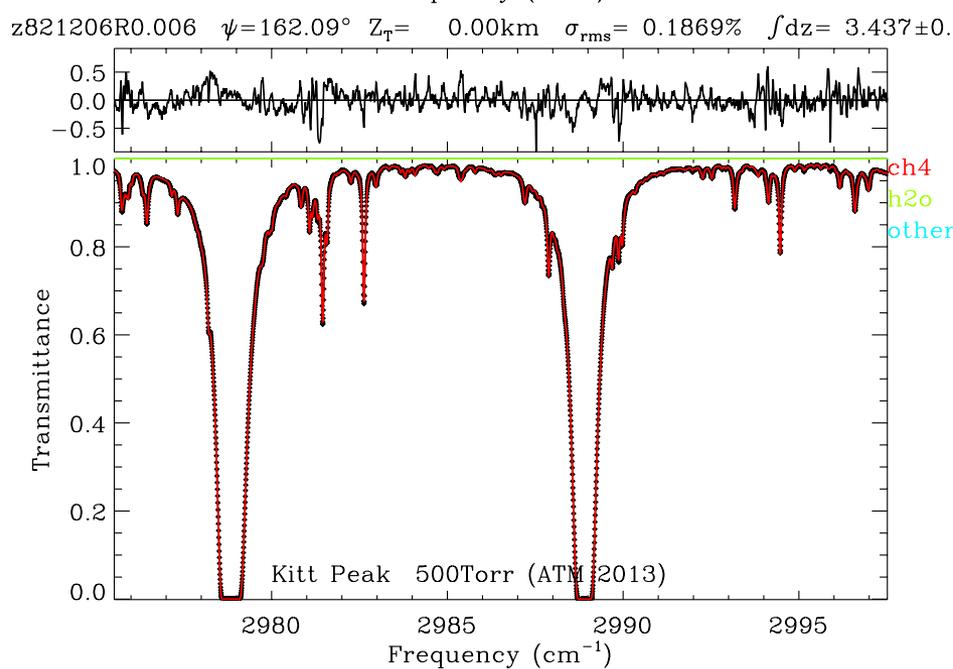
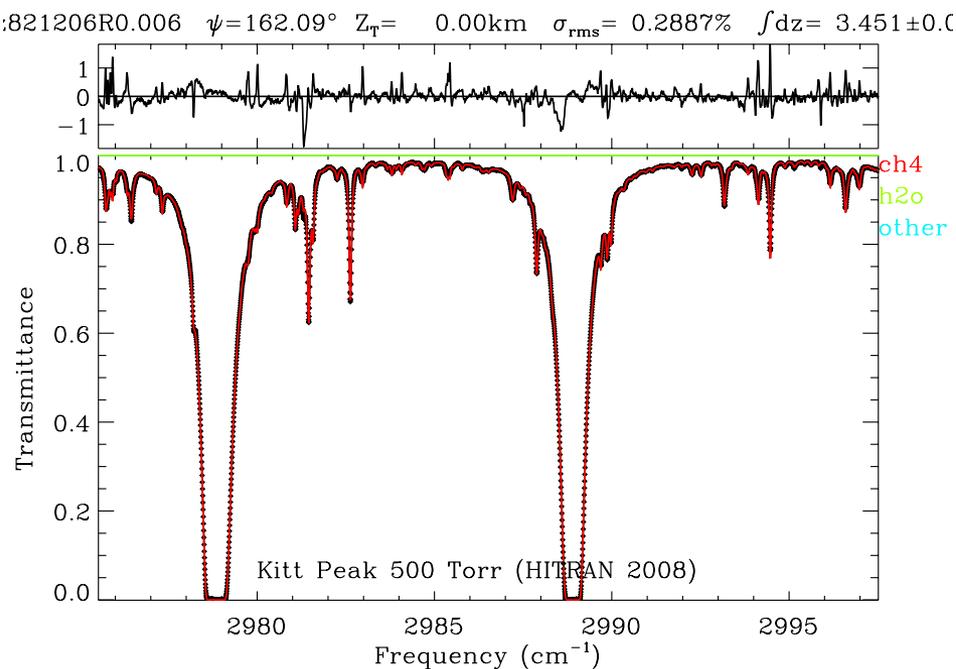
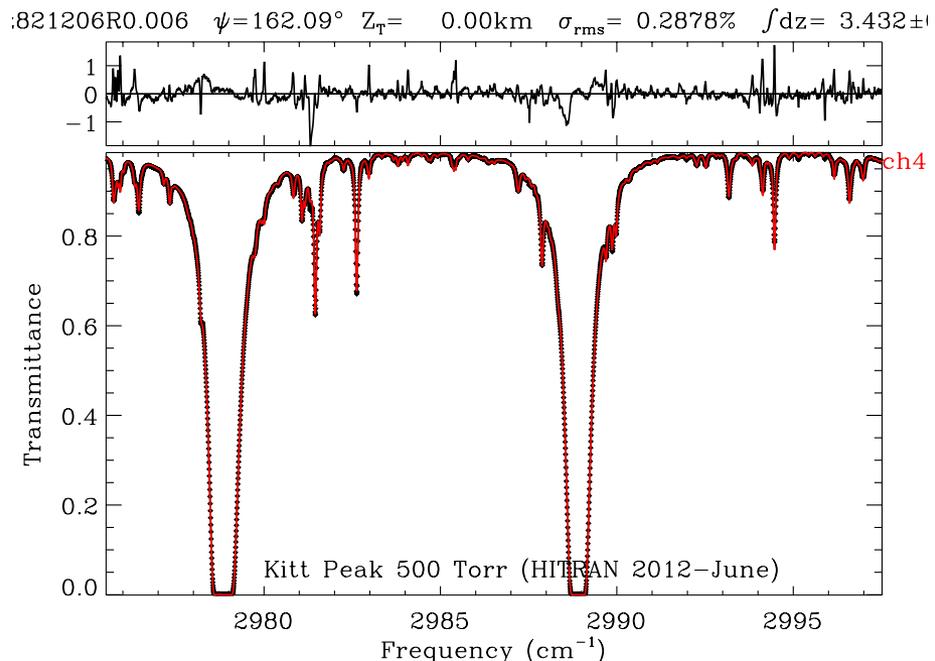


Kitt Peak Lab CH₄ 20 Torr



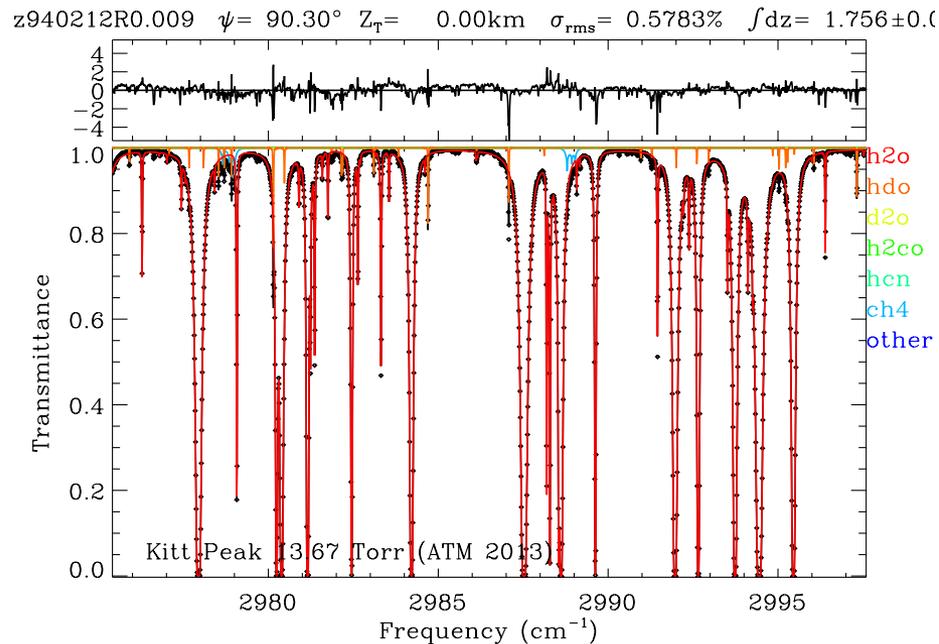
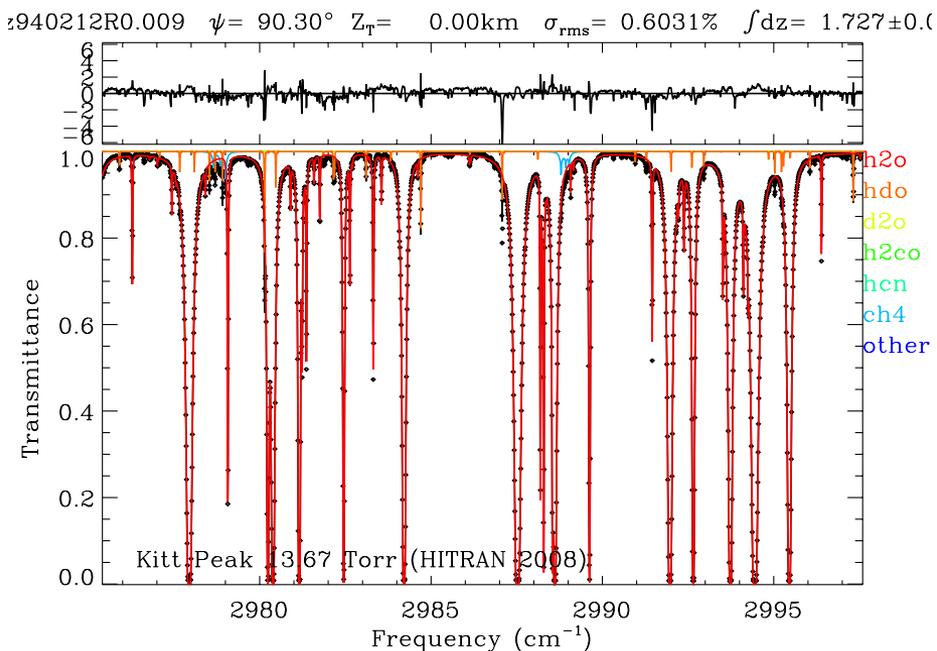
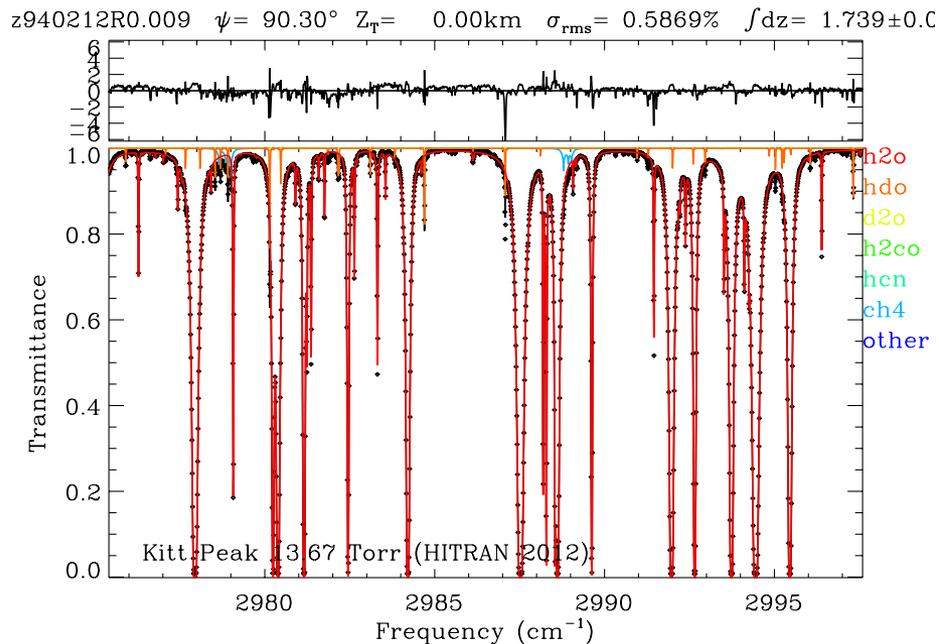
Kitt Peak Lab CH₄ 500 Torr

(Spectrum measured in 1982 !)



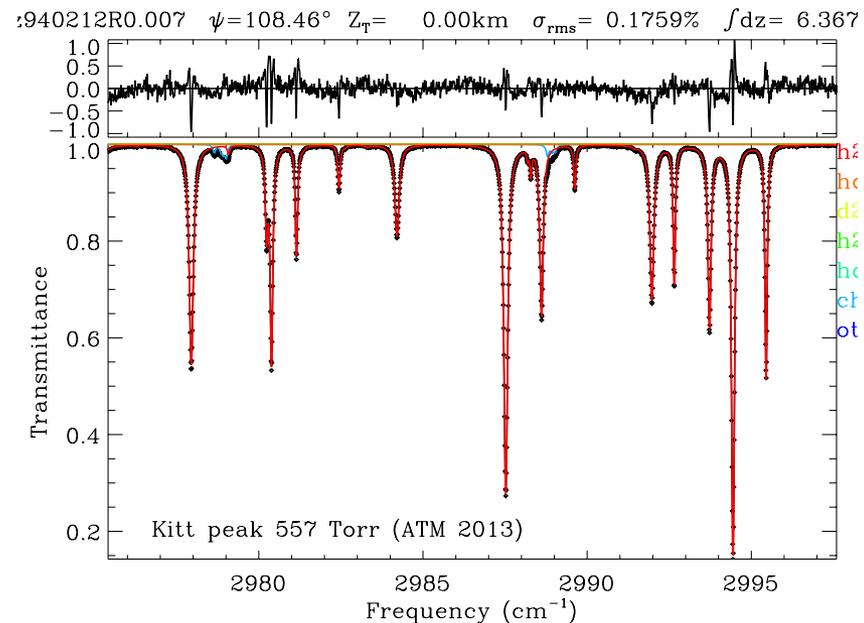
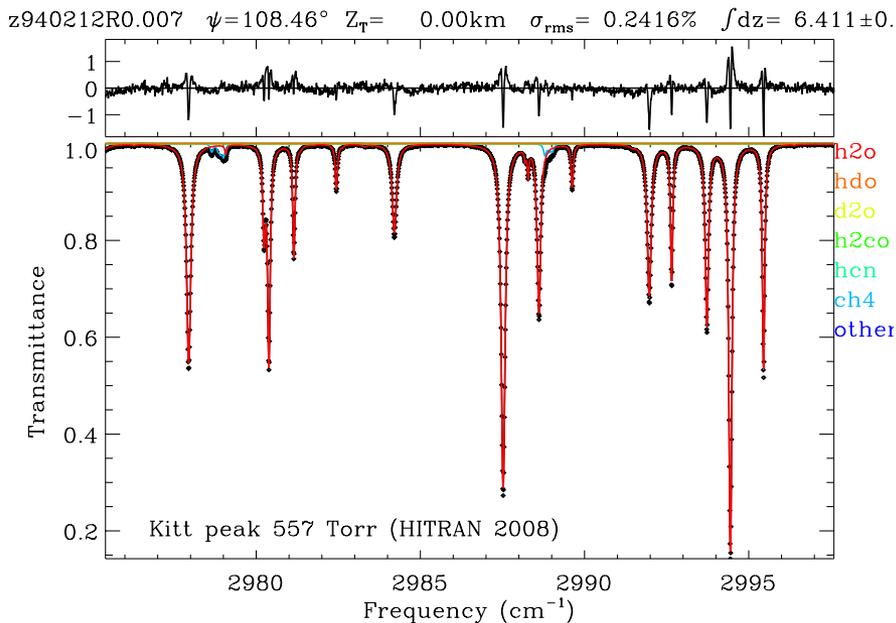
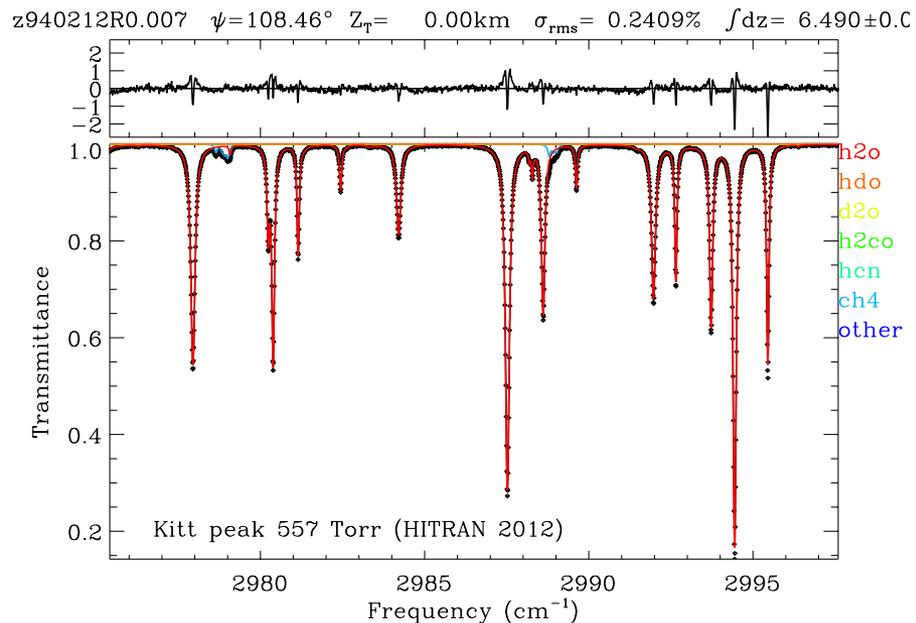
Kitt Peak H₂O (14 Torr)

Spectral residuals sensitive to line positions
& intensities



Kitt Peak H₂O N₂-broadened to 557 Torr

Spectral residuals sensitive to line widths,
pressure shifts, & intensities



Summary/Conclusions

Based on very limited comparisons, the HITRAN 2012 linelist is generally better than HITRAN 2008, but far from perfect.

Significant spectroscopic problems/deficiencies remain. Those causing large residuals are damaging to retrievals employing least-squares fitting methods.

What to do:

- Wait for a better linelist to come along
- Select windows that avoid these spectroscopic problems
- De-weight spectral regions with large residuals in the spectral fitting
- Fix the spectroscopy (simplifies use of wider windows)

In my opinion, an empirical (e.g., PLL) or semi-empirical linelist that fits the lab spectra is better than quantum-mechanically-based linelist that doesn't.

A lot of lab data exists already that has the potential to help resolve many of our current spectroscopic problems. But it is time-consuming work.