HNO_3 Spectroscopy Evaluation

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In July 2006, HITRAN released a complete replacement for HNO_3, based on the work of Flaud et al., [2006] "MIPAS database: Validation of HNO_3 line parameters using MIPAS satellite measurements", ACP, 6, 5037-5048, 2006

I evaluate this new HNO_3 linelist by using it to fit MkIV balloon spectra and PNNL laboratory spectra. The latter are described by Chackerian et al. JQSRT, 82, 429-441, 2003.

[*Why fit MkIV spectra, not ACE ? They are 2⅓ times higher spectral resolution – easier to see spectroscopic problems*]

HNO_3 Fundamentals

HNO_3 has 3N-6 = 9 fundamental vibration-rotation bands

It therefore has

- 9 first overtone bands
- 9x8/2 = 36 simple combination bands

Most of these 9+9+36=54 bands are discernable in solar occultation spectra

How many are in HITRAN ?

458.2	ν_9
580.3	ν_7
646.8	ν_6
763.2	ν_8
879.1	ν_5
1303.2	ν_4
1326.2	ν_3
1709.6	ν_2
3551.7	ν_1

HNO_3 ground-state bands

458.2	**ν_9**	1522.8	$\nu_5 + \nu_6$	2467.9	$\nu_2 + \nu_8$
580.3	**ν_7**	1523.3	$2\nu_8$	2583.5	$\nu_2 + \nu_5$
646.8	**ν_6**	1639.0	$\nu_5 + \nu_8$	2601.2	$2\nu_4$
763.2	**ν_8**	**1709.6**	**ν_2**	2624.1	$\nu_3 + \nu_4$
879.1	**ν_5**	1754.7	$2\nu_5$	2645.1	$2\nu_3$
914.6	**$2\nu_9$**	1757.9	$\nu_4 + \nu_9$	3006.8	$\nu_2 + \nu_4$
1036.4	$\nu_7 + \nu_9$	1780.8	$\nu_3 + \nu_9$	3029.7	$\nu_2 + \nu_3$
1102.8	$\nu_6 + \nu_9$	1879.7	$\nu_4 + \nu_7$	3412.4	$2\nu_2$
1158.3	$2\nu_7$	1902.7	$\nu_3 + \nu_7$	3551.7	ν_1
1205.0	**$\nu_8 + \nu_9$**	1946.1	$\nu_4 + \nu_6$	4006.9	$\nu_1 + \nu_9$
1224.6	**$\nu_6 + \nu_7$**	1969.1	$\nu_3 + \nu_6$	4123.7	$\nu_1 + \nu_7$
1291.0	$2\nu_6$	2062.3	$\nu_4 + \nu_8$	4190.1	$\nu_1 + \nu_6$
1303.2	**ν_4**	2085.2	$\nu_3 + \nu_8$	4306.3	$\nu_1 + \nu_8$
1326.2	**ν_3**	2163.5	$\nu_2 + \nu_9$	4421.9	$\nu_1 + \nu_5$
1334.6	$\nu_5 + \nu_9$	2177.9	$\nu_4 + \nu_5$	4845.2	$\nu_1 + \nu_4$
1340.8	$\nu_7 + \nu_8$	2200.9	$\nu_3 + \nu_5$	4868.1	$\nu_1 + \nu_3$
1407.2	$\nu_6 + \nu_8$	2285.3	$\nu_2 + \nu_7$	5250.8	$\nu_1 + \nu_2$
1456.5	$\nu_5 + \nu_7$	2351.7	$\nu_2 + \nu_6$	7089.2	$2\nu_1$

Bold indicates present in July 2006 HITRAN update

HNO_3 Spectroscopy Evaluation

So the July 2006 HITRAN update for HNO_3 covers 11/54 possible ground-state bands

- 8/9 fundamentals (missing ν_1)
- 1/9 overtones ($2\nu_9$ only)
- 2/36 combination bands
- 4/100+ hot-bands
- 1/5 single-substituted isotopologs

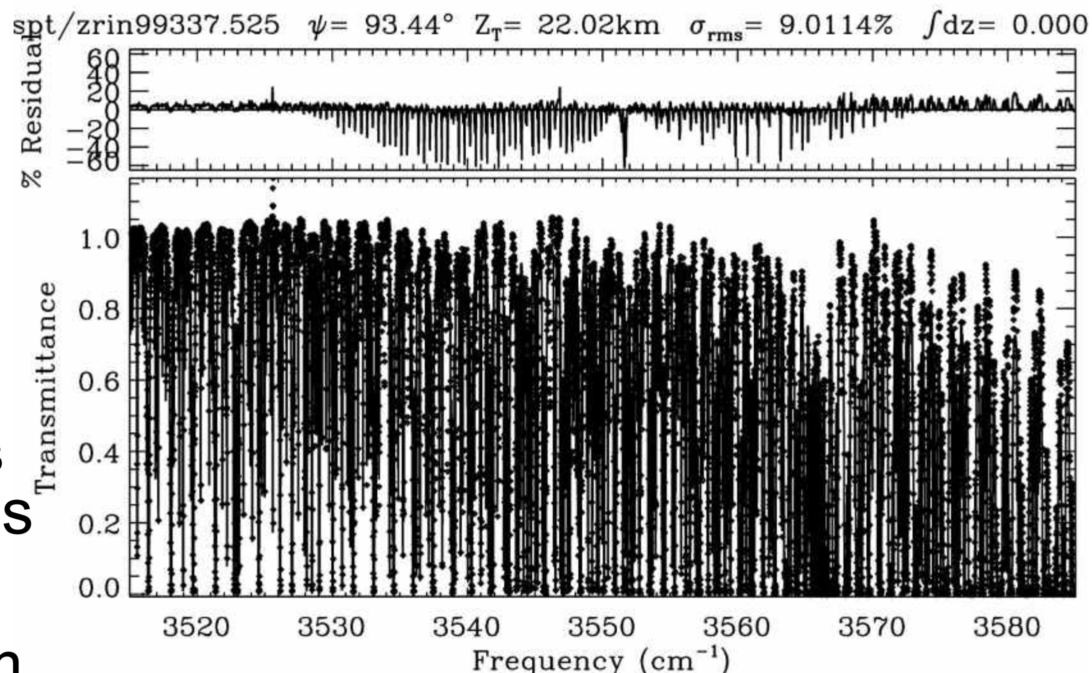
HNO_3 Spectroscopy Evaluation

How well does the July 2006 HITRAN update represent the 11 absorption bands that it covers?

Does it make any real difference that so many HNO_3 bands are missing?

Can they be seen in spectral fits to solar occultation spectra ?

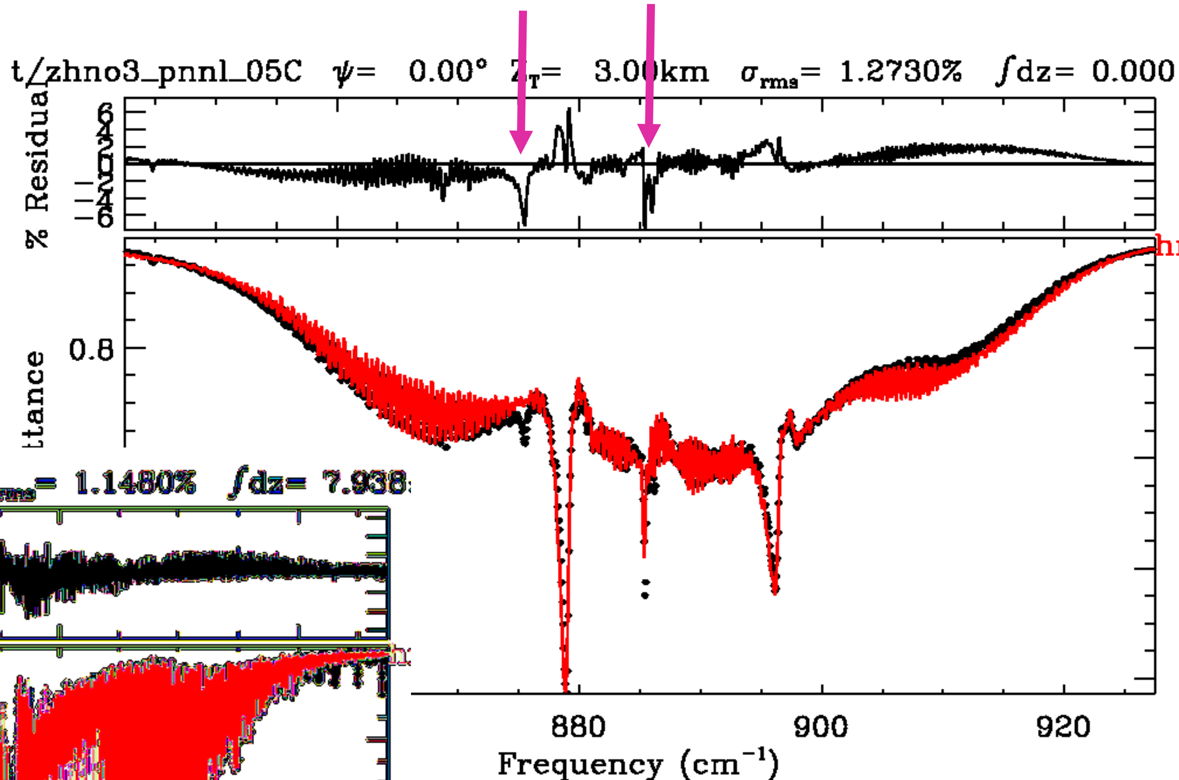
Yes!. The missing HNO_3 lines are 60% deep in this 22 km tangent altitude limb occultation spectrum

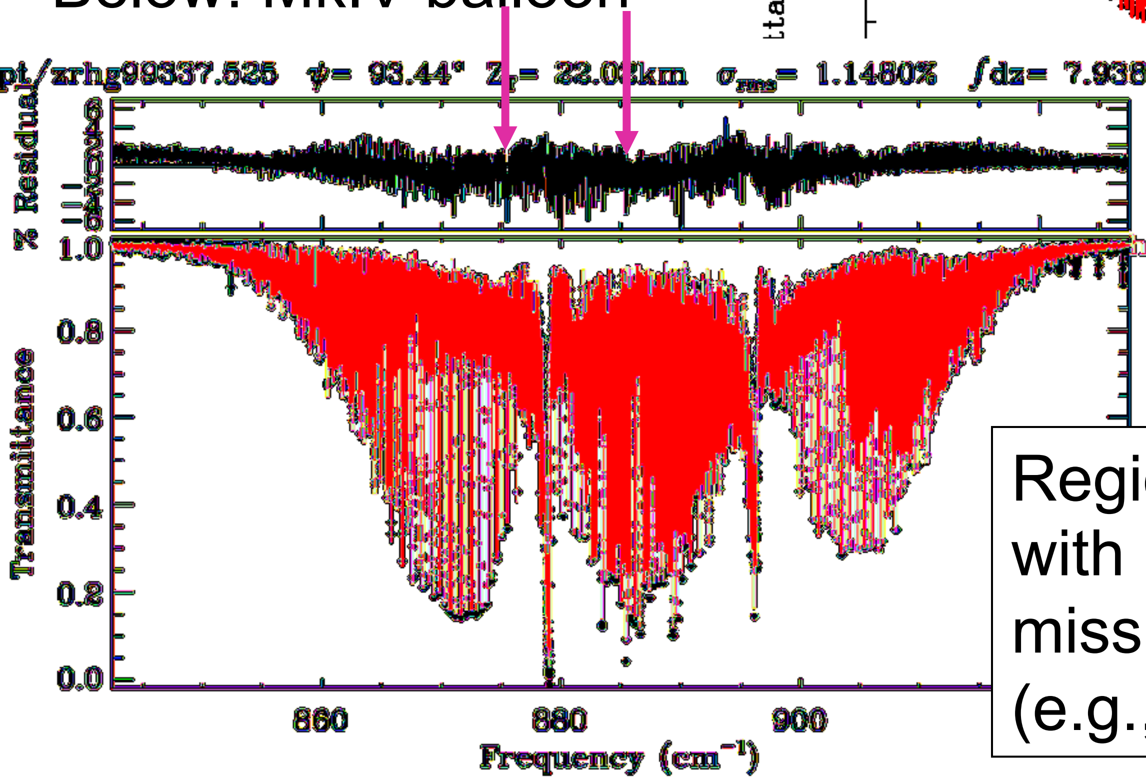


HNO_3 900 cm^{-1}: ν_5 & $2\nu_9$

Black Line: Observation
Red Line: Calculation

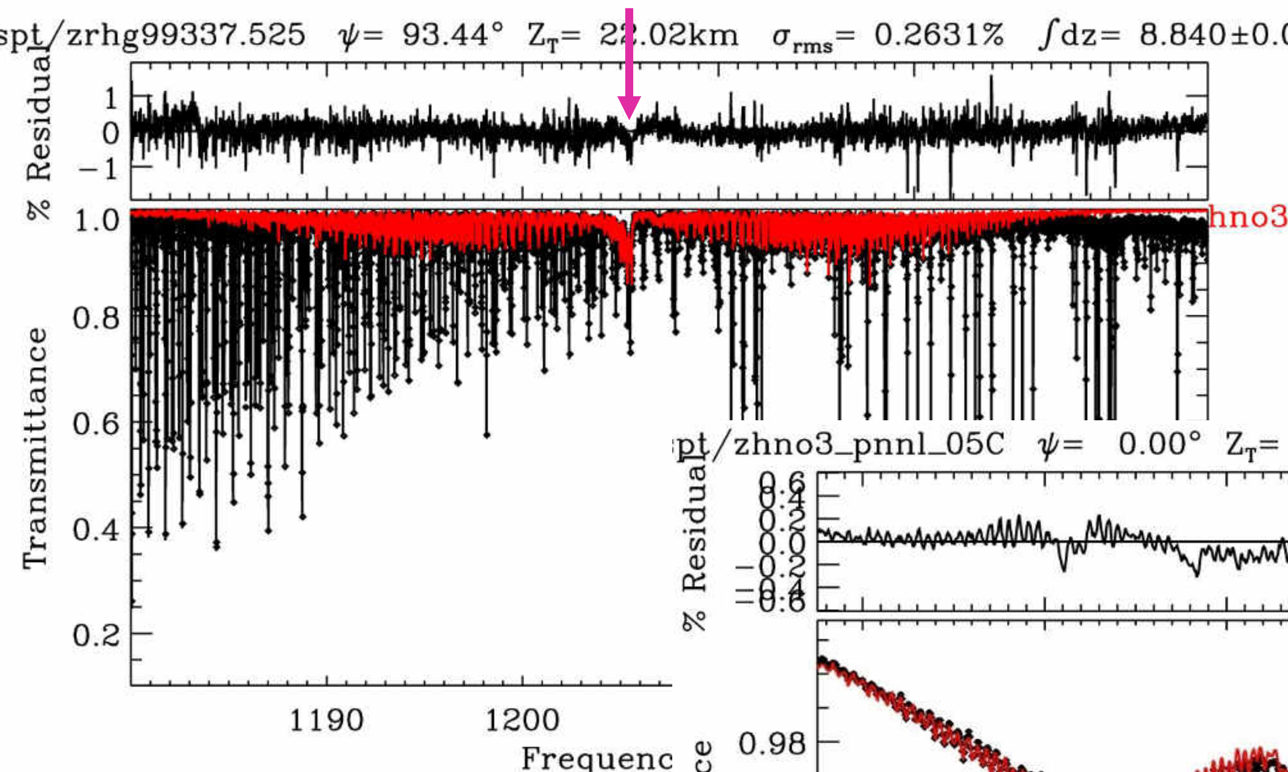
Right: PNNL laboratory
Below: MkIV balloon



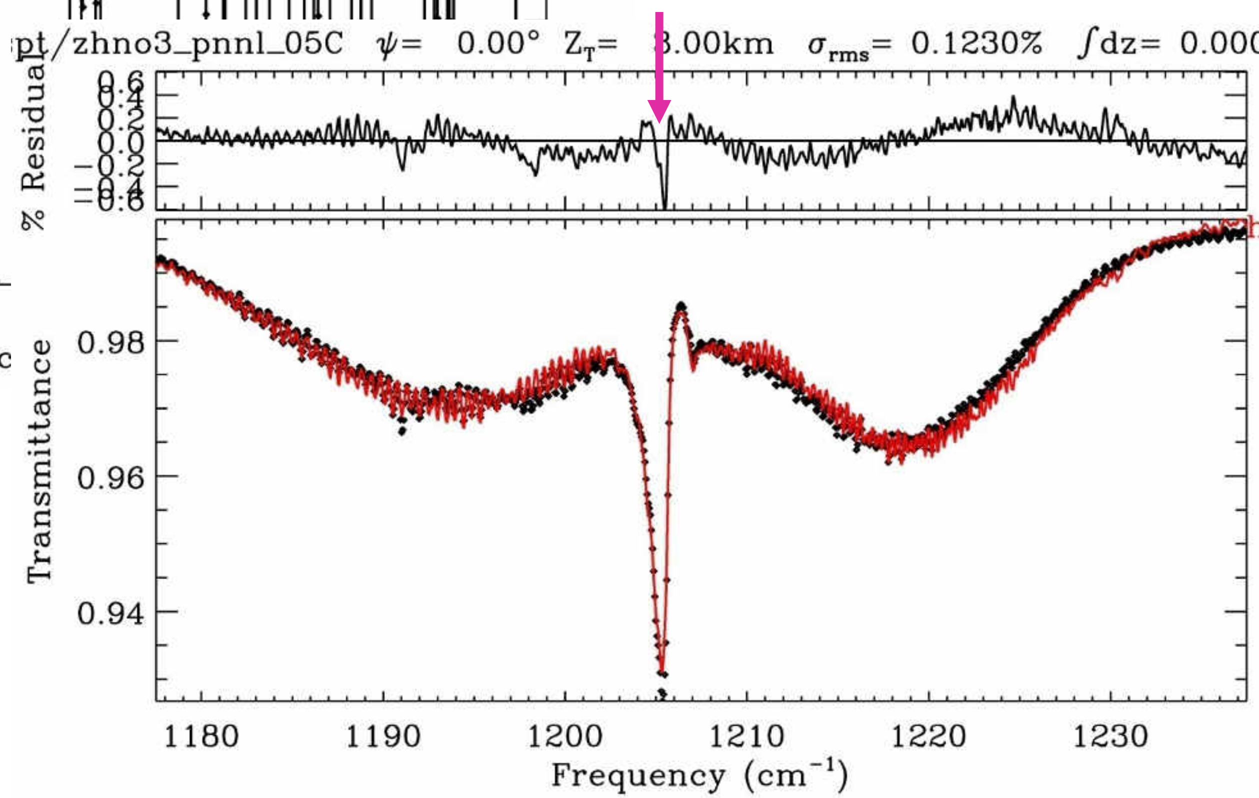


Region is improved compared with HITRAN 2004, but is still missing important features (e.g., purple arrows)

HNO_3 1205 cm^{-1}: $\nu_8+\nu_9$ & $\nu_6+\nu_7$



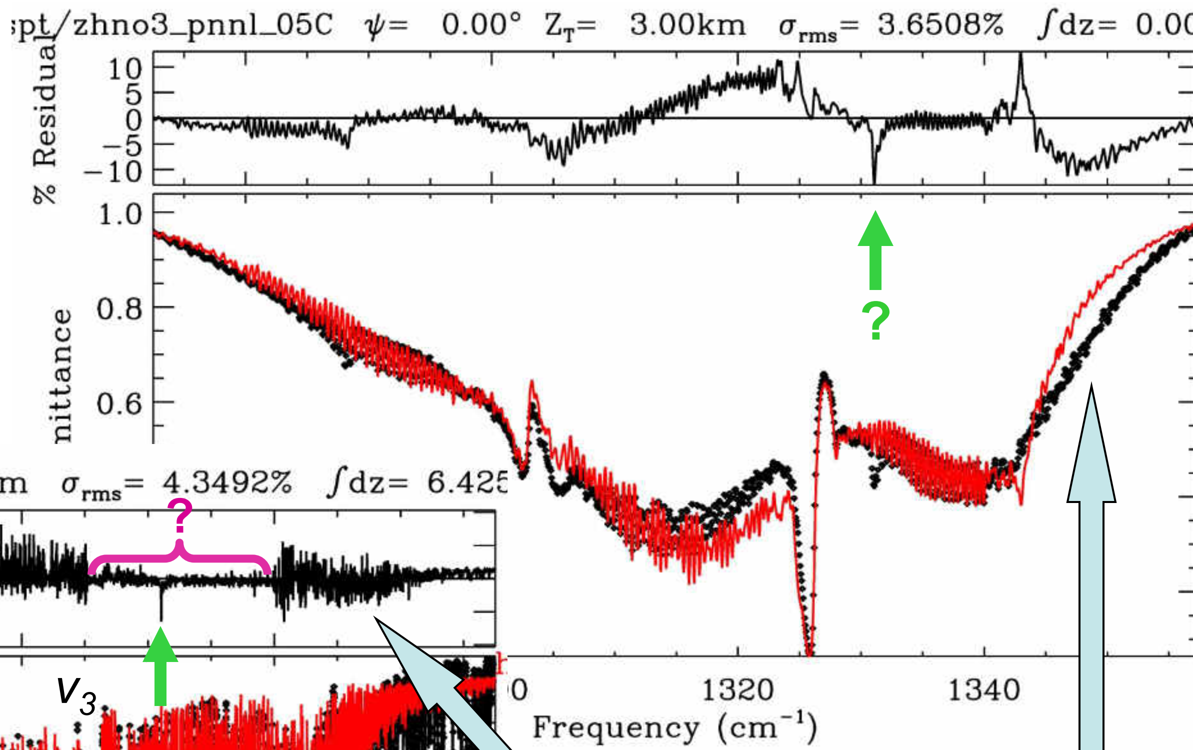
Region is much improved in comparison with HITRAN_2004

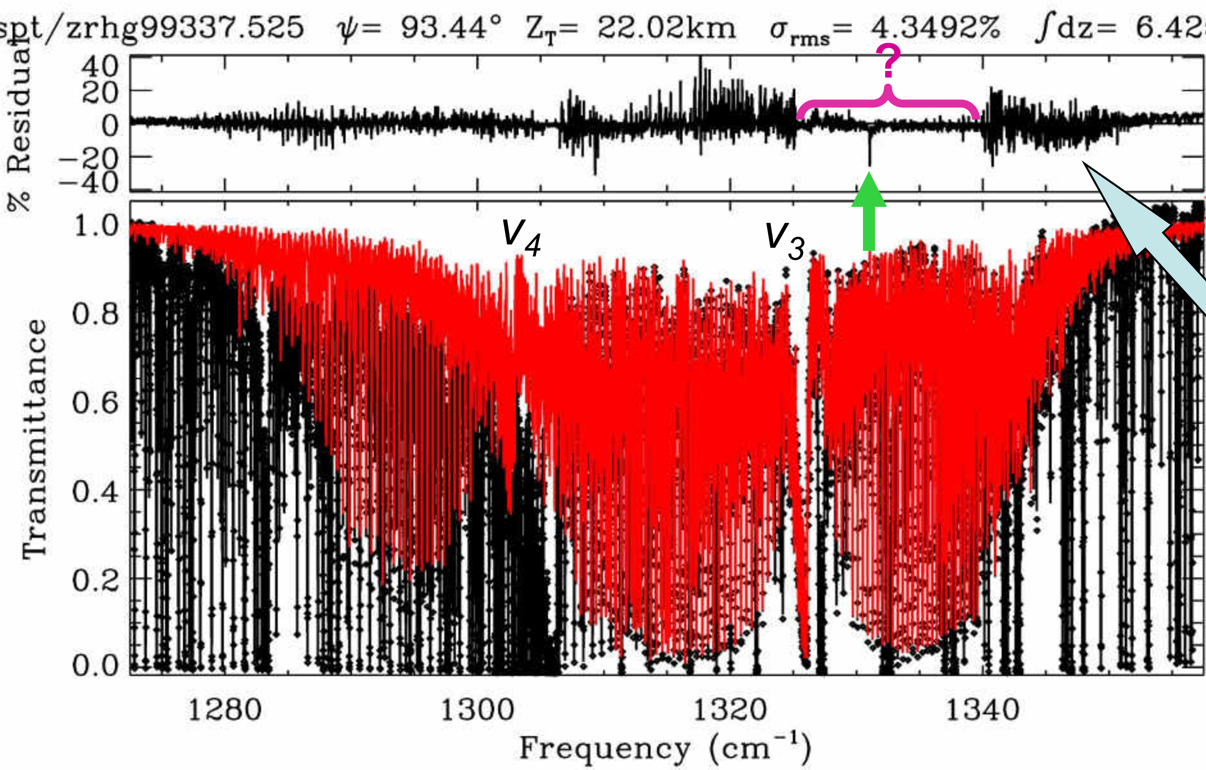


Problem at 1205.5 cm^{-1} seen in fits to MkIV balloon and PNNL spectra

HNO_3 1303 & 1326 cm^{-1} ν_4 & ν_3 bands

The strongest HNO_3 band has serious deficiencies, apart from a 15 cm^{-1}-wide section of the R-branch

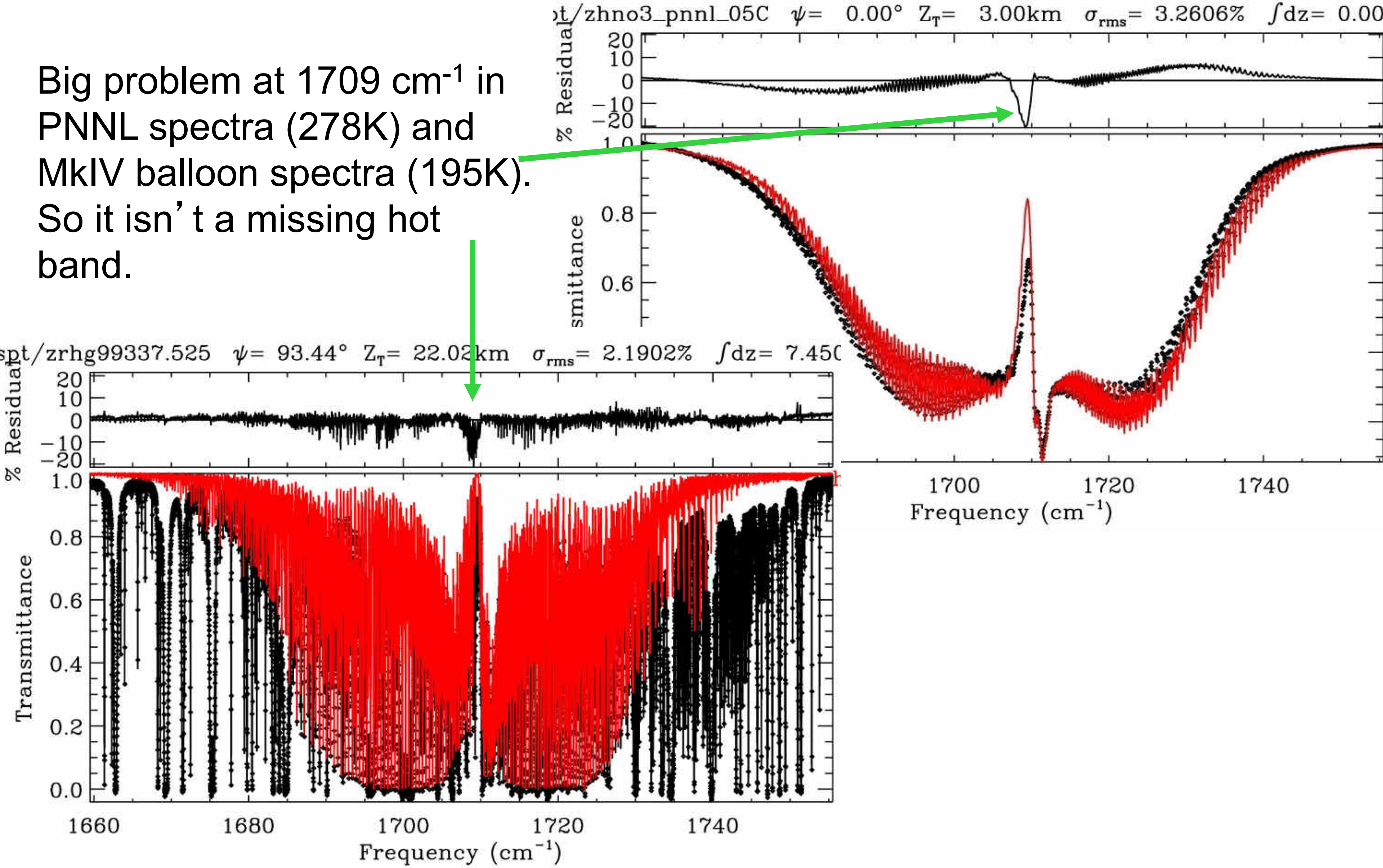




Missing $\nu_5+\nu_9$ and $\nu_7+\nu_8$ HNO_3 bands prevent SO_2 retrieval

HNO_3 1709 cm^{-1} ν_2 band

Big problem at 1709 cm^{-1} in PNNL spectra (278K) and MkIV balloon spectra (195K). So it isn't a missing hot band.



Bands completely missing from HITRAN

In the next section we look at a few of the bands at frequencies above 1770 cm^{-1} that are missing from HITRAN

We evaluate their impact on the surrounding spectral region
by fitting MkIV balloon spectra acquired in the winter polar vortex at 22-23 km tangent altitude (lots of HNO_3).

We also evaluate new, empirical HNO_3 linelists for 3 of the missing bands.

Empirical linelists for missing bands

Lacking spectra acquired at low T, it was not possible to generate an empirical PLL as was done for $C_2H_{6.}$ Use MkIV balloon spectra instead.

Assumed that all HNO_3 bands have the same basic P-Q-R shape with a similar ~0.4 cm^{-1} spacing of the manifolds.

- Use the ν_2 band (1700 cm^{-1}) as template for missing HNO_3 bands.
- Shift and squeeze/stretch the template linelist until it fits the manifold positions of the missing band. Scale the P/Q/R branch intensities.

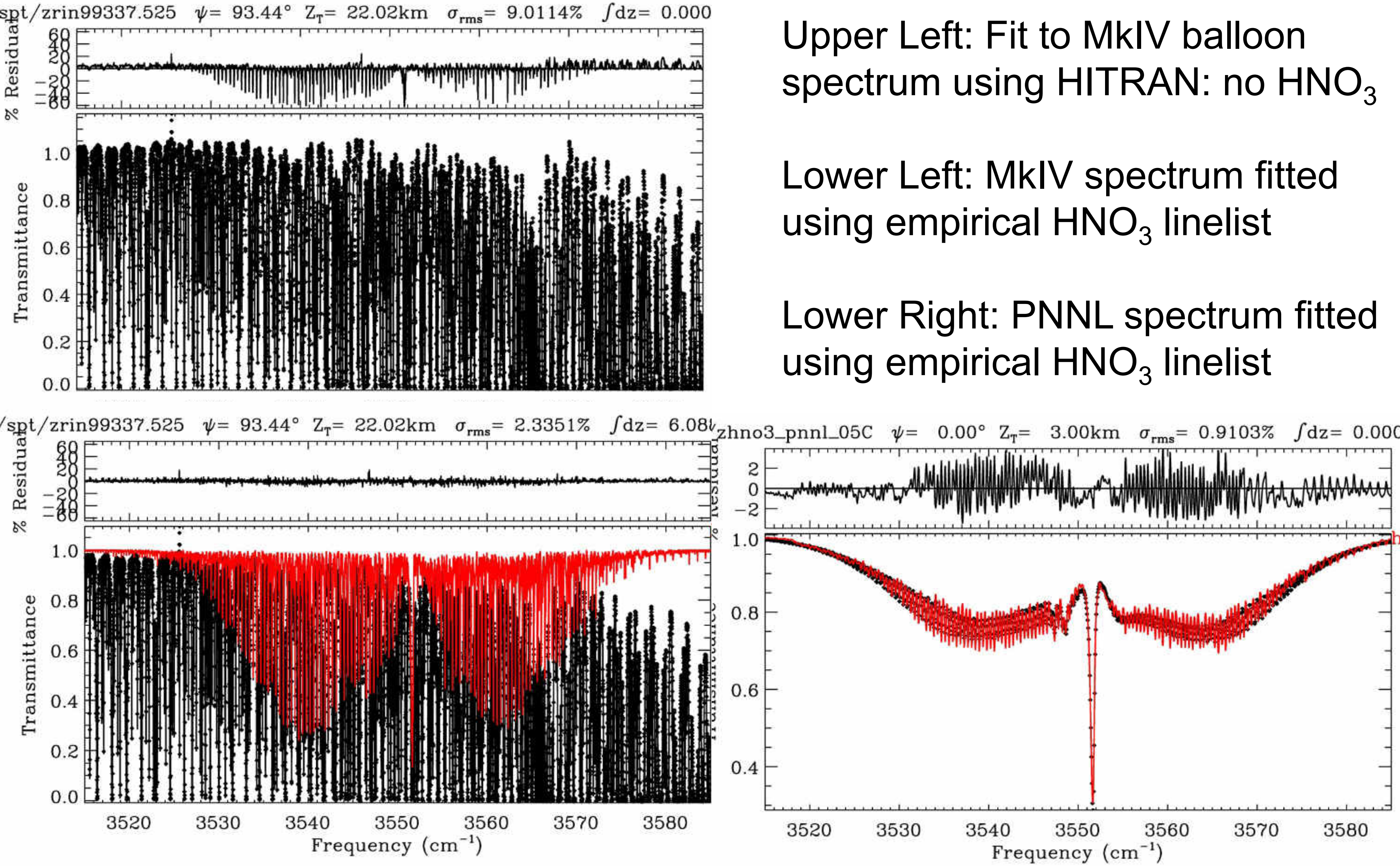
Works well for P & R branches, but Q-branches were difficult.

HNO_3 3551 cm^{-1} ν_1 band

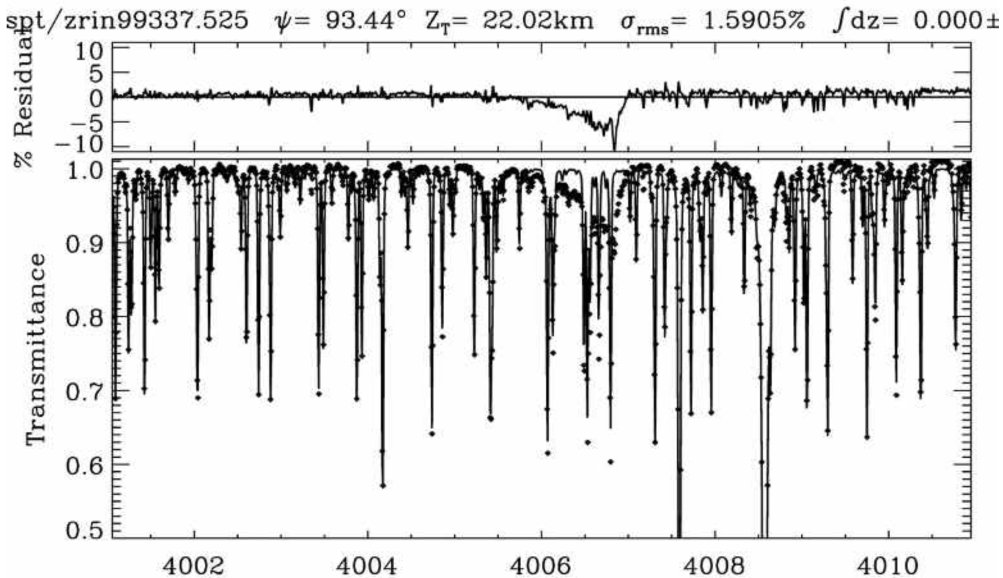
Upper Left: Fit to MkIV balloon spectrum using HITRAN: no HNO_3

Lower Left: MkIV spectrum fitted using empirical HNO_3 linelist

Lower Right: PNNL spectrum fitted using empirical HNO_3 linelist



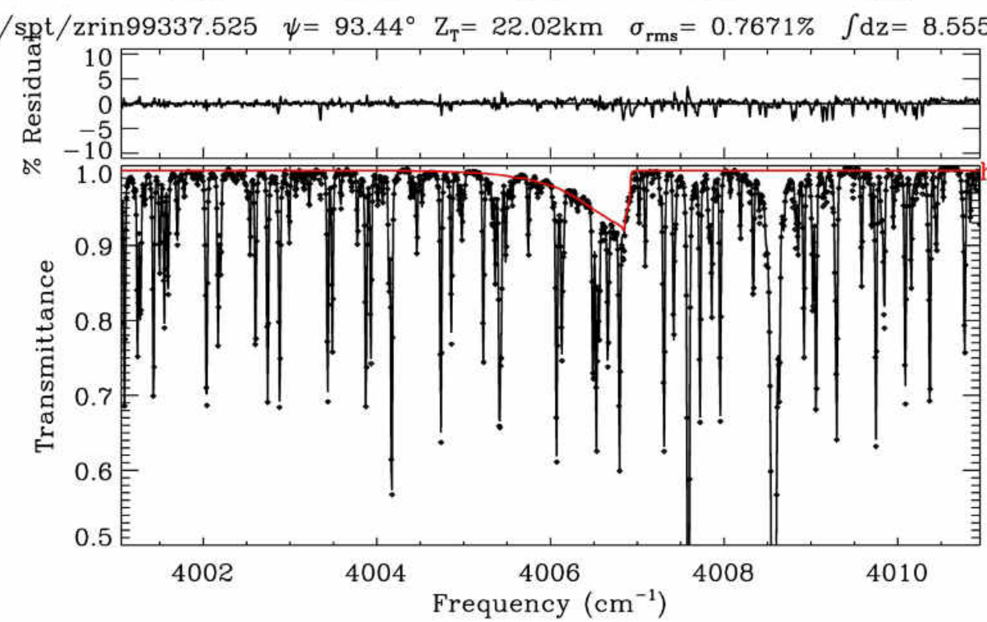
HNO_3 4006 cm^{-1} $\nu_1+\nu_9$ band

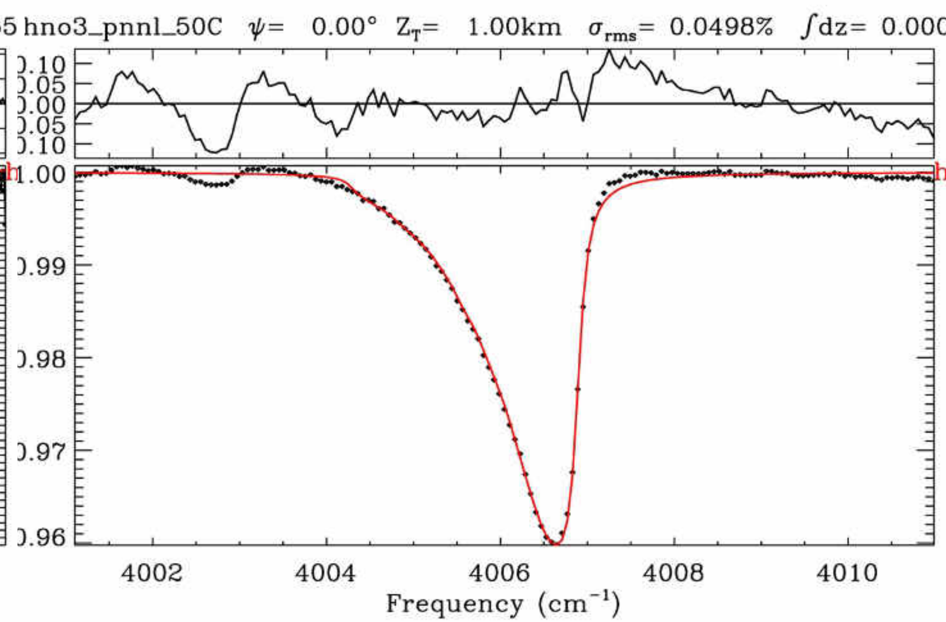


Upper Left: Fit to MkIV balloon spectrum at 22 km tangent altitude

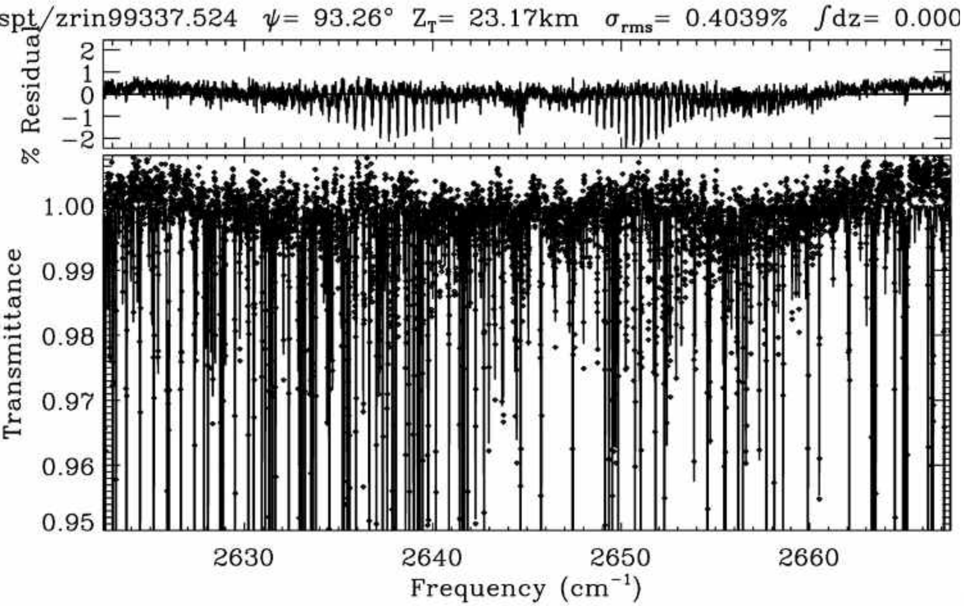
Lower Left: Fit to same spectrum with new kludged HNO_3 linelist

Lower Right: Fit to PNNL spectrum using same kludged HNO3 linelist





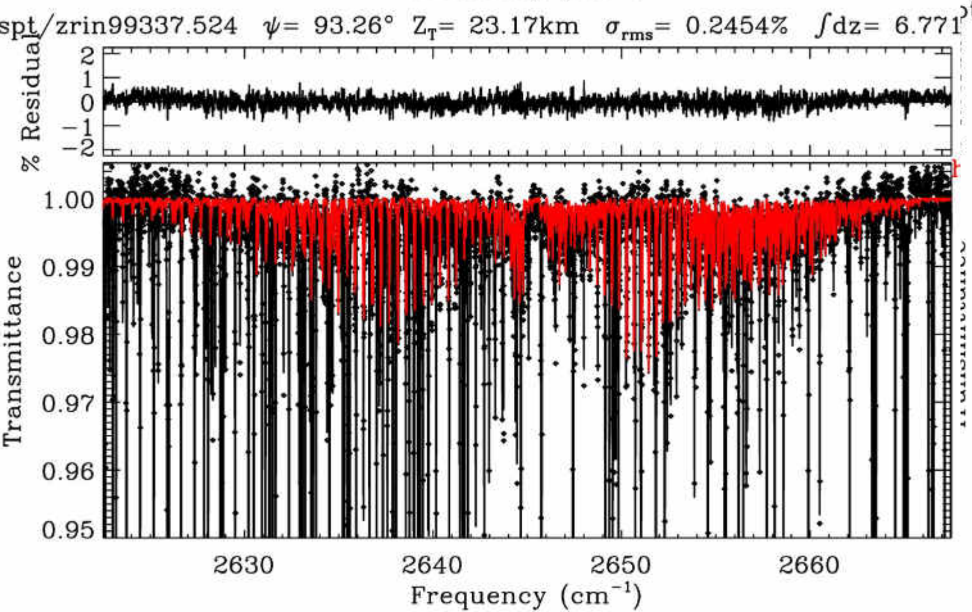
HNO_3 2645 cm^{-1} $2\nu_3$ band

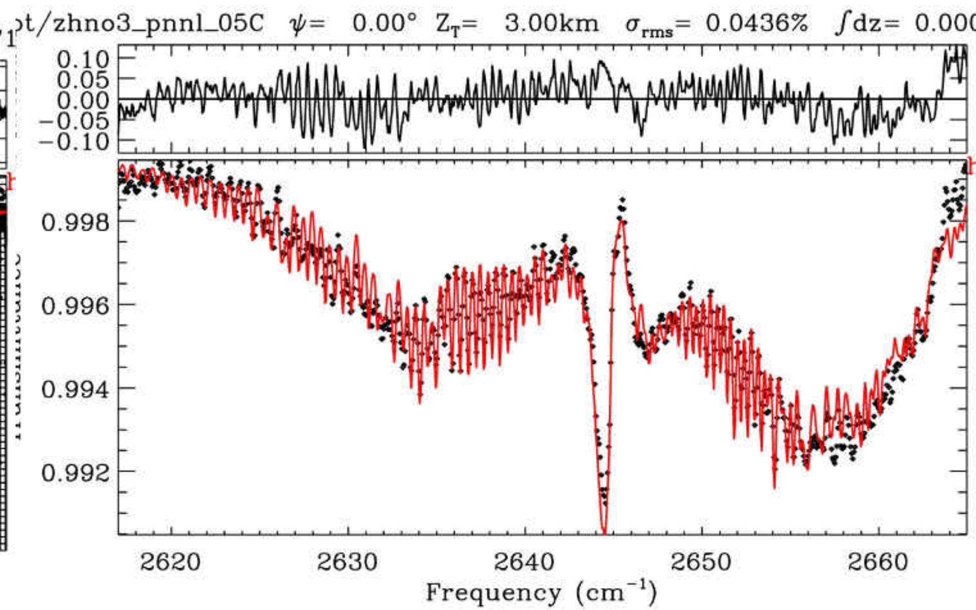


Upper Left: Fit to MkIV balloon spectrum using HITRAN HNO_3

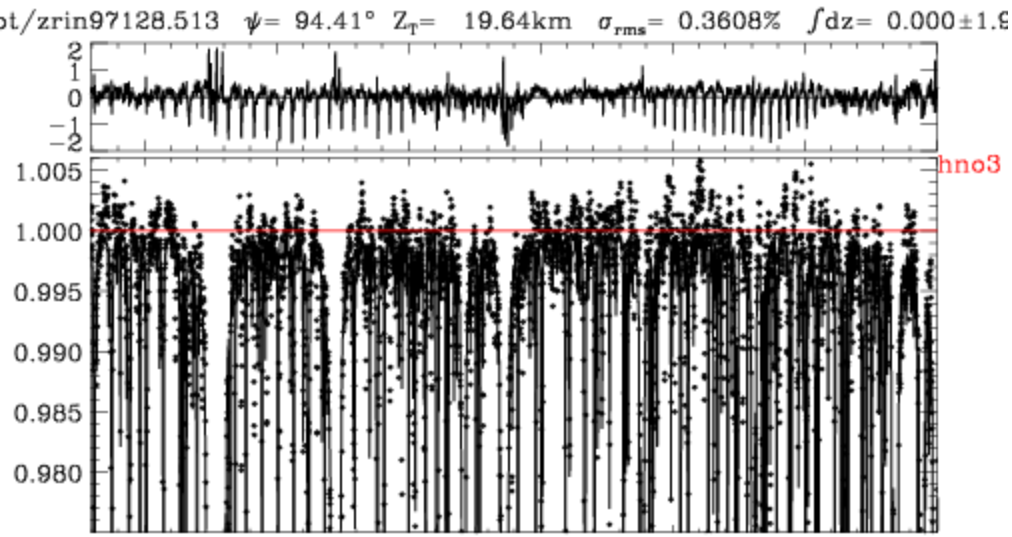
Lower Left: Fit using empirical HNO_3 linelist

Lower Right: Fit to PNNL spectrum using kludged HNO_3 linelist





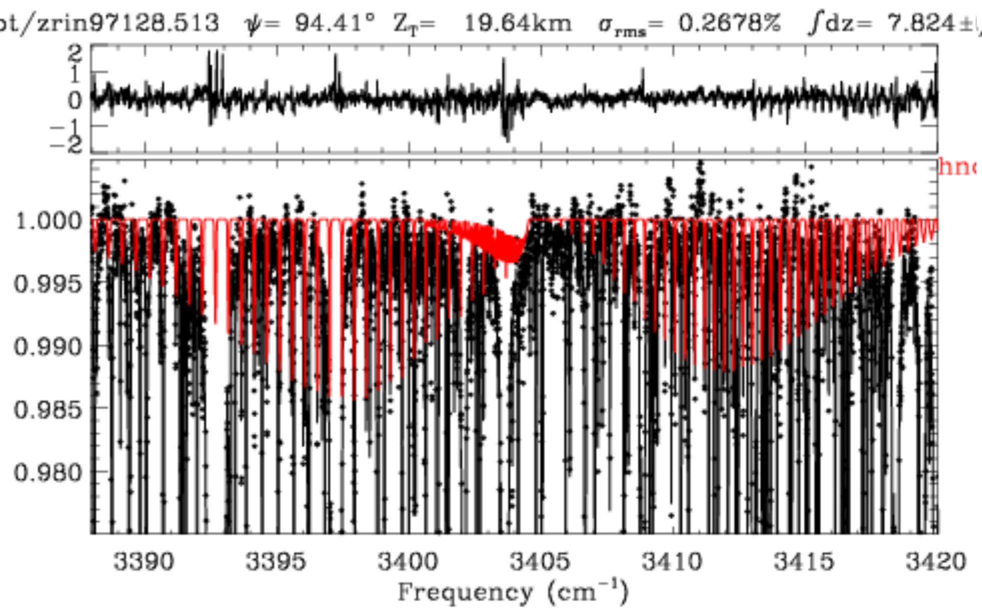
HNO_3 3404 cm^{-1} $2\nu_2$ band

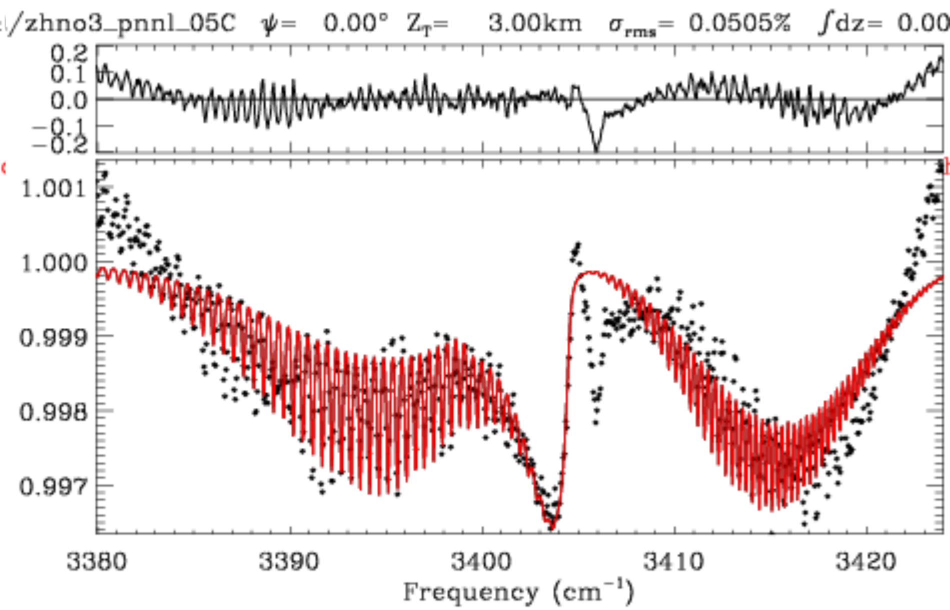


Upper Left: Fit to MkIV balloon spectrum using HITRAN HNO_3

Lower Left: Fit using empirical HNO_3 linelist

Lower Right: Fit to PNNL spectrum using kludged HNO_3 linelist





Comparison with HITRAN 2004

2006 HNO_3 update is a major improvement over HITRAN 2004:

- Was focused on thermal IR (MIPAS & IASI)
- Reduced strength inconsistencies between 900 and 1700 cm^{-1} regions
- Improved fits to the 900 and 1200 cm^{-1} regions
- Introduced J-dependent widths (900 cm^{-1} region only)

But serious deficiencies remain:

- ν_3 band at 1300 cm^{-1} (the strongest) is still unusable (except for a narrow section of the R-branch
- Zero lines above 1770 cm^{-1}.
- Missing the ν_1 fundamental band at 3550 cm^{-1}
- Missing the vast majority of overtone and combination bands
- Missing most hot bands and all heavy isotopologs
- HNO_3 widths are all constant, with the exception of the 900 cm^{-1} region

HNO_3 is the main cause of poor residuals in fits to stratospheric spectra.

Conclusions

HNO_3 spectroscopic deficiencies are a major obstacle to further progress in the use of solar occultation spectra for new research into atmospheric composition.

Detection/Measurement of the following gases is impaired by HNO_3 spectroscopic inadequacies

- *SO_2 at 1340 cm^{-1}*
- *H_2CO at 1700 cm^{-1}*
- *HOCl at 1230 cm^{-1}*
- *HDO at 2645 cm^{-1}*
- *OH & HO_2 at 3400 cm^{-1}*
- *OH & HO_2 at 3550 cm^{-1}*
- *HF at 4000 cm^{-1}*

Improved HNO_3 linelist urgently needed !

Empirical HNO_3 linelists

Created new empirical HNO_3 linelists for:

- $2\nu_3$ at 2645 cm^{-1}
- $2\nu_2$ at 3404 cm^{-1}
- ν_1 at 3551 cm^{-1}
- $\nu_1+\nu_9$ at 4006.6 cm^{-1}

Although these empirical linelists are better than nothing, they do not allow the fitting of MkIV spectra down to the noise level.

These empirical linelists should **not** be used for retrieving HNO_3 itself. They should only be used for fitting other gases of interest in these regions, where HNO_3 is an interferent.

A linelist doesn't have to be perfect to be extremely useful to the remote sensing community.