HNO_3 Spectroscopy Evaluation

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Compiled a HNO_3 linelist consisting of:

- HITRAN 2012 from 0 to 1800 cm^{-1}
- MIPAS-1220-1396pre from 1220 to 1396 cm^{-1}
- Pseudo-line-lists from 1800 to 4100 cm^{-1}

I believe that the first 2 of these are intended for HITRAN 2016.

The MIPAS linelist was the one described by Perrin et al., 2015.

The pseudo-linelists have been discussed elsewhere (not a topic here)

A series of 10 broad windows were defined, each containing a complete HNO_3 absorption band. These windows were fitted in lab spectra (Kitt Peak & PNNL) and atmospheric spectra (MkIV balloon).

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This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

MIPAS database: new HNO_3 line parameters at 7.6 µm validated with MIPAS satellite measurements

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Laboratory Spectra Analyzed

3 PNNL spectra covering 600 to 6000 cm^{-1} (5 to 50C; 1 atm)
1 Kitt peak spectrum covering 550-1400 cm^{-1} (295K; <1 mbar)
5 Kitt peak spectra covering 600-2750 cm^{-1} (273K; <1 mbar)
6 Kitt peak spectra covering 1100-2750 cm^{-1} (296K; <1 mbar)

Not all spectra cover all bands/windows. Out of 15 spectra x 10 windows = 150 possible fits, only 55% could be performed.

MkIV Balloon Spectra

Used 39 spectra from a single occultation (fai07rat.brl) covering altitudes from 10 to 39 km.

Spectral resolution = 0.01 cm^{-1} (57 cm OPD)

All MkIV spectra cover 650-6500 cm^{-1} simultaneously and therefore cover all HNO_3 bands, which makes them very useful for evaluating band-to-band biases.

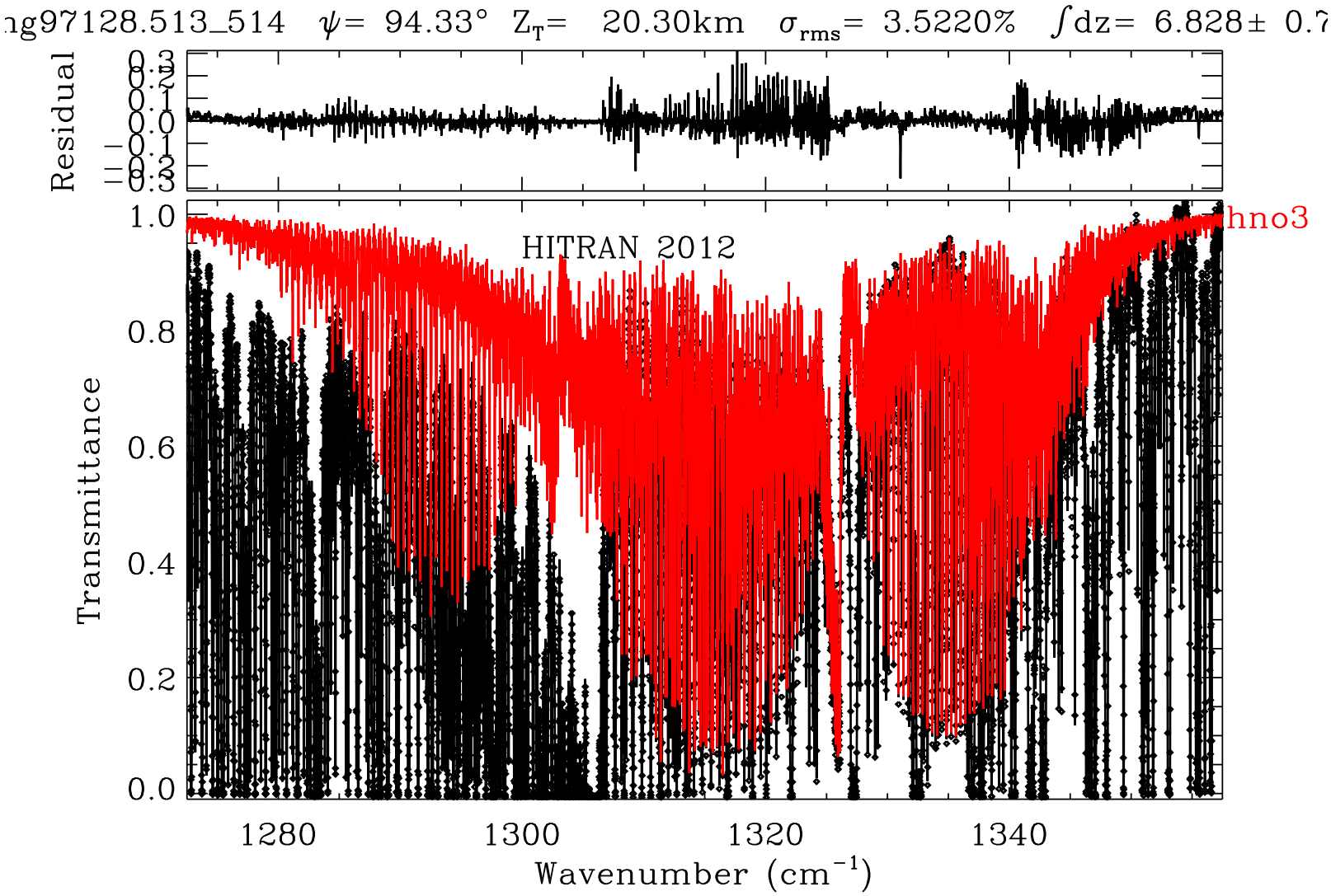
Wide range of temperature, pressures, and HNO_3 slant columns encountered.

VMR Scale factors & RMS Fits

Window (cm-1)	VMR Scale Balloon	VMR Scale Laboratory	% RMS Balloon	% RMS Lab
766 ± 25	0.94±0.03	0.92±0.03	0.80	0.37
885 ± 44	0.99±0.03	0.98±0.02	0.37	0.49
1208 ± 27	1.21±0.03	1.21±0.03	0.26	0.20
1314 ± 45	0.81±0.03	0.81±0.03	0.56	1.84
1314 ± 45	0.89±0.02	0.91±0.03	0.30	1.10
1707 ± 48	0.96±0.04	0.95±0.03	1.46	1.19
2645 ± 32	1.10±0.05	0.92±0.18	0.21	0.15
2999 ± 47	0.86±0.08	1.14±0.28	0.51	0.12
3402 ± 22	0.89±0.07	0.80±0.50	0.22	0.03
3550 ± 35	0.81±0.06	1.17±0.15	0.92	0.58
4000 ± 35	1.01±0.09	1.02±0.10	0.45	0.08

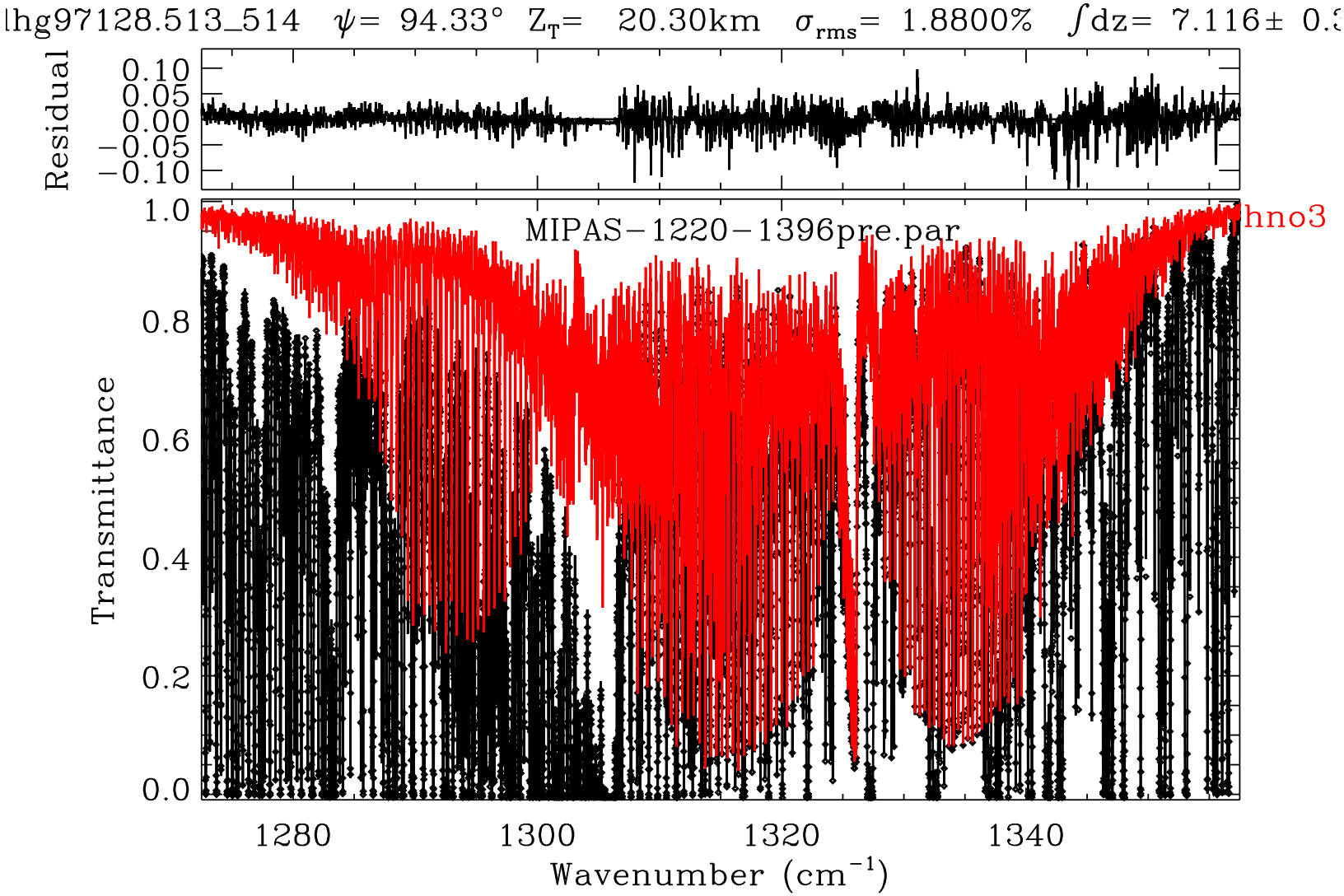
VMR Scaling is the factor that needs to be applied to the line intensities to make bands consistency. Black represents windows fitted with HITRAN 2012 HNO_3 linelist.
Blue represents window fitted with MIPAS-1220-1396pre.par linelist.
Green represent windows fitted with HNO_3 pseudo-linelists.

Example of Balloon fit – HITRAN12



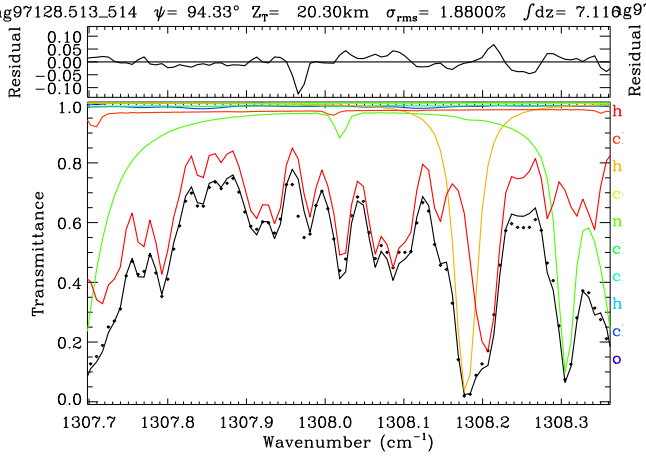
Main absorbers are CH_4, H_2O and HNO_3. Peak residual exceed 30% and the rms is 3.52%

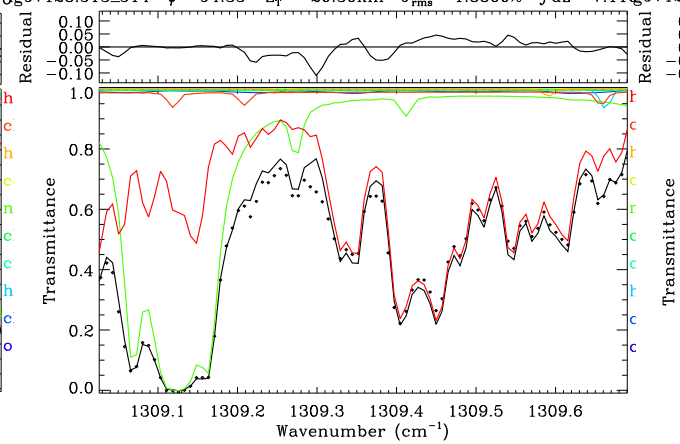
Example of Balloon fit – MIPAS-1220-1396

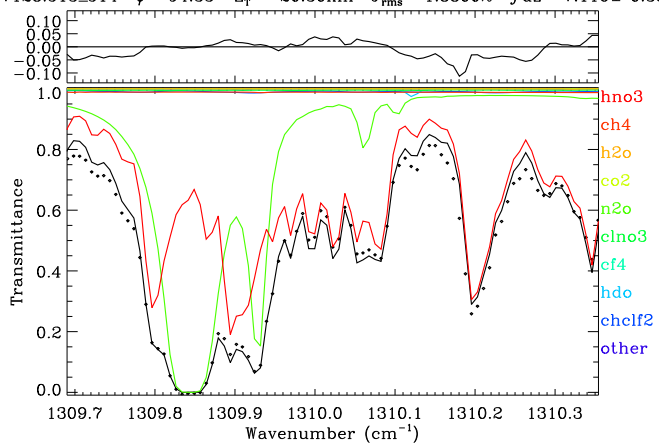


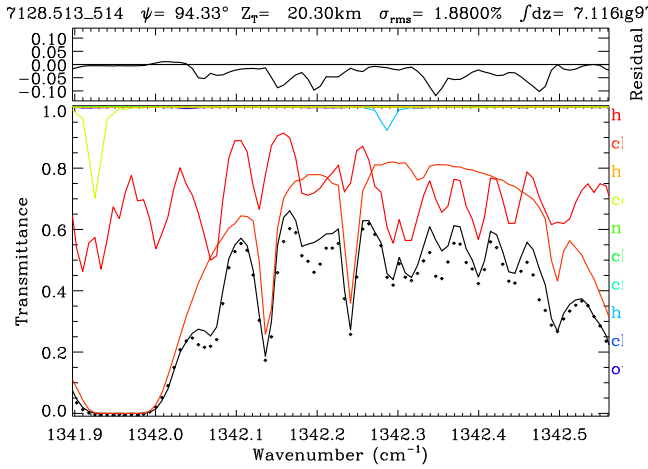
Peak residuals are reduced to 14% with an rms of 1.88 %

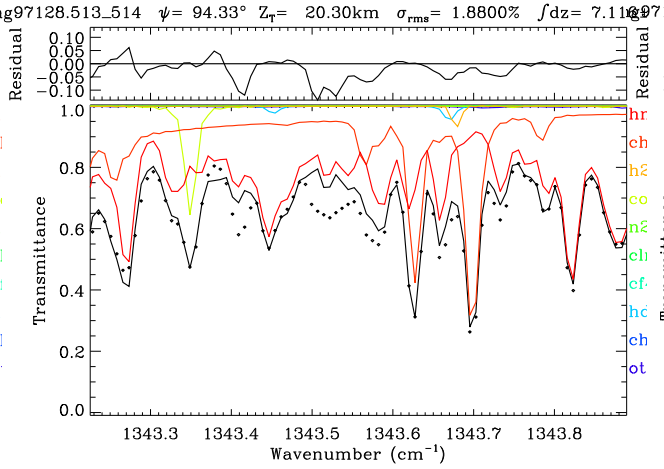
Examples of remaining large residuals in fits to balloon spectra – MIPAS-1220-1396

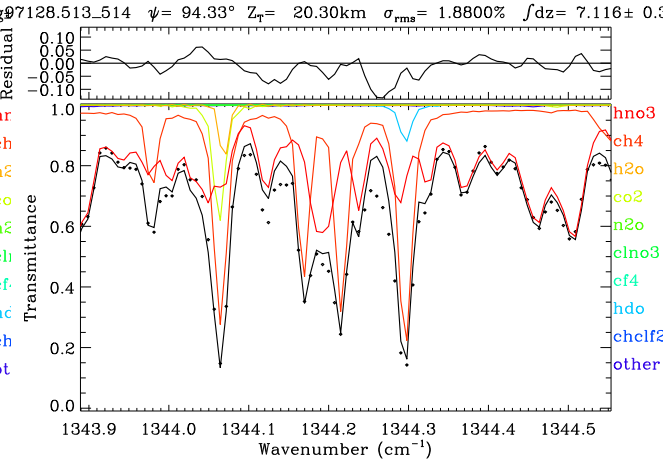




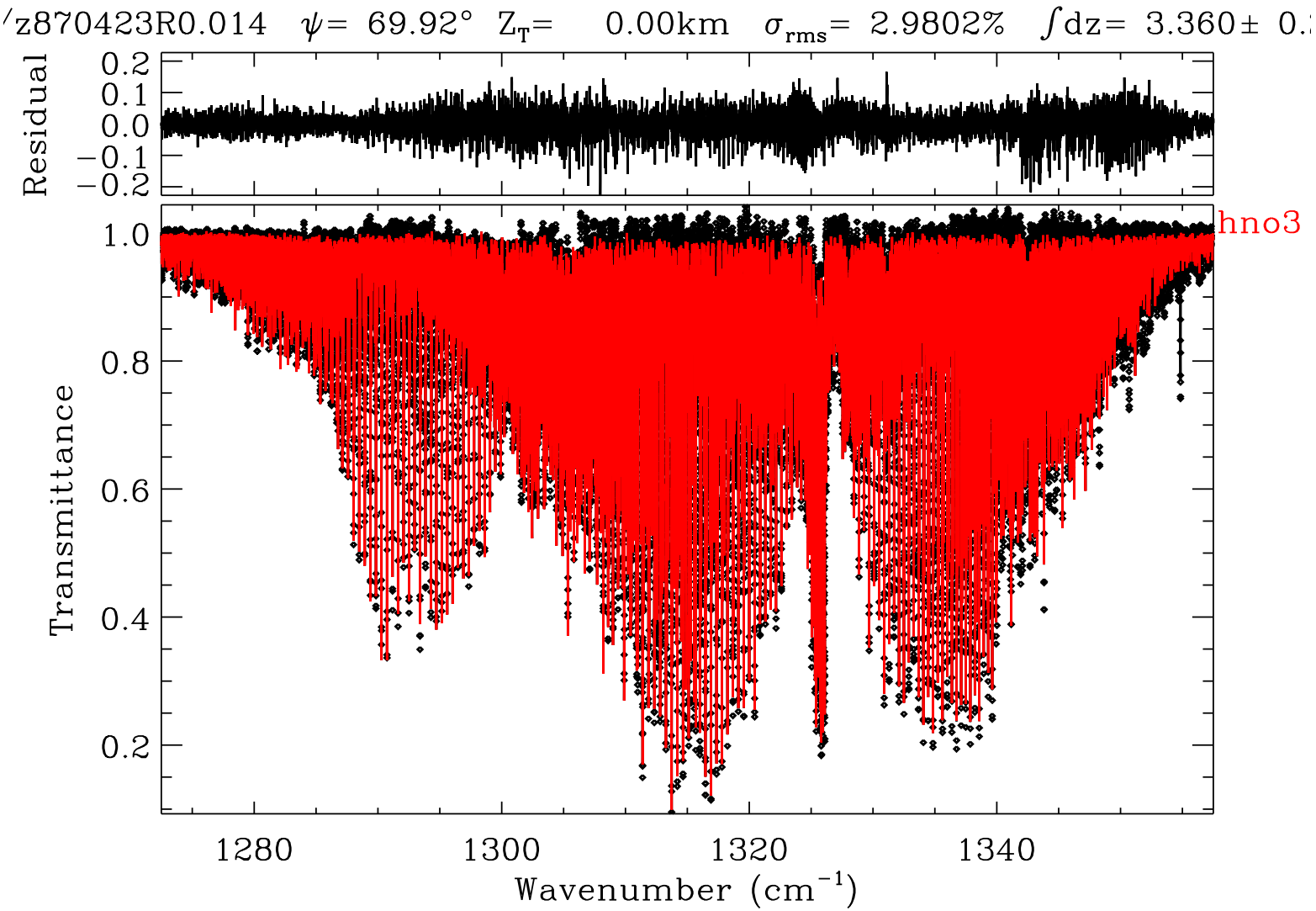




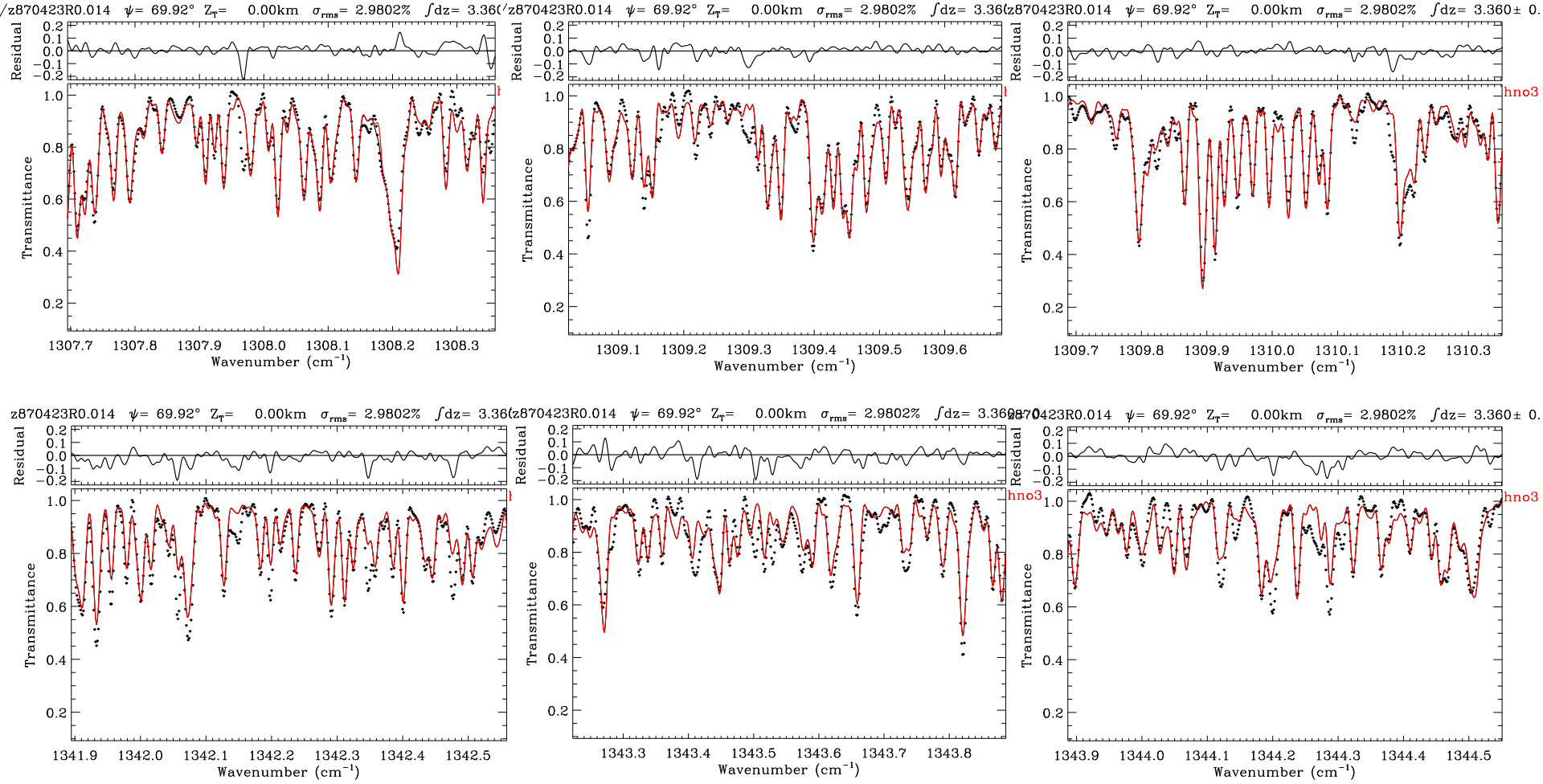




Example of fit to Kitt Peak lab spectrum – MIPAS-1220-1396pre.par linelist

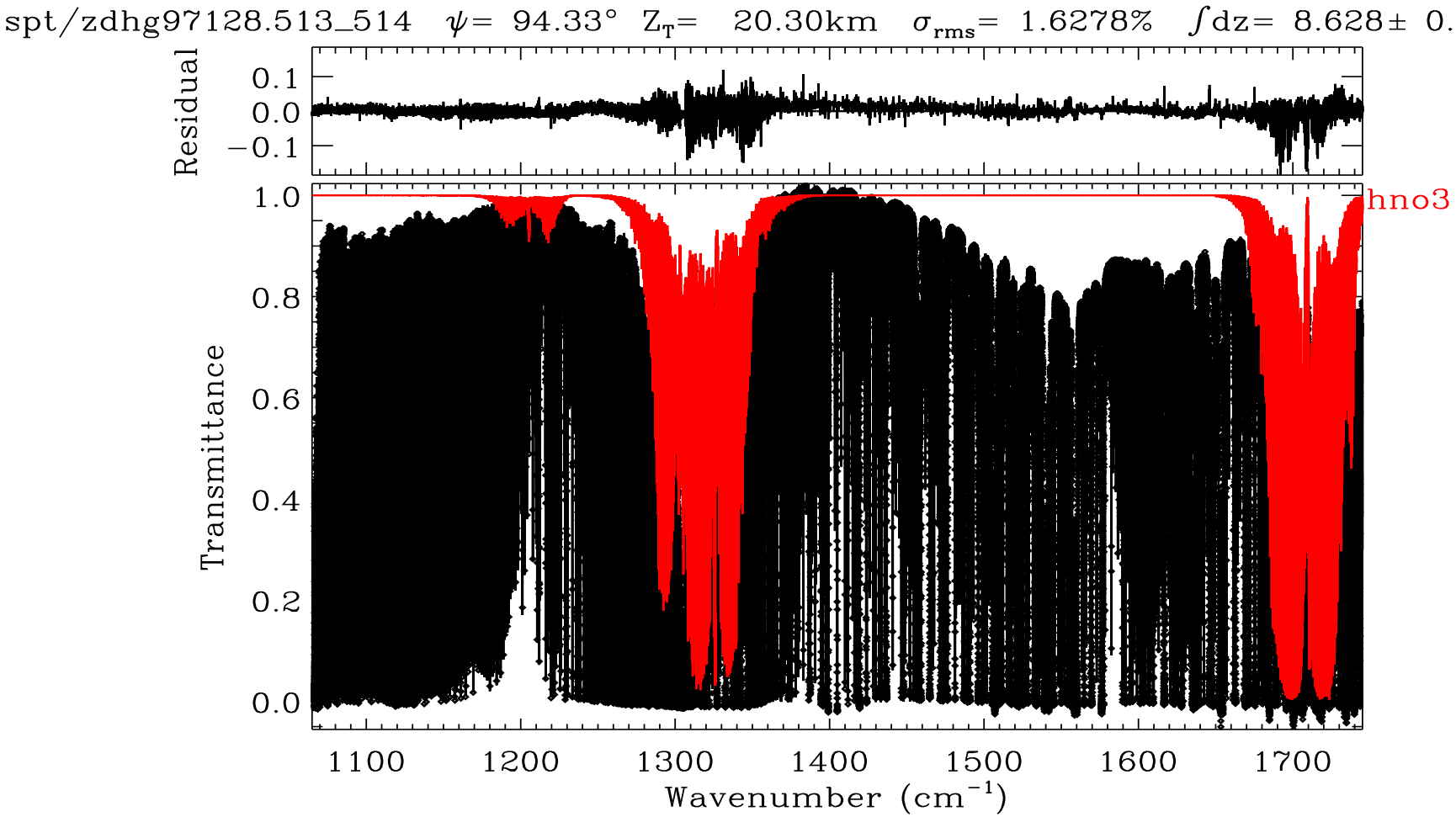


Examples of remaining large residuals in fits to KP lab spectra – MIPAS-1220-1396



Note similarity of these residuals with those shown 2 slide ago in fits to MKIV balloon spectra.

Example of balloon spectral fit



Even using the new MIPAS-1220-1396pre linelist, fits to MKIV balloon spectra in the lower stratosphere (20 km tangent altitude) are still dominated by HNO_3 spectroscopic problems. [With HITRAN_2012 HNO_3 linelist, residuals around 1300-1350 cm^{-1} reached 30%.]

Conclusions

MIPAS-1220-1396pre.par linelist represents a substantial improvement over HITRAN_2012 in the 1300 cm^{-1} region containing the v_3 and v_4 bands:

- Fitting residuals are reduced:
    - Balloon: from 0.56% to 0.30%
    - Laboratory: from 1.84% to 1.10%
- Retrieved HNO_3 amounts are more consistent with those from other windows:
    - Balloon: VSF increased from 0.81 to 0.89
    - Laboratory: VSF increased from 0.81 to 0.91

So, using the new MIPAS linelist, reduces the low bias from 19% to 10% in the 1300 cm^{-1} window, which is a significant improvement over HITRAN 2012.

The new linelist reduces the rms fitting residuals by nearly a factor ~2 in balloon and lab data. But residuals up to 15% remain in fits to balloon spectra and are very similar to those seen in lab spectra, implying a common cause (HNO_3).

Scale factors are surprisingly consistent between lab & balloon spectra

- Intensities in 1208 cm^{-1} band need multiplying by 1.2
- Intensities in 1314 cm^{-1} band need multiplying by 0.9