Aura Spectroscopy Validation

HITRAN 2004

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Solar Occultation Spectra for Spectroscopy Validation

The broad spectral coverage of FTIR solar occultation spectra, together with their high SNR and resolving power, make them very useful for assessing the adequacy of the spectroscopic databases.

•Look for significant omissions in the current linelist (e.g. missing gases, isotopologs, hot-bands, combination bands, overtones)

•Investigate adequacy of physics (e.g. far-wing line shapes, line-mixing)

•Assess relative strengths of bands in different spectral regions (laboratory spectrometers tend to have narrower spectral coverage)

•Assess pressure-dependent parameters (widths, shifts)

•Check spectroscopic parameters of gases for which laboratory measurements are very difficult (e.g. O_2, N_2, low-temperature H_2O,)

Major Deficiencies

Missing line at 1167.3 cm^{-1} (up to 50% deep)

Missing HNO_3 overtone/combination bands at 1340-1355 cm^{-1}

Missing HNO_3 overtone at 2630 cm^{-1}

Missing O_3 band at 4007 cm^{-1}

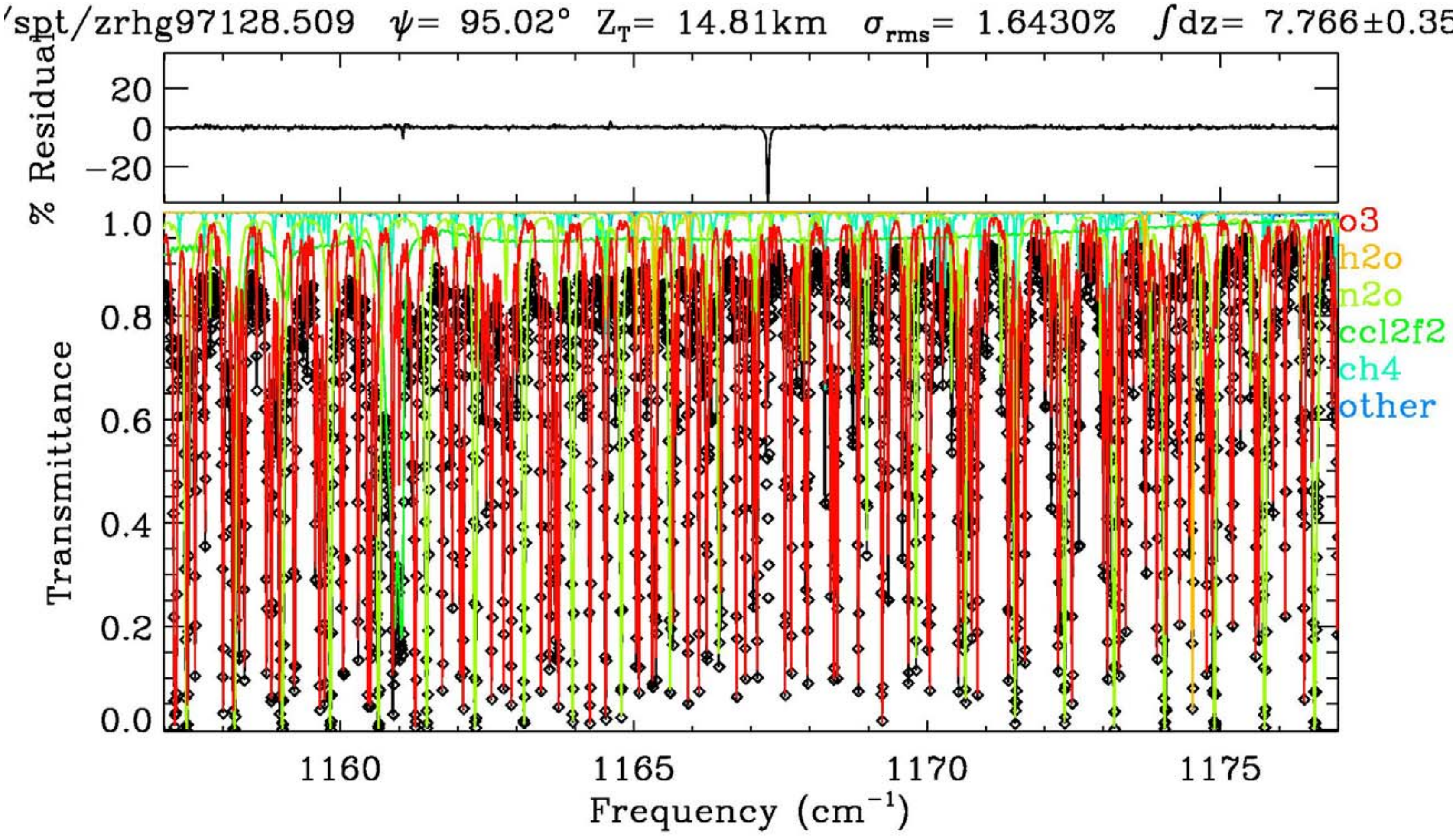
Of course, H_2O spectroscopy is a problem throughout the infrared, but these problems are already well-known and under investigation and will therefore not be a topic of this study.

Missing line at 1167.3 cm-1

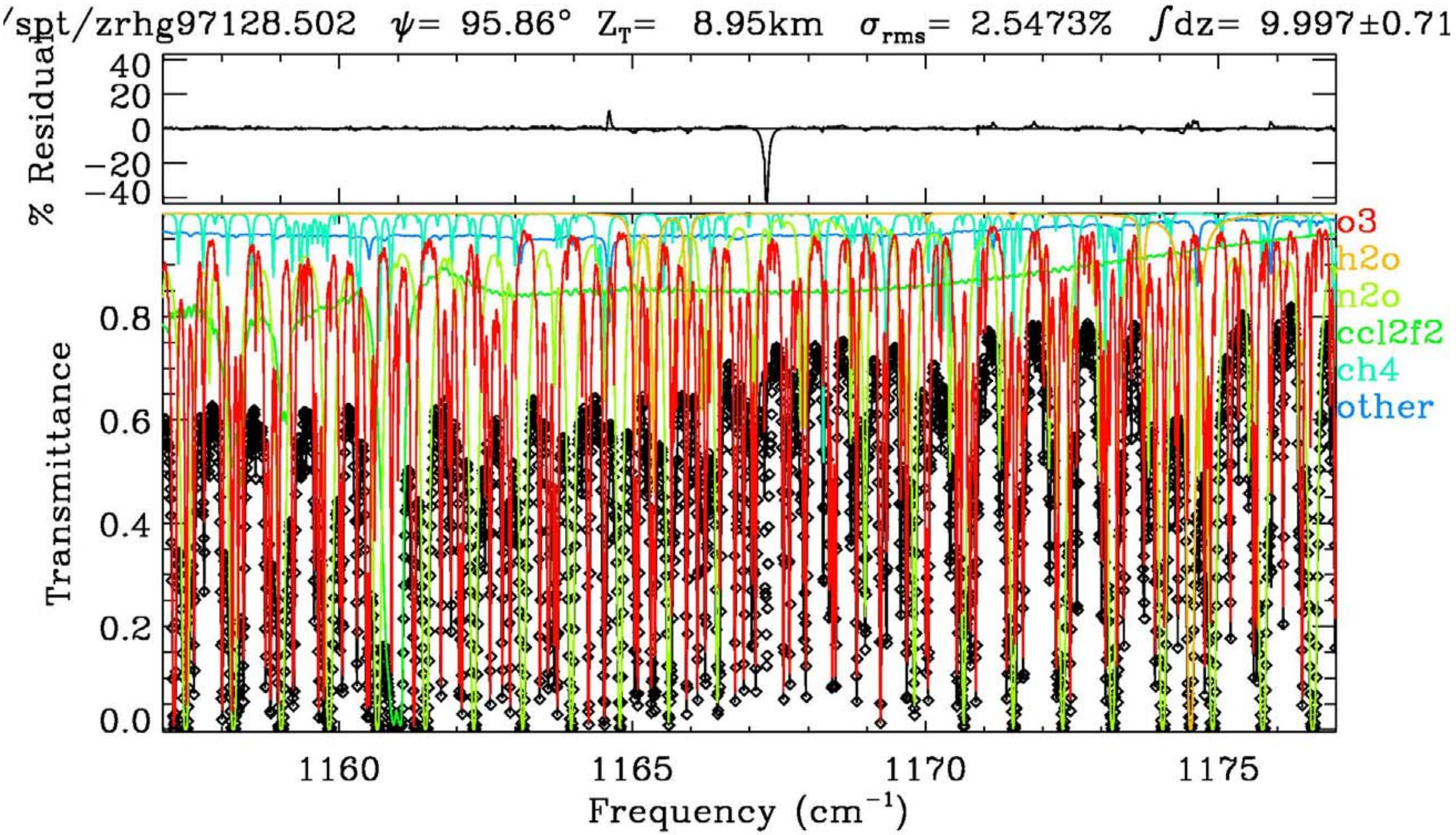
The subsequent plots show fits to MkIV balloon spectra over the 1157 to 1167 cm^{-1} region.

Based on line shape and on altitude variation of residual, we guess that this is a stratospheric gas.

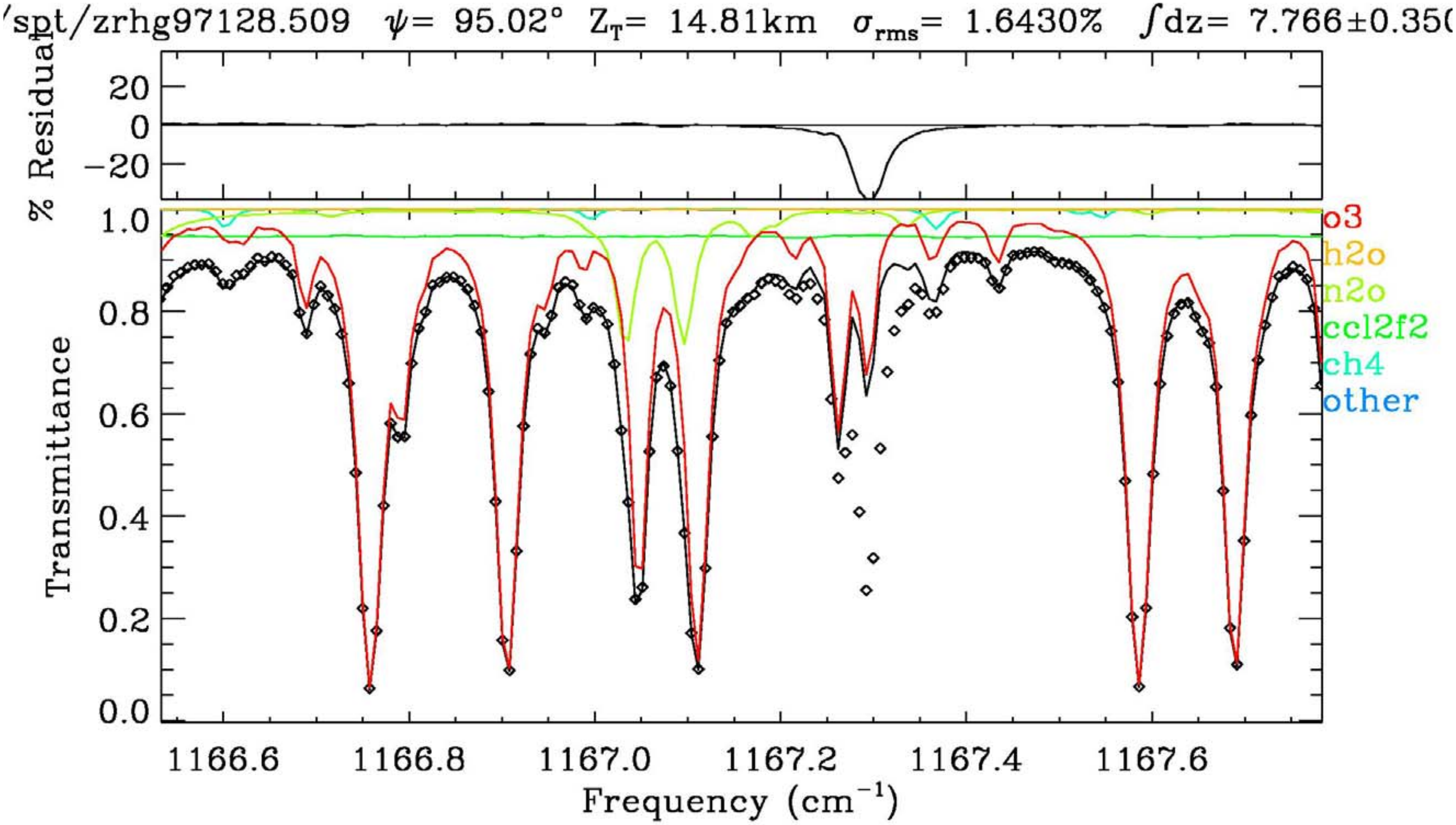
15 km tangent altitude: 1157-1177 cm^{-1}



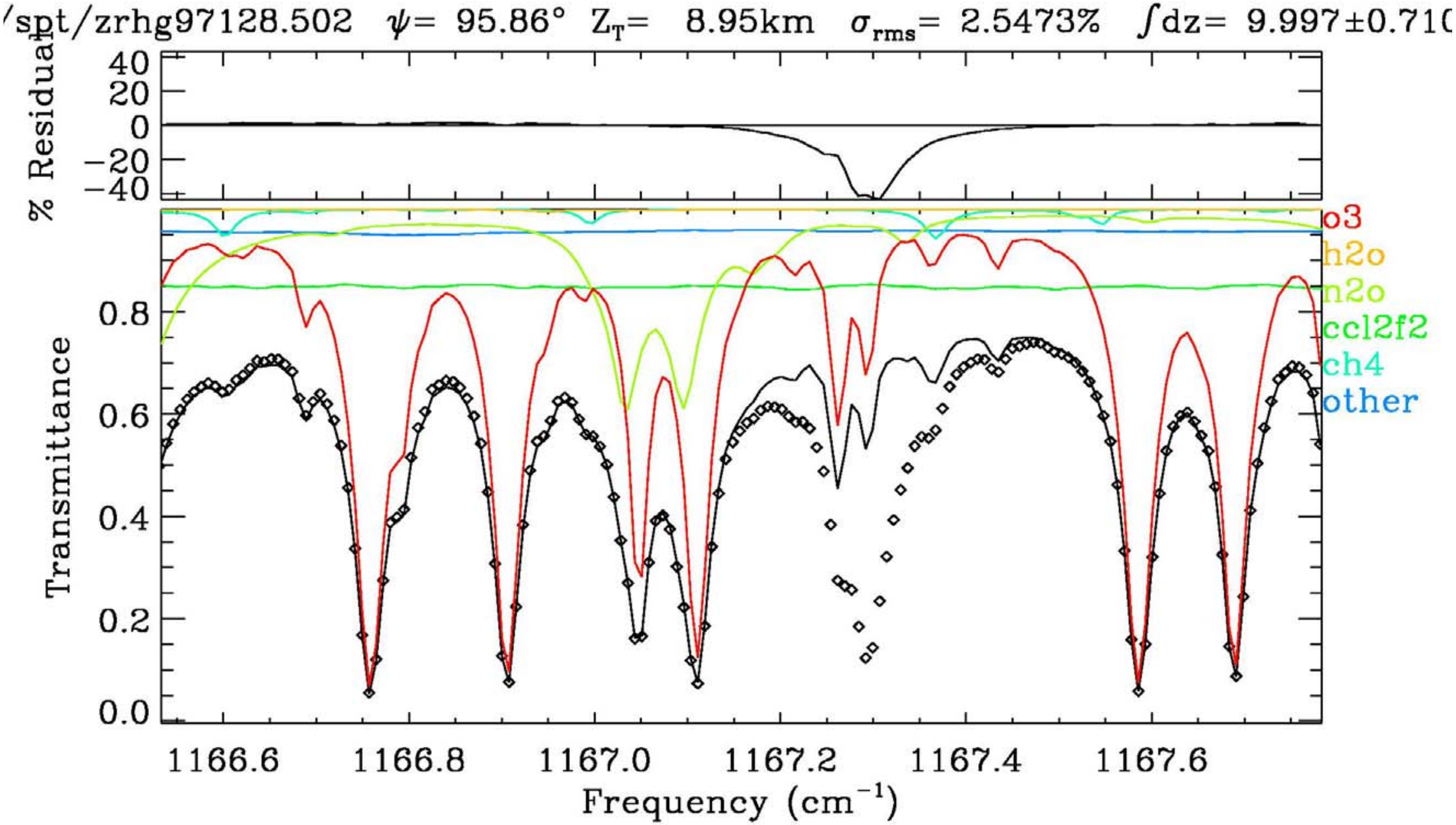
9 km tangent altitude: 1157-1177 cm^{-1}



15 km tangent altitude: 1166-1168 cm^{-1}



9 km tangent altitude: 1166-1168 cm^{-1}



Missing HNO_3 bands: 1340-1355 cm^{-1}

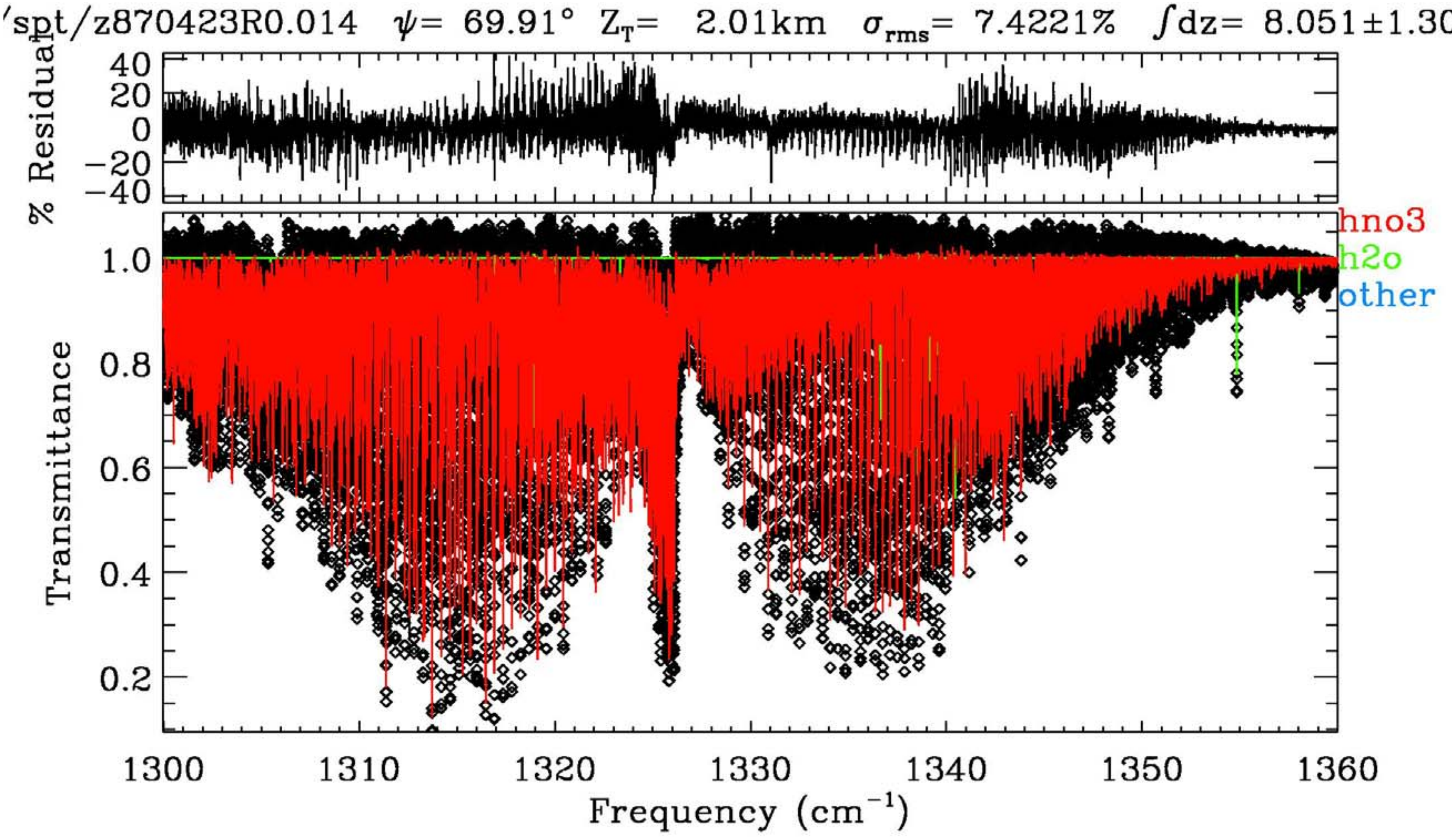
The following 3 plots show fits to a Kitt Peak laboratory spectrum (courtesy of Linda Brown) and MkIV balloon spectra at 15 and 21 km altitude. The strong similarity of the residuals of the lab and balloon spectra confirms their common cause (HNO_3).

The basic ν_3 (1303 cm^{-1}) and ν_4 (1326 cm^{-1}) bands are okay, apart from some extra lines in the 1315 to 1325 cm^{-1} region.

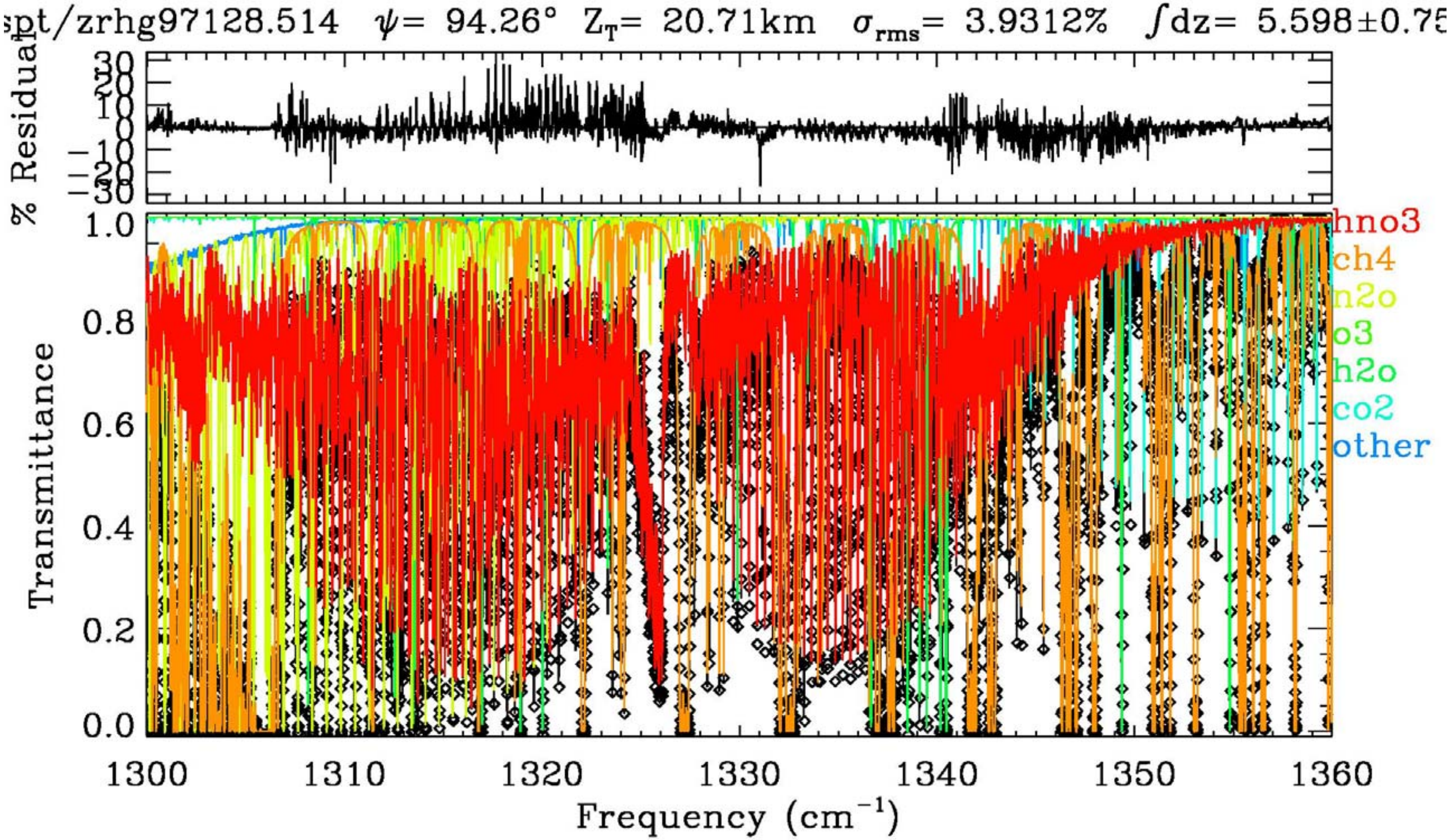
But there are missing lines in the 1340-1355 cm^{-1} region which may arise from missing combination bands ($\nu_5+\nu_9$ or $\nu_7+\nu_8$). Although these bands are ~30x weaker than the fundamental bands, they nevertheless contribute absorption lines up to 10% depth. Since the 1340-1355 cm^{-1} regions the strongest SO_2 lines in the infrared, poor HNO_3 spectroscopy prevents the measurement of SO_2.These missing bands can be seen as –ve residuals in the 1340-1355 cm-1 region.

There is also a prominent dip at 1331.07 cm^{-1}, which is likely also due to HNO_3 since it appears in the laboratory spectrum and since its absorption depth as a function of altitude mirrors that of the HNO3 lines. This produces a 25% residual in fits to the 15 km MkIV balloon spectrum.

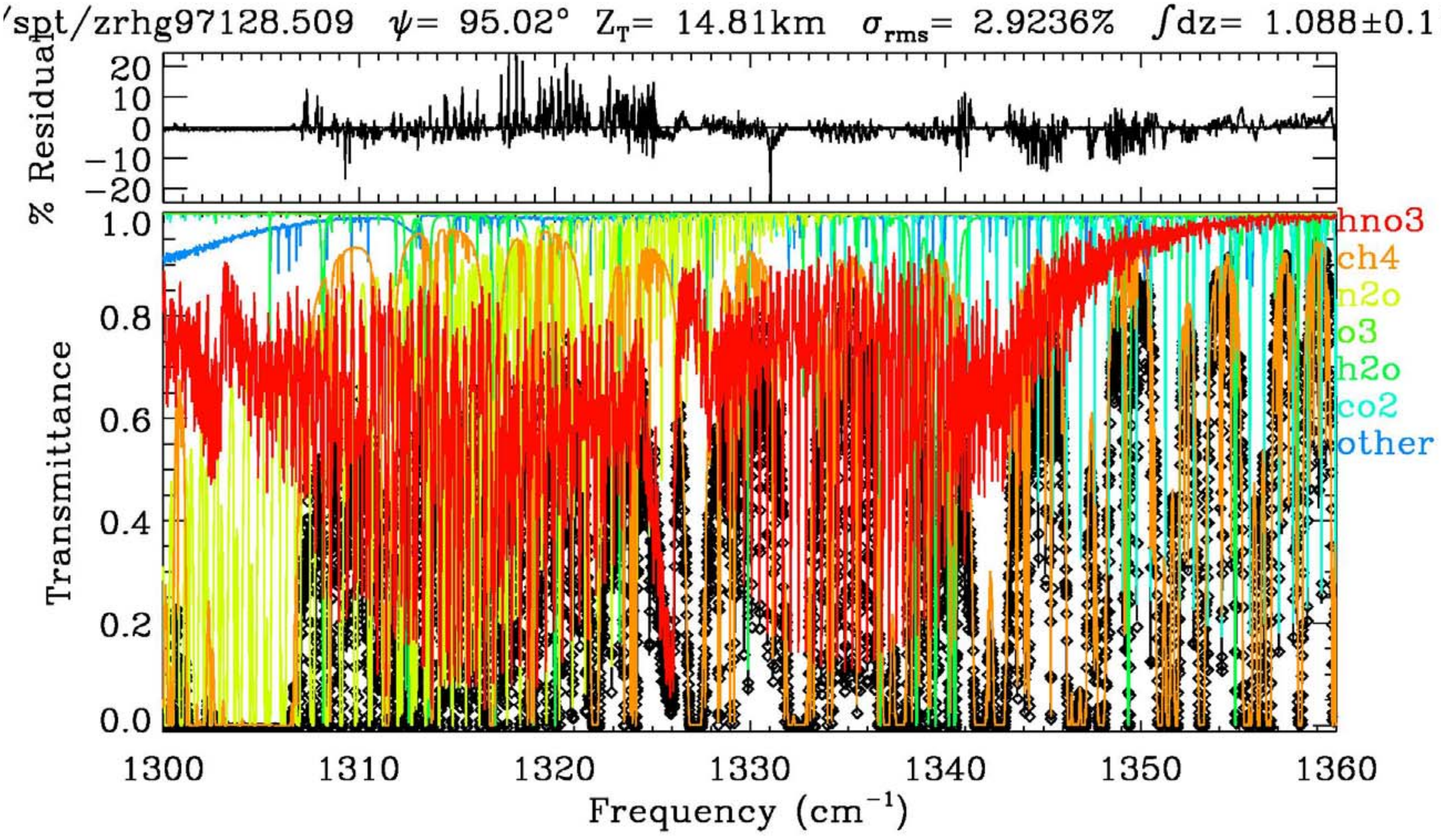
Fit to Kitt Peak laboratory spectrum



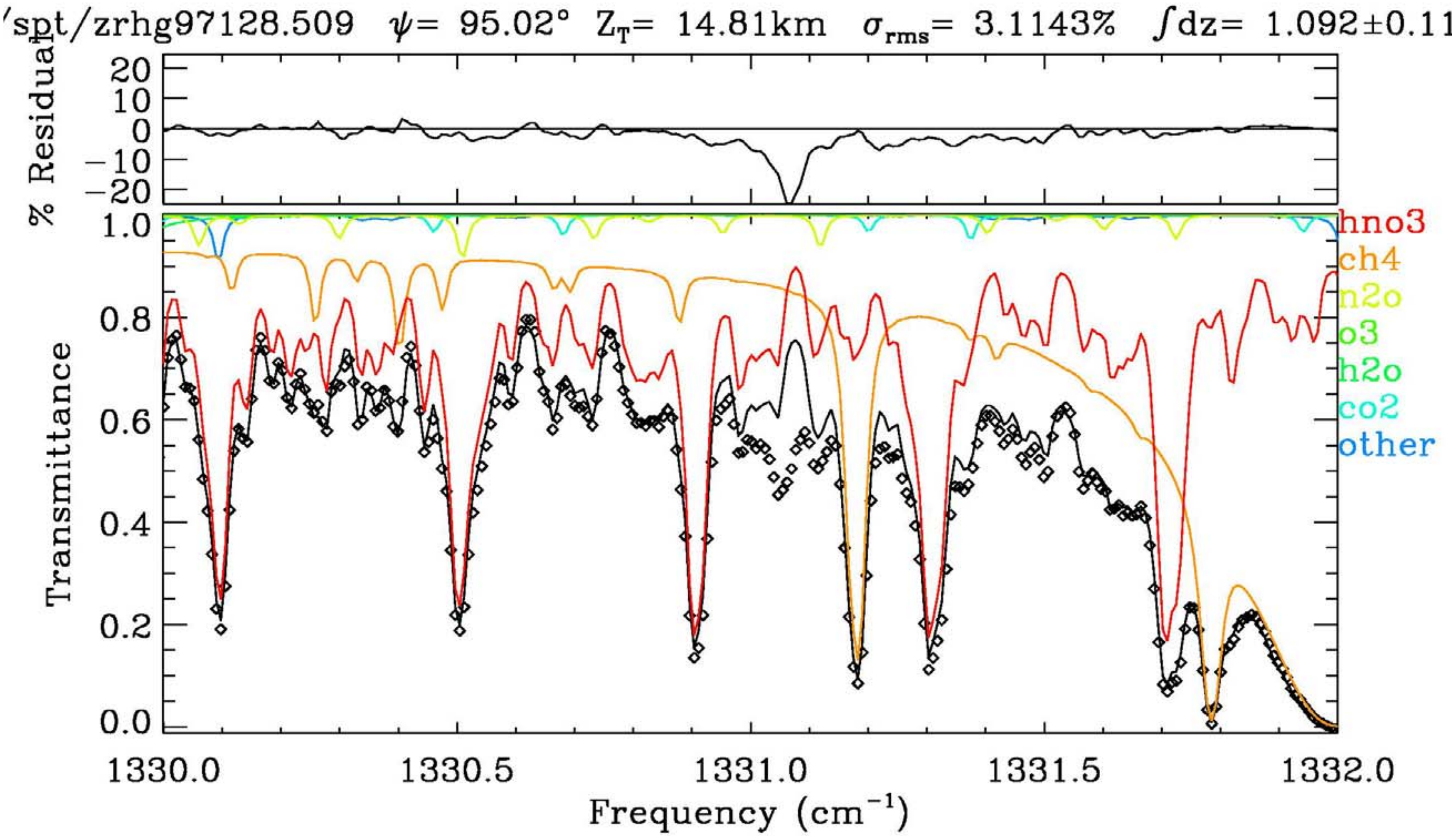
21 km tangent altitude: 1300-1360 cm^{-1}



15 km tangent altitude: 1300-1360 cm^{-1}



15 km tangent altitude: 1330-1332 cm^{-1}



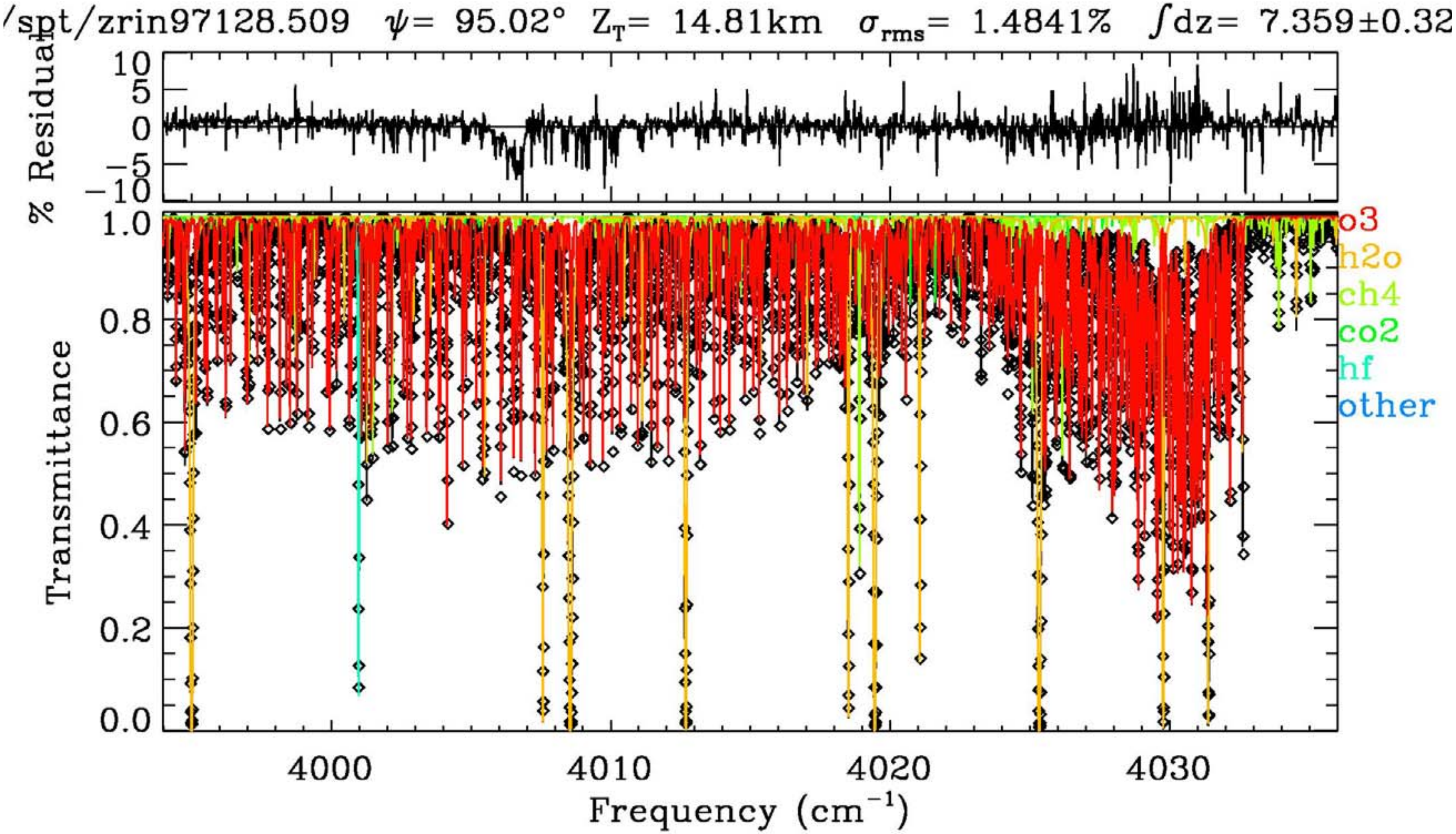
Missing O_3 band: 4007 cm^{-1}

The 3990-4040 cm-1 region is one of the best for limb measurements of O3 in the troposphere or lower stratosphere. This is due to the weakness (i.e. non-saturation) of the O3 lines and the weakness of interfering absorption lines.

Although the HITRAN 2004 lists both the $\nu_1+3\nu_3$ band (4021.85 cm-1) and the $4\nu_3$ band (4001.31 cm-1), there is still a missing band centered around 4007 cm-1 with absorption depths up to 10%.

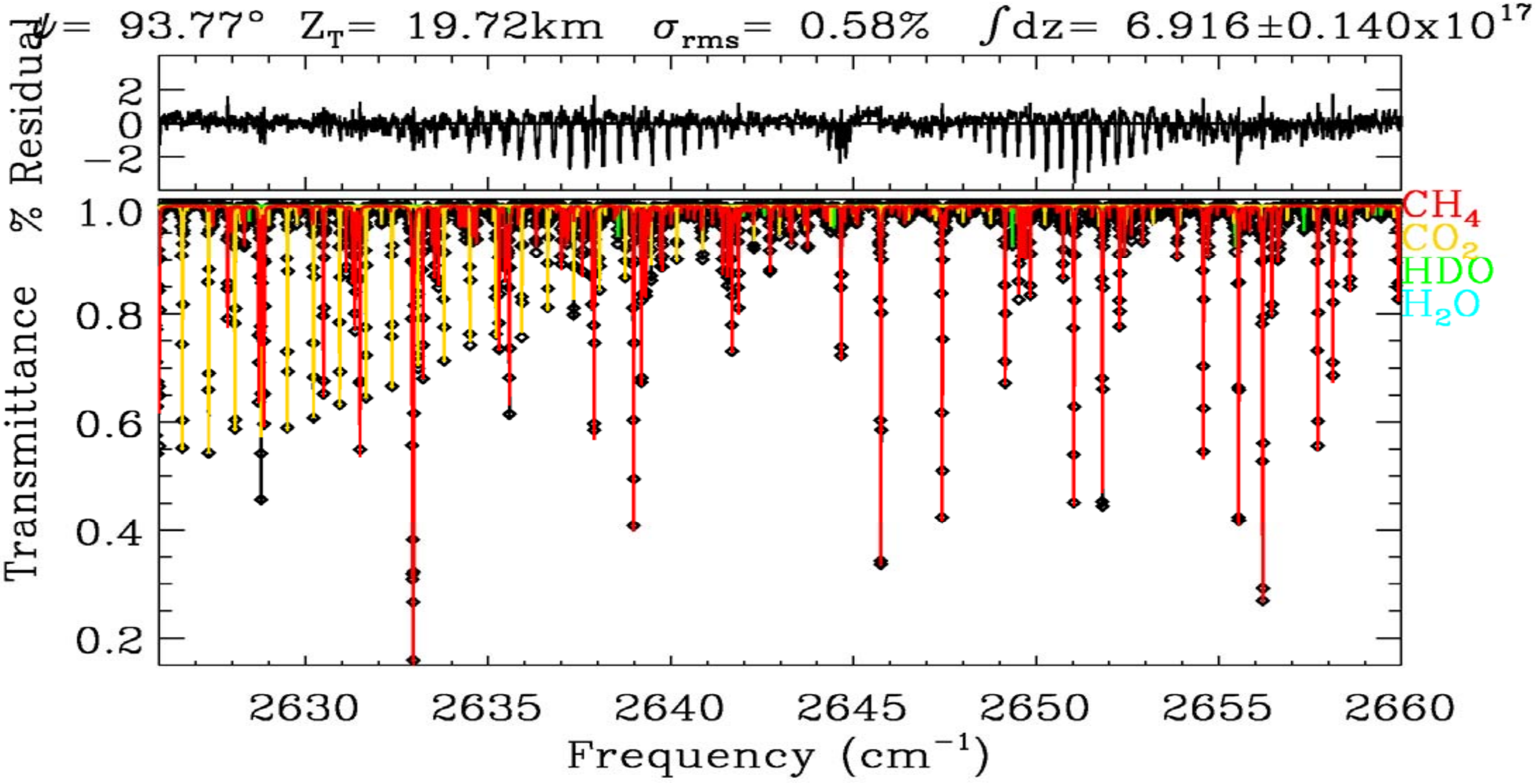
It is also obvious from the subsequent fit to MkIV balloon data that the band head has some line position problem (or line mixing).

15km tangent altitude: 3994-4036 cm^{-1}



Missing $2\nu_4$band of HNO_3 ?

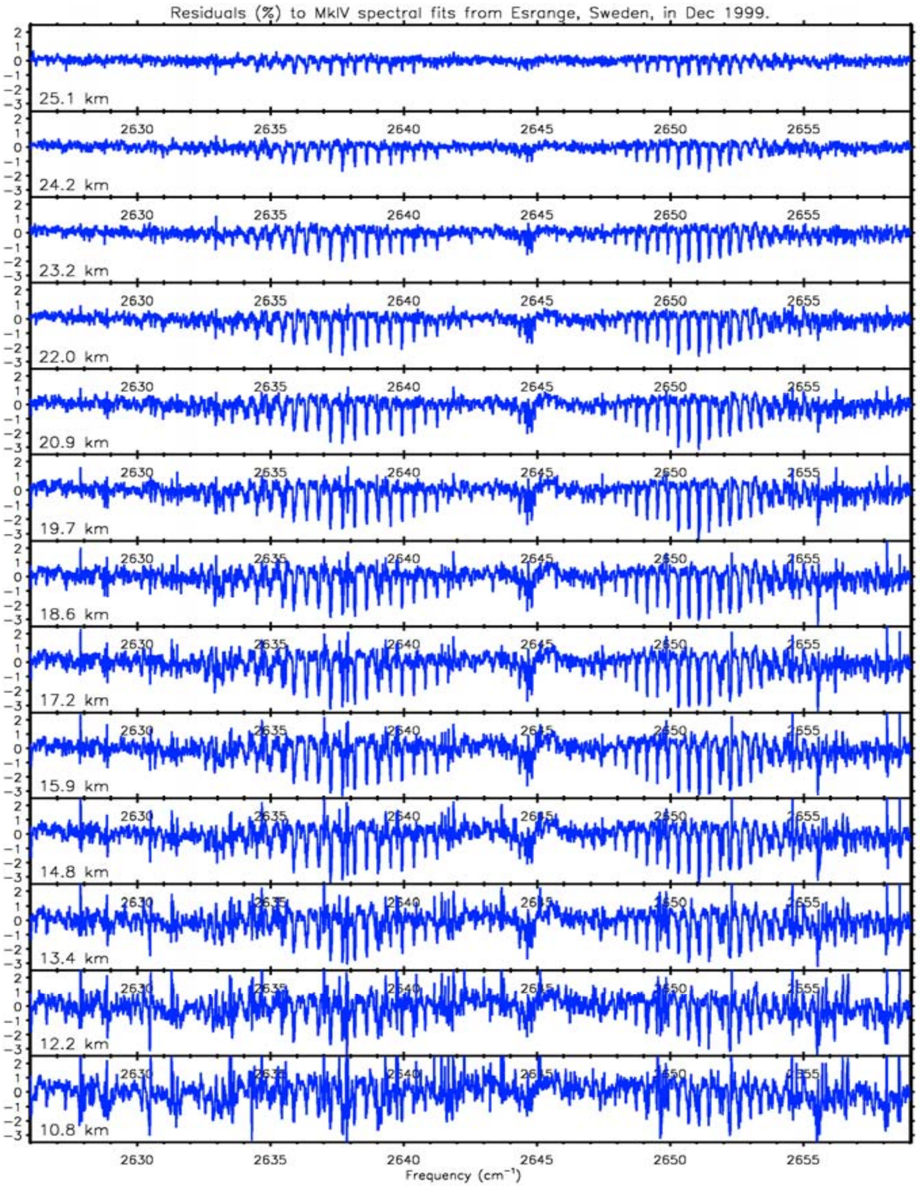
Fit to a MkIV balloon spectrum at 20 km tangent altitude.
Residuals exhibit a P, Q, and R-branch manifolds whose spacing and structure is similar to the ν_4 band of HNO_3 centered at 1326 cm^{-1}



Missing $2v_4$band of HNO_3 ?

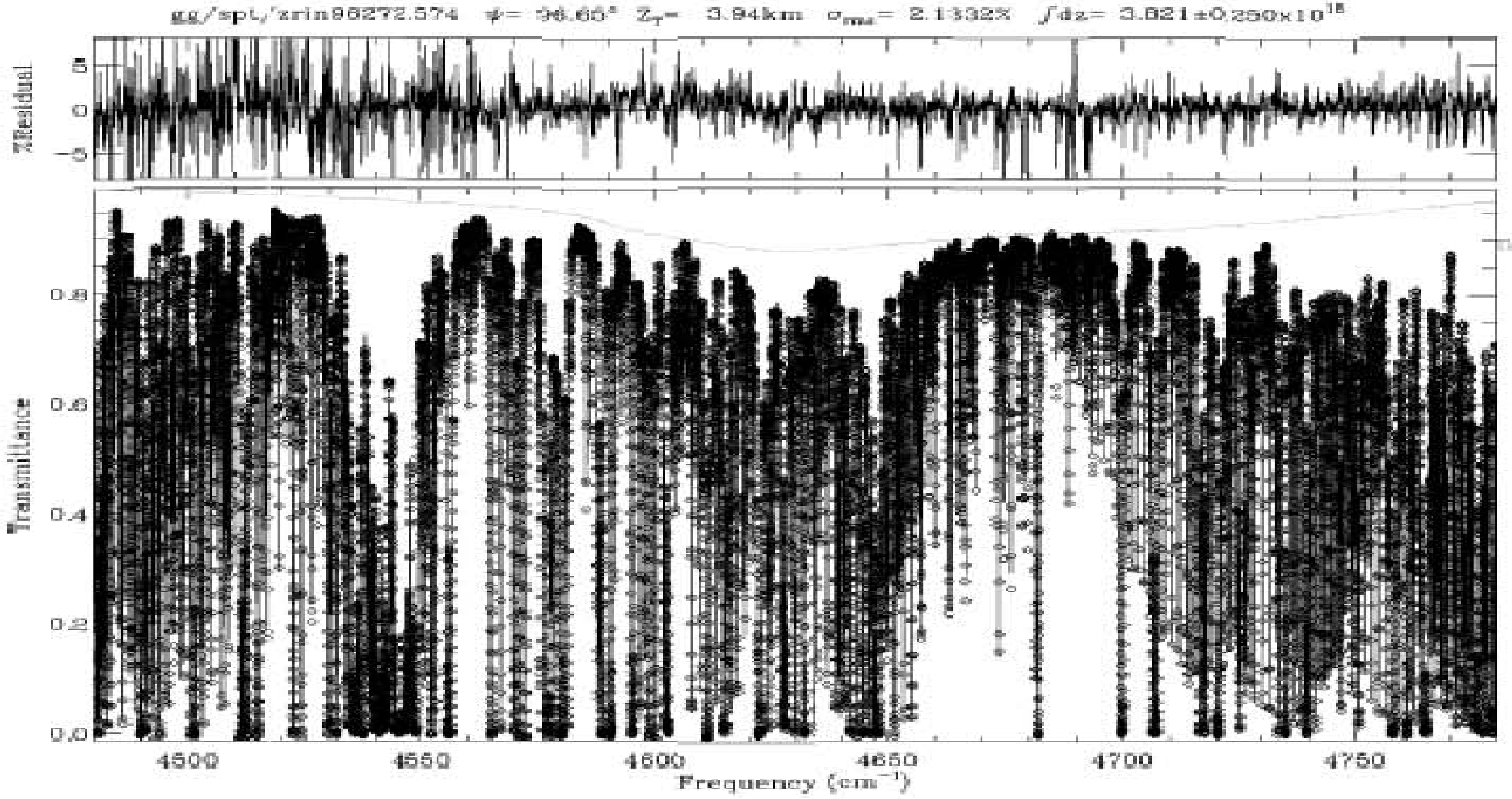
The altitude variation of the depths of these residuals confirms that the concentration of the responsible absorber peaks in the lower stratosphere at ~16 km.

We believe that HNO_3 is the most likely candidate since the band looks like the longer wavelength HNO_3 bands and each of the absorption dips is a manifold containing several lines. Since the HNO_3 v_4 band is centered at 1326 cm^{-1}, a possibility is the $2v_4$ band.



Missing N_2 CIA Overtone

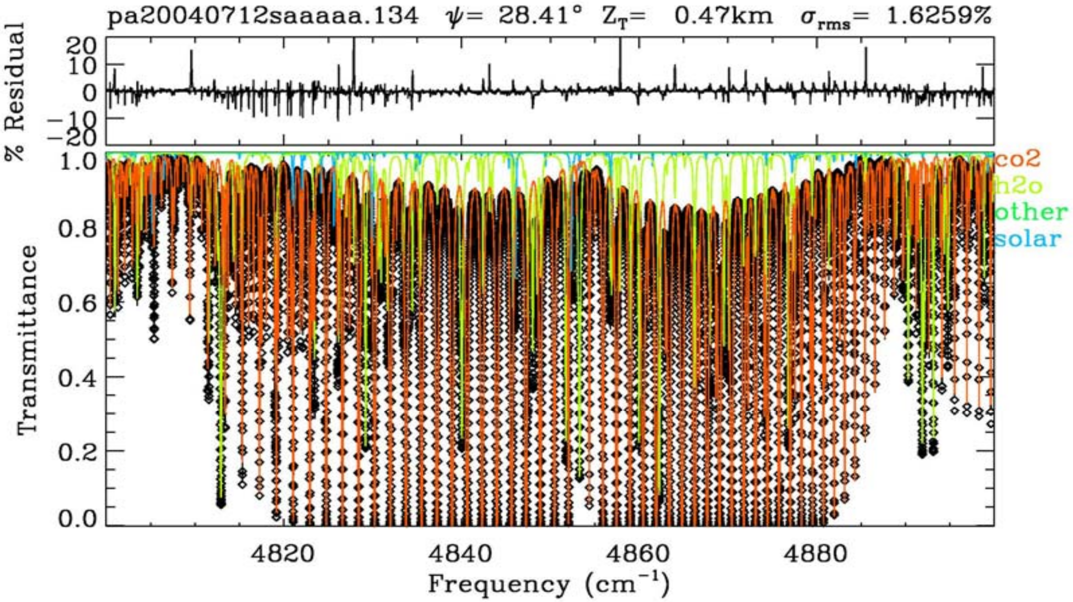
Figure below (courtesy of Paul Wennberg) shows a fit to a MkIV balloon spectrum measured at 4 km altitude. The faint grey line shows the contribution from the N_2 Collision Induced Absorption (CIA) overtone band centered at 4630 cm^{-1}, based on laboratory measurements of SHAPIRO MM & GUSH HP [1966]



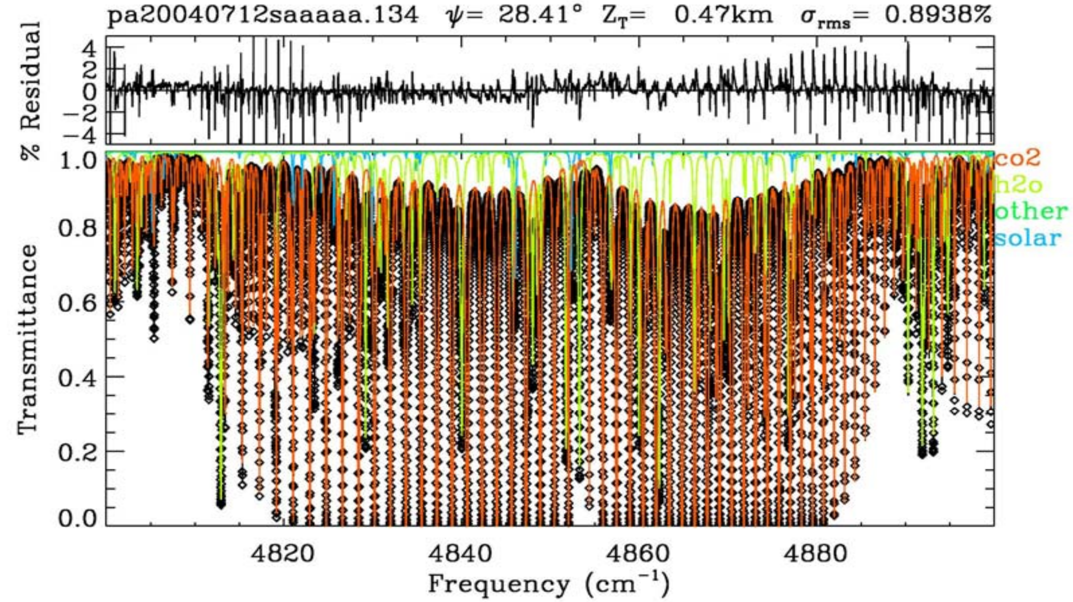
HITRAN 1996 & 2004 comparisons

The following 6 plots show fits to ground-based near-IR spectra acquired from Park Falls (courtesy of Paul Wennberg and Rebecca Washenfelder)

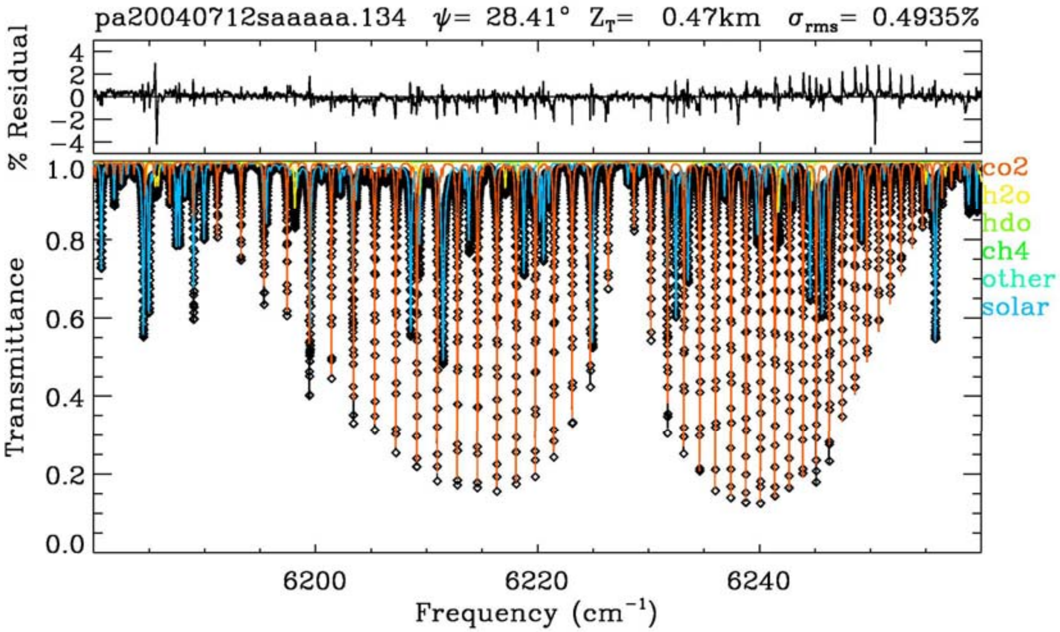
HITRAN 1996



HITRAN 2004



HITRAN 1996



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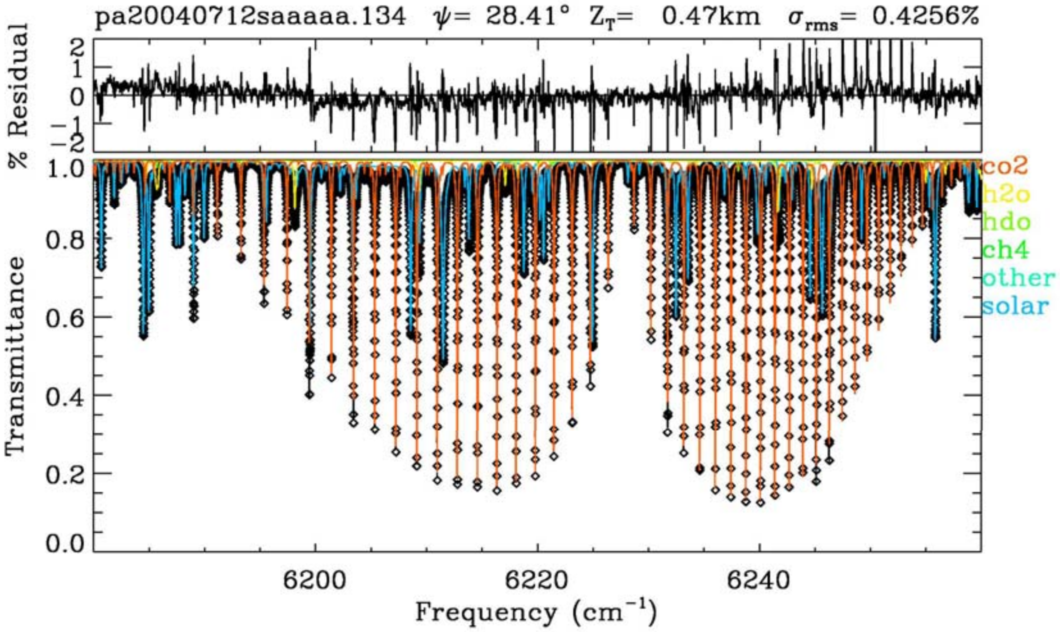
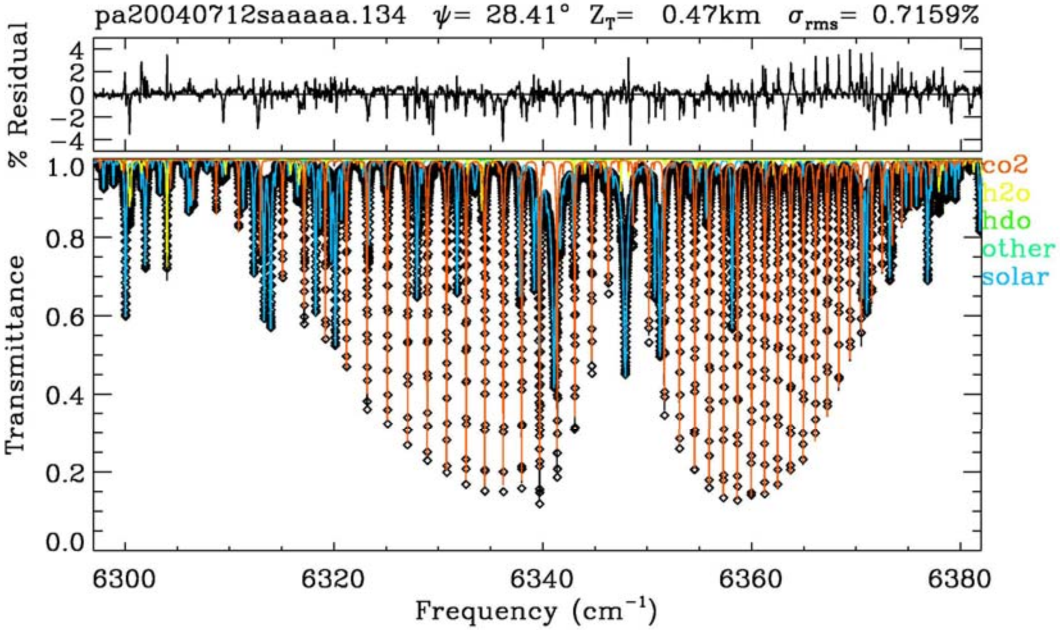


HITRAN 1996



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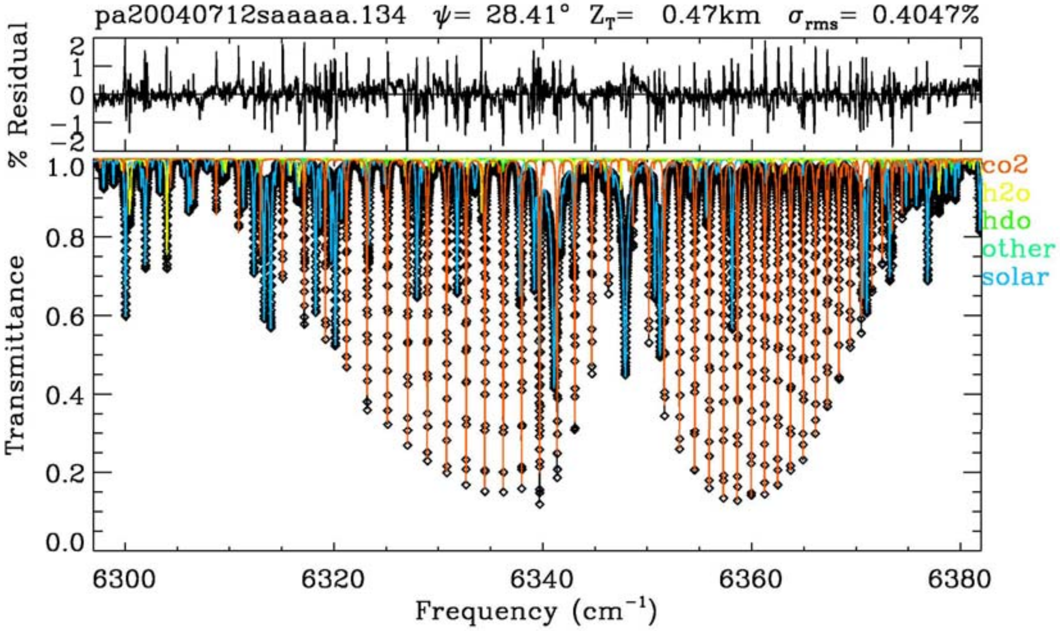
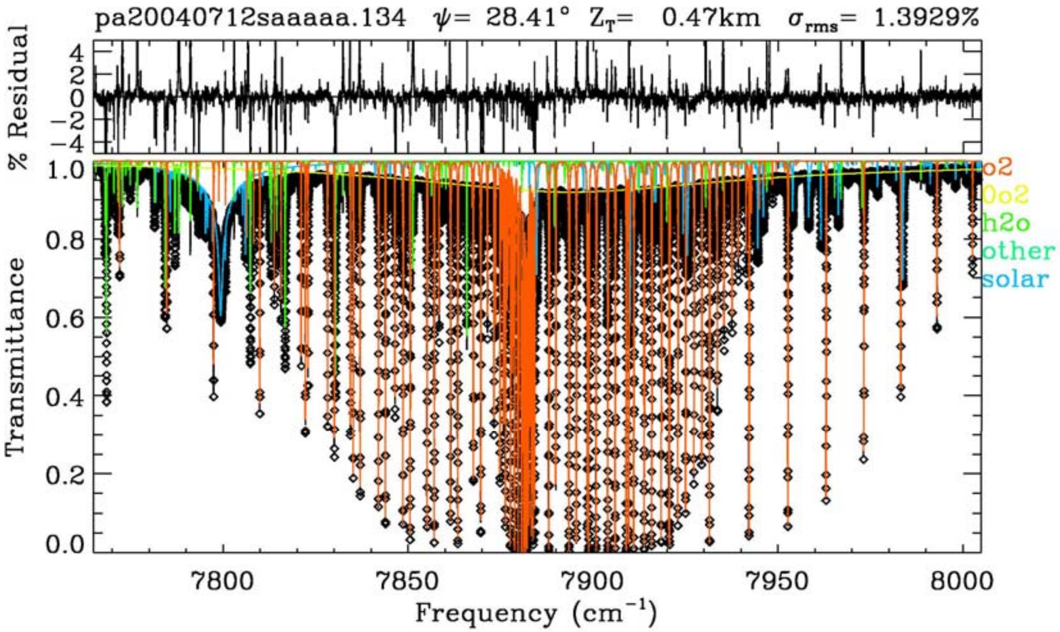


HITRAN 1996



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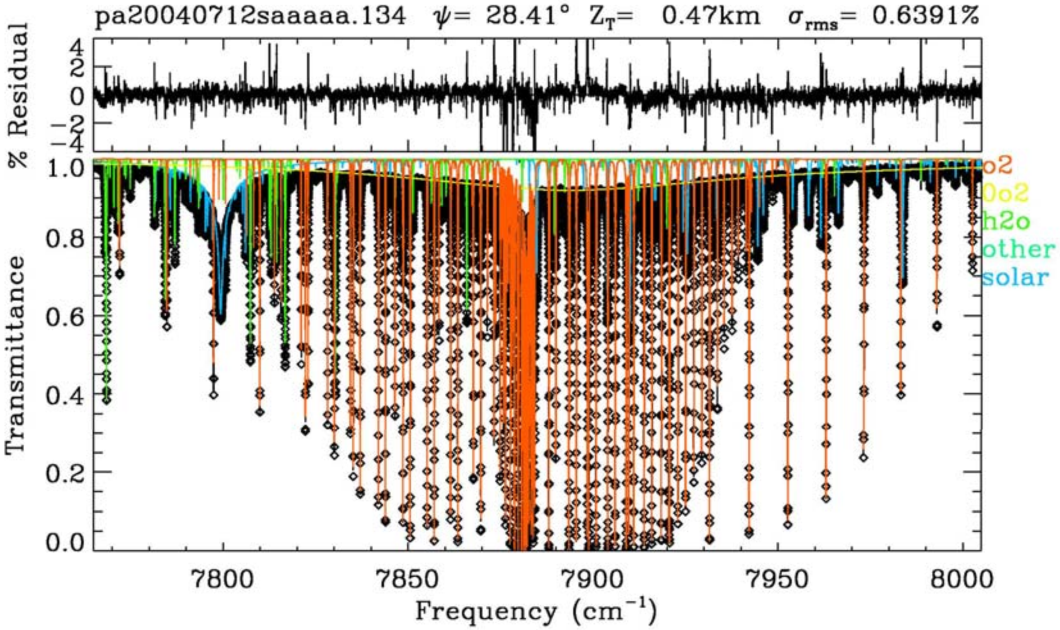

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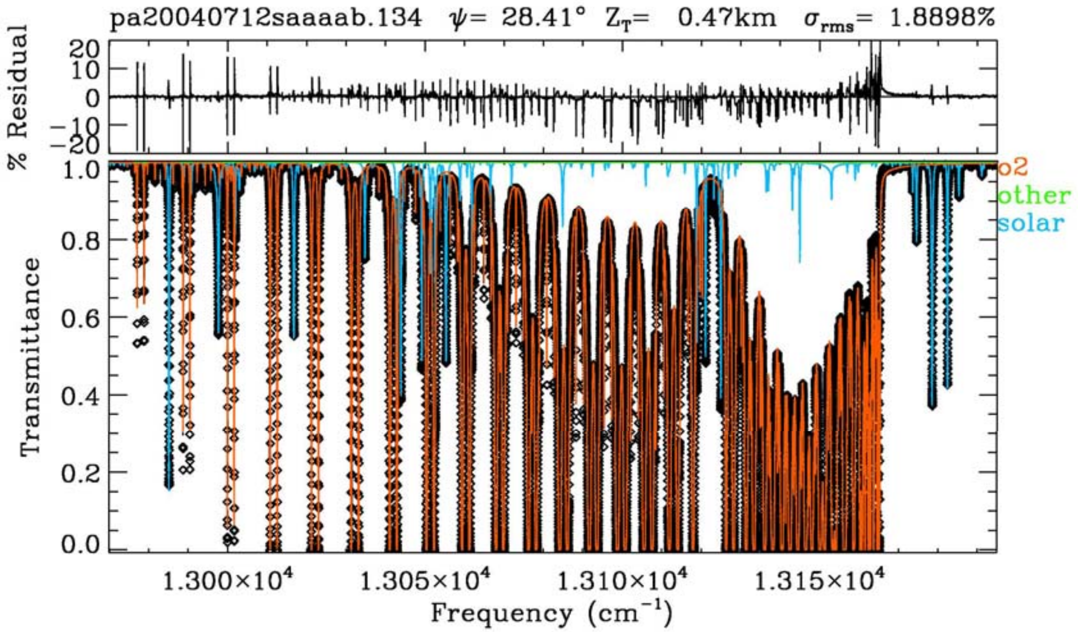

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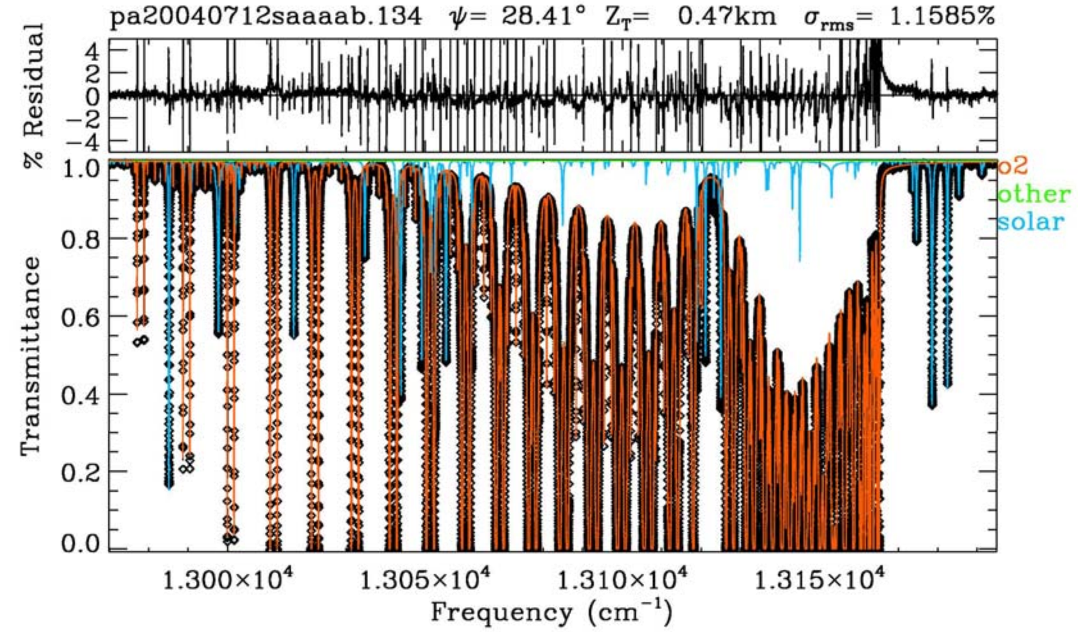

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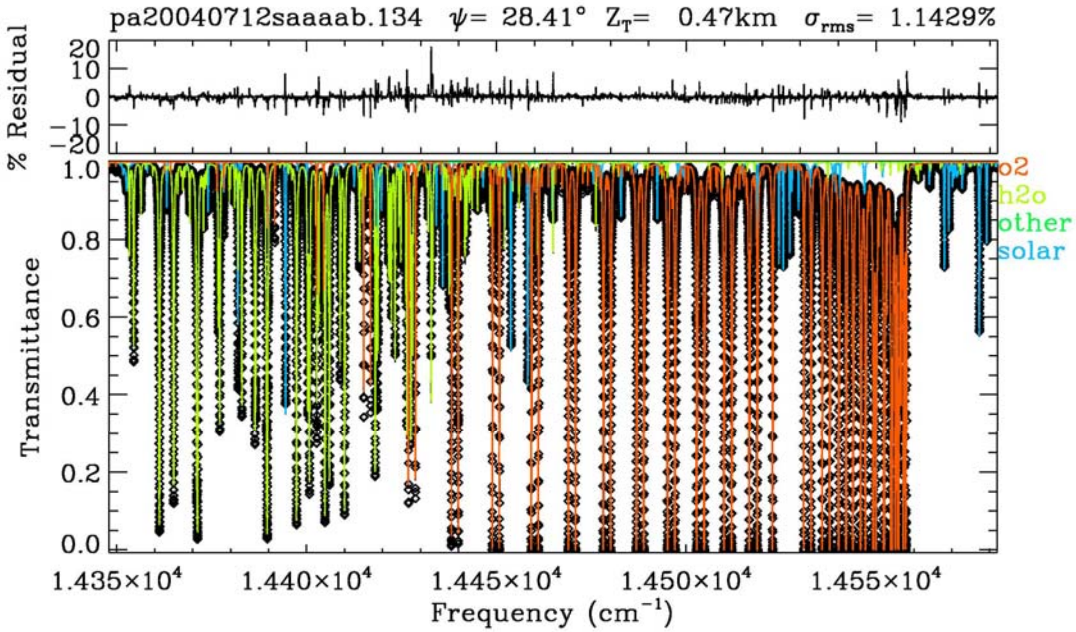

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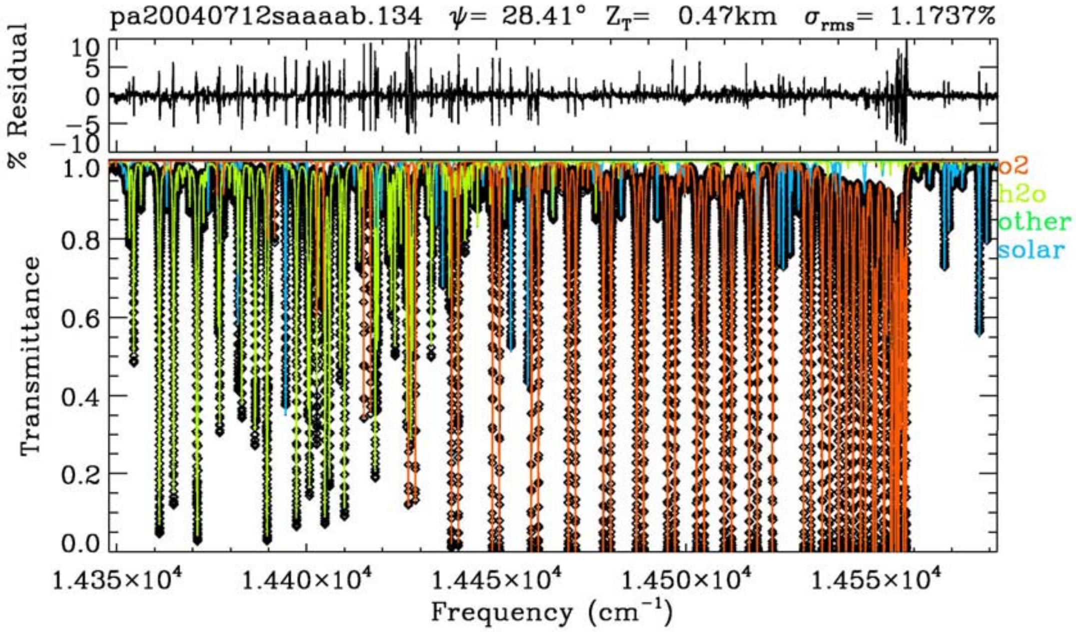

Conclusions

Solar occultation spectrometry has the high SNR and spectral resolving power necessary to:

- Identify weak absorptions due to trace gases and minor isotopomers.

- Identify inadequacies in the spectroscopic database and pinpoint their cause.

In general, fits to MkIV balloon spectra are limited not by the measurement noise but by spectroscopic limitations.

To identify more weakly absorbing trace gases and minor isotopologues requires further spectroscopic improvement. Not just the trace species themselves, but more importantly, the major gases whose absorptions overlap the trace gas absorptions of interest.