Evaluation of HITRAN 2016 O_3 linelist

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2017-01-17

The prospective HIT16 O_3 linelist (O3_hit16_beta.par), received from Iouli Gordon on Oct 27, 2016, was compared with its predecessors (HIT08, HIT12) in terms of the quality of the spectral fits to 194 Kitt Peak lab spectra and 19 MkIV balloon spectra, and in terms of the consistency of retrieved O_3 amounts from different windows.

A fourth linelist (ATM16) was also included. This is based on previous HITRAN versions, but not necessarily the latest for every gas/band. ATM16 also embodies empirical tweaks based on improving fits to lab spectra.

20 broad windows were defined over the 600 to 5000 cm^{-1} region in which discernable O_3 absorption could be seen in Kitt Peak lab and MkIV balloon spectra. The windows chosen for the lab and balloon analyses were very similar in terms of their spectra coverage, but the interfering gases fitted are more extensive for the balloon spectra.

A new linelist, HIT16", generated from O3_hit16_beta.par by empirically adjusting several hundred of the line position based on fits to Kitt Peak lab spectra, was also evaluated.

For the other (non-O_3) gases, the ATM16 linelist was used since it provides the best fits, the HIT16 linelist not yet existing for the other gases.

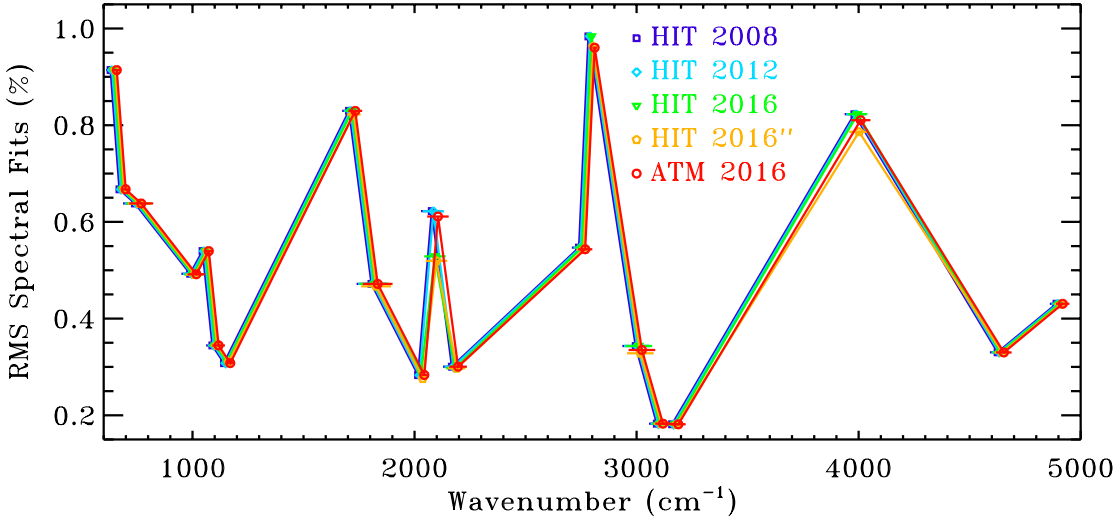
Spectral fitting Windows & RMS (lab)

Center (cm^{-1})	Width (cm^{-1})	Gases fitted	RMS Spectral Fits (%) HIT08	HIT12	HIT16	HIT16"	ATM16
645.0	40.0	o3 h2o co2	0.9141	0.9141	0.9140	0.9140	0.9141
685.0	32.0	o3 h2o co2	0.6674	0.6674	0.6674	0.6674	0.6674
755.0	108.0	o3 h2o	0.6382	0.6382	0.6381	0.6381	0.6382
1003.4	79.0	o3 h2o	0.4928	0.4928	0.4909	0.4909	0.4918
1059.4	32.0	o3 h2o	0.5397	0.5397	0.5397	0.5397	0.5397
1103.5	57.0	o3 h2o	0.3445	0.3445	0.3445	0.3445	0.3445
1156.0	36.0	o3 h2o n2o	0.3079	0.3079	0.3105	0.3105	0.3079
1719.0	62.0	o3 h2o	0.8297	0.8297	0.8297	0.8223	0.8297
1820.0	134.0	o3 h2o	0.4718	0.4718	0.4718	0.4668	0.4718
2029.9	25.7	o3 h2o co ocs co2	0.2831	0.2830	0.2877	0.2867	0.2834
2091.6	96.8	o3 h2o co ocs co2	0.6223	0.6221	0.5288	0.5194	0.6112
2182.0	80.0	o3 h2o co n2o	0.3005	0.3005	0.2974	0.2972	0.3006
2754.5	64.0	o3 hdo	0.5468	0.5468	0.5468	0.5426	0.5434
2797.0	21.0	o3 hdo	0.9837	0.9839	0.9839	0.9591	0.9603
3010.0	120.0	o3 h2o	0.3433	0.3433	0.3434	0.3282	0.3351
3105.0	70.0	o3 h2o	0.1827	0.1827	0.1825	0.1825	0.1827
3174.0	66.0	o3 h2o	0.1814	0.1814	0.1814	0.1814	0.1814
3995.0	88.0	o3 h2o	0.8228	0.8228	0.8228	0.7863	0.8104
4640.0	70.0	o3 h2o	0.3303	0.3303	0.3303	0.3298	0.3300
4905.0	60.0	o3 h2o co2	0.4307	0.4307	0.4306	0.4299	0.4307

Blue highlighted values represent the best rms fitting values. The differences between the RMS values arise solely from O_3 spectroscopy (all other gases fixed to ATM16).

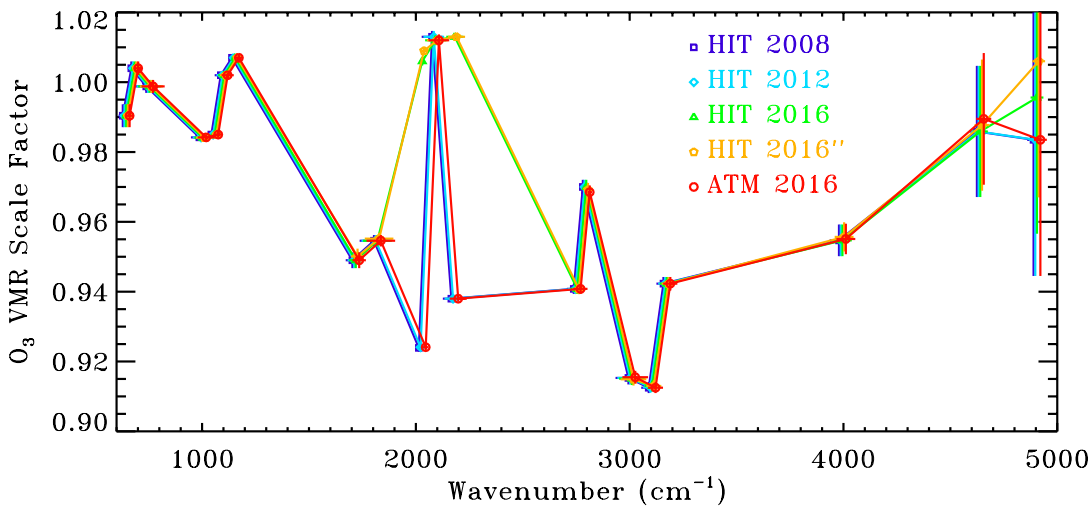
Kitt Peak laboratory spectra: fitting results

Used 194 Kitt Peak lab spectra of O_3 measured from 1984 to 1998, although none covered every window. Due to the limited spectral coverage, only 39% of the potential 20x194 spectral fits could be performed. These lab spectra range from 210 to 300K and from 0.5 to 250 Torr.



Upper Panel: RMS fitting residuals. Their absolute values don't really matter. Their variation from linelist to linelist is more important.

HIT16 produces much improved residuals in the 2090 cm^{-1} window, rms down from 0.63% to 0.52%.



Lower Panel: The VMR Scale Factor represents the retrieved O_3 amount divided by the expected amount, based on nominal cell conditions.

In the 2029 and 2180 cm^{-1} windows the HIT16 and HIT16" linelists yield 8% larger retrieved O_3 amounts.

The 3010 & 3105 cm^{-1} windows now produce the lowest O_3 amounts.

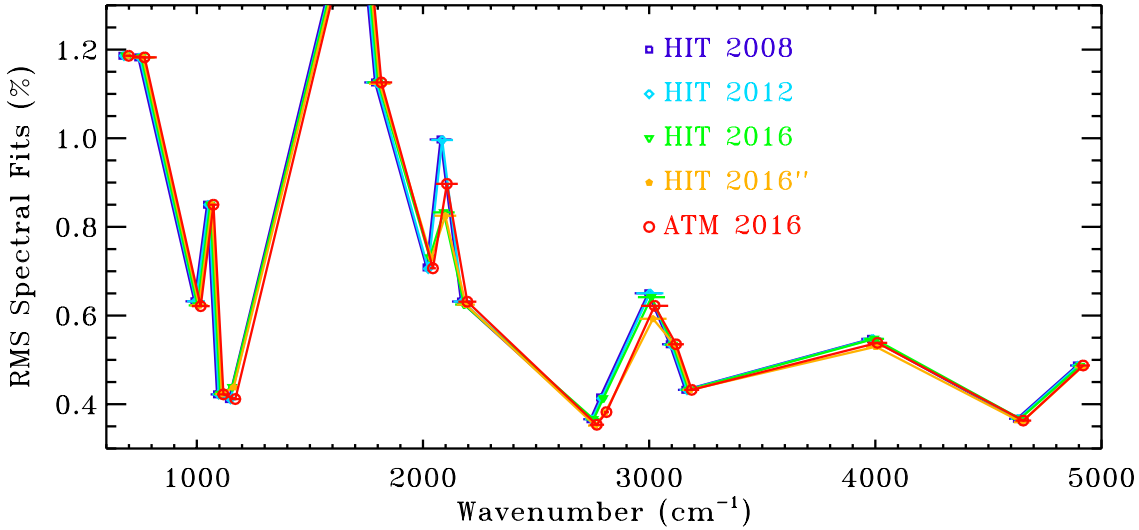
Spectral fitting windows & RMS (balloon)

Center (cm^{-1})	Width (cm^{-1})	Gases fitted	RMS Spectral Fits (%) HIT08	HIT12	HIT16	HIT16″	ATM16
685.0	32.0	o3 h2o co2	1.1861	1.1861	1.1866	1.1866	1.1861
755.0	108.0	o3 h2o co2	1.1825	1.1825	1.1825	1.1825	1.1825
1003.4	79.0	o3 h2o co2 ch4 n2o	0.6322	0.6322	0.6229	0.6229	0.6212
1059.4	32.0	o3 h2o co2	0.8501	0.8501	0.8500	0.8500	0.8501
1103.5	57.0	o3 h2o co2	0.4222	0.4222	0.4230	0.4230	0.4222
1156.0	36.0	o3 h2o n2o	0.4116	0.4116	0.4384	0.4384	0.4116
1719.0	62.0	o3 h2o hno3 n2o5 clno3	1.5932	1.5932	1.5932	1.5929	1.5970
1802.0	95.4	o3 h2o hno3 co2 n2o no	1.1259	1.1259	1.1259	1.1228	1.1259
2029.9	25.7	o3 h2o co2 ocs	0.7086	0.7056	0.7310	0.7298	0.7066
2091.6	96.8	o3 h2o co co2	0.9973	0.9961	0.8328	0.8251	0.8972
2182.0	80.0	o3 h2o co n2o	0.6316	0.6316	0.6248	0.6245	0.6312
2754.5	64.0	o3 hdo ch4	0.3661	0.3659	0.3659	0.3518	0.3536
2797.0	21.0	o3 hdo ch4	0.4153	0.4132	0.4132	0.3796	0.3822
3010.0	120.0	o3 h2o ch4 hcl hno3 ch3cl	0.6503	0.6503	0.6415	0.5926	0.6220
3105.0	69.0	o3 h2o ch4	0.5352	0.5342	0.5340	0.5340	0.5352
3174.0	66.0	o3 h2o ch4 co2	0.4324	0.4323	0.4323	0.4323	0.4324
3995.0	87.0	o3 h2o ch4 co2 hno3 hf	0.5474	0.5474	0.5474	0.5298	0.5384
4640.0	70.0	o3 h2o co2 ch4 n2o	0.3671	0.3671	0.3671	0.3594	0.3630
4905.0	60.0	o3 h2o 1co2 2co2 3co2 co2	0.4874	0.4874	0.4861	0.4832	0.4874

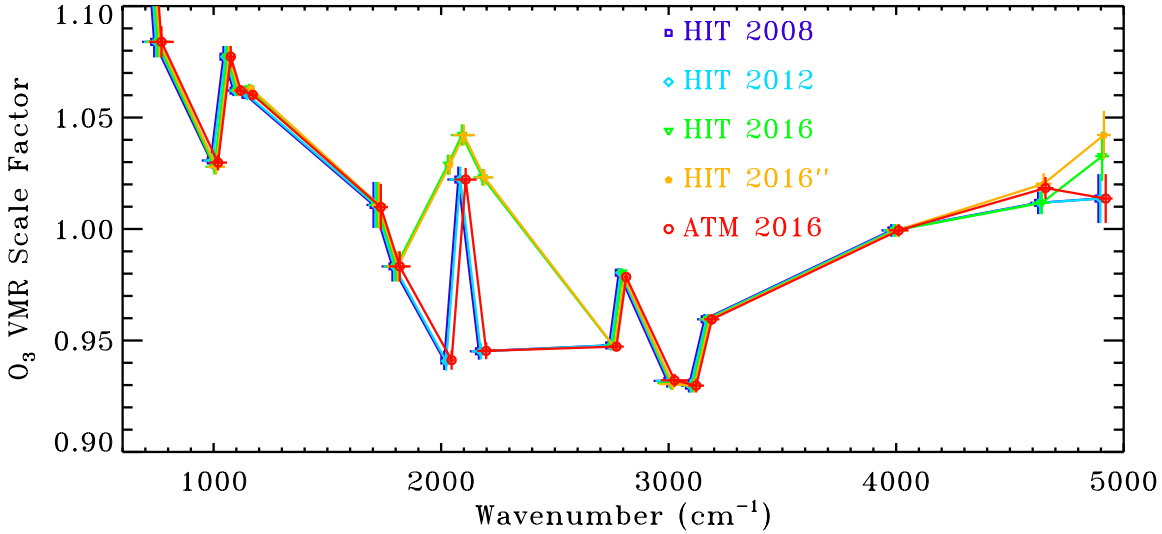
645 cm^{-1} window not used for balloon spectra: region blacked out by CO_2 at most altitudes. Blue highlighted values represent the best rms fitting values. The differences between the RMS values arise solely from O_3 spectroscopy (all other gases fixed to ATM16).

Balloon Fitting Results (da_fai97rat.brl)

An occultation of MkIV balloon spectra was fitted, covering altitudes from 9 to 37 km. Every MkIV spectrum covered every window, so 100% of potential spectral fits were performed



Upper Panel: RMS fitting residuals. Absolute values are dominated by interfering gases (e.g. H_2O & HNO_3 at 1730 cm^{-1}). It is the linelist-to-linelist variations that pertain to O_3.
HIT2016 produces improved rms residuals in 2090 cm^{-1} window.

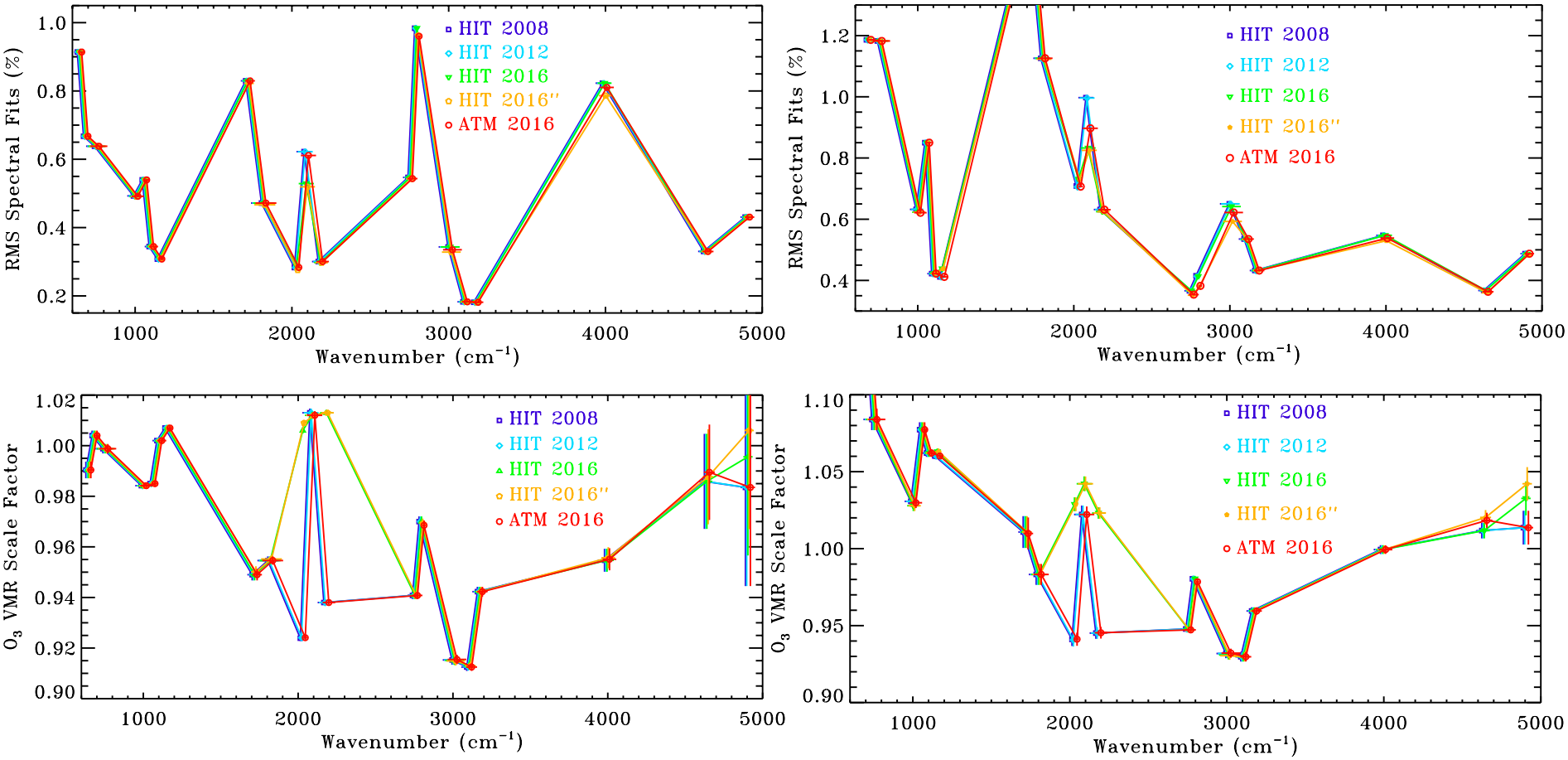


Lower Panel: Retrieved O_3 VMR Scale Factors. HIT16 produces larger retrieved O_3 amounts in the 2000-2250 cm^{-1} region.

All linelists produce their lowest O_3 amounts in the 3010 & 3105 cm^{-1} windows.

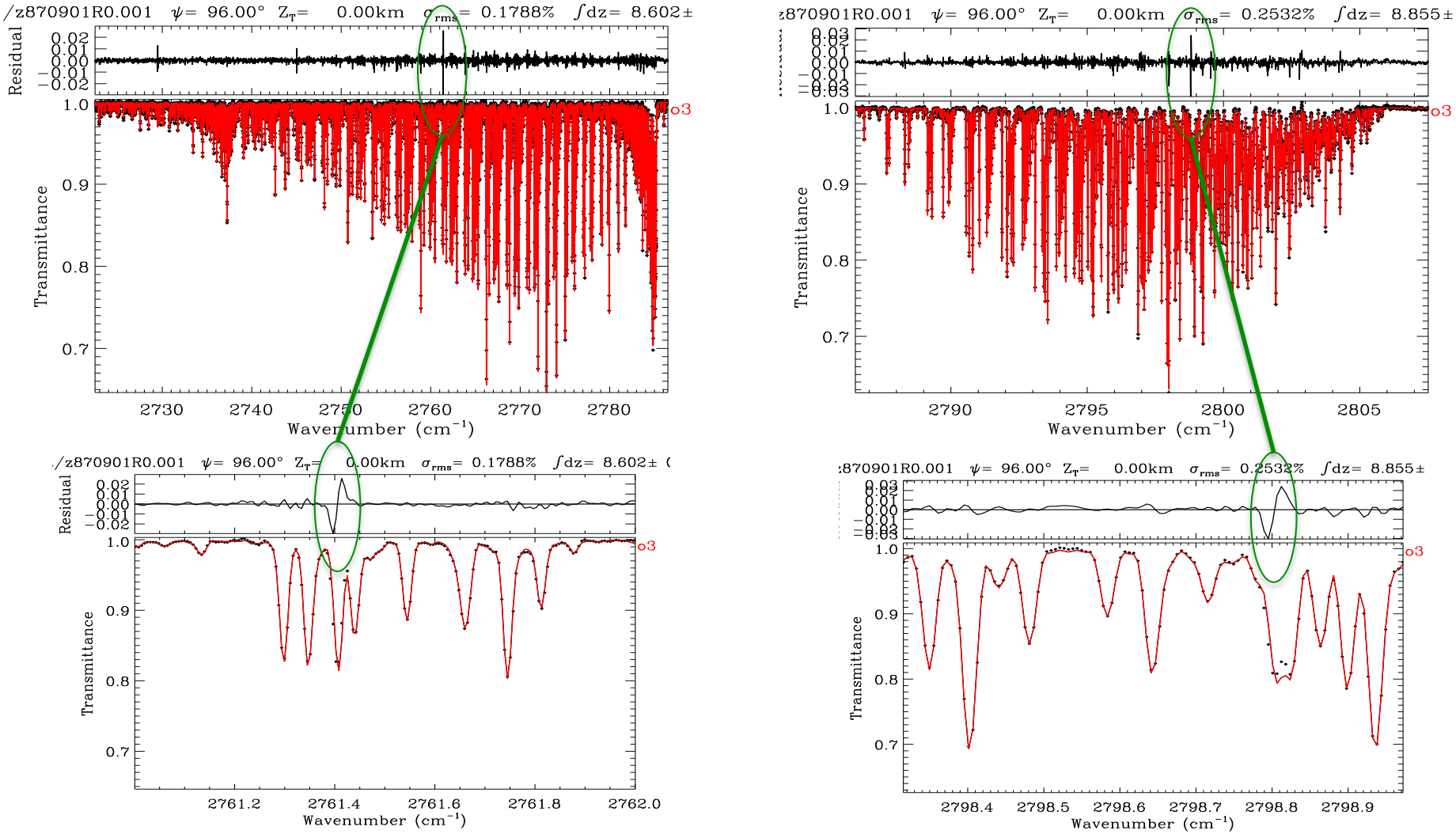
Laboratory (left) and Balloon (right) results

Upper panels show average RMS spectral fitting residuals. The large values at 600-700 cm^{-1} are due to interfering CO_2 . Those around 1730 cm^{-1} are due to atmospheric HNO_3 and H_2O.



Lower panels show average vmr scale factors (VSF). Above 2000 cm^{-1} there is good consistency between balloon and laboratory, but below 2000 cm^{-1} the balloon results are ~5% larger.

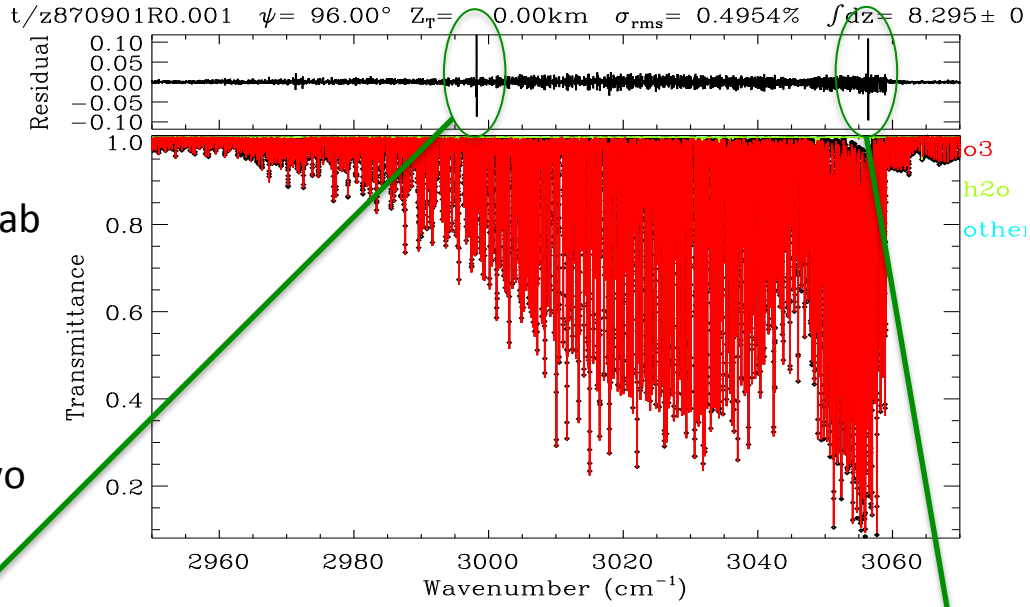
Kitt Peak lab spectral fits: position errors: HIT16

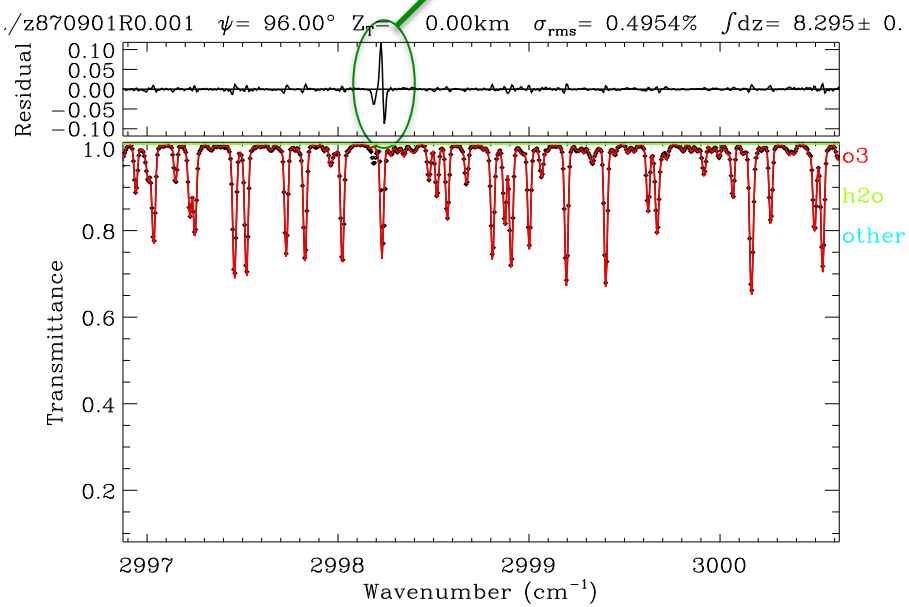


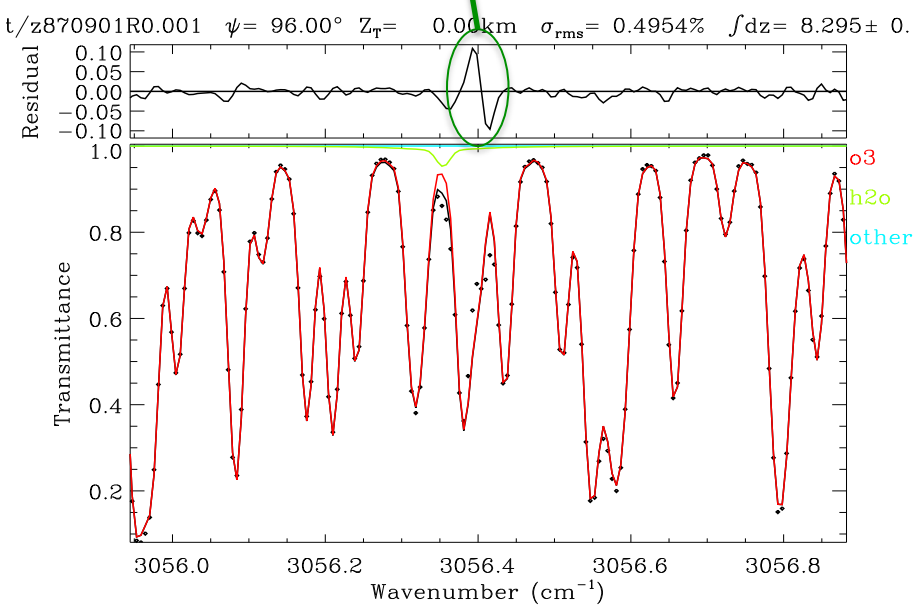
Black points represent measured spectrum, black line is calculated spectrum, red line is O_3 contribution. Residuals are Meas-Calc. Positions of some O_3 "resonance lines" have errors exceeding 1 mK. These were also present in HITRAN 2004, 08, & 12, but not HITRAN 2000.

More line position errors with HIT16

Showing fits to Kitt Peak lab spectra. The residual at 2998.2 cm^{-1} could not be fixed simply by moving lines. In this case the line intensity was split into two lines: one moved left and the other right.



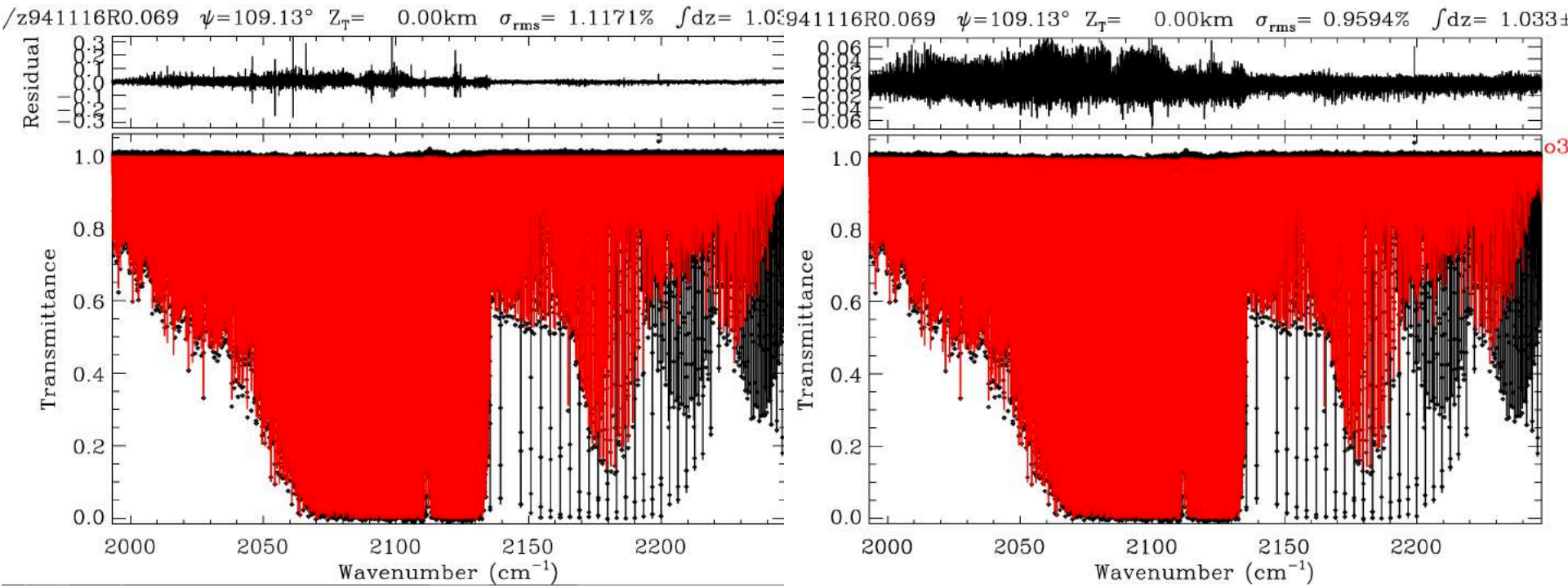




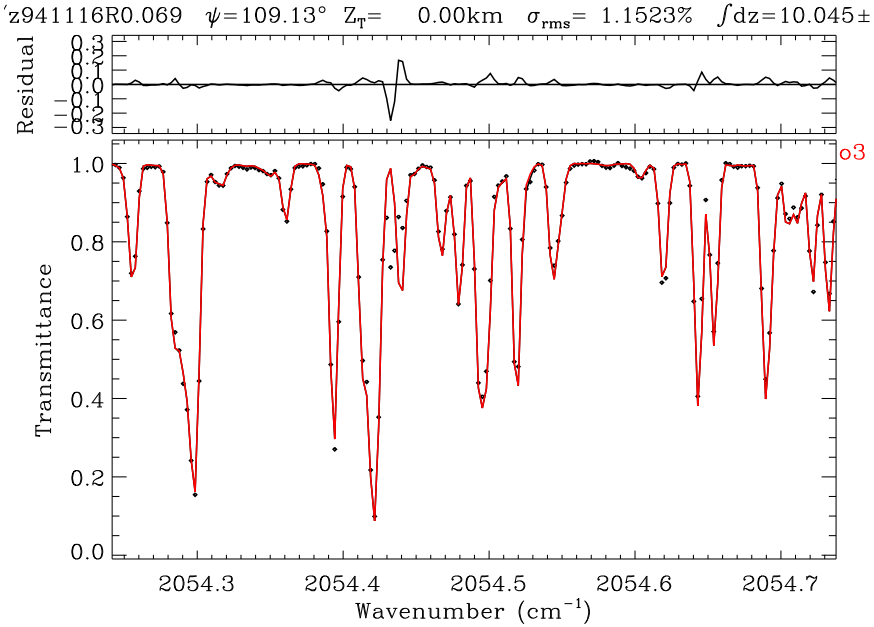
Position Errors in 1995 – 2245 cm^{-1} region

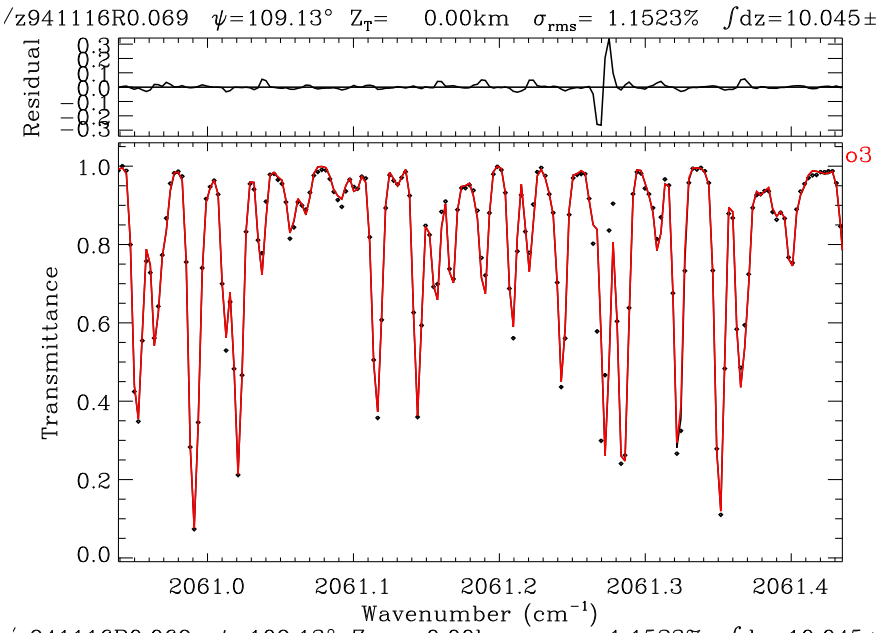
Large residuals were also seen in fits to Kitt Peak lab spectra in the 1995 to 2245 cm^{-1} region using HIT16. Below are fits to spectrum 941116R0.069 taken with 0.47 Torr of O_3 in a 85m long cell at 26C. The spectral resolution is 0.003 cm^{-1} (180 cm OPD).

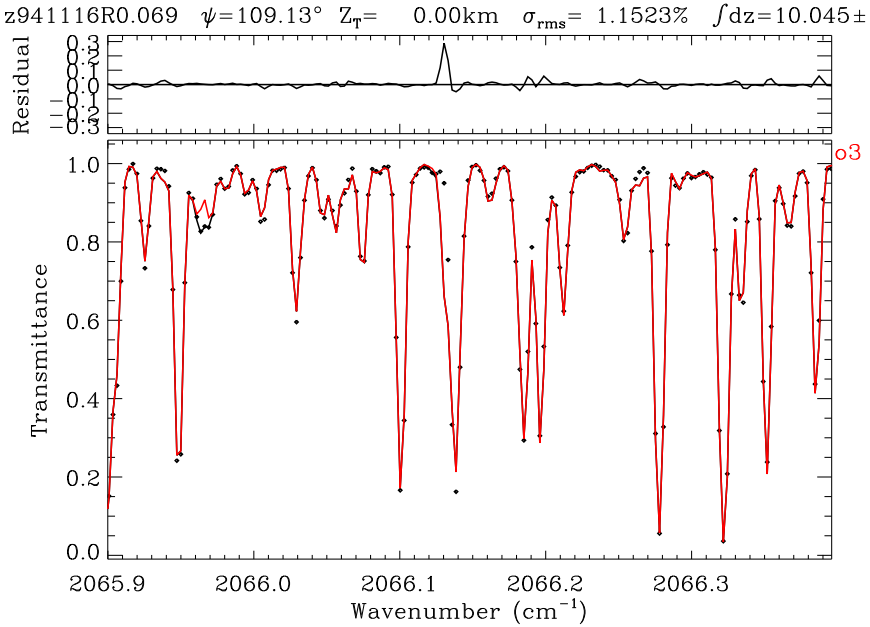
The left panel shows fits with the original O3_hit16_beta.par linelist (HIT16). The right panel show fits after the line positions had been tweaked (HIT16”). Note the factor 4 change in the residual scale. The rms residual fell from 1.12% to 0.96% and the peak residual fell from 33% to 8% in this particular lab spectrum. Interfering CO and N_2O lines (black) are well fitted.

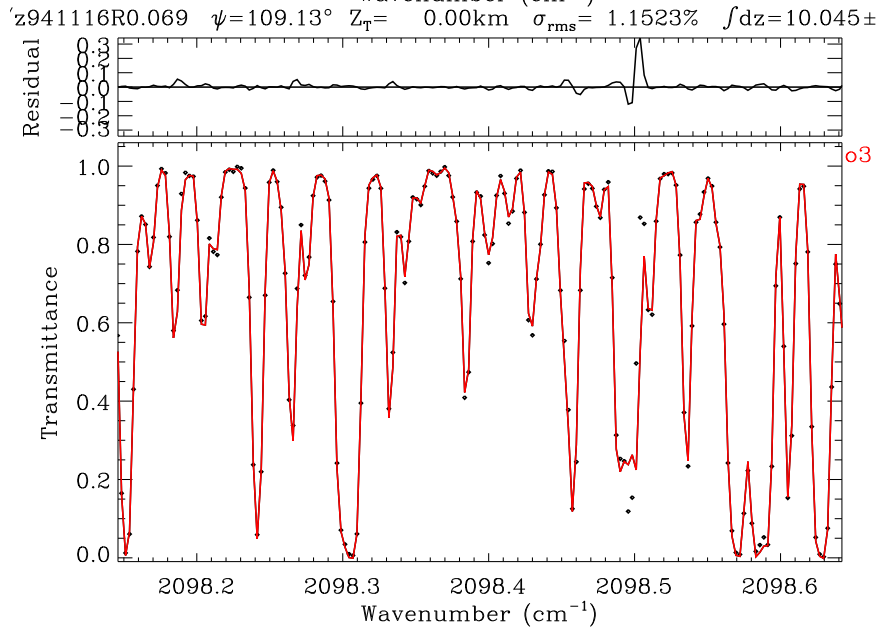


Zoom into position errors: 1995-2150 cm^{-1}

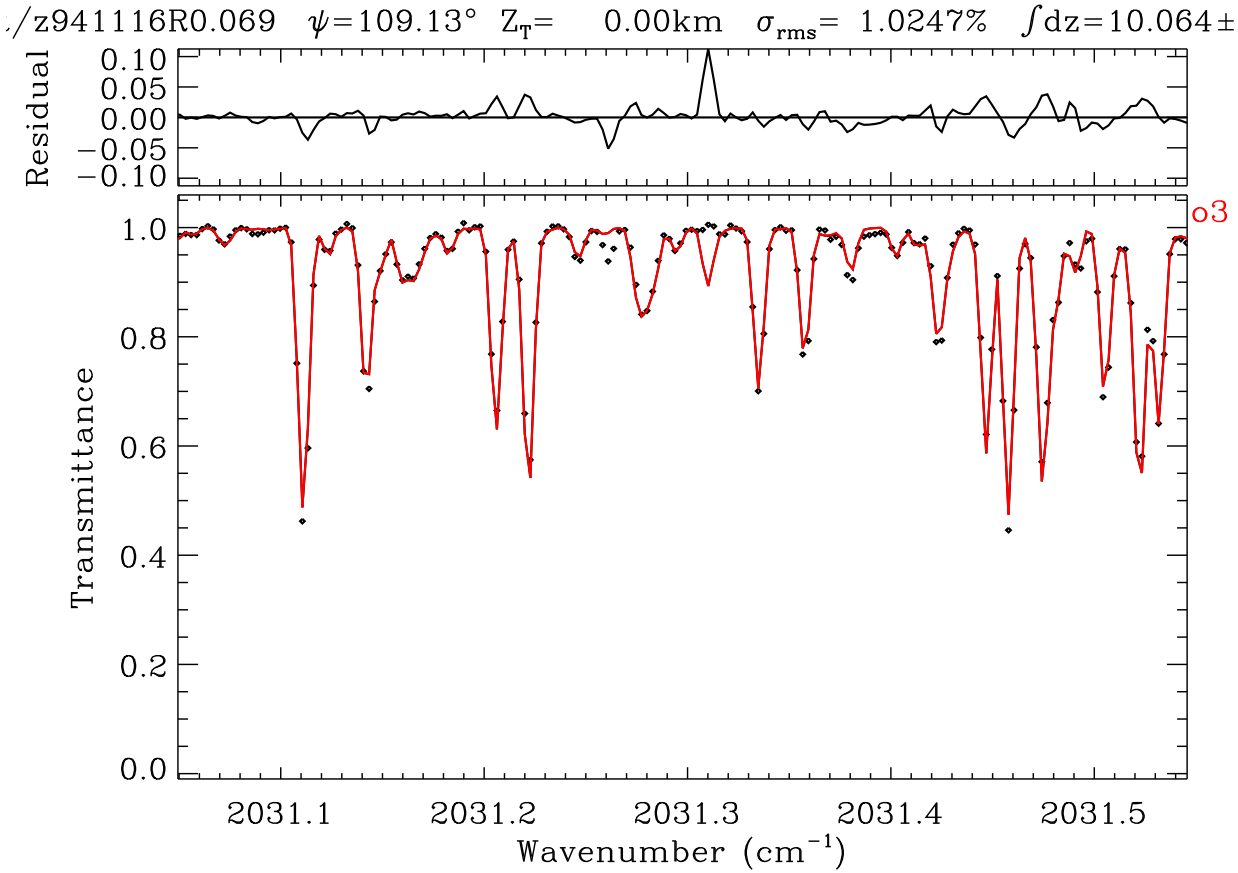








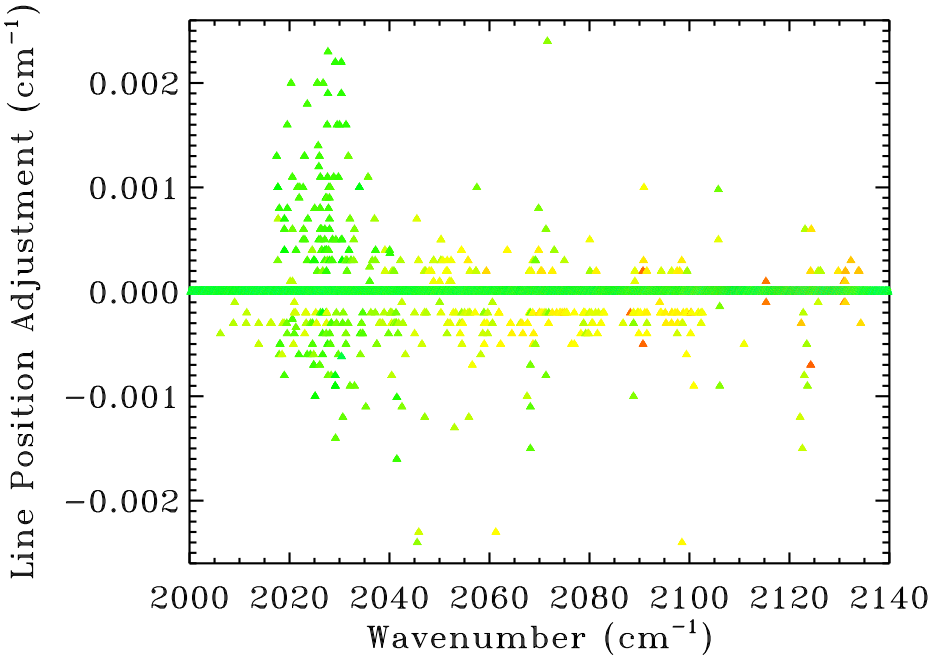
Another residual that is uncorrectable simply by adjusting line positions

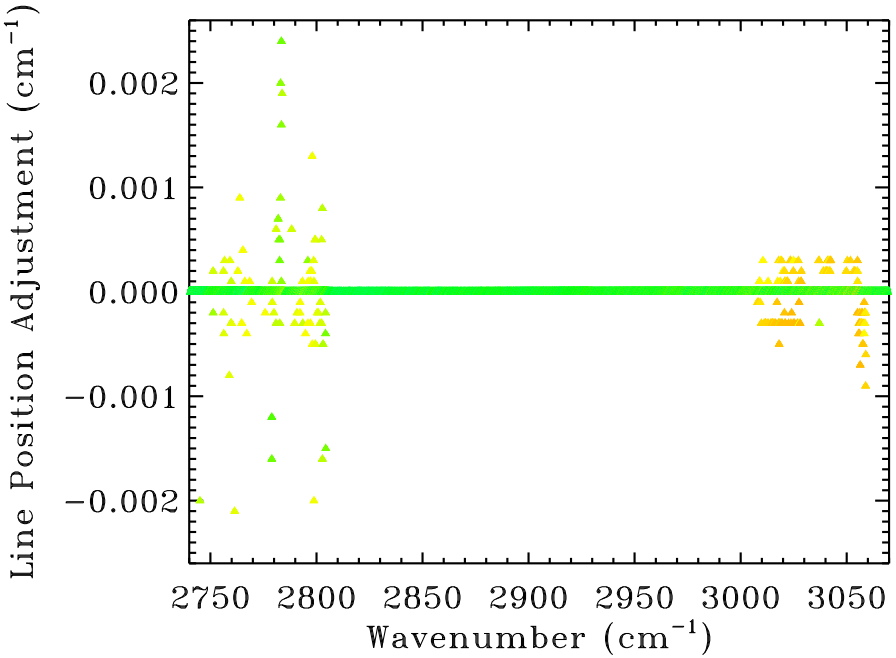


The large residual (11%) at 2031.31 cm^{-1} couldn't be fixed simply by adjusting line positions. Splitting the line intensity 50/50 and moving the resulting lines left and right to 2031.262 cm^{-1} and 2031.381 cm^{-1} remedied this residual.

Line Position Adjustments: 2000-3050 cm^{-1}

Over 300 O_3 lines were found to benefit from an position adjustment, based on fits to Kitt Peak lab spectra. These were in three regions: 2000-2140, 2750-2810, and 3000-3060 cm^{-1}. The largest shifts were 2.5 mK, with the majority under 1 mK. The figures below show the position adjustments, color coded by line intensity (blue=1E-29; green=1E-25, red=1E-21). This figure does not include the two lines that were split and then moved up to 70 mK

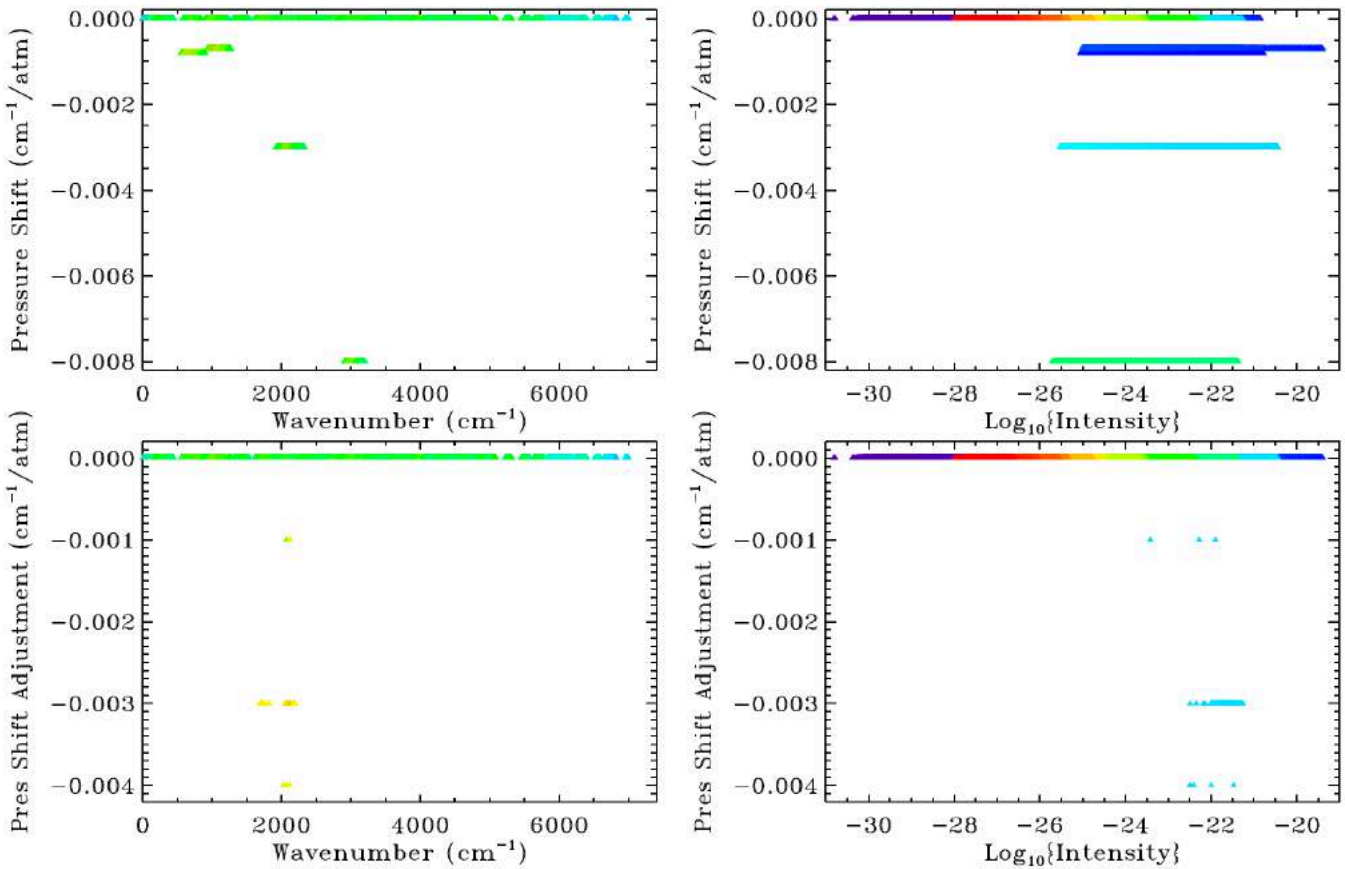




Solid green line at 0.0 mK represents the unmoved lines. Since adjustments were done manually, very few adjustments of 0.1 mK are seen -- these are generally not worth the effort.

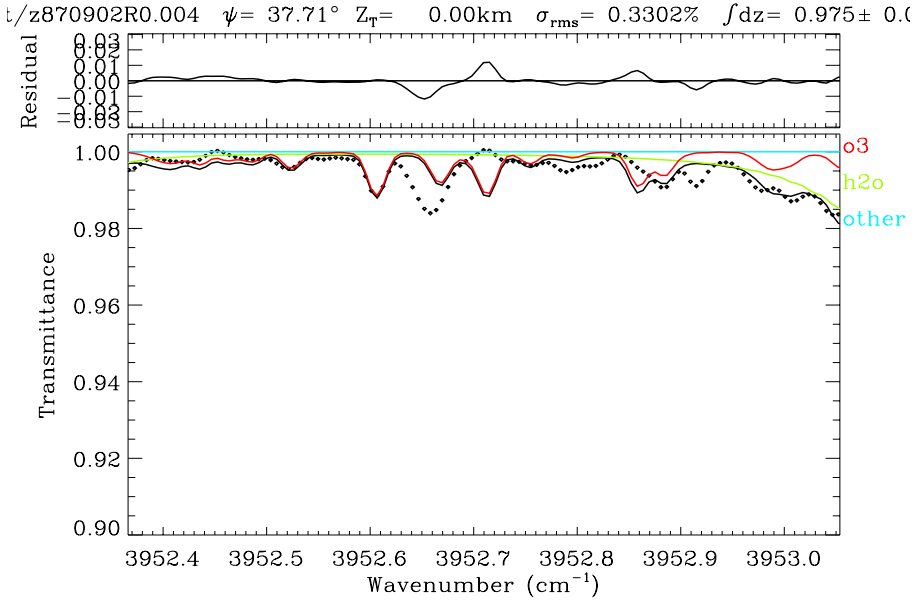
Pressure Shifts

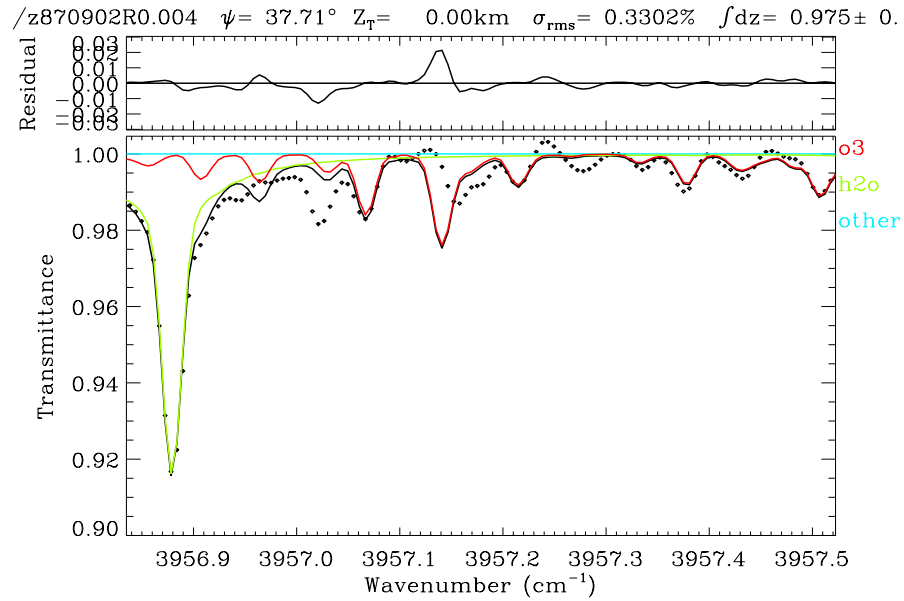
The vast majority of O_3 lines have shifts of zero, even some exceeding 1E-21 in intensity.

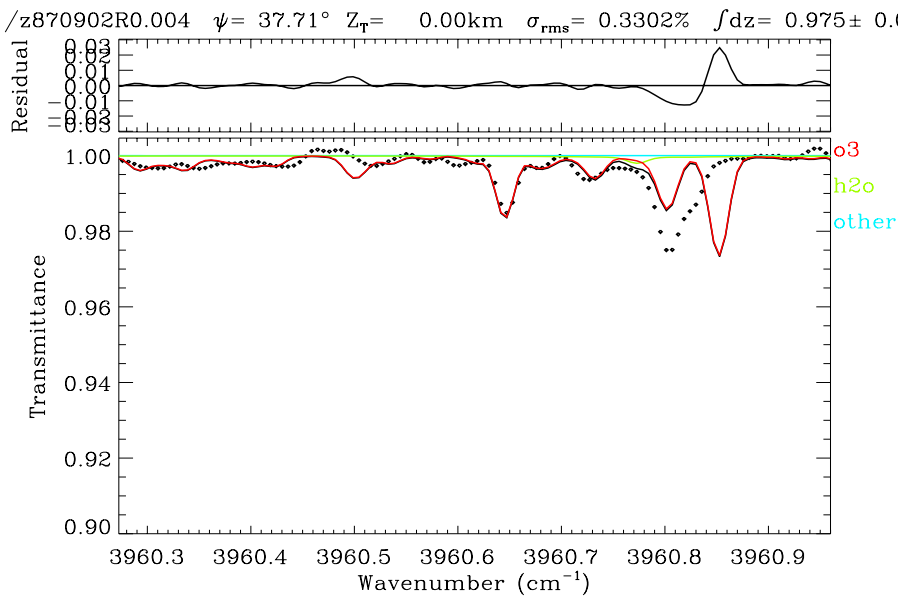


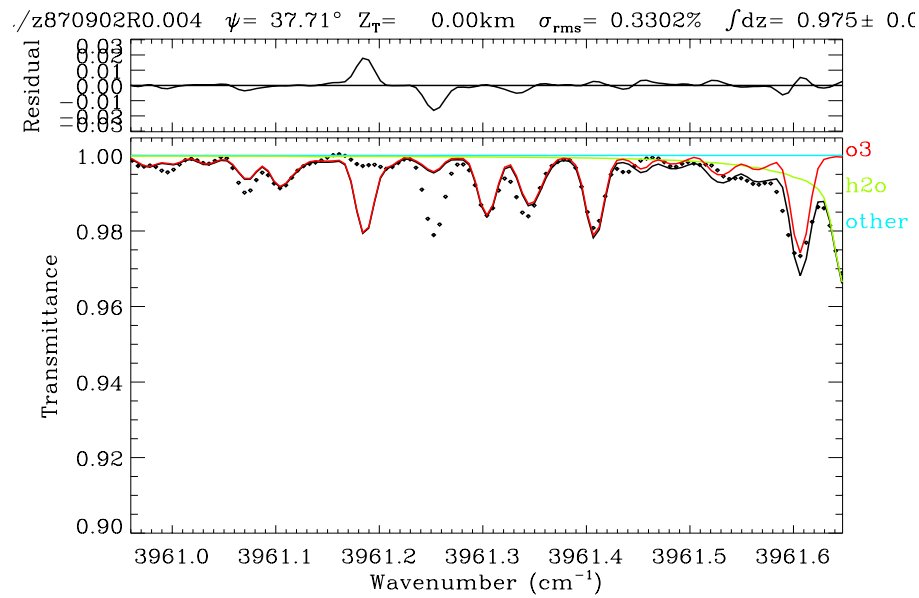
Top panels show original pressure shifts, bottom panels the applied adjustments.
Left panels show shifts versus wavenumber, color-coded by intensity (blue=1E-30; red=1E-20)
Right panels show shifts versus Intensity, color-coded by wavenumber (blue=0; red=7000 cm^{-1})
In 2000 cm^{-1} region, if intensity > 1E-22 and Pressure Shift=0, changed shift to -0.003 cm^{-1}/atm

Some line position errors 3950-4000 cm^{-1}



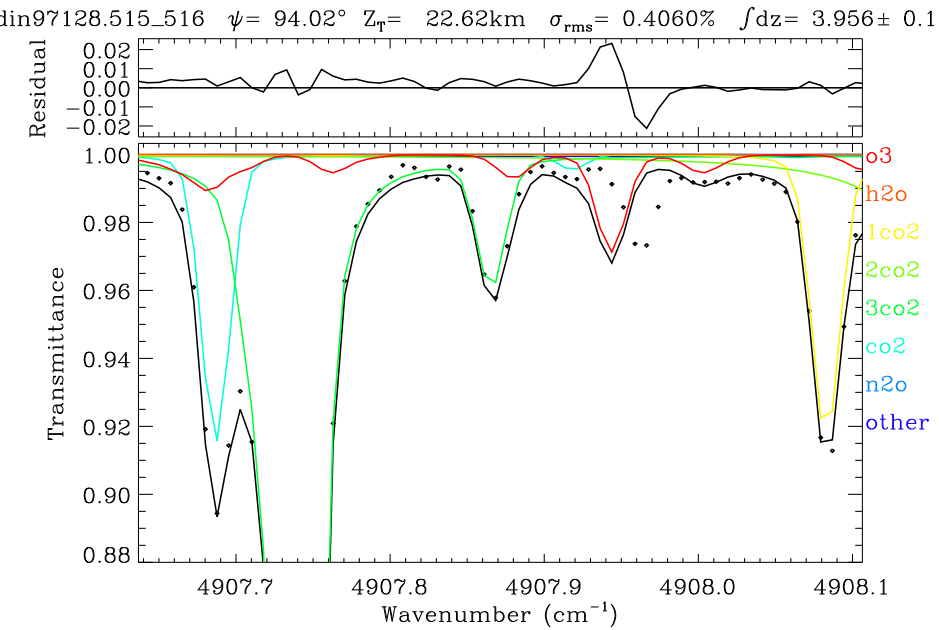


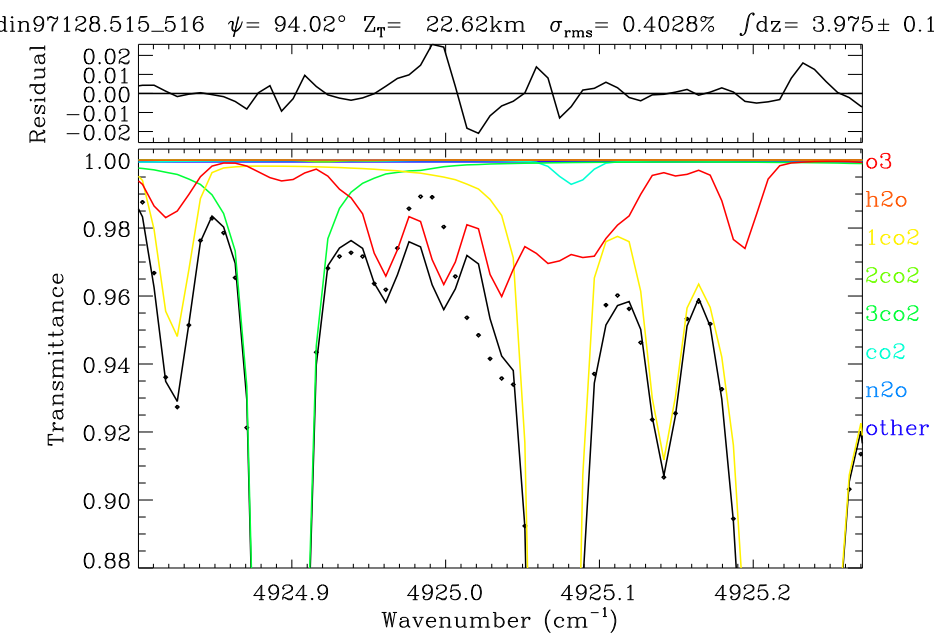


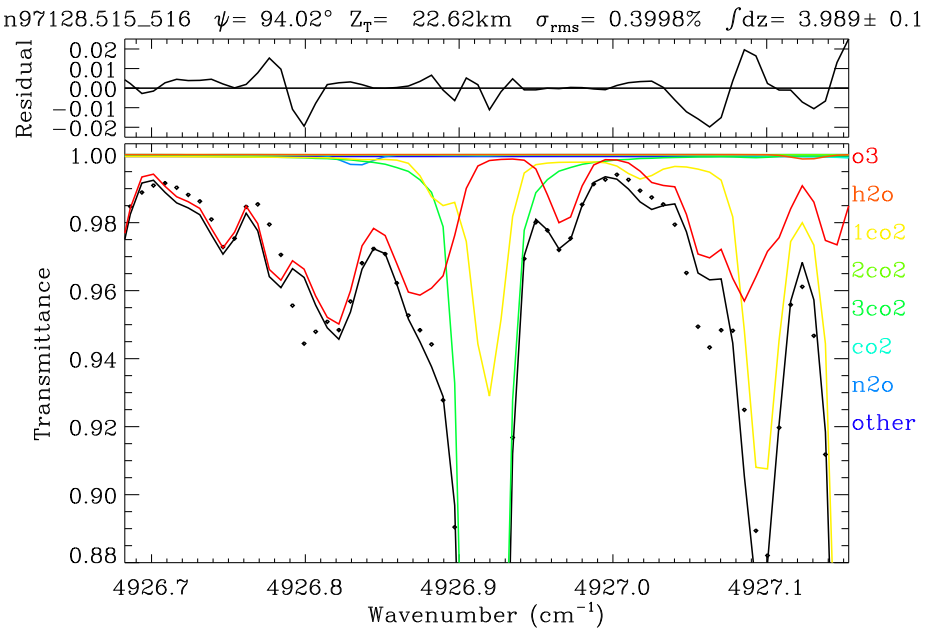


Line position errors around 4900 cm^{-1} in MkIV balloon spectra

[Kitt Peak lab spectra were too noisy in this region]







Summary

Four different O_3 linelists (HIT08, HIT12, HIT16, and ATM16), together with the non-O_3 lines from ATM16, were used to fit Kitt Peak lab spectra of O_3 and MkIV balloon spectra over 20 windows were defined covering significant O_3 absorption bands over 600-5000 cm^{-1}.

A fifth linelist (HIT16") was developed by adjusting O_3 line positions and shifts and was included into the comparison.

The MkIV balloon spectra cover 650-5650 cm^{-1} simultaneously in every spectrum, so every window is fitted in every spectrum, making it easier to quantify window-to-window biases.

The lab spectra collectively cover this same region, but individual lab spectra cover only a few windows. This makes it difficult to determine biases in retrieved O_3 amounts between windows using lab spectra.

In most windows the results are virtually identical between the five different linelists.

Why are the VMR scale factors not more consistent between the balloon and lab spectra?

- The VMR Scale Factors depend not only on the line intensities. They also depend on the positions, for strong lines the widths, and hence the measurement conditions.
- Interfering gases are different between lab and balloon cases.
- Uncertainties in ILS of MkIV & Kitt Peak instruments.

Conclusions

No major problems seem with new HIT16 O_3 linelist. Only in the 2029 cm^{-1} window is it slightly worse than its HITRAN predecessors, and it is certainly much better in the 2091 cm^{-1} window in terms of RMS fitting, and better in the 2182 cm^{-1} window in terms of the consistency of the retrieved O_3 amounts.

The largest residuals seen in fits with HIT16 could be fixed simply by adjusting line positions, typically by less than 1mK, resulting in the HIT16" linelist. In two cases, a single line was split into two weaker lines with the same total intensity, which were adjusted.

HIT16 (and HIT16") produces 8% larger retrieved O_3 amounts at 2182 cm^{-1} than any other linelist, bringing this region into better consistency with the others

The 3000 cm^{-1} region yields the lowest retrieved O_3 amounts, about 5% lower than average, both in fits to Kitt Peak lab and MkIV limb spectra. This indicates errors in line widths or intensities, since the errant line positions were corrected.

Pressure shifts need updating. Most O_3 lines have shifts of zero, even some strong lines. The inconsistency between the lines with and without pressure shifts drive up the residuals in fits to higher-pressure lab spectra.