HITRAN Spectroscopy Evaluation using Solar Occultation FTIR Spectra

Geoffrey C. Toon[1], Jean-Francois Blavier[1], Keeyoon Sung[1], Laurence S. Rothman[2], Iouli Gordon[2]

[1] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA

[2] Harvard-Smithsonian Center for Astrophysics, Cambridge, MA

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The HITRAN 2012 linelist contained several preventable errors. Late delivery of key linelist components left too little time for a thorough validation, and too little time to remedy the problems that were found.

We have tried to automate part of the validation process by fitting atmospheric spectra measured by the MkIV balloon interferometer. By comparing rms fitting residuals with previous HITRAN linelists, errors are quickly identified. This work, applied to HITRAN 2016, will hopefully reduce the number of preventable errors.

Results also provides guidance for future spectroscopic work.

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Approach

Defined 113 contiguous windows covering 700 to 5600 cm^{-1}

Fitted an occultation of MkIV balloon spectra (57 cm OPD) with 20 different tangent altitudes from 9 km to 38 km

Large range of T/P/vmr seen in balloon spectra exposes spectroscopic errors

Used four different linelists: HITRAN 2000, 2004, 2008, 2012

So a total of 113 x 20 x 4 = 9,040 spectral fits were performed with GFIT

Compared rms fitting residuals from HITRAN 2012 linelist with its predecessors

Investigate cases where HITRAN 2012 rms residual is not the best, or is too large

Mainly tests HITRAN line positions, E”, and relative intensities (and completeness)

MkIV Balloon Spectra

From May 1997 balloon flight from Fairbanks, Alaska, part of POLARIS campaign.

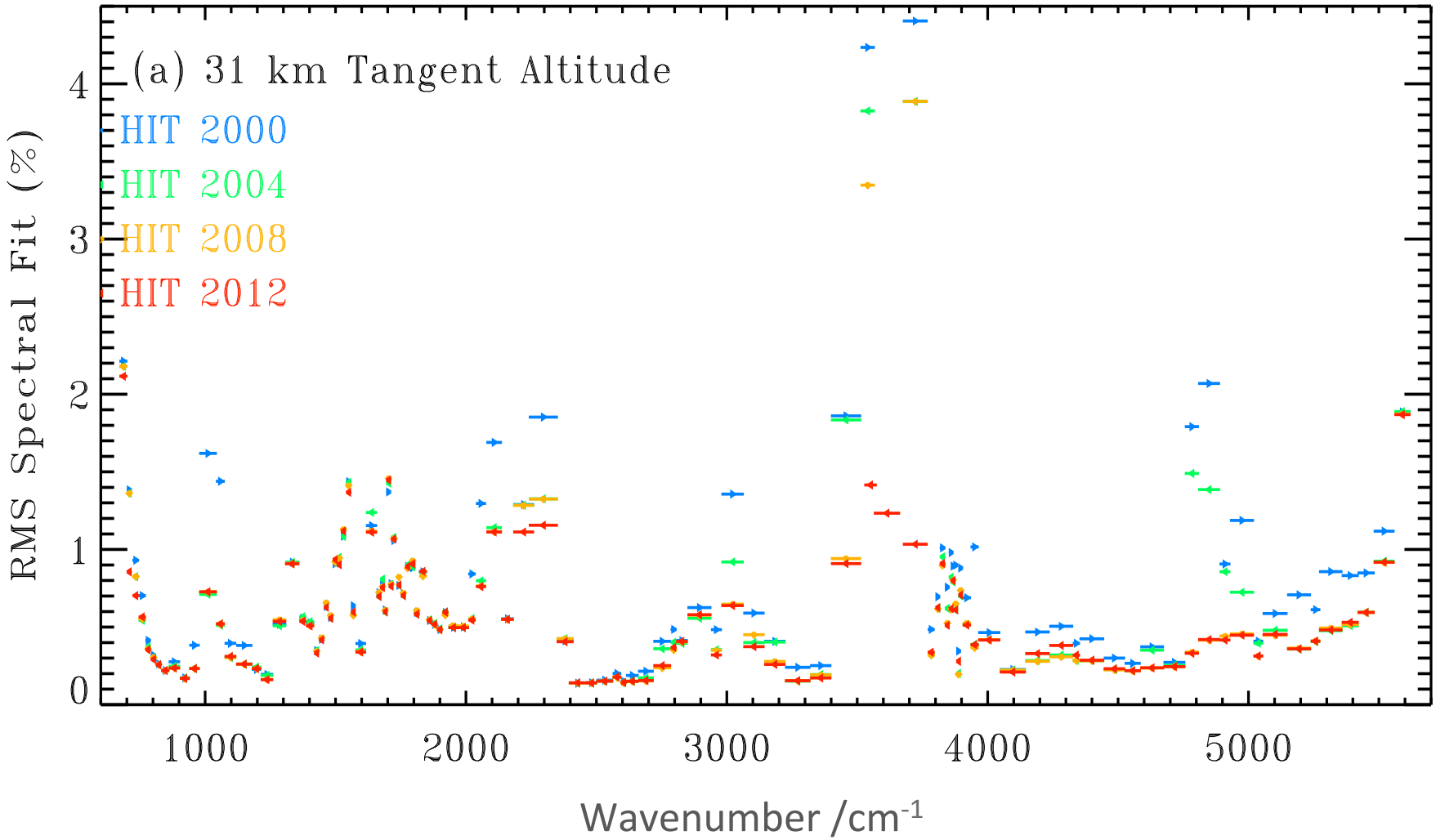
The NASA ER-2 aircraft made dozens of flights over Alaska. There were also frequent ground-based remote-sensing observations. Thus, the atmosphere over Alaska was exceptionally well characterized during POLARIS.

MkIV spectra balloon cover 650-5650 cm^{-1} at 0.01 cm^{-1} resolution (57 cm MOPD)

Spectra were ratioed against a high-sun solar spectrum to remove solar and instrumental features. Observed residuals are therefore predominantly telluric.

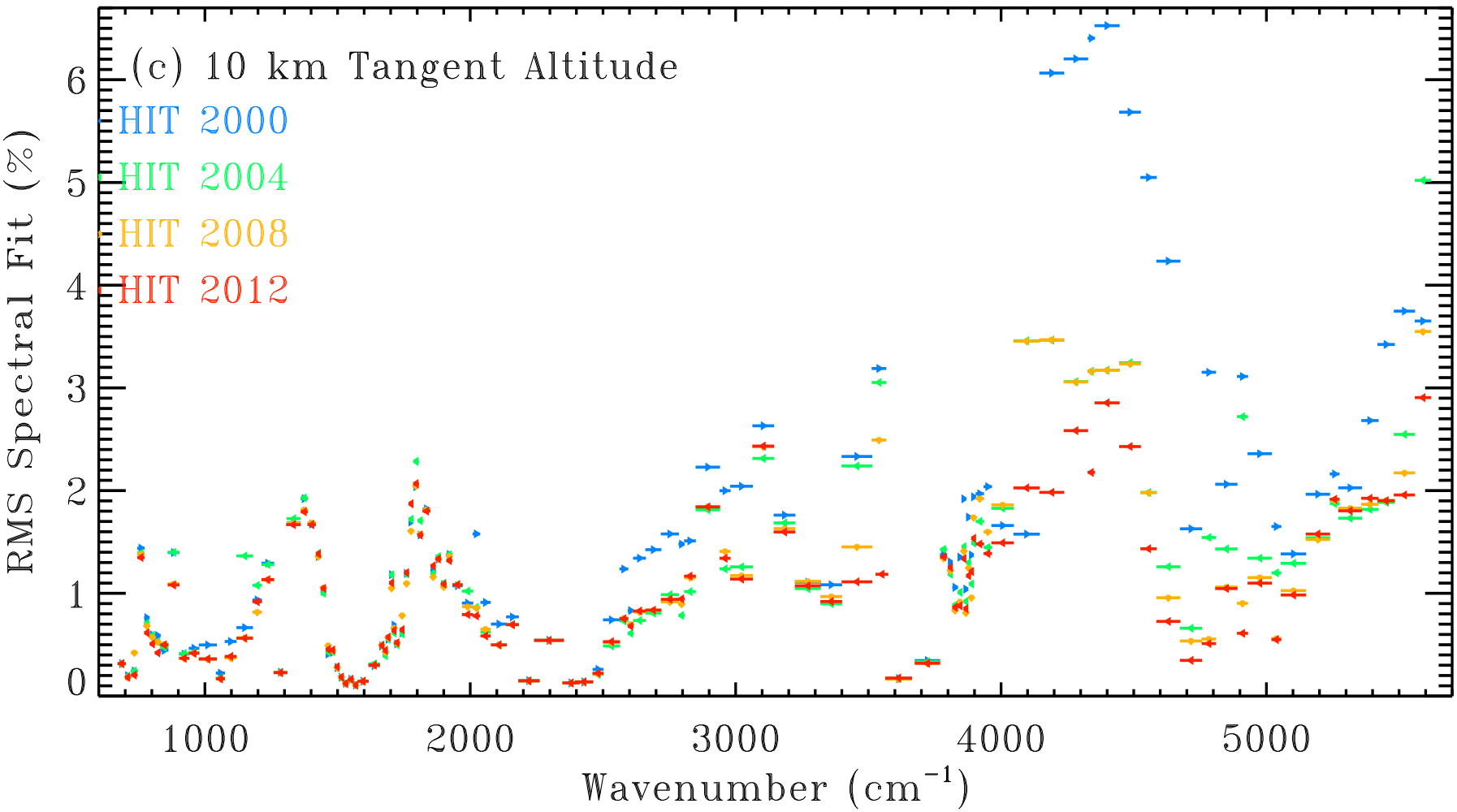
ILS was determined by fits to high altitude (38 km) spectra of CO_2. In any case, the same ILS is used for all linelists, and so does not cause residuals to be different

RMS fitting residuals at 31 km



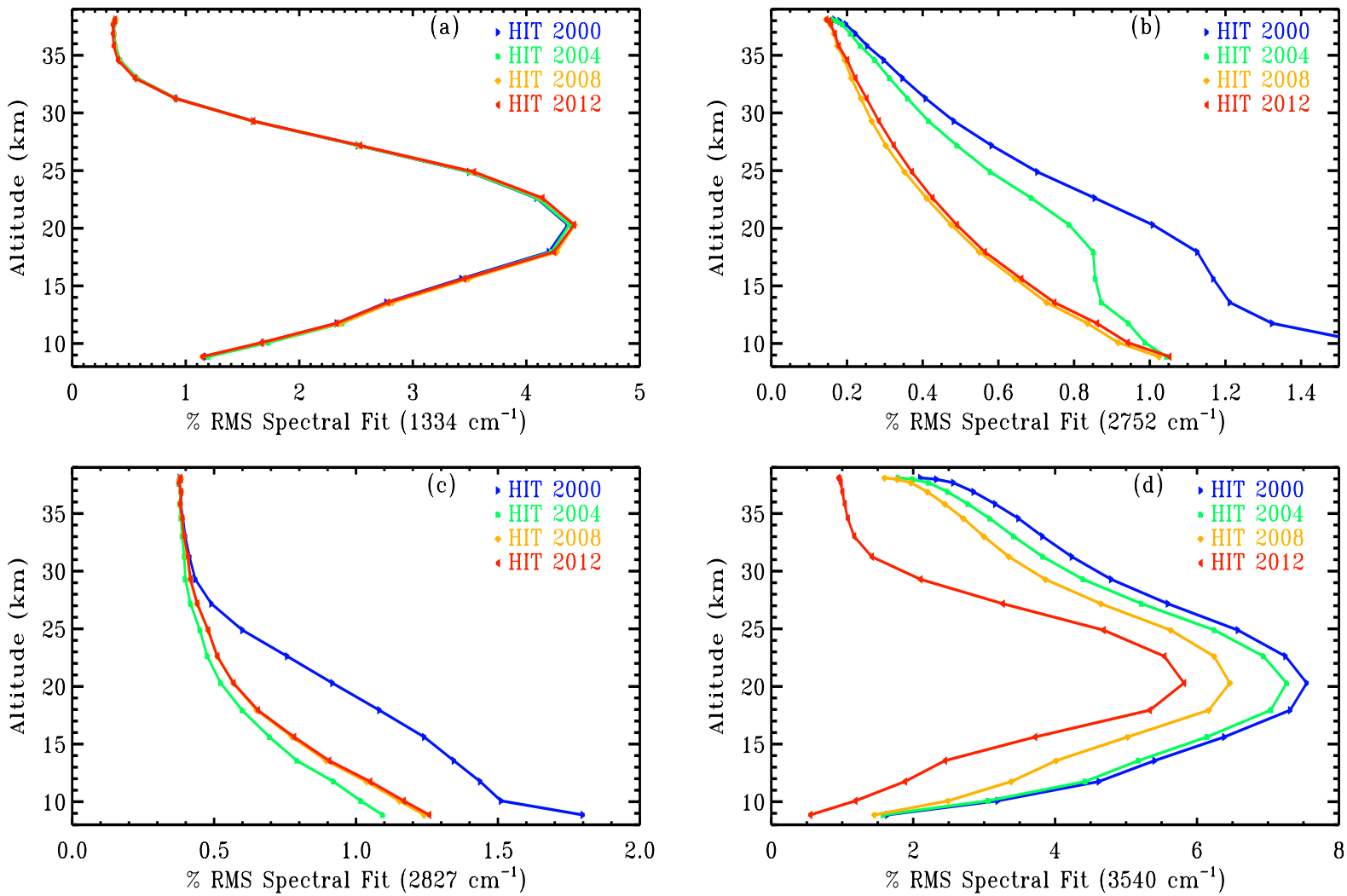
At 31 km, the smallest rms residuals occur in window regions, e.g. 2400-2700 cm^{-1}, with weak absorptions.

RMS Fitting Residuals at 10 km Altitude

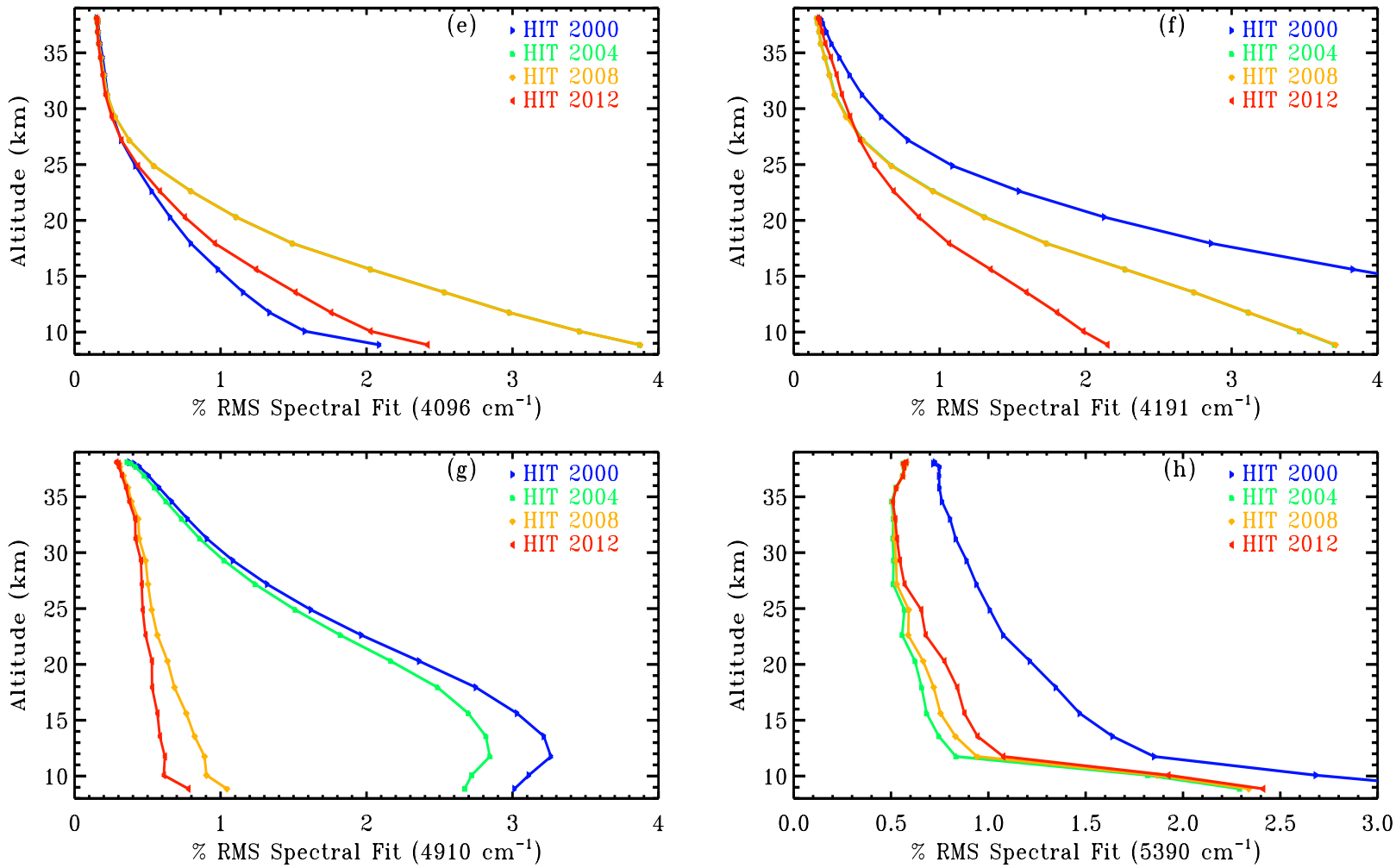


At 10 km, the smallest rms residuals occur in saturated regions, e.g. 1600-1700 cm^{-1}.

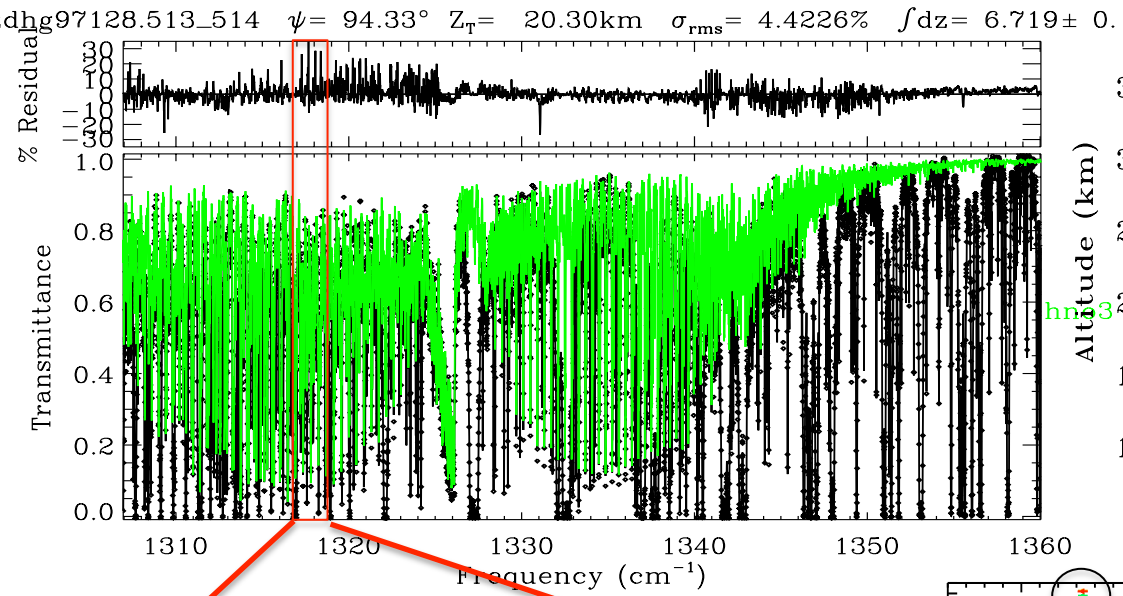
RMS Residuals versus altitude (1/2)

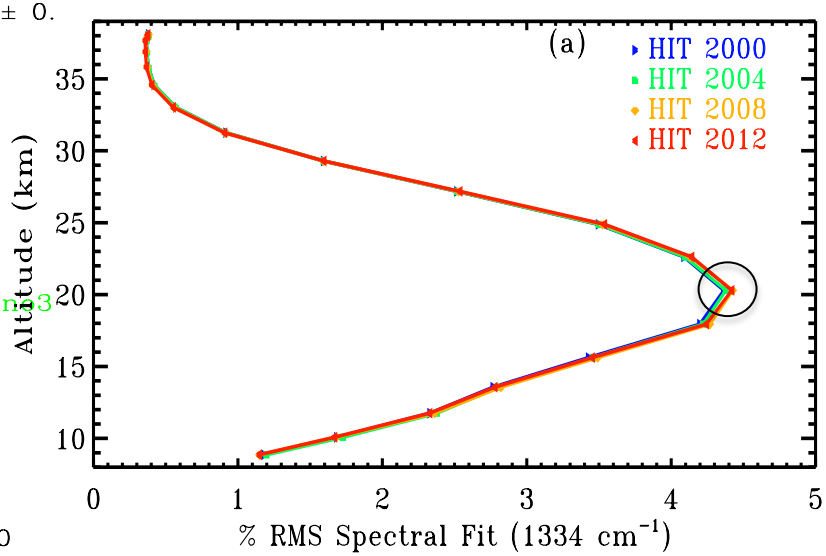


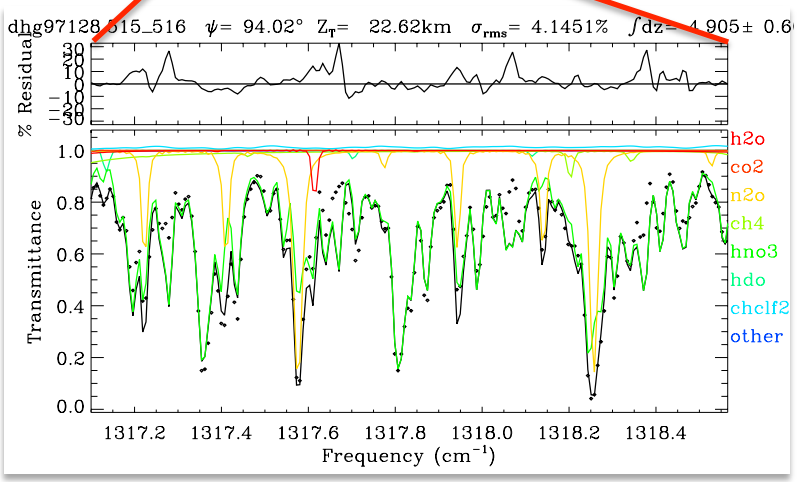
RMS Residuals versus Altitude (2/2)

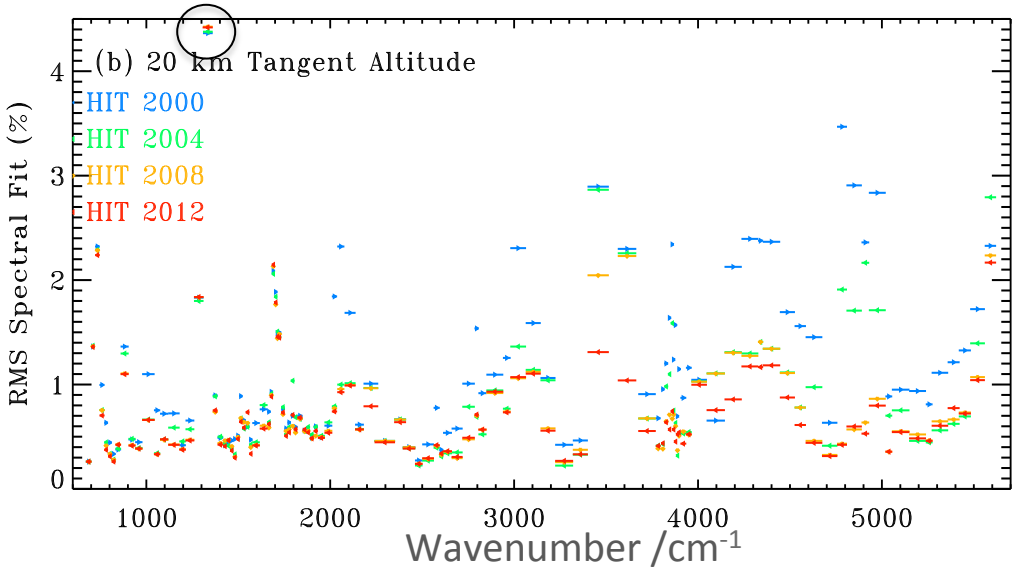


Fit to 1307-1360 cm^{-1} window at 20 km altitude



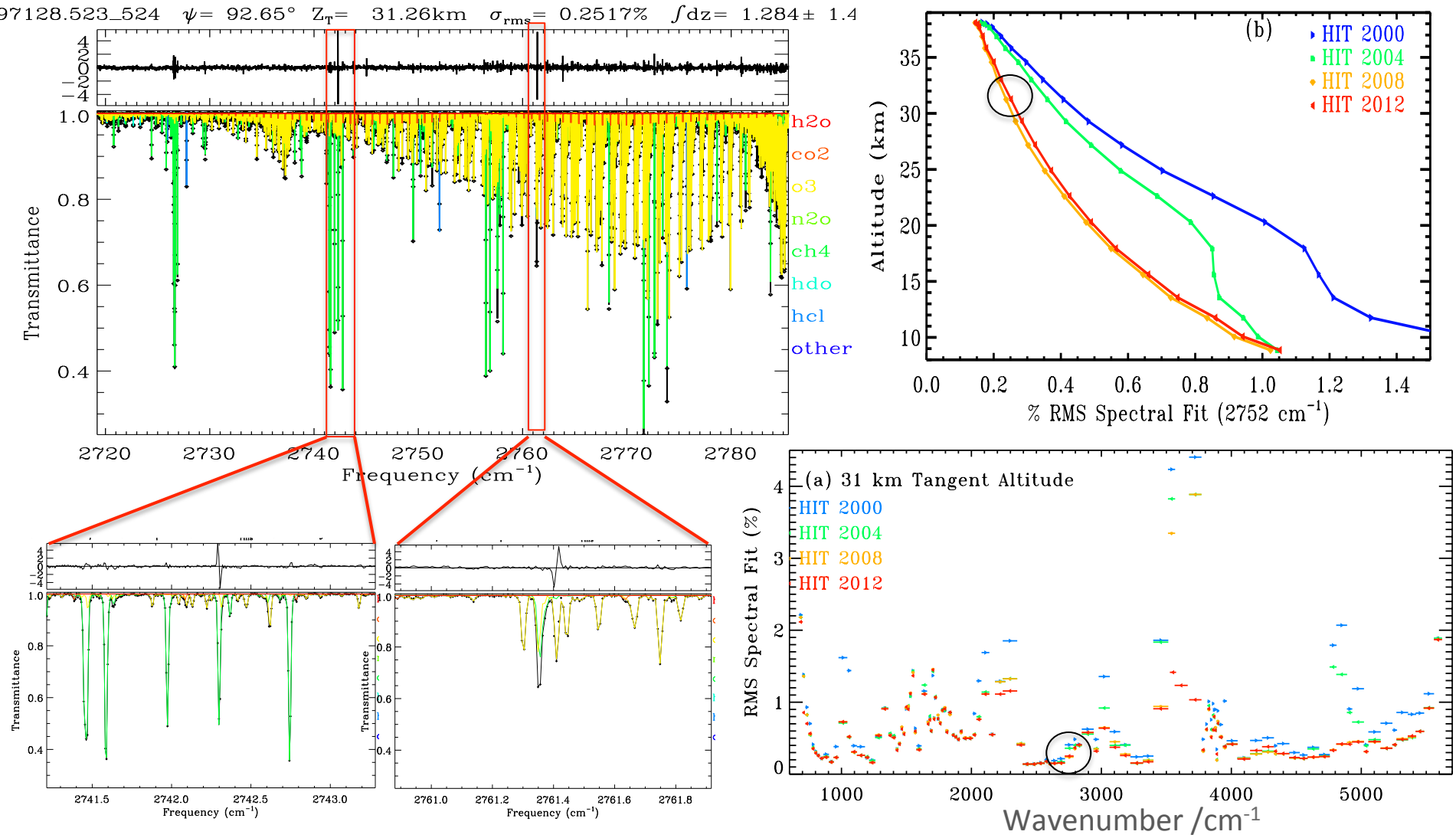






This is the worst window for HITRAN 2012. All 4 HITRAN linelists produce similar residuals, peaking at 20 km altitude. This and the 0.4 cm^{-1} spacing of residuals indicate HNO_3 as the culprit.

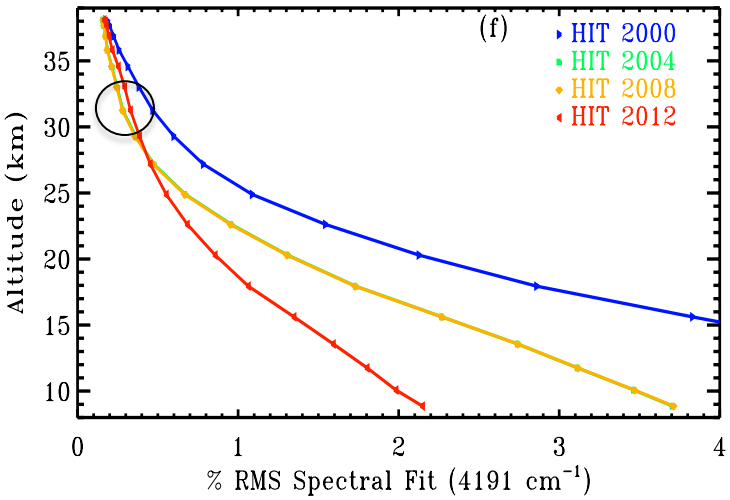
Fit to 2720-2785 cm^{-1} window at 31 km altitude

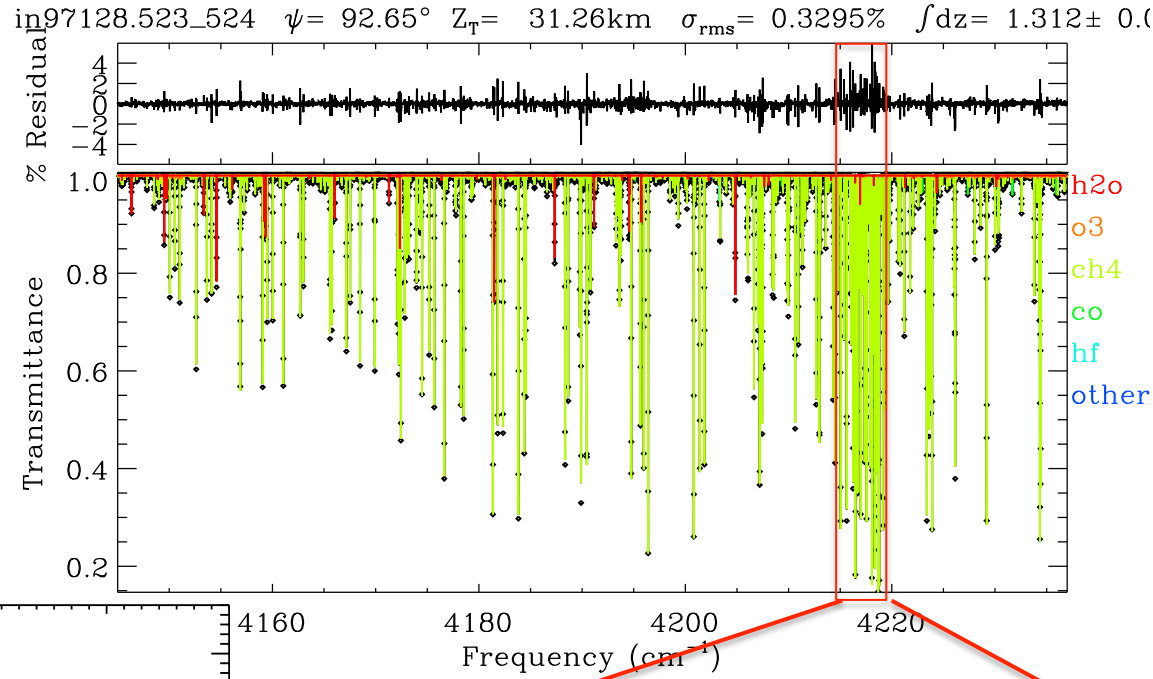


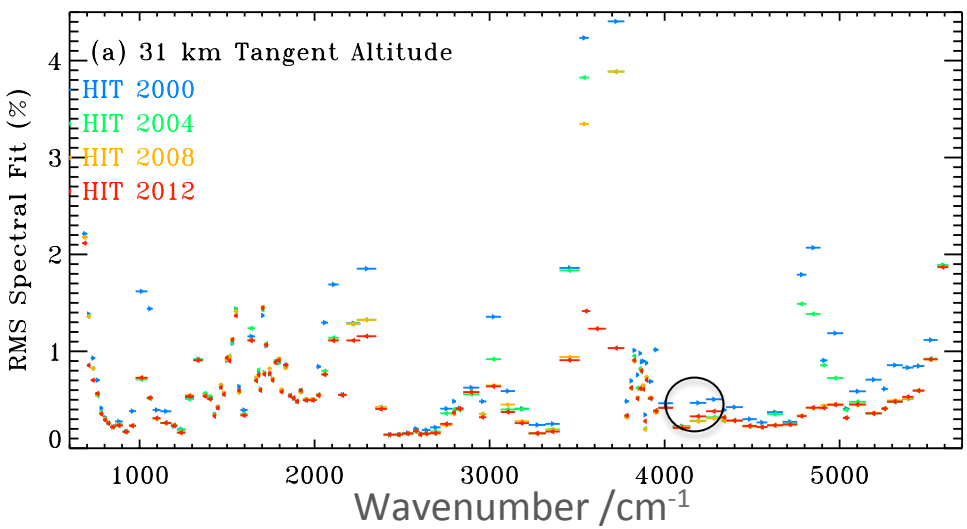
HITRAN 2012 worse than 2008 due to a 0.001 cm^{-1} position error on CH_4 line at 2742.3 cm^{-1}

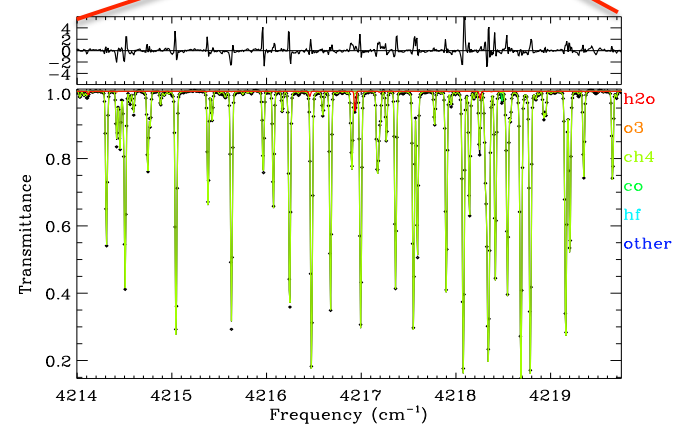
Residual at 2761.4 cm^{-1} due to 0.002 cm^{-1} position error in resonance O_3 line, a perennial problem

Fit to 4145-4236 cm^{-1} window at 31 km altitude



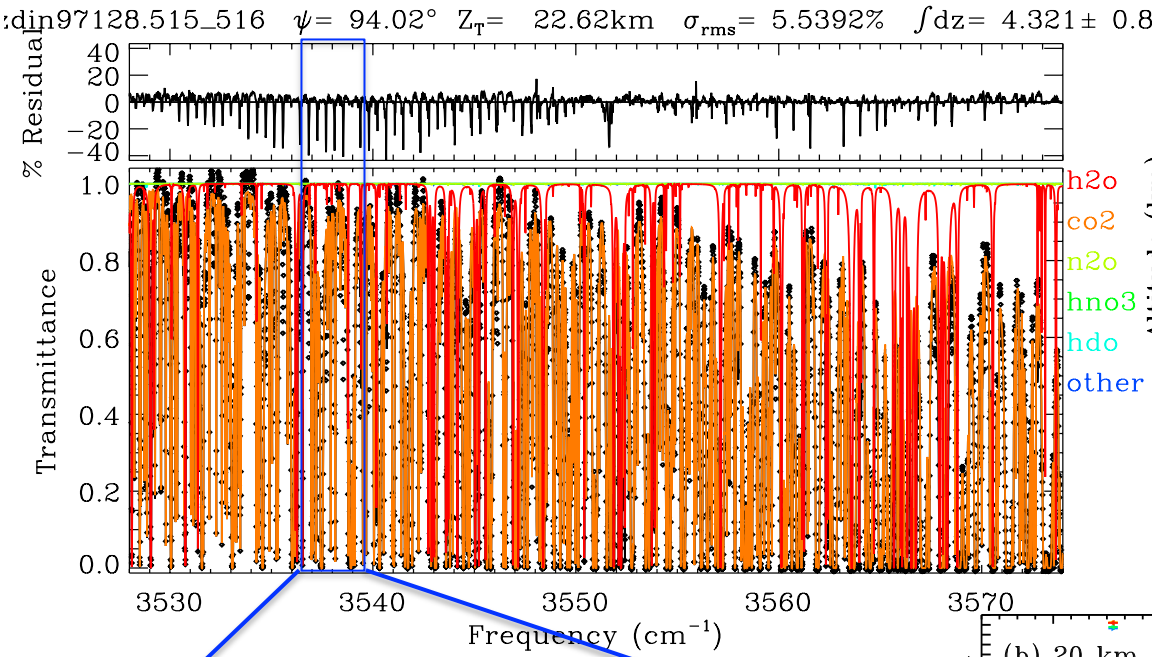


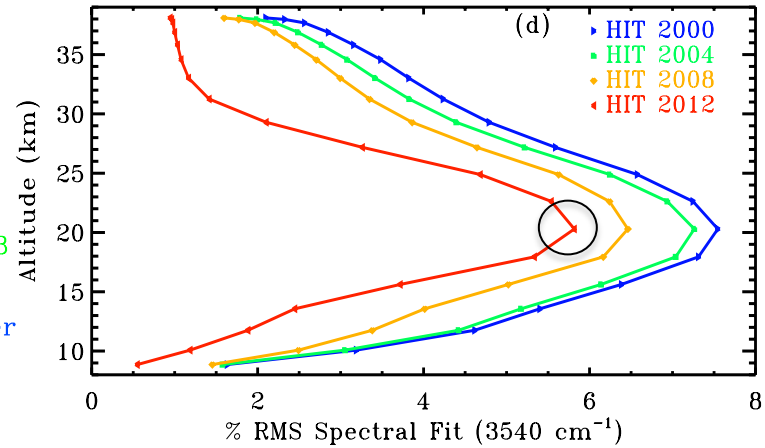


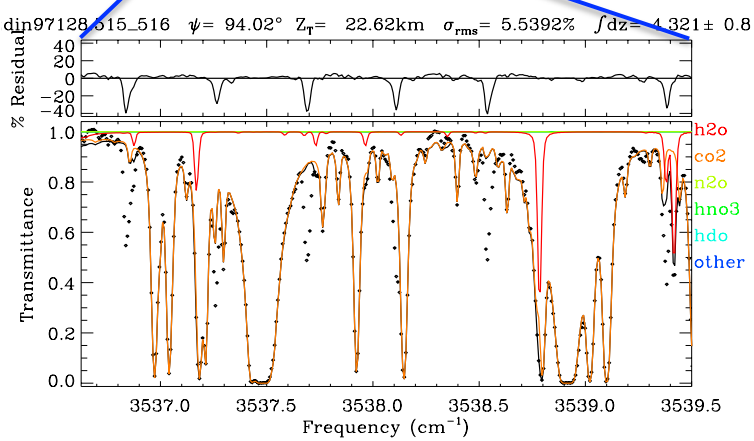


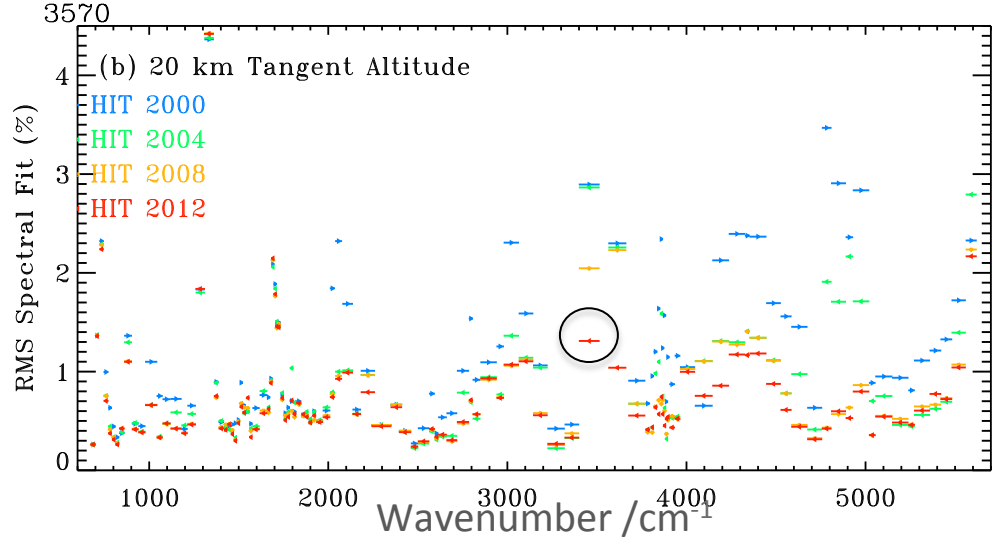
HITRAN 2012 fits are worse than those using HITRAN 2004 or 2008 due to a worsening of the line positions, esp. in $\nu_3+\nu_4$ Q-branch with peak residuals of 6% versus 4% with HITRAN 2004/8

Fit to 3528-3574 cm^{-1} window at 23 km altitude



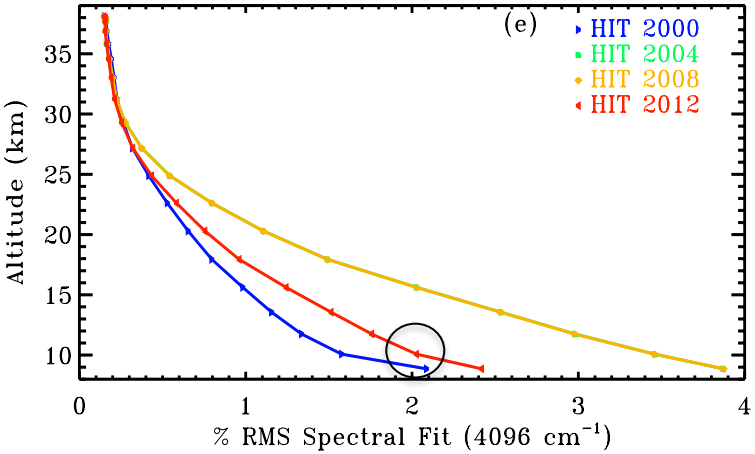


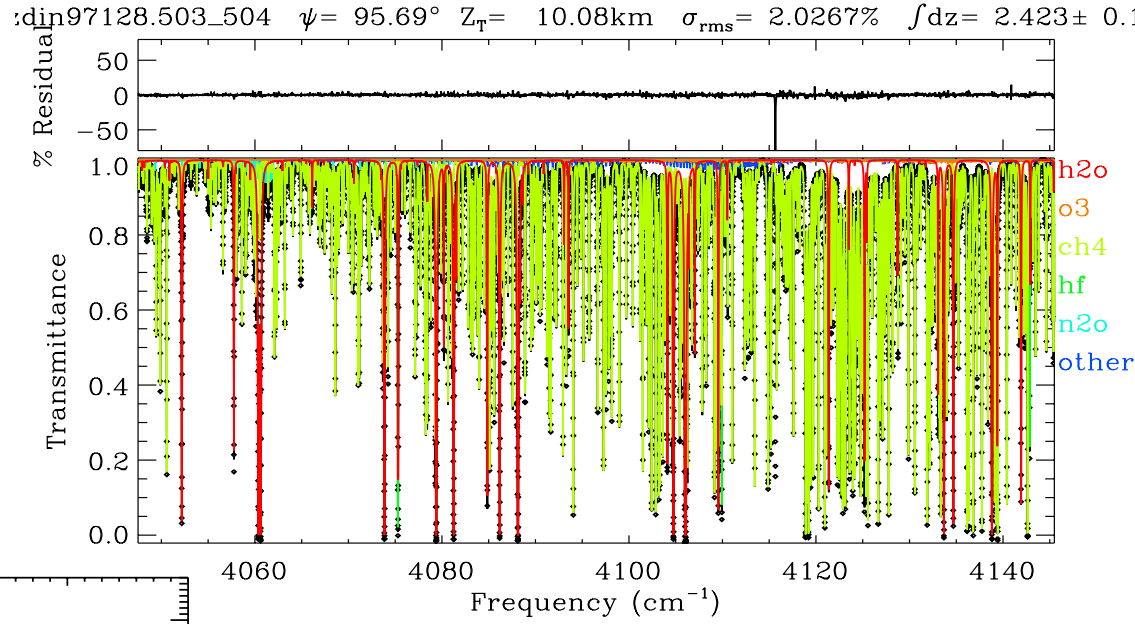


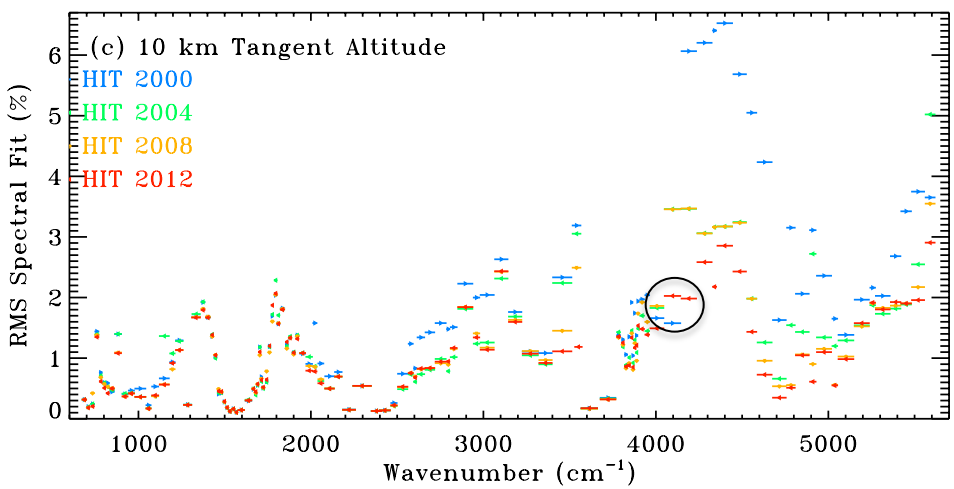


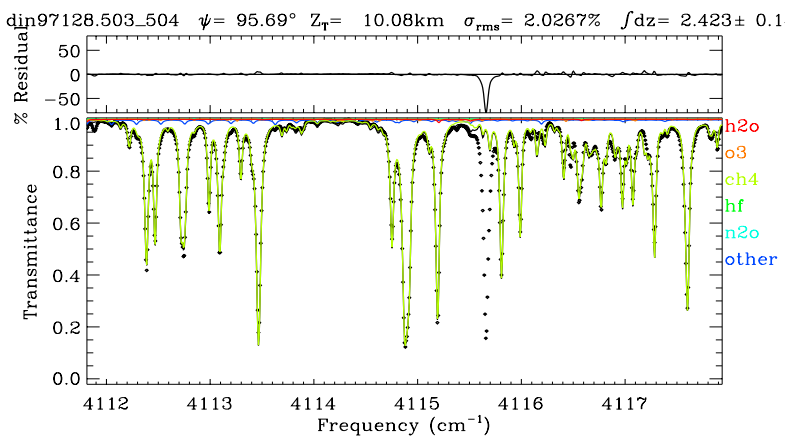
RMS has reduced with each successive HITRAN version (improved CO_2), but residuals at 20 km are now dominated by the missing ν_1 HNO_3 band, whose P- and Q-branches are clearly visible.

Fit to 4048-4145 cm^{-1} window at 10 km altitude



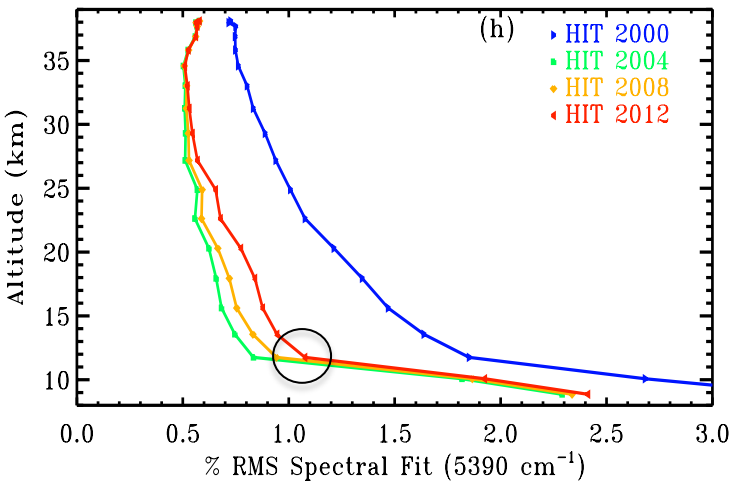


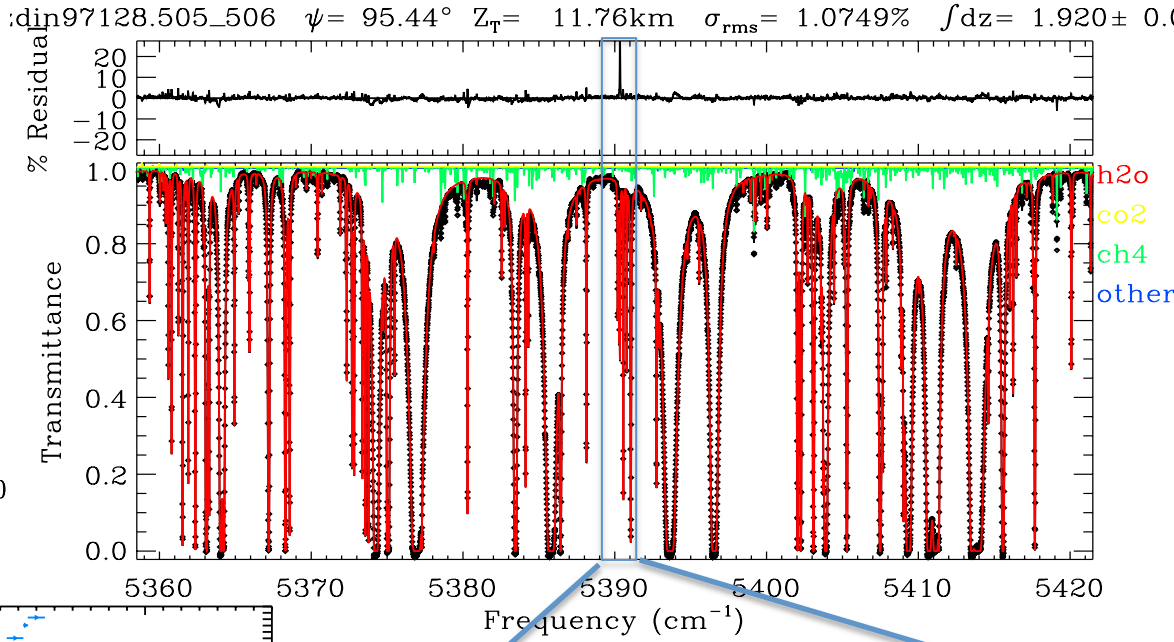


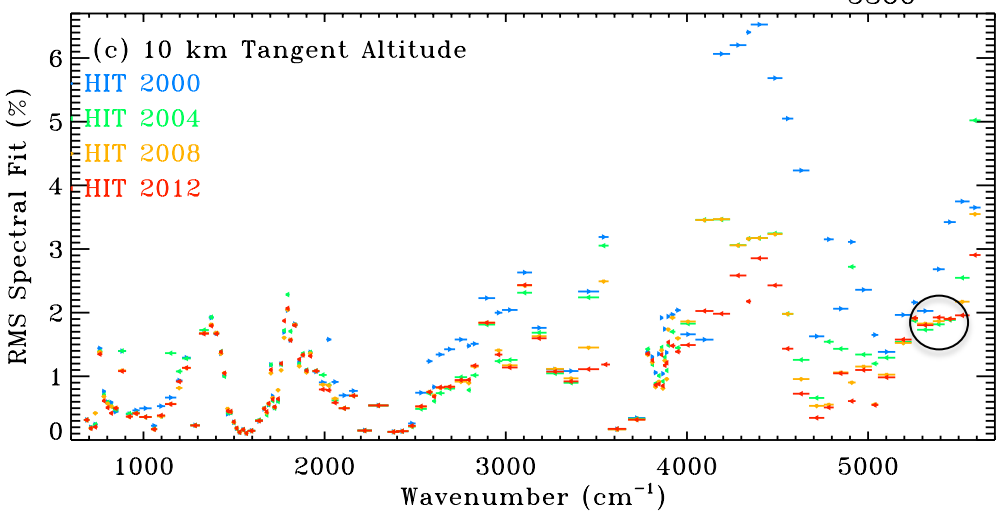


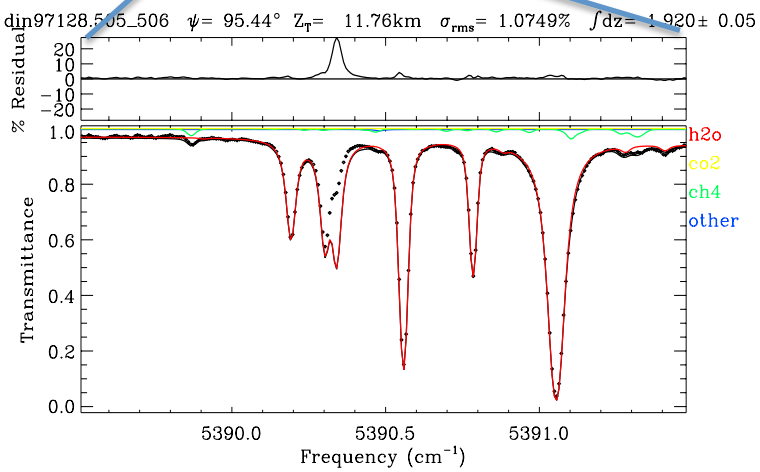
HITRAN 2012 is better than HITRAN 2004/8 despite the huge residual at 4115.659 cm^{-1}, due to a missing CH_4 line which was present in HITRAN 2008. HITRAN 2000 is still best at 10 km

Fit to 5358-5422 cm^{-1} window at 12 km altitude









Large positive residual near 5390.3 cm^{-1}, due to a factor ~4 intensity over-estimate of H_2O line at 5390.339 cm^{-1}, was not present in fits using HITRAN 2004 or 2008.

Average RMS Fitting Residual Table (1/4)

Center	Width	Fitted gases	HIT2000	HIT2004	HIT2008	HIT2012
686.50	29.00	h2o co2 o3 hcn	0.7832	0.7821	0.7826	0.7775
709.00	18.00	h2o co2 o3 clno3 hcn	0.8505	0.8458	0.8406	0.7709
734.00	24.00	h2o co2 o3 clno3 hcn n2o5 hno3	0.8724	0.8282	0.8867	0.7750
759.00	26.00	h2o co2 o3 clno3 hcn n2o5 hno3 ccl4	0.8453	0.7568	0.7555	0.7271
781.50	19.00	h2o co2 o3 clno3 hcn hno3 ccl4 cof2 chclf2	0.5793	0.5216	0.5089	0.4868
802.00	19.00	h2o co2 o3 clno3 hno3 ccl4 chclf2 ho2no2	0.4769	0.4451	0.4439	0.4270
822.00	21.00	h2o co2 o3 clno3 hno3 ccl4 chclf2	0.4201	0.4012	0.4010	0.3837
847.00	29.00	h2o co2 o3 hno3 ccl3f cocl2 ocs	0.3935	0.3950	0.4048	0.4033
882.00	42.00	h2o co2 hno3 ccl2f2 ocs	0.5343	0.5199	0.4963	0.4951
922.00	36.00	h2o co2 hno3 ccl2f2	0.3649	0.3664	0.3525	0.3518
959.00	38.00	h2o co2 o3 sf6	0.4116	0.3769	0.3752	0.3745
1011.00	66.00	h2o co2 o3	1.0686	0.6661	0.6660	0.6661
1058.50	32.00	h2o co2 o3	0.7725	0.4698	0.4689	0.4674
1097.00	43.00	h2o co2 o3 ccl2f2 ccl3f chclf2 hcooh ch4	0.5243	0.4449	0.4407	0.4337
1150.00	60.00	h2o o3 n2o ccl2f2 chclf2 ch4 chf3	0.5065	0.4633	0.4117	0.4109
1197.00	34.00	h2o o3 n2o ch4 hno3 hdo	0.5687	0.6529	0.5690	0.5751
1237.00	46.00	h2o co2 o3 n2o ch4 hno3 hdo n2o5 cof2	0.3971	0.3864	0.3636	0.3610
1285.00	50.00	h2o co2 n2o ch4 hno3 hdo clno3 cf4	0.5191	0.5119	0.5409	0.5222
1334.50	51.00	h2o co2 n2o ch4 hno3 hdo chclf2	0.9875	0.9902	0.9798	0.9702
1374.50	25.00	h2o co2 n2o ch4 hdo	0.9149	0.9188	0.8650	0.8638
1402.50	29.00	h2o co2 ch4 hdo	0.7639	0.7723	0.7330	0.7239
1427.50	15.00	h2o ch4 hdo	0.5890	0.5957	0.5970	0.5788
1446.60	19.00	h2o ch4 hdo	0.6207	0.6108	0.6323	0.6300
1464.50	14.00	h2o ch4 hdo	0.6542	0.6222	0.6329	0.6050
1481.30	15.00	h2o ch4 hdo	0.6156	0.5488	0.5442	0.5389
1498.30	14.00	h2o ch4 hdo	0.7167	0.7080	0.7097	0.7103
1514.00	13.00	h2o ch4 hdo	0.7508	0.6929	0.7167	0.6927
1530.25	17.00	h2o ch4 hdo	0.7086	0.6705	0.6852	0.6734
1550.25	19.00	h2o ch4 hdo	0.8885	0.8817	0.8899	0.9131
1568.00	14.50	h2o ch4 hdo	0.5726	0.5408	0.5359	0.5149
1596.50	39.00	h2o ch4 hdo no2	0.4419	0.4105	0.4026	0.3999
1703.50	16.00	h2o hno3 ch4 n2o o3 clno3 hdo	1.9126	1.9016	1.8346	1.8477

Average RMS Fitting Residuals Table (2/4)

Center	Width	Fitted gases								HIT2000	HIT2004	HIT2008	HIT2012
1713.00	8.00	h2o	hno3	ch4	o3	clno3	hdo			1.0893	1.0874	1.0754	1.0903
1723.50	19.00	h2o	hno3	ch4	n2o	o3	clno3	hdo		1.3430	1.3226	1.3533	1.3318
1743.00	16.00	h2o	hno3	ch4	n2o	o3	clno3	hdo		0.9425	0.9272	0.9451	0.9110
1760.00	15.50	h2o	hno3	ch4	n2o	o3	clno3	hdo		0.8523	0.8253	0.8364	0.8025
1776.50	16.00	h2o	ch4	n2o	o3	clno3	hdo			1.1097	1.1226	1.0380	1.0372
1795.50	20.00	h2o	ch4	n2o	o3	clno3	hdo			1.1413	1.3122	1.0625	1.0893
1811.50	20.00	h2o	ch4	n2o	o3	clno3	hdo			0.7731	0.8125	0.7660	0.7527
1835.00	28.00	h2o	co2	ch4	n2o	o3	hdo	no		0.9972	0.9891	0.9850	0.9912
1860.00	18.00	h2o	co2	ch4	n2o	o3	hdo	no		0.7181	0.7219	0.7216	0.7242
1879.75	19.50	h2o	co2	ch4	n2o	o3	hdo	no		0.7001	0.7120	0.6999	0.6936
1900.00	20.00	h2o	co2	n2o	o3	no				0.6445	0.6581	0.6433	0.6398
1921.00	22.00	h2o	co2	n2o	o3	no	cof2			0.7823	0.7828	0.7453	0.7619
1952.00	36.00	h2o	co2	o3	no	cof2				0.6573	0.6632	0.6705	0.6519
1990.00	41.00	h2o	co2	o3	ocs					0.6818	0.6955	0.6710	0.6473
2023.00	27.00	h2o	co2	o3	co	ocs				1.0450	0.7356	0.7311	0.7117
2057.50	37.00	h2o	co2	o3	co	ocs				1.2226	0.8515	0.8505	0.8178
2108.00	58.00	h2o	co2	o3	co	n2o	ocs			1.3032	0.9914	0.9819	0.9809
2159.00	46.00	h2o	co2	o3	co	n2o				0.6961	0.6721	0.6709	0.6717
2221.00	78.00	h2o	co2	o3	co	n2o				0.6723	0.6564	0.6554	0.6155
2296.75	109.50	h2o	co2	o3	n2o					0.7585	0.6813	0.6812	0.6562
2380.00	63.00	h2o	co2	ch4						0.5471	0.5242	0.5245	0.5148
2428.50	67.00	h2o	co2	o3	n2o	ch4				0.2834	0.2823	0.2835	0.2835
2481.50	39.00	h2o	co2	o3	n2o	ch4				0.2871	0.2714	0.2745	0.2754
2532.00	62.00	h2o	co2	o3	n2o	ch4				0.3501	0.3130	0.3181	0.3192
2578.70	31.50	h2o	co2	o3	n2o	ch4				0.4244	0.3592	0.3629	0.3652
2604.35	20.10	h2o	co2	o3	n2o	ch4				0.3451	0.3215	0.3284	0.3306
2637.70	46.60	h2o	co2	o3	n2o	ch4				0.3931	0.3322	0.3368	0.3380
2690.10	58.20	h2o	co2	o3	n2o	ch4				0.4159	0.3504	0.3322	0.3357
2752.35	66.30	h2o	co2	o3	n2o	ch4	hdo	hcl		0.5636	0.5020	0.4032	0.4124
2796.10	21.20	h2o	o3	n2o	ch4	hdo	hcl			0.6344	0.5066	0.4839	0.4952
2827.85	42.30	h2o	o3	n2o	ch4	hdo	hcl			0.6879	0.5901	0.6121	0.6140
2895.00	90.00	h2o	o3	n2o	ch4	hdo	no2	hcl	ocs	0.9387	0.8526	0.8626	0.8642
2960.00	40.00	h2o	o3	ch4	hdo	hcl	c2h6			0.6876	0.5154	0.5153	0.4878

Average RMS Fitting Residuals Table (3/4)

Center	Width	Fitted gases							HIT2000	HIT2004	HIT2008	HIT2012
3022.00	84.00	h2o	o3	ch4	hcl	c2h6			1.3087	0.9698	0.7652	0.7470
3104.00	80.00	h2o	o3	ch4					0.8145	0.6101	0.6485	0.6291
3184.00	80.00	h2o	co2	o3	ch4				0.5578	0.5438	0.4516	0.4345
3272.00	96.00	h2o	co2	o3	ch4	hcn			0.4141	0.3050	0.3173	0.3195
3360.00	80.00	h2o	co2	n2o	hcn				0.4281	0.3536	0.3642	0.3437
3457.00	114.00	h2o	co2	o3	n2o				1.8789	1.8396	1.0458	0.9821
3540.00	53.00	h2o	co2	n2o	hno3	hdo			3.7889	3.4543	3.0314	1.5992
3614.00	99.00	h2o	co2	o3	n2o	hno3	hdo		1.1080	1.1064	1.0899	0.7537
3722.50	93.50	h2o	co2	o3	n2o	hf	hdo		1.2539	1.0290	1.0221	0.7967
3783.50	25.00	h2o	co2	o3	n2o	hf	ch4	hdo	0.7361	0.5463	0.5319	0.5452
3809.00	13.00	h2o	co2	o3	n2o	ch4	hdo		1.0882	0.8435	0.8252	0.8642
3827.00	20.00	h2o	co2	o3	n2o	hf	ch4	hdo	1.2517	1.1096	0.9578	0.9768
3845.00	13.00	h2o	co2	o3	n2o	ch4	hdo		1.1898	0.9487	0.8168	0.7485
3860.00	9.00	h2o	co2	o3	n2o	ch4	hdo		1.4591	1.1815	0.8833	0.8999
3867.50	4.00	h2o	co2	o3	n2o	ch4	hdo		1.2018	0.9846	0.9659	0.8738
3877.60	15.00	h2o	co2	o3	n2o	hf	ch4	hdo	1.5634	0.9905	0.9908	0.8799
3888.50	4.50	h2o	co2	o3	n2o	ch4	hdo		0.4811	0.3476	0.3506	0.4131
3896.50	9.50	h2o	ch4	hdo					1.2353	0.8601	0.8780	0.8822
3920.00	30.00	h2o	n2o	hf	ch4	hdo			0.9541	0.7462	0.7637	0.6754
3950.00	30.00	h2o	co2	o3	ch4	hdo			1.2557	0.5896	0.5758	0.5815
4006.00	83.00	h2o	co2	o3	ch4	hf			0.6472	0.5929	0.5927	0.5785
4096.50	98.00	h2o	o3	n2o	ch4	hf			0.4394	0.4757	0.4751	0.4383
4191.00	92.00	h2o	o3	ch4	co	hf			0.6709	0.5244	0.5215	0.5199
4282.00	90.00	h2o	o3	ch4	co				0.7023	0.5527	0.5450	0.5885
4340.00	26.00	h2o	o3	ch4	co				0.5918	0.5095	0.5095	0.5122
4399.50	93.00	h2o	n2o	ch4					0.6325	0.5147	0.5147	0.5114
4486.00	80.00	h2o	ch4						0.5400	0.4747	0.4734	0.4609
4556.00	60.00	h2o	co2	ch4					0.5412	0.4591	0.4590	0.4390
4630.50	89.00	h2o	co2	o3	n2o	ch4			0.6140	0.5390	0.4248	0.4126
4716.00	82.00	h2o	co2	n2o	ch4				0.4972	0.4211	0.3904	0.3689
4783.00	52.00	h2o	co2						1.7564	1.4177	0.4701	0.4610
4849.00	82.00	h2o	co2						2.0143	1.3789	0.6120	0.6163
4910.00	40.00	h2o	co2	o3					1.0928	1.0312	0.5964	0.5389

Average RMS Fitting Residuals Table (4/4)

Center	Width	Fitted gases					HIT2000	HIT2004	HIT2008	HIT2012
4975.00	90.00	h2o	co2	n2o			1.3605	0.9442	0.7133	0.6971
5037.50	35.00	h2o	co2	n2o	ch4	hdo	0.6236	0.5795	0.4366	0.4356
5102.00	94.00	h2o	co2	n2o	ch4	hdo	0.8164	0.7176	0.6426	0.6410
5194.00	90.00	h2o	co2	ch4			0.9068	0.5432	0.5640	0.5483
5257.00	35.00	h2o	co2	ch4			0.8469	0.6084	0.6213	0.6177
5315.50	88.00	h2o	co2	ch4			1.0393	0.6653	0.7101	0.6865
5390.00	63.00	h2o	co2	ch4			1.1273	0.7307	0.7536	0.7911
5451.00	64.00	h2o	ch4				1.2288	0.8195	0.8366	0.8290
5520.00	78.00	h2o	ch4				1.5419	1.3215	1.2153	1.1957
5590.00	60.00	h2o	ch4				2.2967	2.4974	2.2599	2.1792

Summary/Conclusions

Comparing rms fitting residuals (new linelist versus previous linelists) provides a quick method of validation and for identifying problems.

The HITRAN 2000 linelist produces the best fits in 2 cases; the 2004 linelist in 25 cases; the 2008 linelist in 20 cases, and the 2012 linelist in 65 cases.

Atmospheric spectra are used only to assess the HITRAN linelist and to identify problems. To actually fix the problems requires laboratory spectra.

Results also show regions/gases for which further spectroscopic work would be beneficial

Future Work

Analyze lower altitude spectra where H_2O plays a much more important role and where errors in line widths and shifts become more important. This will require inclusion of line mixing effects which above 10 km are small.

Sub-dividing some of the windows, such that we would end up with more the 113 windows with a narrower average width, would provide more specificity in the identification of regions where the rms fits worsen. For example, in a wide window improvements in the spectroscopy of gas A can mask a worsening of gas B.

Examine the band-to-band consistency of the retrieved gas amounts.

Evaluate HITRAN 2016 when it comes out later this year. This can now be done quickly (a few days) since the windows and spectra are already defined and the scripts for running the GFIT code and making the plots already exist.

ATM 2016 linelist

ATM 2016 linelist is a “greatest hits” compilation based on HITRAN, but including empirical fixes of obvious problems. It is used by the TCCON network.

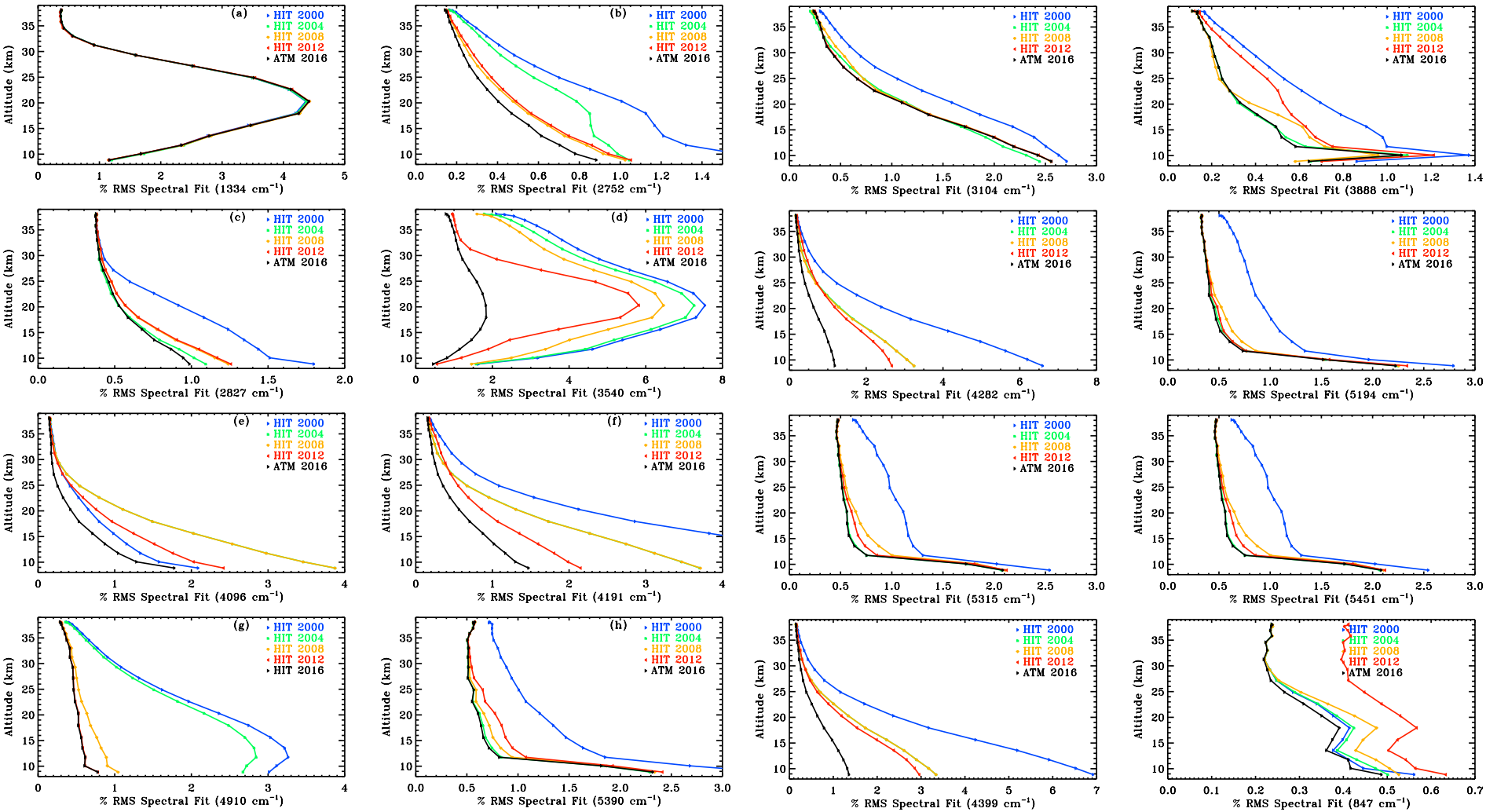
Previously described paper did not include ATM 2016 because it is not documented in a publication and it would not be a fair comparison (ATM is 4 years later)

When HITRAN 2012 linelist came out, ATM linelist was updated for gases/region that were improved.

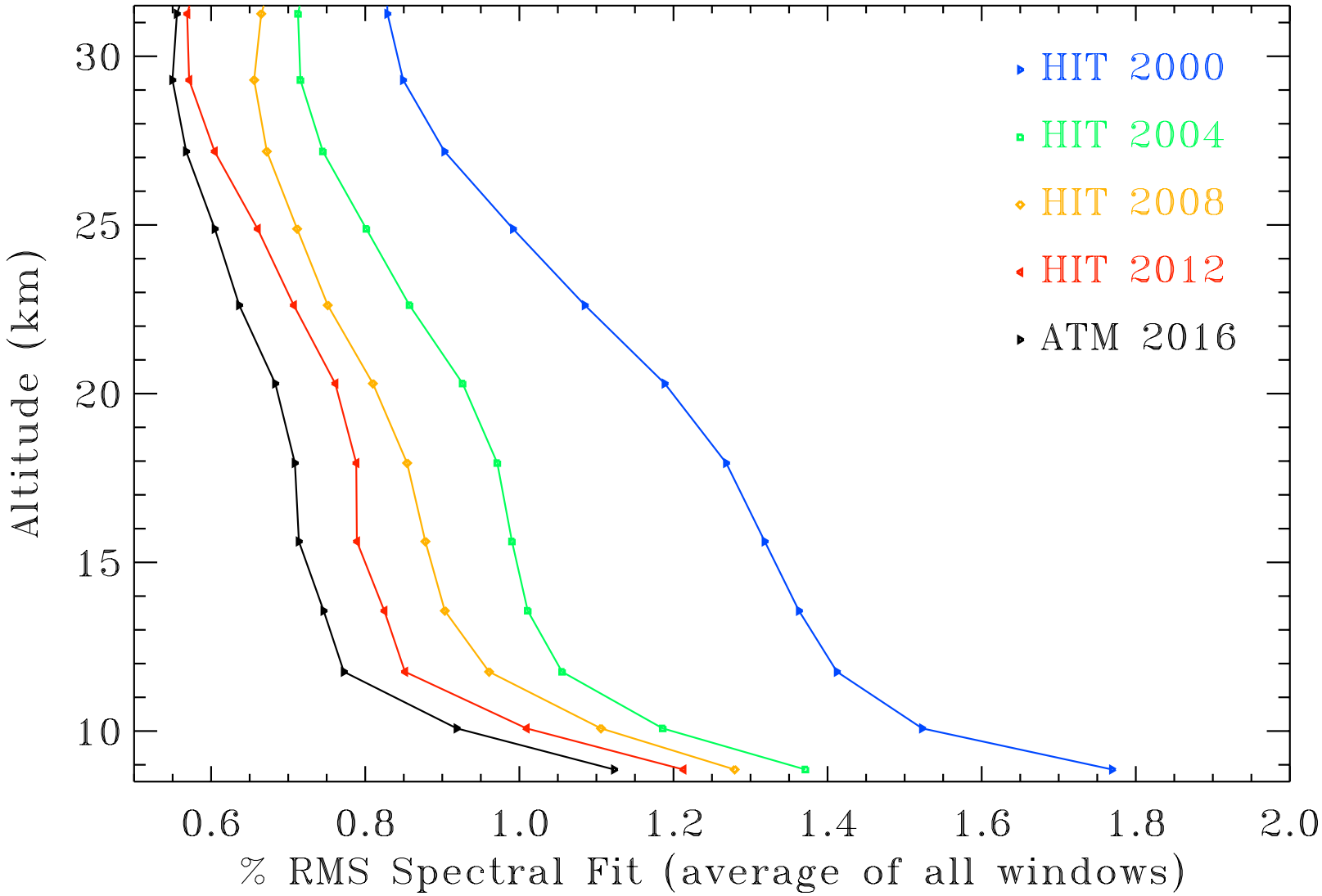
In regions that didn’t improve, no update.

So it should be no surprise that in terms of the rms residuals ATM2016 linelist is as good as the best HITRAN linelist in nearly every window.

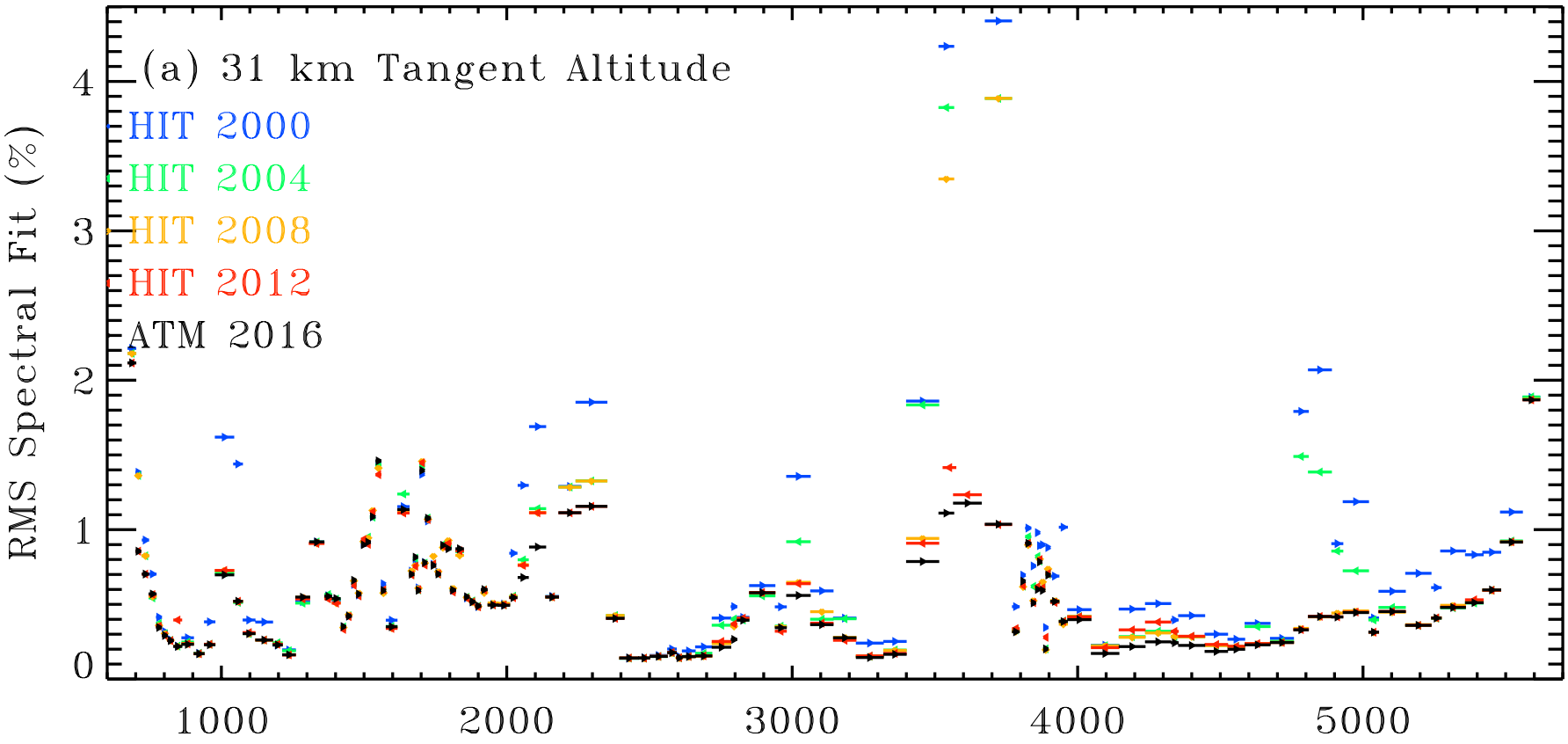
Comparisons Including ATM 2016 Linelist



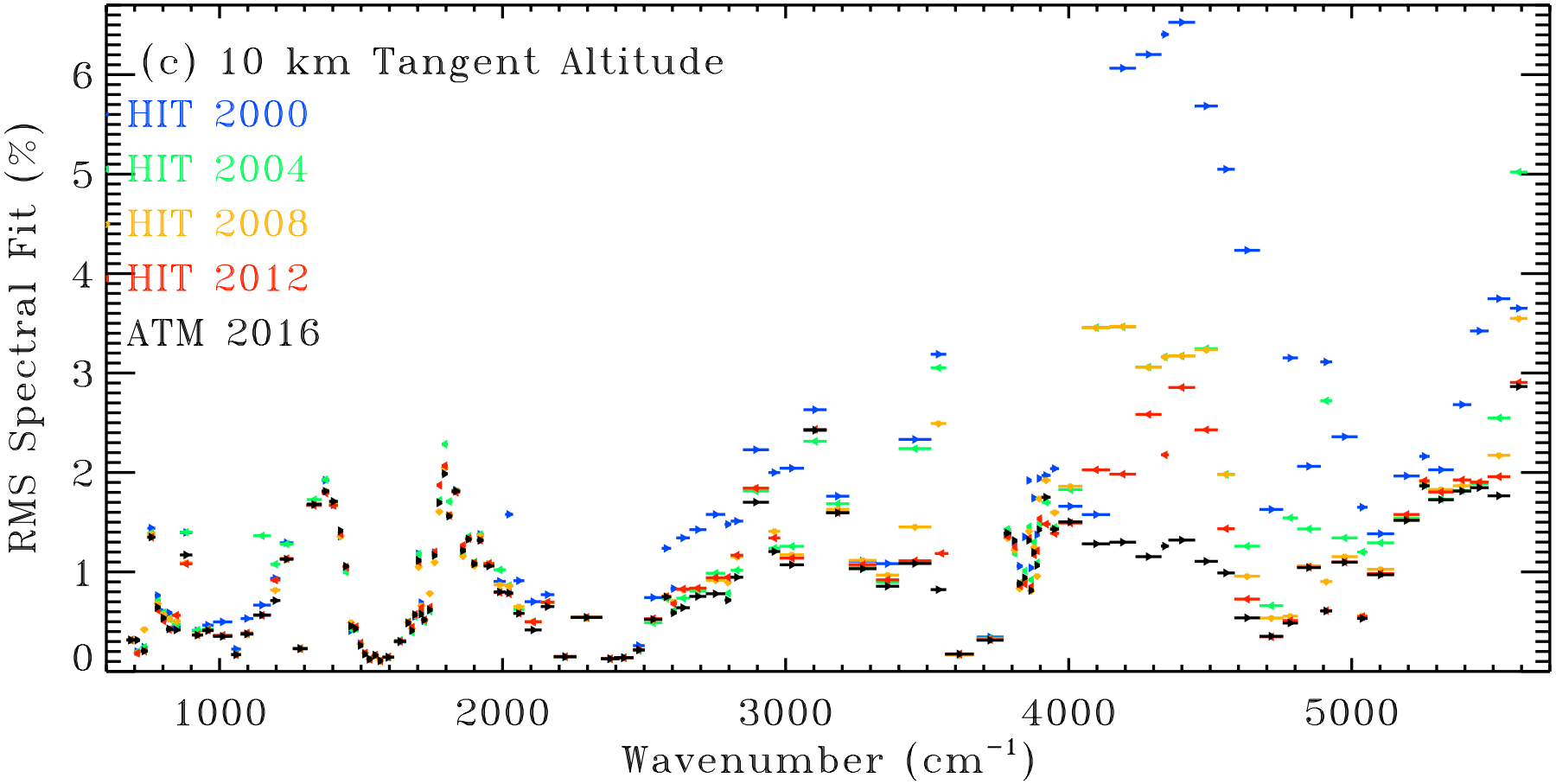
Average RMS Fit versus Altitude



RMS fits at 31 km altitude



RMS fits at 10 km Altitude



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Worldwide spectroscopy community whose work is encapsulated in the HITRAN linelists.