CO_2 spectroscopy Evaluation: 670 to 9500 cm^{-1}

Geoffrey C. Toon
Jet Propulsion Laboratory
California Institute of Technology
2024-06-16

In Jan 2024, I obtained a new CO_2 HITEMP linelist: "co2_HITEMP__ALL_sorted_E30.zip", containing 544,355 lines covering 10 to 18,410 cm^{-1}. Decided to compare its performance with earlier HITRAN versions and with the ATM_2019 list which is a version that I maintain and was last edited for CO_2 in 2019.

The GFIT algorithm was used to fit lab and atmospheric spectra:
- Kitt Peak laboratory CO_2 spectra over windows in the 620-8300 cm^{-1} region: 290K to 303K,
- TCCON ground-based solar absorption spectra of the atmosphere covering 4000 to 8500 cm^{-1} (240 to 310K, 0.9 atm)
- MkIV balloon solar occultation spectra of the atmosphere: 650-5650 cm^{-1}; 220K to 250K; 0.25 to 0.003 atm)
- MkIV ground-based solar absorption spectra of the atmosphere: 650-5650 cm^{-1}; 240K-315K; 0.65 to 1 atm)

Examined the average rms fitting residuals, the retrieved CO_2 amounts, and their window-to-window consistencies.

For gases other than CO_2, the latest ATM linelist was used in every case, so any differences between linelists are entirely attributable to CO_2 spectroscopy.
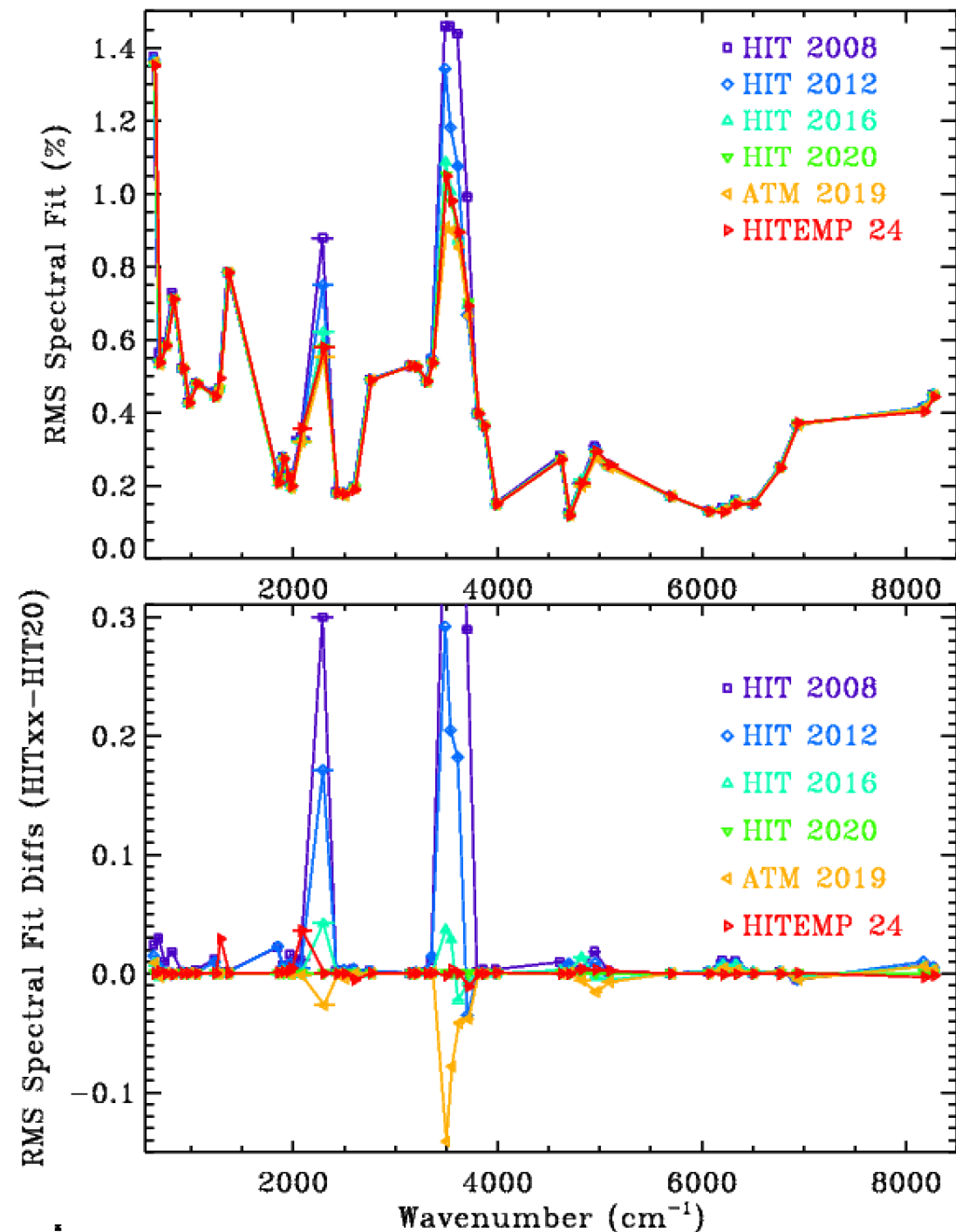
RMS fitting residuals to Kitt Peak lab spectra

148 Kitt Peak laboratory CO_2 spectra were analyzed over 44 windows. Not all spectra covered all windows, but on average there were 42 spectra (28%) covering each window. 146 spectra were 290-303K. There were two cold ones at 235K and 270K, but covering only 600-1400 cm^{-1} at 15 Torr. So the lab spectra at my disposal won't be able to confirm the T-dependence of air-broadened widths or shifts.

Upper panel shows the average rms fitting residuals obtained from each window (in collate_results.rpt), plotted versus the wavenumber of each window. They RMS values vary considerably from window to window, depending on the depth of the CO_2 lines, the resolution of the spectra, interfering gas (e.g., H_2O) amounts.

Bottom panel shows the difference in the residuals wrt the HIT 2020 rms residuals. Negative values, signifying improvements, are seen since 2008/12 in the 2200-2300 and 3400-3700 cm^{-1} regions.

Absolute RMS values are meaningless: they depend on the chosen spectra and analysis methods (fitted parameters, assumed lineshape, window limits, etc.). But RMS variations from linelist to linelist are significant because they depend only on the CO_2 spectroscopy.

Average RMS Fitting Residuals over 148 lab Spectra (mainly KP)

Same data as plotted on previous slide.

Fitted 45 windows covering 600 to 8400 cm^{-1}, temperatures from 290 to 303K.

All fits were performed with Voigt lineshapes and without LM.

atm19 was the best overall (0.4164%), closely followed by hit20 (0.4239%).

HITEMP24 came in third place (0.4254%), but achieved the best fits in most windows above 3800 cm^{-1} and in almost every window above 5500 cm^{-1}.

iwin	fcen	width/2	Nrow	hit08	hit12	hit16	hit20	atm19	hitemp		
1	644.65	26.15	32	1.3756	1.3664	1.3605	1.3515	1.3605	1.3515	6	1
2	693.35	24.35	32	0.5649	0.5405	0.5321	0.5349	0.5321	0.5368	5	1
3	754.50	32.75	37	0.5933	0.5839	0.5835	0.5832	0.5835	0.5831	6	1
4	828.35	33.25	42	0.7294	0.7107	0.7105	0.7110	0.7105	0.7104	6	1
5	925.00	36.05	62	0.5222	0.5219	0.5209	0.5210	0.5209	0.5212	5	1
6	980.00	21.05	64	0.4274	0.4269	0.4265	0.4263	0.4269	0.4266	4	1
7	1056.40	46.90	65	0.4814	0.4795	0.4785	0.4788	0.4783	0.4791	5	1
8	1239.50	20.30	67	0.4561	0.4536	0.4444	0.4441	0.4444	0.4442	4	1
9	1280.60	19.90	67	0.4666	0.4665	0.4649	0.4649	0.4649	0.4941	5	6
10	1367.40	25.90	67	0.7852	0.7847	0.7836	0.7835	0.7836	0.7836	4	1
11	1857.40	8.25	40	0.2290	0.2295	0.2077	0.2068	0.2077	0.2077	4	2
12	1906.50	35.50	40	0.2782	0.2770	0.2739	0.2715	0.2724	0.2733	4	1
13	1958.00	14.30	40	0.2308	0.2268	0.2259	0.2240	0.2242	0.2259	4	1
14	1982.50	8.50	40	0.2095	0.2019	0.1935	0.1935	0.1935	0.1979	5	1
15	2082.00	89.00	40	0.3326	0.3259	0.3208	0.3210	0.3194	0.3571	5	6
16	2299.00	101.00	40	0.8783	0.7495	0.6209	0.5786	0.5521	0.5788	5	1
17	2432.00	33.50	40	0.1813	0.1815	0.1795	0.1793	0.1787	0.1793	5	2
18	2502.00	35.00	40	0.1793	0.1796	0.1769	0.1766	0.1725	0.1766	5	2
19	2601.00	48.00	40	0.1968	0.1971	0.1936	0.1932	0.1932	0.1881	6	2
20	2760.00	31.00	41	0.4911	0.4908	0.4886	0.4886	0.4886	0.4891	5	1
21	3155.00	21.00	39	0.5279	0.5283	0.5277	0.5279	0.5277	0.5282	5	2
22	3207.00	25.00	39	0.5269	0.5266	0.5262	0.5254	0.5262	0.5255	4	1
23	3309.00	24.50	39	0.4866	0.4874	0.4855	0.4853	0.4855	0.4855	4	2
24	3364.00	26.00	39	0.5465	0.5499	0.5361	0.5352	0.5361	0.5358	4	2
25	3496.30	31.30	39	1.4587	1.3424	1.0876	1.0507	0.9095	1.0489	5	1
26	3548.85	21.25	42	1.4596	1.1816	1.0058	0.9771	0.8990	0.9804	5	1
27	3618.50	48.60	42	1.4399	1.0760	0.8717	0.8943	0.8526	0.8944	5	1
28	3712.60	46.60	44	0.9923	0.6677	0.6949	0.7029	0.6648	0.6920	5	1
29	3811.00	37.00	44	0.3986	0.3969	0.3969	0.3969	0.3970	0.3969	6	1
30	3872.00	16.00	45	0.3667	0.3631	0.3631	0.3631	0.3631	0.3631	6	1
31	3992.00	41.00	42	0.1516	0.1483	0.1482	0.1481	0.1482	0.1490	4	1
32	4622.00	41.00	42	0.2814	0.2731	0.2745	0.2717	0.2718	0.2716	6	1
33	4705.00	42.00	32	0.1244	0.1261	0.1194	0.1180	0.1190	0.1177	6	2
34	4825.50	78.50	36	0.2062	0.2050	0.2167	0.2031	0.1973	0.2067	5	3
35	4962.00	58.00	36	0.3090	0.2993	0.2876	0.2905	0.2749	0.2938	5	1
36	5096.00	76.00	36	0.2573	0.2551	0.2501	0.2553	0.2483	0.2575	5	6
37	5696.00	9.00	29	0.1703	0.1703	0.1702	0.1702	0.1702	0.1702	6	2
38	6072.00	49.00	36	0.1302	0.1306	0.1301	0.1285	0.1288	0.1285	6	2
39	6211.00	64.00	35	0.1392	0.1369	0.1355	0.1283	0.1327	0.1275	6	1
40	6338.00	62.00	36	0.1594	0.1575	0.1565	0.1491	0.1522	0.1485	6	1
41	6506.00	62.00	31	0.1506	0.1511	0.1513	0.1502	0.1506	0.1501	6	3
42	6769.00	41.00	32	0.2503	0.2508	0.2505	0.2490	0.2503	0.2486	6	2
43	6940.00	60.00	32	0.3662	0.3661	0.3680	0.3711	0.3662	0.3717	2	6
44	8175.00	36.00	28	0.4128	0.4158	0.4120	0.4059	0.4120	0.4028	6	2
45	8271.00	41.00	28	0.4501	0.4502	0.4483	0.4450	0.4483	0.4433	6	2

Mean % RMS over windows: 0.4749   0.4456   0.4267   0.4239   0.4164   0.4254

CO_2 VMR Scale Factors (VSF) averaged over 148 (mainly KP) laboratory spectra

The plotted values represent the scaling of the CO_2 vmr that was necessary to achieve best fit. These values are averaged over all spectra in which that window could be fitted. It shows how consistent the spectroscopy is from window to window. In a perfect world, these values would all be 1.0.

The error bars represent the standard deviation from this mean value of the individual VSF values of each spectrum. Points with errors > 0.5 are omitted.

The table below shows the results after an additional averaging over windows. HITEMP24 has the mean values closest to 1.0, but HIT20 has the smallest window-to-window variation.
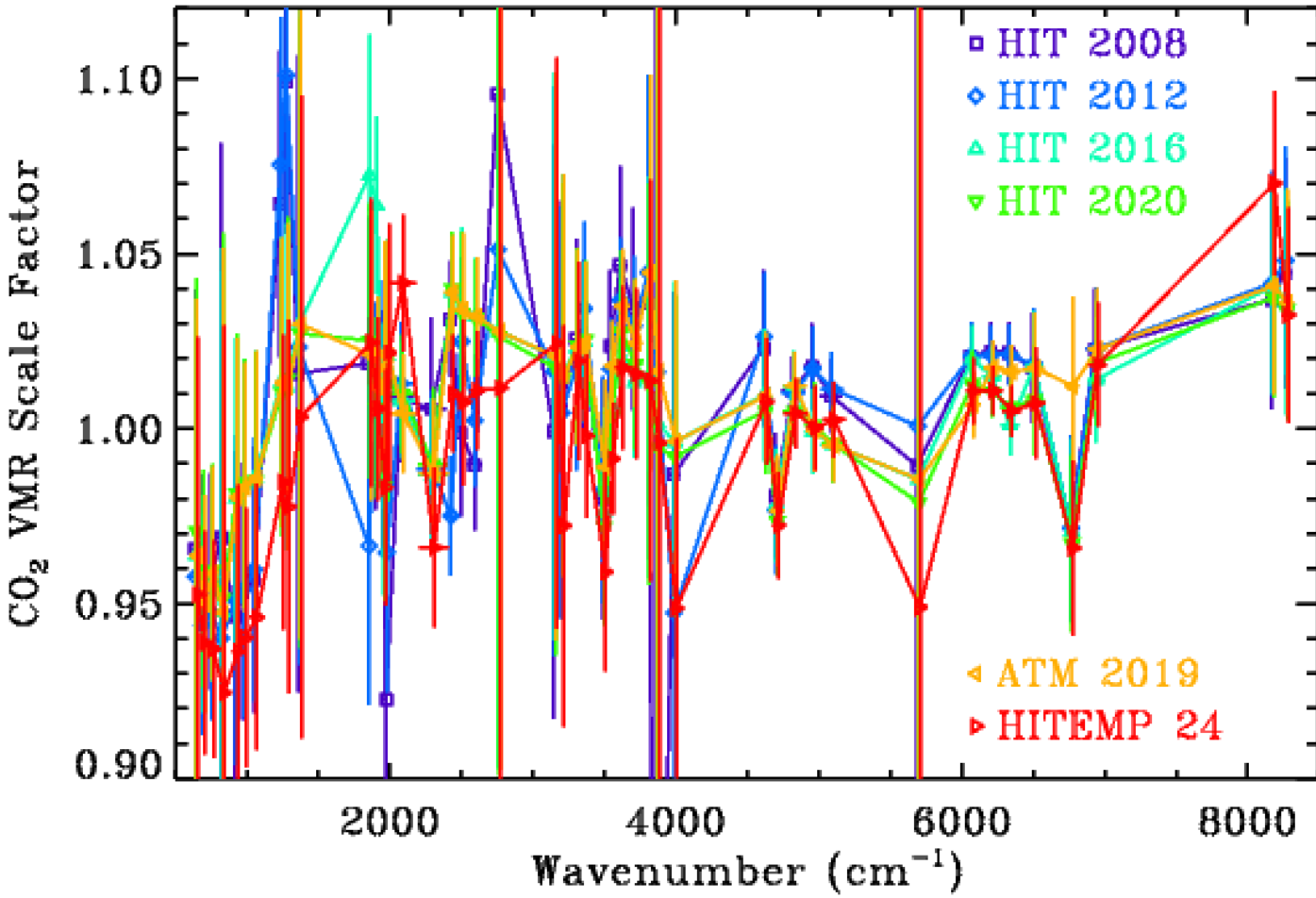

Table shows the VSF factors for each linelist averaged over the 44 windows. It is desirable that the mean values be close to 1.0 and that the standard deviation from the mean be small.

	hit08	hit12	hit16	hit20	atm19	hitemp24
Average VSF (over windows):	1.0135	1.0126	1.0094	1.0069	1.0117	1.0034
RMS deviation from mean:	±0.0189	±0.0202	±0.0181	±0.0154	±0.0156	±0.0190

iwin	fcen	Width/2	Nspec	hit08	hit12	hit16	hit20	atm19	hitemp24
1	644.65	26.15	32	0.9657	0.9577	0.9637	0.9706	0.9637	0.9526
2	693.35	24.35	32	0.9549	0.9439	0.9500	0.9572	0.9500	0.9388
3	754.50	32.75	37	0.9564	0.9477	0.9587	0.9594	0.9587	0.9370
4	828.35	33.25	42	0.9689	0.9401	0.9475	0.9515	0.9475	0.9245
5	925.00	36.05	62	0.9463	0.9511	0.9802	0.9814	0.9804	0.9363
6	980.00	21.05	64	0.9535	0.9539	0.9842	0.9844	0.9832	0.9402
7	1056.40	46.90	65	0.9569	0.9597	0.9859	0.9853	0.9858	0.9461
8	1239.50	20.30	67	1.0642	1.0753	1.0131	1.0103	1.0131	0.9848
9	1280.60	19.90	67	1.0991	1.1010	1.0119	1.0141	1.0119	0.9777
10	1367.40	25.90	67	1.0157	1.0232	1.0298	1.0272	1.0298	1.0033
11	1857.40	8.25	40	1.0187	0.9666	1.0723	1.0251	1.0211	1.0246
12	1906.50	35.50	40	1.0037	1.0096	1.0638	1.0060	1.0118	1.0057
13	1958.00	14.30	40	0.9993	1.0098	0.9859	0.9836	1.0215	0.9831
14	1982.50	8.50	40	0.9226	0.9646	1.0208	1.0128	1.0208	1.0217
15	2082.00	89.00	40	1.0088	1.0129	1.0081	1.0099	1.0044	1.0416
16	2299.00	101.00	40	1.0056	0.9886	0.9869	0.9897	0.9870	0.9661
17	2432.00	33.50	40	1.0313	0.9751	1.0390	1.0398	1.0389	1.0100
18	2502.00	35.00	40	0.9989	1.0249	1.0342	1.0330	1.0340	1.0075
19	2601.00	48.00	40	0.9897	1.0023	1.0321	1.0316	1.0321	1.0109
20	2760.00	31.00	41	1.0955	1.0511	1.0279	1.0263	1.0277	1.0116
21	3155.00	21.00	39	0.9991	1.0163	1.0206	1.0173	1.0206	1.0244
22	3207.00	25.00	39	1.0057	1.0046	1.0152	1.0144	1.0152	0.9723
23	3309.00	24.50	39	1.0255	1.0179	1.0233	1.0236	1.0233	1.0194
24	3364.00	26.00	39	1.0241	1.0344	1.0247	1.0253	1.0247	0.9979
25	3496.30	31.30	39	0.9799	0.9824	0.9759	0.9719	0.9890	0.9590
26	3548.85	21.25	42	1.0237	1.0170	1.0066	1.0034	1.0179	0.9914
27	3618.50	48.60	42	1.0467	1.0367	1.0234	1.0278	1.0350	1.0174
28	3712.60	46.60	44	1.0342	1.0295	1.0131	1.0184	1.0244	1.0156
29	3811.00	37.00	44	1.0357	1.0445	1.0148	1.0128	1.0445	1.0137
30	3872.00	16.00	45	0.7264	1.0162	1.0017	0.9944	1.0164	0.9960
31	3992.00	41.00	42	0.9869	0.9473	0.9962	0.9920	0.9963	0.9487
32	4622.00	41.00	42	1.0230	1.0262	1.0096	1.0051	1.0094	1.0077
33	4705.00	42.00	32	0.9808	0.9767	0.9779	0.9736	0.9765	0.9724
34	4825.50	78.50	36	1.0108	1.0101	1.0122	1.0051	1.0123	1.0044
35	4962.00	58.00	36	1.0178	1.0171	0.9991	1.0011	0.9995	1.0002
36	5096.00	76.00	36	1.0093	1.0114	0.9954	0.9956	0.9952	1.0025
37	5696.00	9.00	29	0.9894	1.0007	0.9855	0.9789	0.9855	0.9490
38	6072.00	49.00	36	1.0206	1.0207	1.0198	1.0129	1.0068	1.0108
39	6211.00	64.00	35	1.0219	1.0210	1.0150	1.0105	1.0174	1.0108
40	6338.00	62.00	36	1.0217	1.0210	1.0009	1.0061	1.0162	1.0051
41	6506.00	62.00	31	1.0173	1.0184	1.0177	1.0081	1.0173	1.0072
42	6769.00	41.00	32	0.9717	0.9716	0.9708	0.9672	1.0121	0.9659
43	6940.00	60.00	32	1.0227	1.0228	1.0140	1.0188	1.0227	1.0183
44	8175.00	36.00	28	1.0369	1.0415	1.0408	1.0373	1.0408	1.0701
45	8271.00	41.00	28	1.0445	1.0481	1.0361	1.0339	1.0361	1.0325
Average VSF (over windows)				**1.0137**	**1.0128**	**1.0094**	**1.0069**	**1.0117**	**1.0034**
RMS deviation from mean				**±0.0194**	**±0.0206**	**±0.0181**	**±0.0153**	**±0.0156**	**±0.0190**

CO_2 VMR Scale Factors (VSF) averaged over the 148 lab spectra for each of the 44 windows, for each of the 6 tested linelists.

The HITEMP linelist has an overall mean VSF of 1.0034, which is very close to the nominal value of 1. But its rms window-to-window variation is 1.90% which is larger than that of HIT20 or ATM19
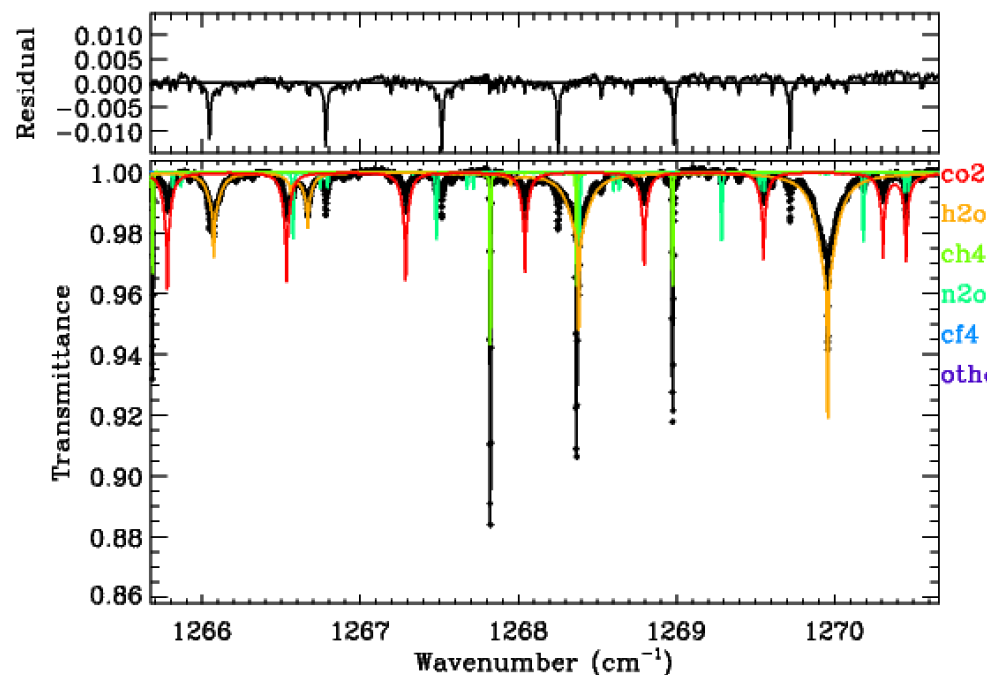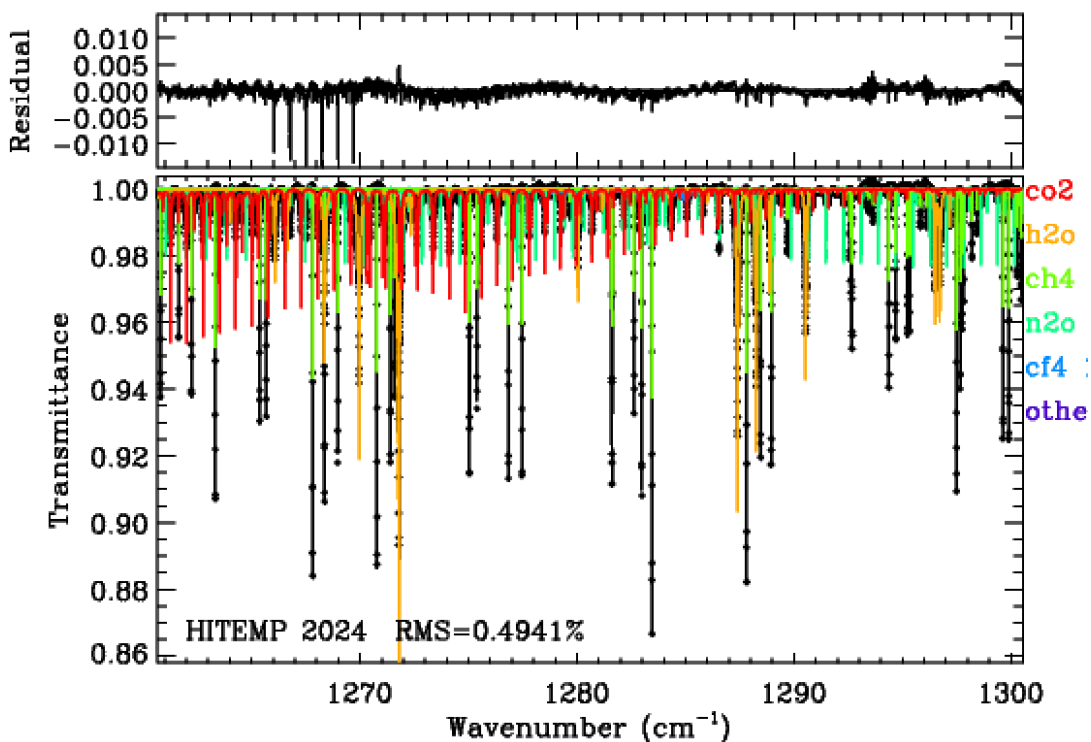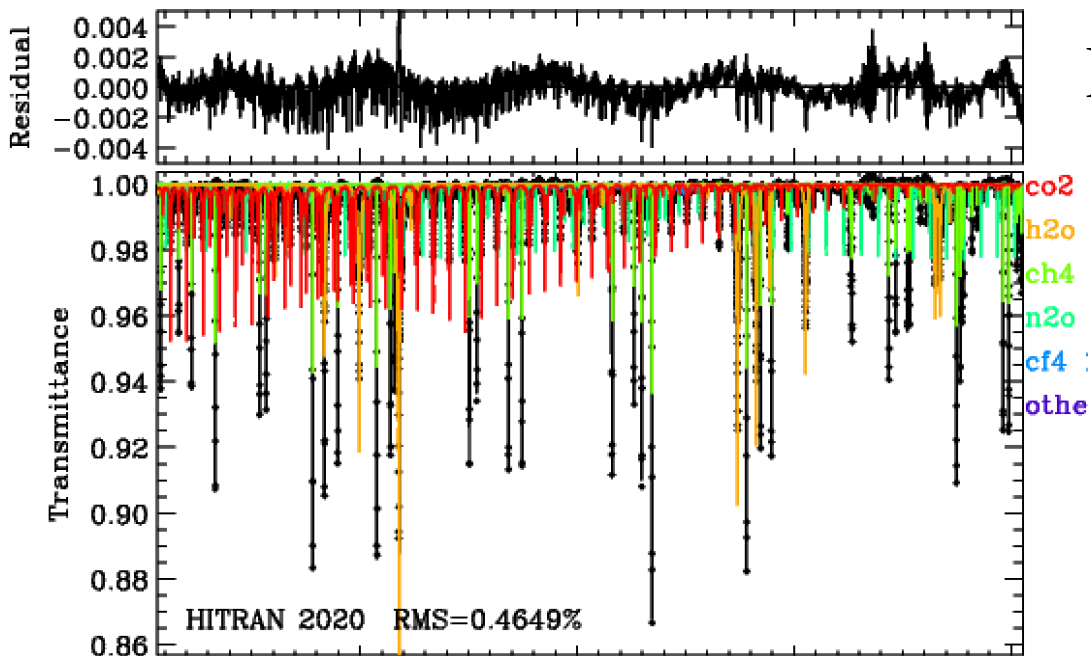
Example of Deficiency in HITEMP CO_2 Linelist

In fits to KP lab spectra, HITEMP 2024 linelist produced significantly larger residuals in 1280 cm^{-1} window than any other linelist.

Top-Left: Average spectral fit to 67 Kitt Peak lab spectra using HITRAN 2020 linelist. Peak residual is 0.5% due to H_2O.

Bottom-Left: Fits to same spectra using HITEMP. Peak residual is 1.5%. Six CO_2 lines seem to be missing.

Below: Zoom into the 6 missing lines.

# Another Example of a Deficiency in HITEMP

In fits to KP lab spectra, HITEMP 2024 linelist produced larger residuals in 2082 cm^{-1} window than any other linelist.

Top-Left: Spectral fit to 67 Kitt Peak lab spectra using HITRAN 2020 linelist. Peak residual is 4% due to H$_2$O. RMS fittinf residual is 0.192%

Bottom-Left: Fits to same spectrum using HITEMP 2024 linelist. RMS fitting residual is 0.308%

Although largest residuals are due to contaminating H$_2$O, the poorer HITEMP24 residuals are due to less consistent line positions and intensities between the various CO$_2$ bands/branches.

This problem is also seen in MkIV balloon spectra (later).
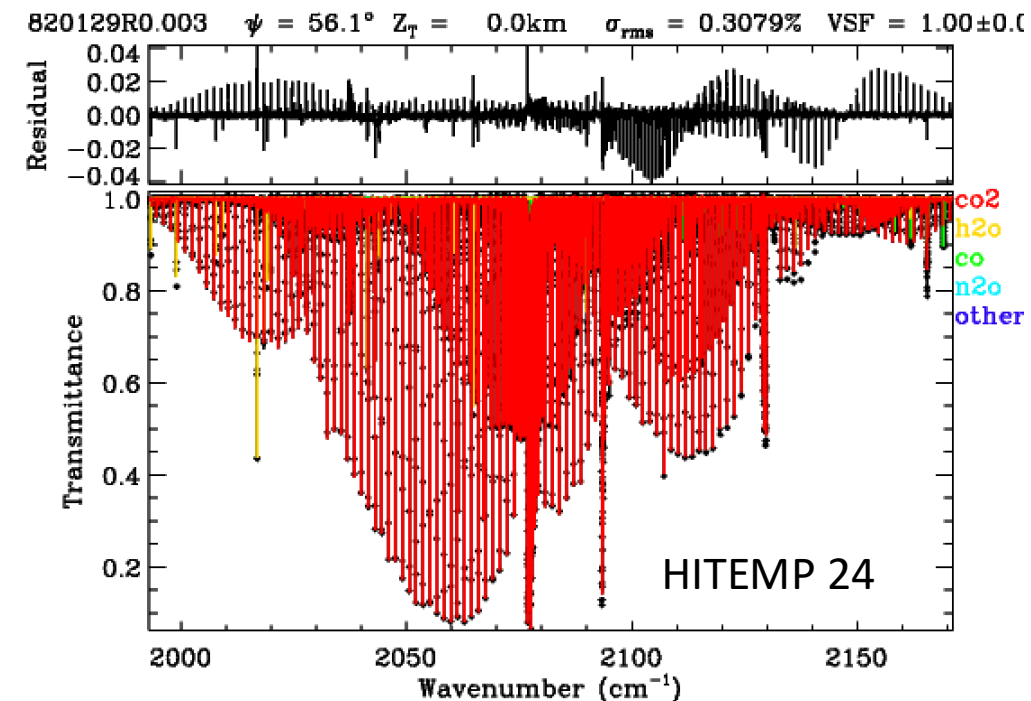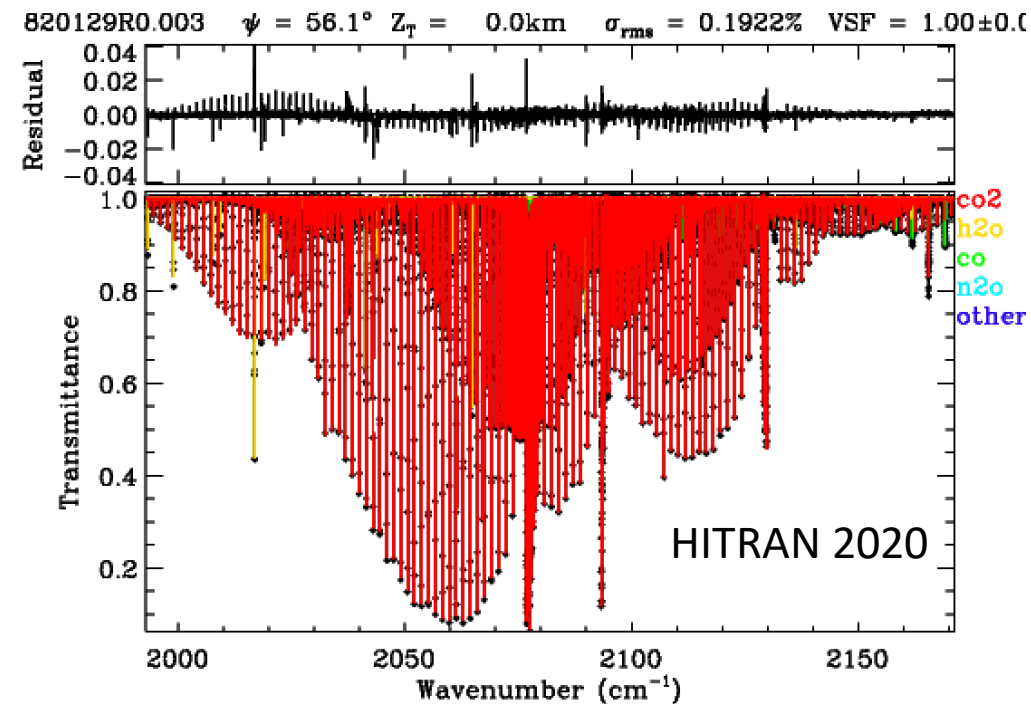
MkIV Balloon Atmospheric Spectra – RMS fitting residuals 670-5200 cm^{-1}

Fitted a sample of 17 MkIV balloon spectra in 35 windows.

iwin	fcen	width/2	Nspec	hit08	hit12	hit16	hit20	atm19	hitemp24		
1	694.60	23.60	17	1.6396	1.5976	1.5857	1.5806	1.5857	1.5832	4	1
2	754.50	32.75	17	0.8863	0.8341	0.8282	0.8424	0.8253	0.8456	5	1
3	827.20	34.30	17	0.3889	0.3820	0.3818	0.3837	0.3818	0.3847	5	1
4	925.00	36.05	17	0.3522	0.3512	0.3511	0.3519	0.3511	0.3525	5	6
5	980.00	21.05	17	0.4698	0.4686	0.4685	0.4699	0.4695	0.4706	3	6
6	1056.40	46.90	17	0.4230	0.4229	0.4227	0.4230	0.4225	0.4234	5	6
7	1239.50	20.30	17	0.3279	0.3270	0.3273	0.3274	0.3273	0.3276	2	1
8	1280.60	19.90	17	0.4735	0.4727	0.4725	0.4725	0.4725	0.9087	5	6
9	1367.40	25.90	17	0.9983	0.9998	0.9990	0.9987	0.9987	0.9989	1	2
10	1857.90	7.65	17	0.5510	0.5512	0.5496	0.5499	0.5496	0.5501	5	2
11	1906.50	35.50	17	0.6993	0.7014	0.7016	0.6985	0.6987	0.7000	4	3
12	1958.00	14.30	17	0.5467	0.5452	0.5508	0.5491	0.5450	0.5496	5	3
13	1982.50	8.50	17	0.4921	0.4829	0.4823	0.4830	0.4823	0.4890	5	1
14	2082.50	88.50	17	0.7170	0.7114	0.7101	0.7091	0.7078	0.7558	5	6
15	2299.30	125.15	17	0.9010	0.8192	0.7025	0.6821	0.6891	0.6748	6	1
16	2430.60	32.10	17	0.1546	0.1538	0.1539	0.1539	0.1538	0.1539	5	1
17	2501.90	34.80	17	0.2265	0.2254	0.2259	0.2259	0.2257	0.2259	2	1
18	2601.00	48.00	17	0.3004	0.2993	0.2993	0.2995	0.2993	0.2997	5	1
19	2760.00	31.00	17	0.3042	0.3020	0.3017	0.3016	0.3017	0.3016	6	1
20	3155.00	19.00	17	0.5480	0.5468	0.5457	0.5450	0.5457	0.5449	6	1
21	3206.75	20.25	17	0.2817	0.2752	0.2708	0.2673	0.2708	0.2680	4	1
22	3309.00	24.50	17	0.2594	0.2370	0.2338	0.2320	0.2338	0.2337	4	1
23	3364.00	26.00	17	0.3016	0.2752	0.2642	0.2586	0.2642	0.2625	4	1
24	3496.30	31.30	17	1.8285	1.3117	0.6930	0.6418	0.4208	0.6371	5	1
25	3548.80	21.20	17	2.3090	0.9894	0.8583	0.8369	0.6881	0.8395	5	1
26	3618.50	48.60	17	3.1751	1.0762	0.9391	0.9622	0.9164	0.9620	5	1
27	3713.10	46.20	17	2.2614	1.0556	1.0533	1.0656	1.0531	1.0705	5	1
28	3811.20	37.00	17	0.9146	0.8869	0.8866	0.8867	0.8868	0.8868	3	1
29	3871.90	15.80	17	1.0367	0.9843	0.9842	0.9841	0.9843	0.9843	4	1
30	3991.00	42.00	17	0.5391	0.5376	0.5376	0.5376	0.5376	0.5380	5	1
31	4622.10	41.40	17	0.3164	0.2914	0.2911	0.2893	0.2895	0.2895	4	1
32	4705.00	42.00	17	0.2972	0.2774	0.2823	0.2773	0.2738	0.2779	5	1
33	4825.95	78.05	17	0.5100	0.5146	0.5678	0.5248	0.5101	0.5322	1	3
34	4962.00	58.00	17	0.5834	0.5570	0.5547	0.5409	0.5271	0.5437	5	1
35	5096.00	76.00	17	0.5089	0.5069	0.5032	0.5070	0.5006	0.5110	5	6

Mean % RMS over windows: 0.7578 0.5992 0.5709 0.5674 0.5540 0.5822
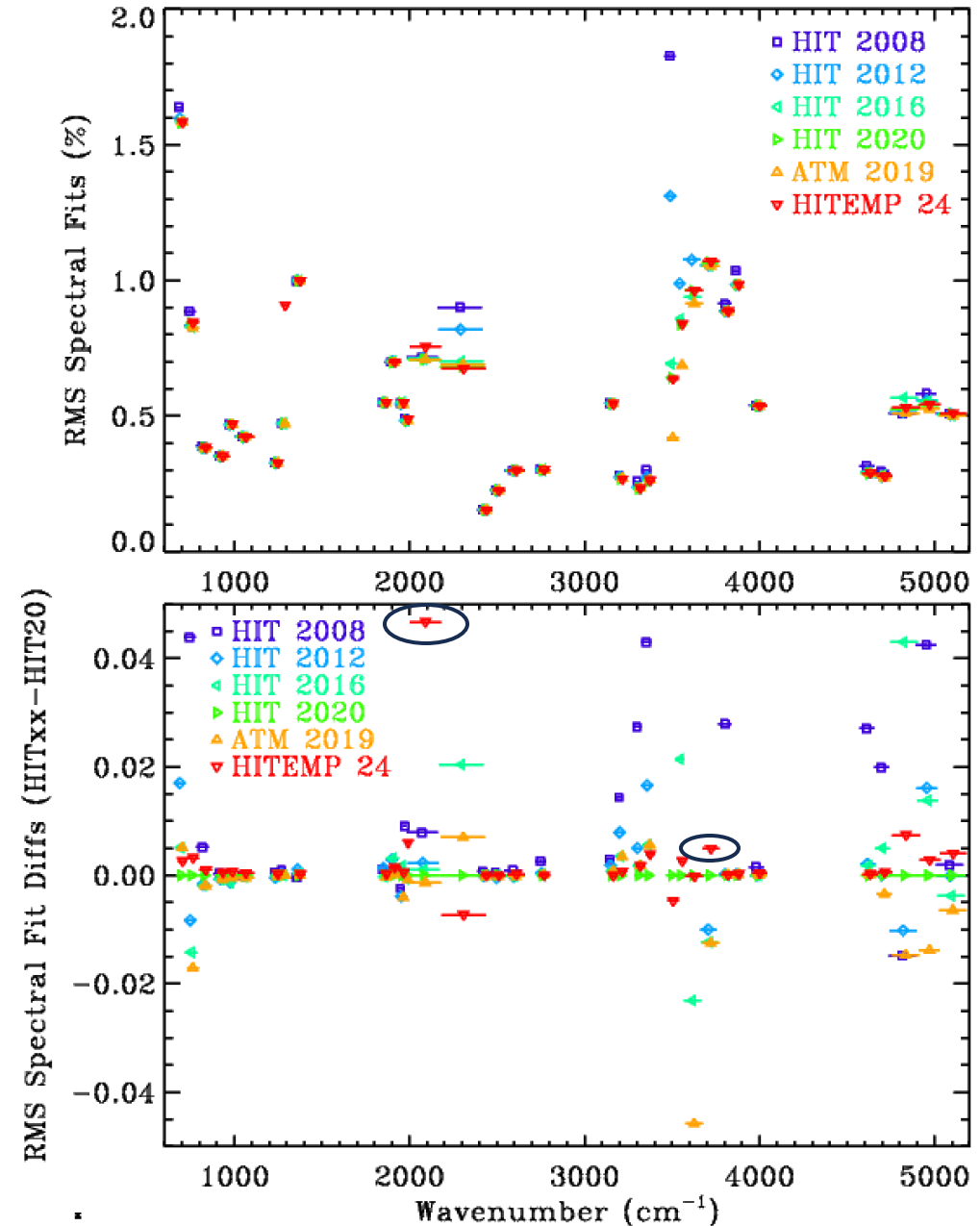
Example of deficiency in HITEMP24 seen in MkIV balloon spectral fits at ~2150 cm⁻¹

Spectral fits to MkIV balloon spectrum at 17.9 km tangent altitude.

Top panel shows fit using HITRAN 2020 CO_2 linelist. The residual at 2076 cm⁻¹ is due to neglect of LM at the Q-branch.

Bottom panels shows fit using HITEMP_24 CO_2 linelist. There seems to be an inconsistency in the line intensities: below 2148 cm-1 the lines are too weak; above they are too strong.
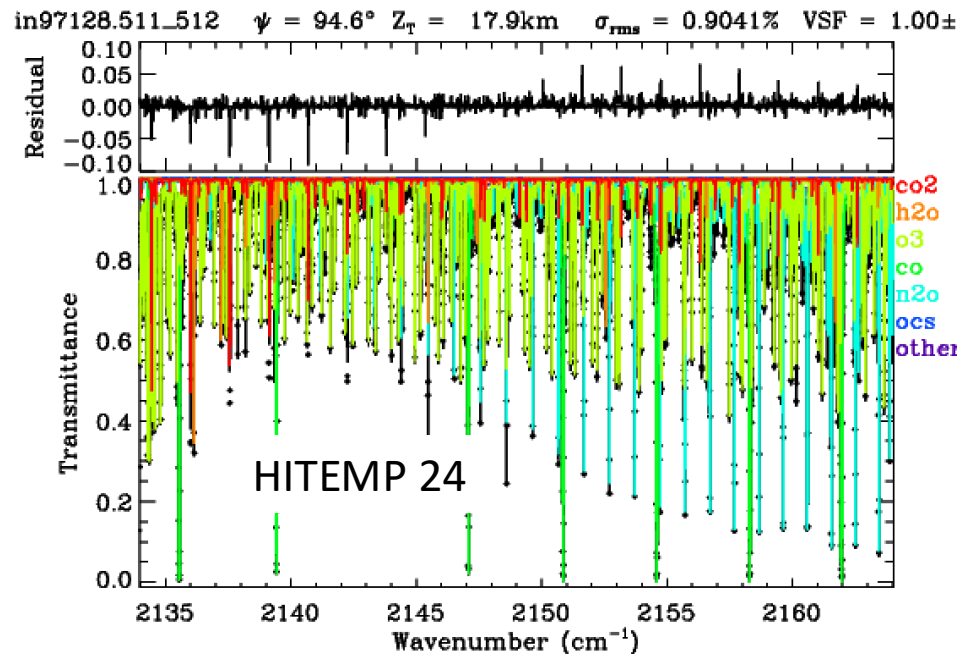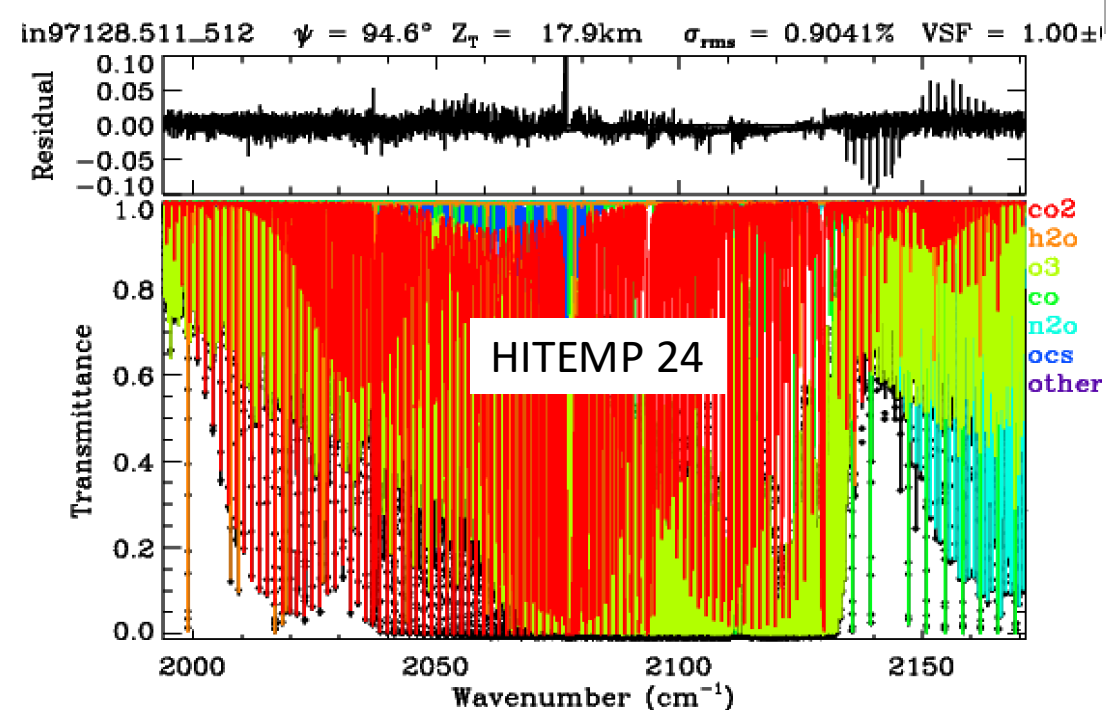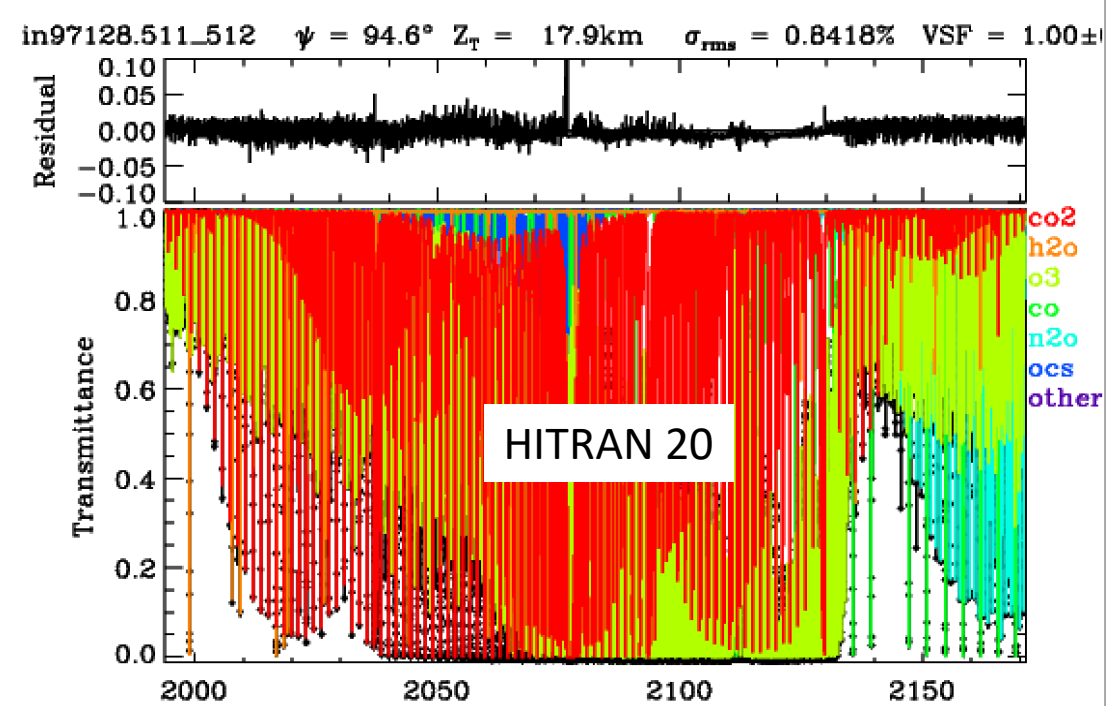
MkIV Balloon Atmospheric Spectra – VSFs

iwin	fcen	width/2	Nspec	hit08	hit12	hit16	hit20	atm19	hitemp24
1	694.60	23.60	17	1.1082	1.0899	1.0972	1.1115	1.0972	1.0947
2	754.50	32.75	17	1.0391	1.0200	1.0317	1.0430	1.0319	1.0229
3	827.20	34.30	17	1.0124	1.0034	1.0119	1.0203	1.0119	0.9937
4	925.00	36.05	17	1.0075	0.9971	1.0356	1.0393	1.0378	0.9941
5	980.00	21.05	17	1.0251	0.9981	1.0441	1.0476	1.0500	1.0026
6	1056.40	46.90	17	0.9768	0.9626	0.9968	1.0034	0.9990	0.9669
7	1239.50	20.30	17	1.0393	1.0313	1.0400	1.0407	1.0400	1.0172
8	1280.60	19.90	17	1.0379	1.0265	1.0429	1.0433	1.0429	1.0116
9	1367.40	25.90	17	1.0384	1.0380	1.0533	1.0543	1.0532	1.0312
10	1857.90	7.65	17	1.0229	0.9738	1.0572	1.0068	1.0069	1.0061
11	1906.50	35.50	17	0.9902	0.9963	1.0544	0.9984	1.0005	1.0013
12	1958.00	14.30	17	0.9841	0.9974	0.9620	0.9575	0.9996	0.9585
13	1982.50	8.50	17	0.9561	0.9977	0.9878	0.9705	0.9879	0.9848
14	2082.50	88.50	17	0.9997	1.0104	1.0112	1.0180	1.0053	1.0482
15	2299.30	125.15	17	1.0206	0.9892	0.9901	1.0031	0.9903	0.9844
16	2430.60	32.10	17	0.9939	0.9386	0.9941	0.9937	0.9941	0.9654
17	2501.90	34.80	17	0.9799	1.0101	1.0064	1.0052	1.0053	0.9802
18	2601.00	48.00	17	0.9881	1.0058	1.0086	1.0080	1.0085	0.9874
19	2760.00	31.00	17	1.0376	0.9782	1.0208	1.0180	1.0203	1.0021
20	3155.00	19.00	17	0.9904	1.0063	1.0104	1.0106	1.0104	1.0183
21	3206.75	20.25	17	0.9967	0.9968	1.0071	1.0067	1.0071	0.9619
22	3309.00	24.50	17	1.0084	1.0127	1.0168	1.0168	1.0168	1.0196
23	3364.00	26.00	17	1.0155	1.0299	1.0171	1.0187	1.0171	0.9885
24	3496.30	31.30	17	0.9453	0.9737	0.9786	0.9815	0.9854	0.9723
25	3548.80	21.20	17	0.9861	1.0001	0.9906	0.9985	1.0002	0.9904
26	3618.50	48.60	17	1.0281	1.0187	1.0122	1.0286	1.0085	1.0238
27	3713.10	46.20	17	1.0571	1.0455	1.0307	1.0461	1.0450	1.0477
28	3811.20	37.00	17	1.0182	1.0343	1.0051	1.0034	1.0343	1.0044
29	3871.90	15.80	17	0.0719	1.0206	1.0152	1.0127	1.0209	0.9999
30	3991.00	42.00	17	0.9585	0.9299	0.9742	0.9729	0.9756	0.9273
31	4622.10	41.40	17	1.0266	1.0286	1.0136	1.0123	1.0123	1.0141
32	4705.00	42.00	17	0.9879	0.9848	0.9873	0.9878	0.9852	0.9880
33	4825.95	78.05	17	0.9941	0.9914	0.9889	0.9938	0.9943	0.9939
34	4962.00	58.00	17	1.0054	1.0050	0.9898	1.0013	0.9845	1.0036
35	5096.00	76.00	17	0.9864	0.9913	0.9779	0.9898	0.9744	0.9997
Average VSF (over windows)				1.0037	1.0016	1.0108	1.0110	1.0094	0.9935
RMS deviation from mean				±0.0182	±0.0266	±0.0190	±0.0181	±0.0179	±0.0198
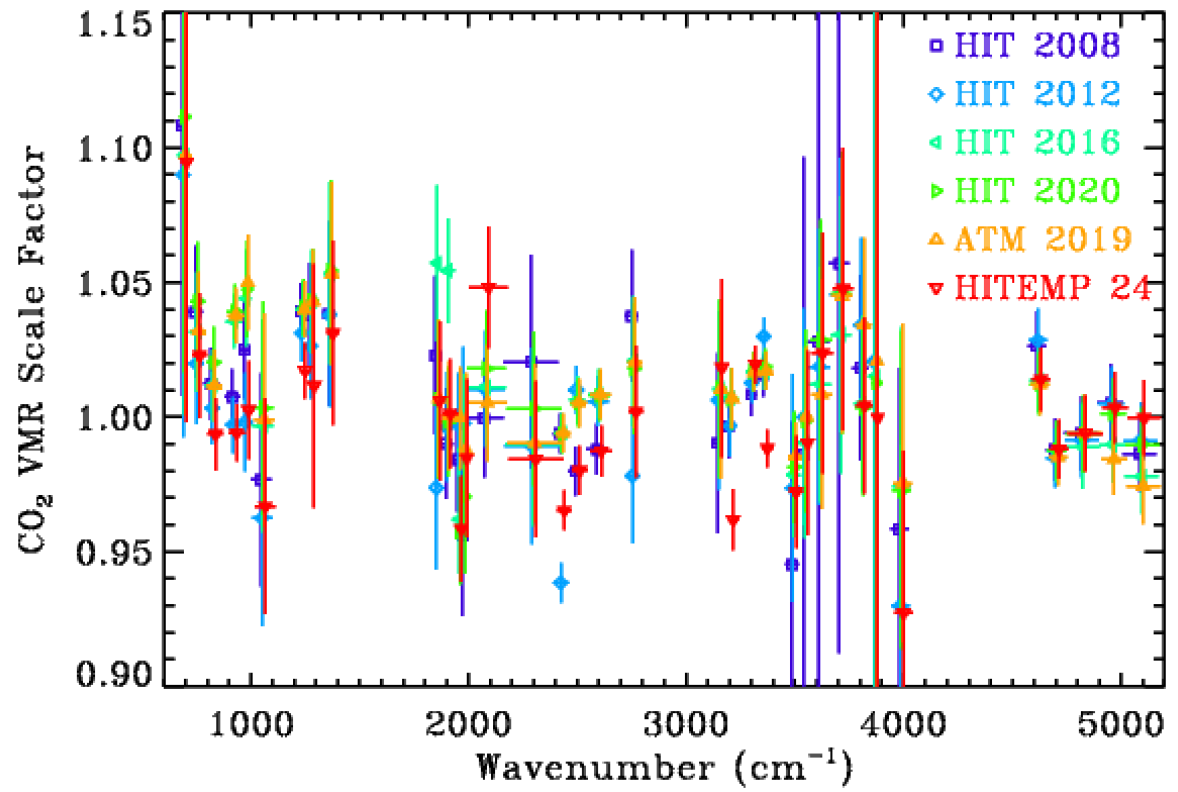
Fitted a sample of 17 MkIV balloon spectra in 35 windows. These represent a variety of conditions from T=220 to 260K and P=200 mbar to 3 mbar

ATM19 has the smallest mean RMS fitting residual, in this spectral region (5760-5200 cm-1) and the smallest window-to-window variations.

Examples of spectral fits at ~3600 cm^{-1}

Average spectral fit to 17 MkIV balloon spectra covering 10-37 km tangent altitude.

Although dominant residuals are due to H$_2$O, poor CO$_2$ line positions in HITEMP 24 linelist (Top panel) cause increased residuals, in comparison with ATM19 linelist (bottom panel).

Top panel shows fits using HITEMP. Orange ovals indicate residuals not present in lower panel (ATM19).
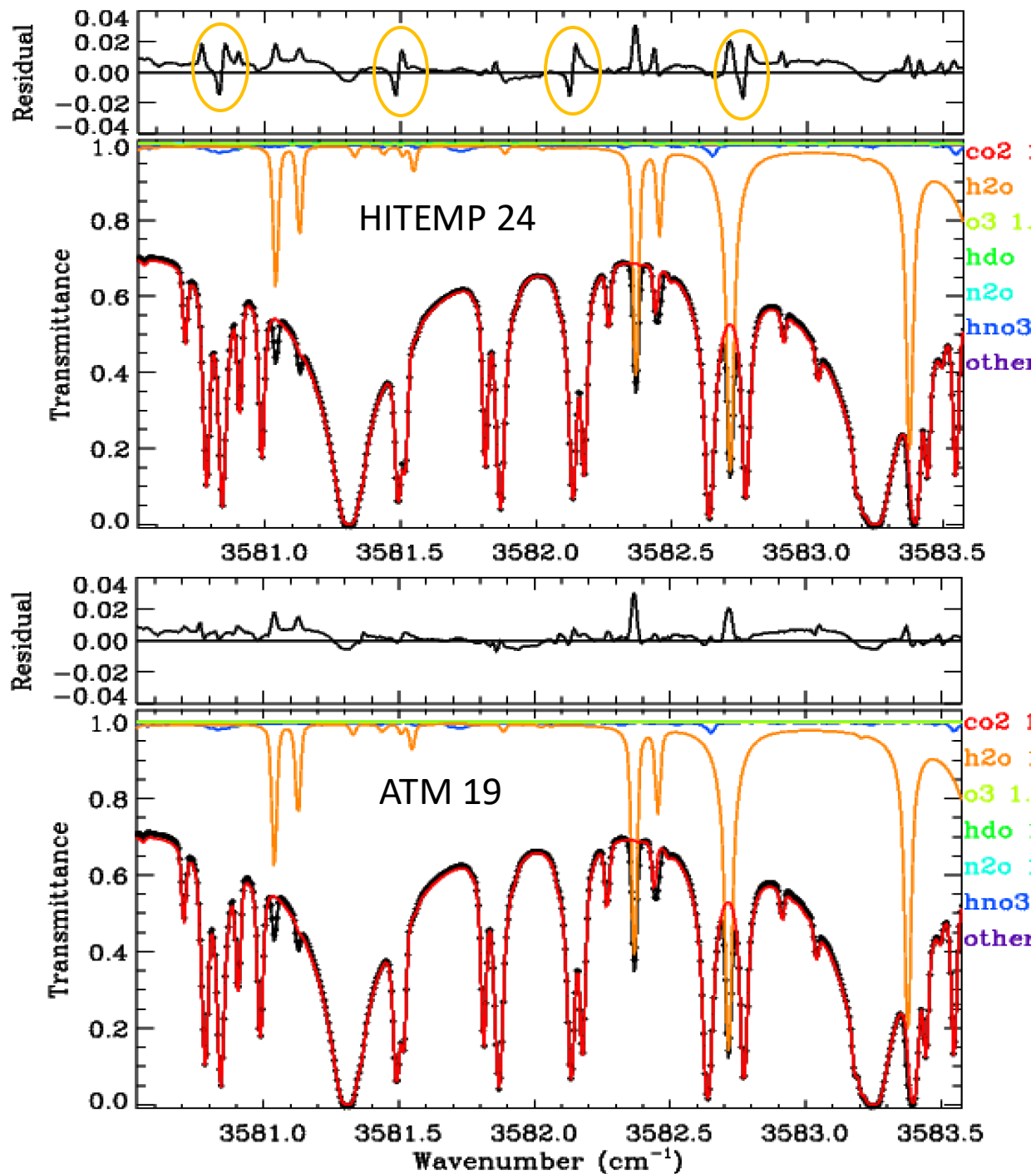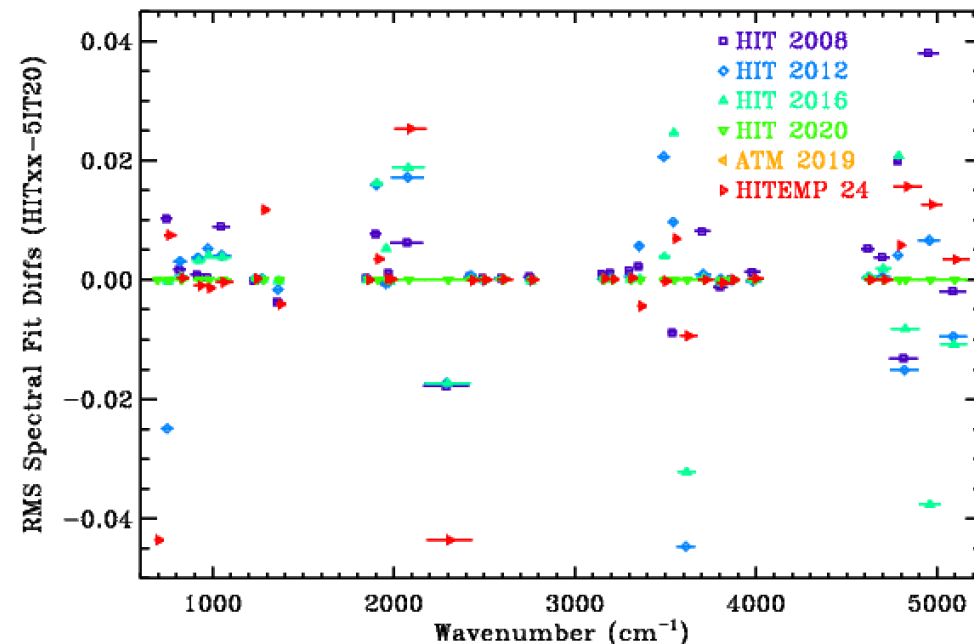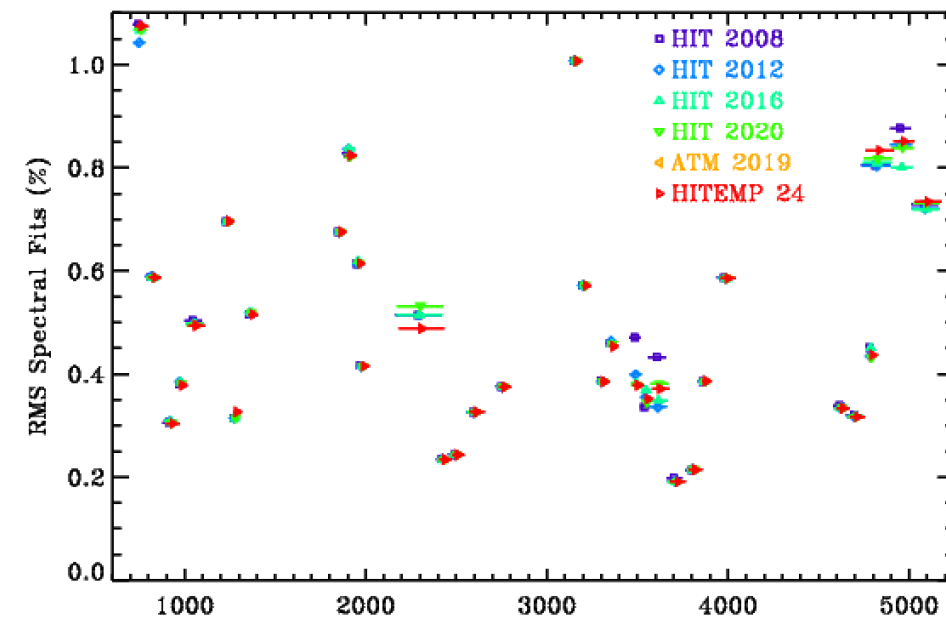
MkIV Ground-based Atmospheric Spectra – RMS fitting residuals 670-5200 cm^{-1}

Fitted a sample of 86 MKIV ground-based spectra in 36 windows. These represent a variety of conditions from T=-30C to +40C; 15° < SZA <88°

| iwin	fcen	width/2	Nspec	hit08	hit12	hit16	hit20	atm19	hitemp24		
1	694.60	23.60	86	2.0074	1.9858	1.9688	2.1140	1.9688	2.0704	5	4
2	755.20	32.05	86	1.0779	1.0427	1.0673	1.0676	1.0178	1.0751	5	1
3	827.20	34.30	86	0.5886	0.5900	0.5875	0.5869	0.5875	0.5872	4	2
4	925.00	36.05	86	0.3058	0.3086	0.3081	0.3049	0.3059	0.3039	6	2
5	980.00	21.05	86	0.3802	0.3850	0.3839	0.3798	0.3793	0.3784	6	2
6	1056.40	46.90	86	0.5034	0.4986	0.4983	0.4945	0.4949	0.4941	6	1
7	1239.50	20.30	86	0.6960	0.6963	0.6963	0.6961	0.6963	0.6963	1	6
8	1280.60	19.90	86	0.3148	0.3149	0.3148	0.3147	0.3148	0.3264	4	6
9	1367.40	25.90	86	0.5159	0.5180	0.5195	0.5196	0.5200	0.5155	6	5
10	1857.90	7.65	86	0.6759	0.6759	0.6757	0.6757	0.6756	0.6757	5	2
11	1910.30	29.70	86	0.8283	0.8365	0.8368	0.8206	0.8385	0.8241	4	5
12	1960.45	11.85	86	0.6140	0.6137	0.6196	0.6143	0.6138	0.6144	2	3
13	1981.50	8.50	86	0.4164	0.4150	0.4150	0.4153	0.4150	0.4154	5	1
14	2082.50	88.50	86	1.1172	1.1282	1.1298	1.1110	1.1181	1.1363	4	6
15	2299.30	125.15	86	0.5142	0.5147	0.5147	0.5320	0.5148	0.4884	6	4
16	2430.60	32.10	86	0.2347	0.2349	0.2344	0.2342	0.2344	0.2341	6	2
17	2501.90	34.80	86	0.2437	0.2434	0.2434	0.2434	0.2433	0.2434	5	1
18	2605.00	42.00	86	0.3263	0.3262	0.3263	0.3261	0.3263	0.3262	4	5
19	2760.00	31.00	86	0.3756	0.3750	0.3750	0.3751	0.3750	0.3751	5	1
20	3159.00	15.20	86	1.0079	1.0071	1.0071	1.0069	1.0071	1.0071	4	1
21	3206.75	18.50	86	0.5726	0.5718	0.5716	0.5715	0.5716	0.5716	4	1
22	3309.00	22.50	86	0.3866	0.3856	0.3852	0.3851	0.3852	0.3854	4	1
23	3360.50	22.00	86	0.4602	0.4637	0.4582	0.4580	0.4582	0.4536	6	2
24	3496.30	31.30	86	0.4712	0.3991	0.3824	0.3785	0.3805	0.3783	6	1
25	3548.80	21.20	86	0.3360	0.3545	0.3694	0.3448	0.3534	0.3517	1	3
26	3618.50	48.60	86	0.4331	0.3360	0.3485	0.3807	0.3544	0.3713	2	1
27	3713.50	41.55	86	0.1989	0.1917	0.1911	0.1908	0.1918	0.1908	6	1
28	3811.20	37.00	86	0.2137	0.2150	0.2144	0.2149	0.2147	0.2144	1	2
29	3871.60	24.50	86	0.3861	0.3861	0.3861	0.3861	0.3861	0.3861	6	6
30	3991.00	42.00	86	0.5869	0.5854	0.5856	0.5856	0.5856	0.5858	2	1
31	4627.00	34.40	86	0.3388	0.3340	0.3342	0.3336	0.3339	0.3336	6	1
32	4705.00	41.00	86	0.3207	0.3174	0.3188	0.3169	0.3168	0.3169	5	1
33	4790.00	10.00	86	0.4508	0.4350	0.4517	0.4309	0.4359	0.4367	4	3
34	4825.95	77.95	86	0.8051	0.8032	0.8101	0.8183	0.7868	0.8339	5	6
35	4962.00	58.00	86	0.8768	0.8454	0.8012	0.8388	0.7945	0.8514	5	1
36	5094.75	73.25	86	0.7289	0.7213	0.7200	0.7308	0.7202	0.7342	**3**	**6**

Mean % RMS over windows: 0.5642 0.5571 0.5570 0.5611 0.5532 0.5606

MkIV Ground-based Atmospheric Spectra – VSFs 670-5100 cm^{-1}

Fitted a sample of 86 MKIV ground-based spectra over 36 windows representing a wide variety of conditions from T=-30C to +40C. Retrieved VSFs shown in table and figure. Greyed out values indicate windows that are blacked out from the ground.

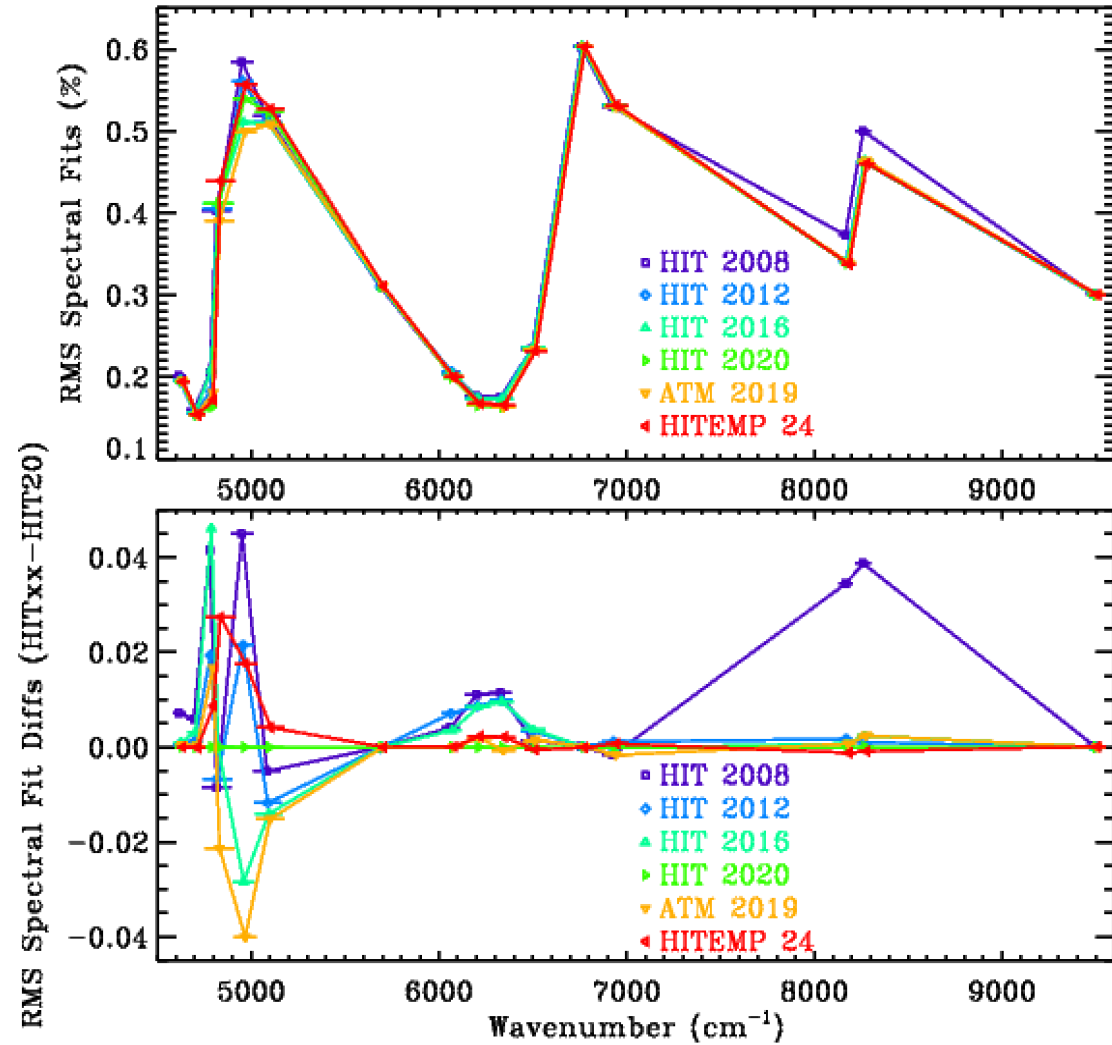| iwin	fcen	width/2	Nspec	hit08	hit12	hit16	hit20	atm19	hitemp24
1	694.60	23.60	86	0.8965	0.8269	0.8219	0.8718	0.8219	0.8641
2	755.20	32.05	86	0.9748	0.9599	0.9731	0.9714	0.9737	0.9471
3	827.20	34.30	86	0.9480	0.9533	0.9605	0.9570	0.9605	0.9279
4	925.00	36.05	86	0.9727	0.9658	1.0026	1.0021	1.0024	0.9556
5	980.00	21.05	86	0.9904	0.9686	1.0128	1.0114	1.0100	0.9639
6	1056.40	46.90	86	0.9649	0.9607	0.9946	0.9934	0.9939	0.9530
7	1239.50	20.30	86	1.0032	1.0036	1.0094	1.0037	1.0094	0.9774
8	1280.60	19.90	86	0.9284	0.9218	0.9349	0.9321	0.9349	0.8741
9	1367.40	25.90	86	1.0566	1.0650	1.0764	1.0716	1.0767	1.0444
10	1857.90	7.65	86	1.0581	1.0070	1.0967	1.0438	1.0444	1.0420
11	1910.30	29.70	86	0.9479	0.9632	1.0210	0.9587	0.9710	0.9593
12	1960.45	11.85	86	0.9776	0.9924	0.9488	0.9502	0.9996	0.9487
13	1981.50	8.50	86	0.9919	1.0228	1.0137	0.9829	1.0142	0.9859
14	2082.50	88.50	86	0.9339	0.9520	0.9524	0.9567	0.9462	0.9909
15	2299.30	125.15	86	0.9447	0.9235	0.9231	0.9342	0.9231	0.9168
16	2430.60	32.10	86	0.9856	0.9434	0.9933	0.9870	0.9933	0.9575
17	2501.90	34.80	86	0.9677	1.0062	1.0004	0.9933	0.9923	0.9657
18	2605.00	42.00	86	0.9771	1.0028	1.0034	0.9969	1.0034	0.9737
19	2760.00	31.00	86	1.0316	0.9829	1.0229	1.0148	1.0227	0.9966
20	3159.00	15.20	86	0.8342	0.8517	0.8540	0.8540	0.8540	0.8572
21	3206.75	18.50	86	1.0013	1.0034	1.0140	1.0116	1.0140	0.9646
22	3309.00	22.50	86	0.9967	1.0026	1.0068	1.0057	1.0068	1.0062
23	3360.50	22.00	86	1.0041	1.0288	1.0145	1.0088	1.0145	0.9750
24	3496.30	31.30	86	0.9770	0.9798	0.9709	0.9757	0.9779	0.9657
25	3548.80	21.20	86	0.9877	0.9763	0.9642	0.9740	0.9760	0.9639
26	3618.50	48.60	86	0.5212	0.7156	0.7298	0.6862	0.8797	0.7161
27	3713.50	41.55	86	0.0867	0.1293	0.1287	0.1545	0.1293	0.1616
28	3811.20	37.00	86	1.0824	1.0971	1.0632	1.0613	1.0970	1.0602
29	3871.60	24.50	86	3.4321	4.0655	4.0908	4.0434	4.0659	3.9938
30	3991.00	42.00	86	1.2724	1.2860	1.3394	1.3347	1.3454	1.2586
31	4627.00	34.40	86	0.9993	0.9989	0.9823	0.9750	0.9742	0.9744
32	4705.00	41.00	86	0.9998	0.9911	0.9918	0.9845	0.9889	0.9821
33	4790.00	10.00	86	0.9940	0.9916	0.9942	0.9918	0.9976	0.9866
34	4825.95	77.95	86	0.9996	0.9983	0.9973	0.9964	1.0011	0.9960
35	4962.00	58.00	86	1.0106	1.0093	0.9970	1.0035	0.9933	1.0043
36	5094.75	73.25	86	0.9909	0.9979	0.9845	0.9911	0.9811	1.0015
Average VSF (over window				0.9832	0.9833	0.9965	0.9930	0.9950	0.9693
RMS deviation from mean				±0.0166	±0.0204	±0.0145	±0.0147	±0.0144	±0.0171
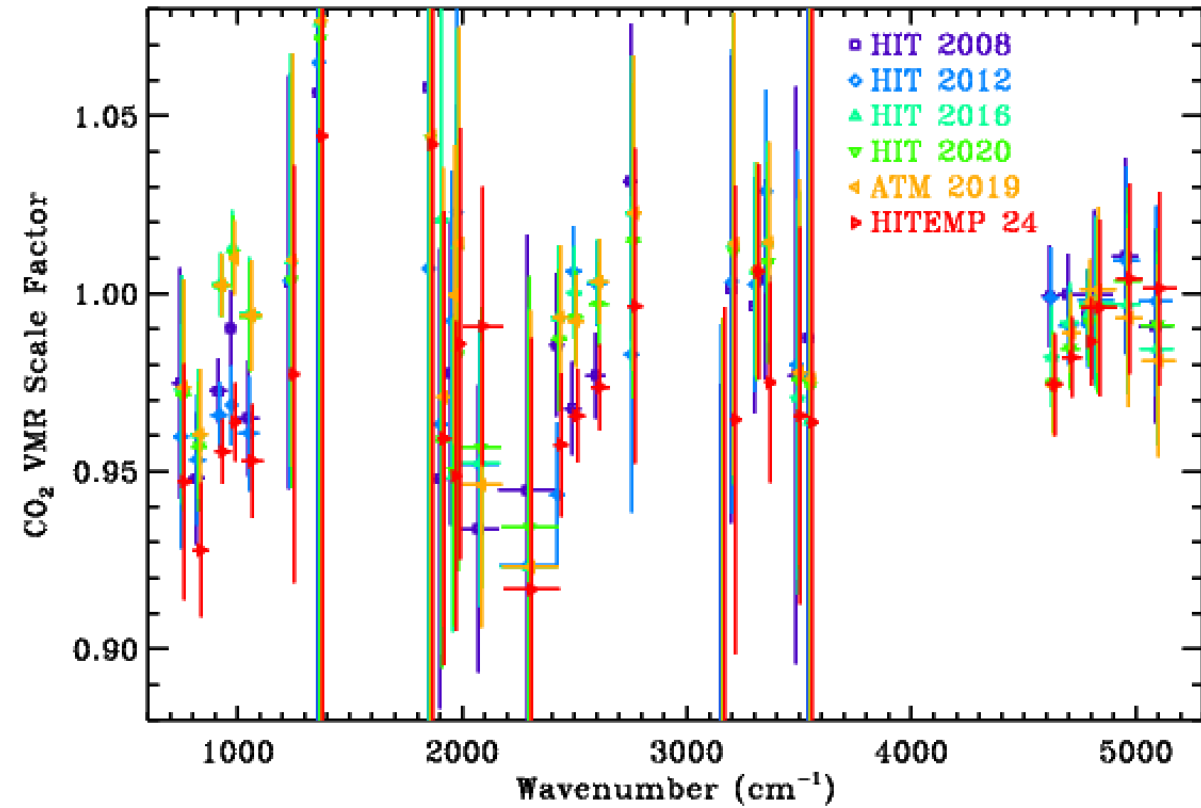
In figure above, points with errors > 0.4 are omitted. This happens in blacked out regions, e.g., 1400-1800 cm^{-1} & 3600 to 4000 cm^{-1}.

HITEMP24 has a low bias and greater window-to-window variation that HIT16 or HIT20 or ATM19

TCCON Ground-based Atmospheric Spectra – RMS fitting residuals

TCCON uses InGaAs detector covering 4000-9600 cm-1. Fitted 16 windows covering CO_2 bands in this range. Fitted a sample of 65 TCCON spectra representing a wide variety of conditions from T=-25 to +35C.

The HITEMP_24 linelist has an overall mean VSF of 1.0034, which is very close to the nominal value of 1. But the rms window-to-window variation is 1.90% which is larger than that of HIT20 or ATM19.
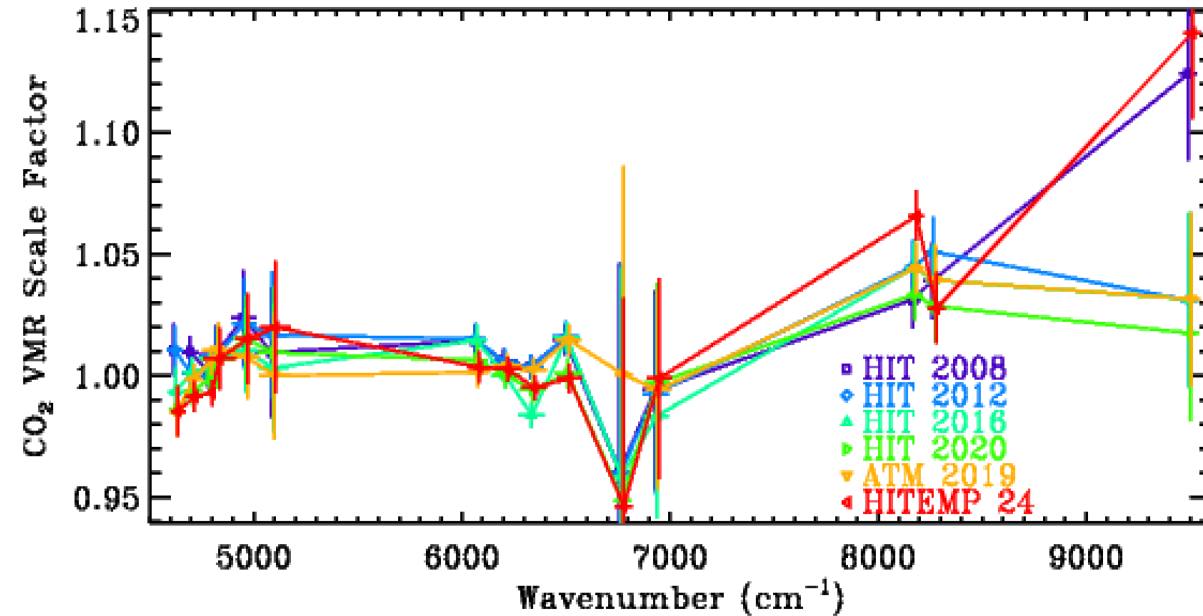

iwin	fcen	width/2	Nspec	hit08	hit12	hit16	hit20	atm19	hitemp24		
1	4627.00	34.40	65	0.2015	0.1950	0.1954	0.1944	0.1949	0.1944	6	1
2	4705.00	41.00	65	0.1598	0.1550	0.1570	0.1538	0.1540	0.1537	6	1
3	4790.00	10.00	65	0.2047	0.1826	0.2094	0.1632	0.1799	0.1719	4	3
4	4825.95	77.95	65	0.4035	0.4052	0.4121	0.4119	0.3905	0.4393	5	6
5	4962.00	58.00	65	0.5844	0.5609	0.5110	0.5394	0.4993	0.5570	5	1
6	5094.75	73.25	65	0.5181	0.5114	0.5091	0.5232	0.5080	0.5273	5	6
7	5696.00	9.00	65	0.3106	0.3106	0.3107	0.3107	0.3107	0.3107	2	6
8	6071.70	48.70	65	0.2036	0.2066	0.2030	0.1995	0.1996	0.1996	4	2
9	6211.00	64.00	65	0.1760	0.1737	0.1734	0.1650	0.1669	0.1673	4	1
10	6338.00	60.55	65	0.1748	0.1733	0.1730	0.1634	0.1627	0.1655	5	1
11	6506.25	60.75	65	0.2339	0.2357	0.2361	0.2324	0.2339	0.2318	6	3
12	6769.00	41.10	65	0.6032	0.6033	0.6032	0.6031	0.6032	0.6030	6	2
13	6937.50	59.50	65	0.5293	0.5321	0.5308	0.5310	0.5293	0.5317	5	2
14	8175.00	36.00	65	0.3731	0.3404	0.3394	0.3387	0.3394	0.3375	6	1
15	8271.00	41.00	65	0.5001	0.4624	0.4638	0.4614	0.4638	0.4605	6	1
16	9499.00	41.00	63	0.3005	0.3002	0.3002	0.3002	0.3002	0.3003	**5**	1

% RMS fits over windows: 0.3423 0.3343 0.3330 0.3307 0.3273 0.3345

TCCON Ground-based Atmospheric Spectra – Retrieved VSFs

Used 16 windows covering CO_2 bands in this range Fitted a sample of 65 TCCON spectra representing a wide variety of conditions from T=-25C to +35C. From 1 airmass to 15 airmasses.

The main interfering gases are telluric H_2O & CH_4, and solar Fraunhofer lines.

Points with errors >0.5 are omitted (e.g. 5696 cm^{-1} window).

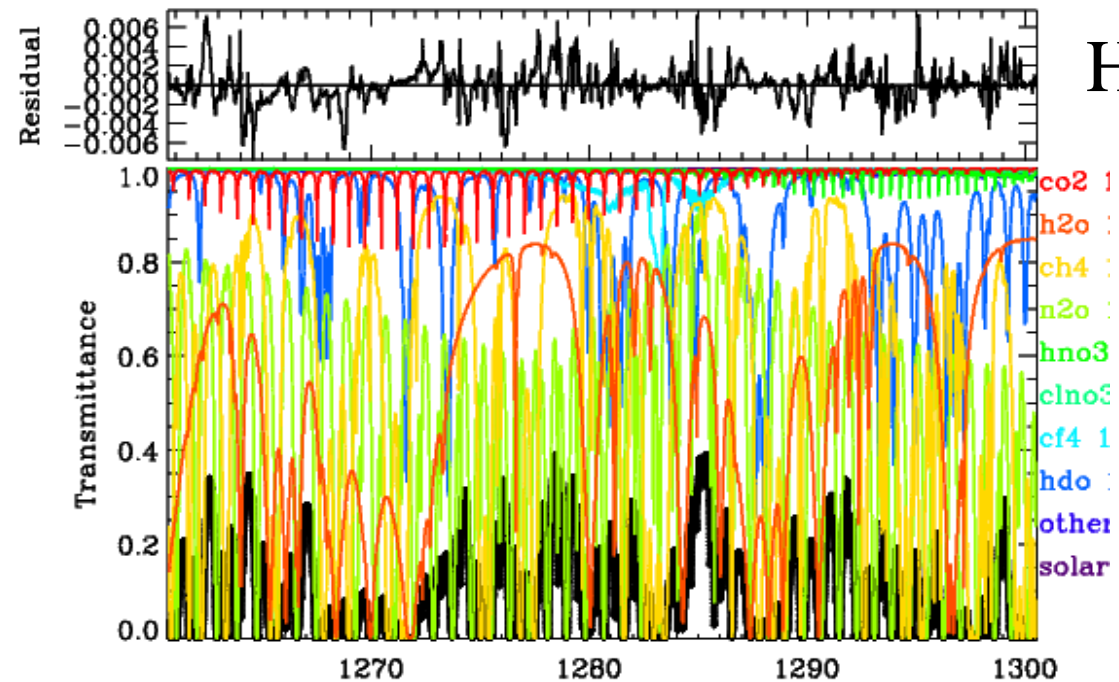| iwin	fcen	width/2	Nspec	hit08	hit12	hit16	hit20	atm19	hitemp24
1	4627.00	34.40	65	1.0107	1.0105	0.9934	0.9863	0.9849	0.9855
2	4705.00	41.00	65	1.0098	1.0010	1.0016	0.9939	0.9987	0.9914
3	4790.00	10.00	65	1.0019	0.9994	1.0035	0.9989	1.0061	0.9931
4	4825.95	77.95	65	1.0088	1.0083	1.0074	1.0067	1.0107	1.0070
5	4962.00	58.00	65	1.0237	1.0215	1.0104	1.0151	1.0076	1.0153
6	5094.75	73.25	65	1.0097	1.0168	1.0033	1.0095	1.0000	1.0199
7	5696.00	9.00	65	1.3459	1.3436	1.2893	1.2762	1.2893	1.2366
8	6071.70	48.70	65	1.0144	1.0151	1.0146	1.0064	1.0015	1.0036
9	6211.00	64.00	65	1.0060	1.0057	1.0001	1.0004	1.0041	1.0027
10	6338.00	60.55	65	1.0037	1.0036	0.9839	0.9942	1.0025	0.9952
11	6506.25	60.75	65	1.0149	1.0160	1.0157	1.0009	1.0149	0.9989
12	6769.00	41.10	65	0.9606	0.9602	0.9587	0.9488	1.0006	0.9464
13	6937.50	59.50	65	0.9941	0.9927	0.9834	0.9972	0.9941	0.9989
14	8175.00	36.00	65	1.0312	1.0449	1.0444	1.0334	1.0444	1.0657
15	8271.00	41.00	65	1.0391	1.0510	1.0393	1.0286	1.0393	1.0278
16	9499.00	41.00	63	1.1240	1.0310	1.0315	1.0175	1.0315	1.1408
Average VSF (over windows)				**1.0101**	**1.0094**	**1.0043**	**1.0007**	**1.0062**	**1.0014**
RMS deviation from mean				**±0.0105**	**±0.0117**	**±0.0147**	**±0.0094**	**±0.0111**	**±0.0173**

The HITEMP linelist has an overall mean VSF of 1.0014, which is very close to the nominal value of 1. But the rms window-to-window variation is 1.73% which is much larger than any other linelist.

In the 9499 cm^{-1} window (#16) HITEMP24 linelist gives a mean VSF (averaged over 65 spectra) of 1.14. This is ~10% larger than all other linelists (except HIT08) and significant in comparison with error bars (unlike 5696 cm^{-1} bias).
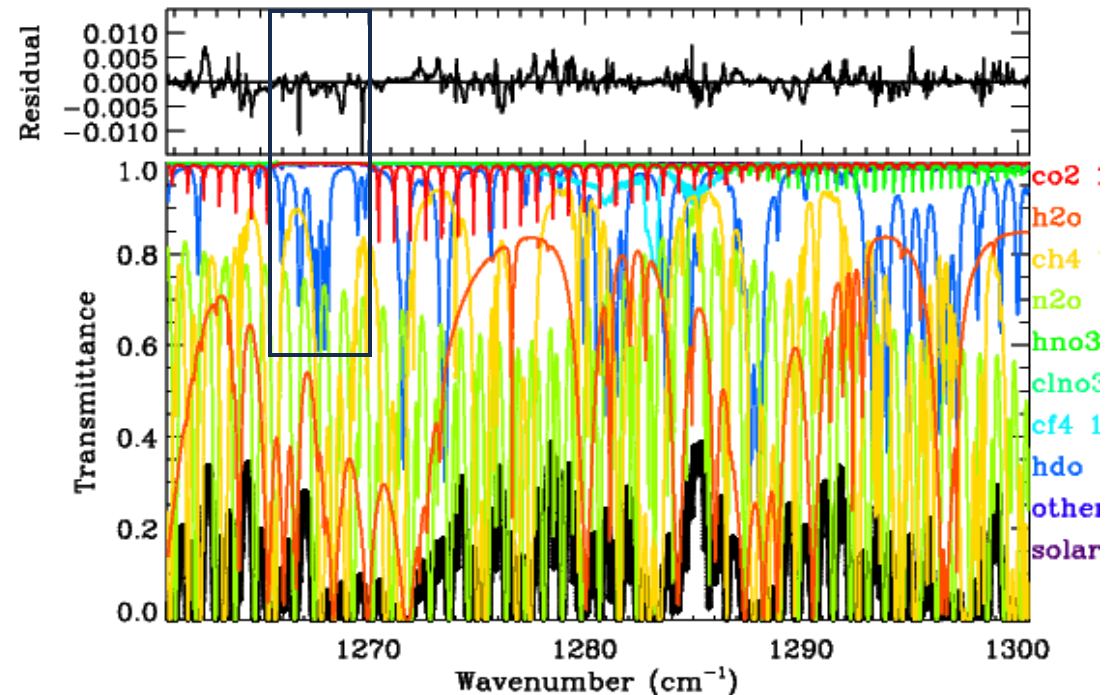
HITEMP Deficiency seen in ground-based spectra

HITEMP 2024 linelist produced significantly larger residuals in 2082 cm^{-1} window than any other linelist.

Top-Left: Average spectral fit to 86 ground-based MkIV spectra spectra using HITRAN 2020 linelist. Peak residual is 0.7% due to H_2O. Average rms fitting residual is 0.3148%

Bottom-Left: Fits to same spectra using HITEMP linelist. Peak residual has doubled to 1.5%. Average rms fitting residual has increased to 0.3264%. Two of the six missing CO_2 lines produce large residuals. The other 4 are blacked out by H_2O and N_2O and are therefore inconspicuous in the residuals.

Summary and Conclusions

Four spectral datasets (Kitt Peak Lab, MkIV balloon, MkIV ground, TCCON ground) have been fitted using six linelists over 46 windows covering 670 to 9500 cm^{-1}. (Above 9500 cm^{-1}, I have no useful lab spectra; paths too short)

Above 5500 cm^{-1}, HITEMP 2024 CO$_2$ linelist gives better fits than the other linelists.

At lower wavenumbers HITEMP does not fit as well as HIT16, HIT20 or ATM19, although it could be improved by fixing obvious deficiencies (e.g., the six missing lines at 1266-1270 cm^{-1}; intensities around 2148 cm^{-1})

In terms of VSFs, below 1500 cm^{-1} the HITEMP24 linelist gives retrieved CO$_2$ amounts (VSFs) that are 3-5% lower than HIT20 or ATM19. But at higher wavenumbers, they are similar.

The window-to-window consistency of the retrieved VSF amounts is poorer for HITEMP at all wavenumbers.

It is nice to see how much the CO$_2$ linelist has improved since 2008. Although the improvements in new editions of HITRAN are sometimes quite small, their cumulative effects are substantial.

Reminder, Voigt lineshape without line-mixing was used through out this work.

ATM 2020 CO$_2$ Linelist

atm.161 20190223
A major change in the ATM CO2 linelist. Most lines have been replaced by HIT2016 except for:
- Using atm16.161 over 3419-3923 and 5750-6598 cm-1
- Using HIT2008 over 6715 - 7000 cm-1
- For isotopologs 10,11,12, using HIT16b throughout.
- Scaling CO2 line intensities by 1.05 over 1800 to 1993 cm-1
- Scaling ^{12}CO2 line intensities by 0.96 over 6720 to 6800 cm-1

On top of these, ad hoc corrections (mainly position adjustments) were applied where beneficial. This work is described in the PPT presentation "CO2 Spectroscopy Evaluation: 670 to 7000 cm-1".
https://mark4sun.jpl.nasa.gov/report/CO2_Spectroscopy_Evaluation_20190503-compressed.pdf