Ozone Spectroscopy Evaluation Update

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Defined 37 broad windows in which O_3 absorption can be seen in atmospheric and lab spectra.

Fitted MkIV atmospheric spectra (balloon & ground-based) and Kitt Peak O_3 laboratory spectra using 11 different O_3 linelists, keeping that same linelist (ATM) for all other gases. Changes in results from linelist to linelist are therefore solely due to O_3.

Examined the RMS fitting residuals and the window-to-window consistency of the retrieved O_3 amounts using:

- 17 MkIV balloon spectra covering 10-37 km tangent altitude, 650-5650 cm^{-1}, 0.01 cm^{-1} resolution (60 cm OPD)
- 78 MkIV ground-based spectra covering surface temperatures of -35C to +35C, 650-5650 cm^{-1}; (120 cm OPD)
- 190 Lab spectra: 2 from Alain Barbe; 188 from Kitt Peak (6 of which are enriched in ^{18}O)

No TCCON spectra are used in this study because from the ground O_3 absorptions cannot be seen above 3300 cm^{-1}

This report updates the previous O_3 evaluation, reported in Nov 2020:
https://mark4sun.jpl.nasa.gov/report/O3_Spectroscopy_Eval_2020_11_30.pdf

Main change since Nov 2020 evaluation:

New linelist added to the evaluation (in addition to the 10 already present in the Nov 2020 evaluation):

SMPO_20d: 496,702 lines, covering 0 - 6997 cm^{-1} from the file:

- 80466372 Jan 14 SMPO-hitraned-for-Geoff-v4.par (received from Iouli Gordon on 12/23/2020)

Linelists Evaluated

HIT 2008: 409,686 lines covering 0 to 5786 cm^{-1} (Not evaluated)
HIT 2012: 422,116 lines covering 0 to 6997 cm^{-1}
HIT 2016: 449,570 lines covering 0 to 6997 cm^{-1}
ATM 2016: 449,570 lines covering 0 to 6967 cm^{-1}. Basically, HIT 2016 with a few tweaks
HIT 2016d: 449,590 lines covering 0 to 6997 cm^{-1}. Basically HIT16 with empirical intensity scalings and position shifts
Ten 18b: 238,990 lines covering 0-3700 cm^{-1}. Linelist received from Jonathan Tennyson May 25, 2018.
Main isotopolog (666) only. Supplemented with HIT16d for heavy O_3. This linelist replaces TEN 2018a sent May 11, 2018.
HIT 2020a: 457,872 lines covering 0 to 6997 cm^{-1} Received from Iouli on May 1, 2020 (03_hit16_plusMikh-update)
Birk_19: 95,280 lines covering 600-1220 cm-1 (gap 850-980 cm^{-1} filled with HIT16)
Tenn_20: 449,569 lines covering 0 - 6697 cm^{-1}, obtained from the file:

- 72830178 Oct 27 O3_HITRAN2016-modified-by-UCL-intensities.par

SMPO_20: 505,868 lines covering 0 - 6997 cm^{-1} from the file:

- 81961123 Nov 12 SMPO-hitraned-for-Geoff-v2.par (received from Iouli Gordon in Nov 2020)

Birk_20: 99,186 lines covering 600 -1220 cm^{-1} (gap 850-980 cm^{-1} filled with HIT16) from the following files:

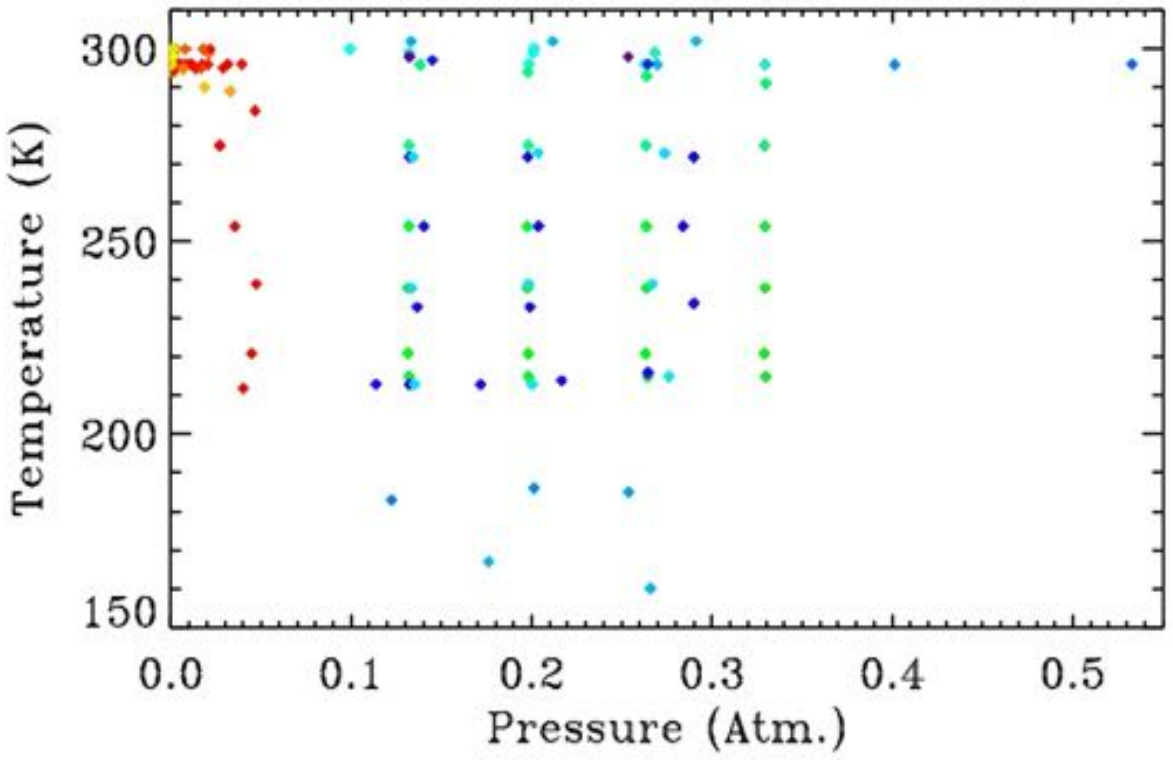
- 5932686 Oct 8 O3_nu2_export_full_HITRAN_with_Sscaled_gamma(J=KA)_updates_140920_V2.hit
- 4246622 Oct 8 O3_nu1_export_full_HITRAN_with_sigma_s_gamma(J=KA)_updates_140920_V3.hit
- 7639286 Oct 8 O3_nu3_export_full_HITRAN16_with_sigma_s_gammaeff_delta_updates_240720.hit

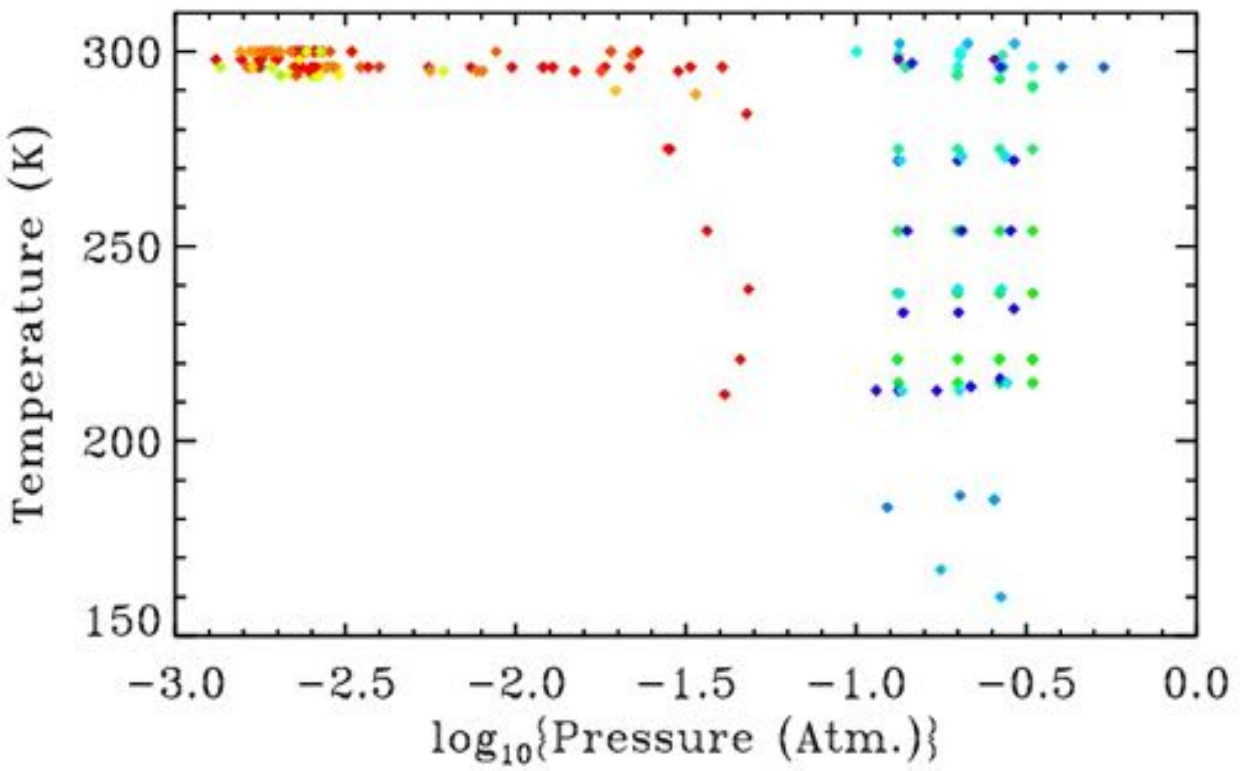
Lines above 1180 cm^{-1} are not included in the evaluation (Manfred said that they weren't his).

SMPO_20d: 496,702 lines, covering 0 - 6997 cm^{-1} from the file:

- 80466372 Jan 14 SMPO-hitraned-for-Geoff-v4.par (received from Iouli Gordon on 12/23/2020)

Measurement Conditions for the 190 Kitt Peak lab O_3 spectra





Same data are plotted twice: **Left** versus Pressure, **Right** versus $\log_{10}$[Pressure].

Points are color coded by O_3 VMR: Blue < 0.05, Red > 0.95

Majority of spectra were measured on pure gas samples (red) at low pressure (<3 mbar) and ~296 K

MkIV balloon spectra were measured between 0.3 Atm & 210 K and 0.003 Atm & 240 K and so were generally at higher pressure and colder temperatures than the KP lab measurements.

Properties of the 37 windows used in fitting (Kitt Peak lab spectra)

#	Center	Width	MIT	A	I	F	Parameters to fit	Gases to fit	Iso_bar	S_max	S_tot	S_bar	W_bar	E"_bar
1	648.65	36.12	15	2	1	0	ncbf=15 fs xo cf	: o3 h2o co2 hcooh	1.01	5.12E-22	8.25E-20	2.15E-22	0.0757	484.0
2	684.45	33.02	15	2	1	0	ncbf=11 fs xo cf	: o3 h2o co2	1.01	1.22E-21	1.68E-19	4.54E-22	0.0765	287.0
3	752.40	102.82	15	2	1	0	ncbf=16 fs xo xf	: o3 h2o co2	1.01	1.66E-21	3.45E-19	5.00E-22	0.0754	351.7
4	832.15	56.70	15	2	1	0	ncbf=18 fs xo xf	: o3 h2o co2	1.00	1.13E-22	6.80E-21	4.49E-23	0.0729	958.7
5	1003.40	81.02	15	2	1	0	ncbf=14 fs xo cf	: o3 h2o	1.02	3.94E-20	8.27E-18	1.67E-20	0.0769	376.3
6	1060.00	32.52	15	2	1	0	ncbf=8 fs xo cf	: o3 h2o	1.00	4.06E-20	6.41E-18	2.12E-20	0.0761	308.3
7	1092.86	33.36	15	2	1	0	ncbf=11 fs xo cf	: o3 h2o hcooh	1.02	5.74E-22	1.10E-19	2.60E-22	0.0739	416.8
8	1119.75	20.40	15	2	1	0	ncbf=10 fs xo cf	: o3 h2o hcooh	1.01	2.02E-21	8.23E-20	1.00E-21	0.0731	305.7
9	1161.90	48.60	15	2	1	0	ncbf=11 fs xo cf	: o3 h2o	1.00	7.68E-22	8.56E-20	2.30E-22	0.0735	565.4
10	1199.25	22.20	15	2	1	0	ncbf=9 fs xo cf	: o3 h2o	1.00	9.40E-23	8.53E-21	4.50E-23	0.0721	878.2
11	1716.40	112.05	15	2	1	0	ncbf=12 fs zo cf	: o3 h2o	1.00	1.65E-22	5.97E-20	6.59E-23	0.0767	366.0
12	1775.44	44.93	15	2	1	0	ncbf=10 fs xo cf	: o3 h2o hcooh	1.00	4.04E-23	7.45E-21	1.33E-23	0.0760	362.4
13	1812.50	24.50	15	2	1	0	ncbf=8 fs xo cf	: o3 h2o	1.00	1.05E-22	7.21E-21	4.40E-23	0.0740	306.0
14	1837.50	24.50	15	2	1	0	ncbf=8 fs xo cf	: o3 h2o	1.00	4.20E-23	4.28E-21	1.96E-23	0.0748	400.9
15	1865.00	29.40	15	2	1	0	ncbf=8 fs xo cf	: o3 h2o	1.00	2.63E-23	2.61E-21	1.42E-23	0.0742	476.0
16	1914.62	54.90	15	2	1	0	ncbf=8 fs xo cf	: o3 h2o	1.01	8.47E-24	1.55E-21	2.18E-24	0.0747	1139.7
17	1957.12	28.25	15	2	1	0	ncbf=9 fs xo cf	: o3 h2o	1.03	9.00E-24	1.46E-21	1.91E-24	0.0747	1200.5
18	1994.00	39.00	15	2	1	0	ncbf=8 fs xo cf	: o3 h2o	1.06	3.27E-23	7.99E-21	1.02E-23	0.0731	961.3
19	2028.22	27.05	15	2	1	0	ncbf=7 fs xo cf	: o3 h2o	1.09	5.43E-23	2.21E-20	2.04E-23	0.0750	903.3
20	2062.00	34.02	15	2	1	0	ncbf=8 fs xo cf	: o3 h2o co	1.03	1.53E-21	1.64E-19	4.00E-22	0.0723	706.1
21	2095.15	32.40	15	2	1	0	ncbf=7 fs xo cf	: o3 h2o co	1.01	3.52E-21	6.19E-19	1.66E-21	0.0779	280.4
22	2128.57	34.45	15	2	1	0	ncbf=7 fs xo cf	: o3 h2o co	1.00	3.60E-21	5.61E-19	1.85E-21	0.0763	299.3
23	2188.00	64.40	15	2	1	0	ncbf=7 fs xo cf	: o3 h2o co n2o	1.01	1.61E-22	1.78E-20	4.59E-23	0.0729	426.9
24	2253.60	62.80	15	2	1	0	ncbf=7 fs xo cf	: o3 h2o co co2 n2o	1.00	4.78E-23	6.22E-21	1.12E-23	0.0730	637.7
25	2754.00	63.02	15	2	1	0	ncbf=11 fs xo cf	: o3 hdo	1.01	7.63E-23	1.79E-20	2.93E-23	0.0767	379.3
26	2797.50	21.02	15	2	1	0	ncbf=5 fs xo cf	: o3 hdo	1.00	7.49E-23	1.12E-20	3.87E-23	0.0765	288.1
27	2860.00	40.02	15	2	1	0	ncbf=10 fs xo cf	: o3 h2o hdo ch4	1.00	3.89E-24	3.55E-22	1.29E-24	0.0716	620.0
28	2916.00	72.02	15	2	1	0	ncbf=13 fs xo xf	: o3 h2o hdo ch4	1.00	8.83E-24	2.65E-21	2.72E-24	0.0747	1263.1
29	3011.00	114.02	15	2	1	0	ncbf=17 fs xo xf	: o3 h2o	1.00	4.28E-22	1.52E-19	1.94E-22	0.0766	331.2
30	3105.00	70.02	15	2	1	0	ncbf=11 fs xo xf	: o3 h2o	1.00	5.74E-23	6.20E-21	1.74E-23	0.0725	426.9
31	3164.50	45.02	15	2	1	0	ncbf=10 fs xo xf	: o3 h2o	1.00	2.16E-23	4.61E-21	9.79E-24	0.0769	331.6
32	3197.00	20.02	15	2	1	0	ncbf=7 fs xo xf	: o3 h2o	1.00	2.23E-23	3.48E-21	1.18E-23	0.0765	292.0
33	3985.88	69.76	15	2	1	0	ncbf=7 fs xo xf	: o3 h2o	1.00	3.84E-23	8.24E-21	1.56E-23	0.0767	335.7
34	4029.75	17.98	15	2	1	0	ncbf=7 fs xo xf	: o3 h2o	1.00	4.16E-23	5.93E-21	2.17E-23	0.0764	259.8
35	4640.00	70.02	15	2	1	0	ncbf=11 fs xo xf	: o3 h2o	1.00	2.87E-24	9.92E-22	1.25E-24	0.0767	279.2
36	4888.85	66.70	15	2	1	0	ncbf=8 fs xo xf	: o3 h2o	1.00	1.83E-24	6.56E-22	6.06E-25	0.0772	272.8
37	4927.35	10.35	15	2	1	0	ncbf=6 fs xo xf	: o3 h2o	1.00	2.13E-24	2.25E-22	1.17E-24	0.0765	214.6

RMS Fitting residuals to Kitt Peak lab spectra

iwin	fcen	HWid	Nrow Npp	hit12	atm16	hit16	hit16d	ten18b	hit20a	birk19	tenn20	smpo20	birk20	smpo20d
1	648.65	18.06	105/190	0.5065	0.5064	0.5064	0.5060	0.5069	0.5064	0.5064	0.5061	0.5081	0.5064	0.5065
2	684.45	16.51	105/190	0.7019	0.7019	0.7019	0.7019	0.7034	0.7019	0.7020	0.7022	0.7037	0.7019	0.7022
3	752.40	51.41	105/190	1.1137	1.1136	1.1136	1.1136	1.1137	1.1136	1.1137	1.1136	1.1151	1.1136	1.1136
4	832.15	28.35	159/190	0.5975	0.5975	0.5975	0.5975	0.5974	0.5975	0.5973	0.5974	0.5974	0.5973	0.5975
5	1003.40	40.51	162/190	0.3895	0.3880	0.3880	0.3868	0.3909	0.3880	0.3846	0.3889	0.3930	0.3846	0.3885
6	1060.00	16.26	162/190	0.3525	0.3524	0.3523	0.3504	0.3664	0.3523	0.3512	0.3633	0.3550	0.3496	0.3513
7	1092.86	16.68	162/190	0.2514	0.2514	0.2514	0.2507	0.2675	0.2514	0.2513	0.2698	0.2514	0.2514	0.2520
8	1119.75	10.20	162/190	0.1903	0.1903	0.1903	0.1898	0.2040	0.1903	0.1903	0.2073	0.1905	0.1903	0.1906
9	1161.90	24.30	162/190	0.1717	0.1742	0.1742	0.1711	0.1765	0.1742	0.1711	0.1784	0.1719	0.1711	0.1712
10	1199.25	11.10	162/190	0.1572	0.1581	0.1581	0.1571	0.1575	0.1581		0.1578	0.1570		0.1573
11	1716.40	56.03	60/190	0.5691	0.5626	0.5691	0.5626	0.5646	0.5691		0.5620	0.5585		0.5585
12	1775.44	22.47	60/190	0.5893	0.5863	0.5893	0.5829	0.5886	0.5893		0.5883	0.5795		0.5795
13	1812.50	12.25	60/190	0.2494	0.2475	0.2494	0.2460	0.2498	0.2494		0.2494	0.2465		0.2465
14	1837.50	12.25	60/190	0.3003	0.2919	0.3003	0.2887	0.2996	0.3003		0.3002	0.2851		0.2852
15	1865.00	14.70	60/190	0.2268	0.2223	0.2268	0.2219	0.2268	0.2268		0.2267	0.2178		0.2178
16	1914.62	27.45	60/190	0.1456	0.1456	0.1456	0.1446	0.1454	0.1456		0.1456	0.1449		0.1450
17	1957.12	14.12	60/190	0.1510	0.1512	0.1512	0.1502	0.1499	0.1512		0.1503	0.1504		0.1504
18	1994.00	19.50	60/190	0.1769	0.1773	0.1774	0.1754	0.1754	0.1774		0.1756	0.1748		0.1747
19	2028.22	13.52	60/190	0.1652	0.1700	0.1704	0.1639	0.1702	0.1704		0.1671	0.1612		0.1608
20	2062.00	17.01	60/190	0.2976	0.2575	0.2620	0.2536	0.2775	0.2620		0.2432	0.2492		0.2489
21	2095.15	16.20	60/190	0.5065	0.4052	0.4079	0.4010	0.4194	0.4079		0.3985	0.4012		0.4007
22	2128.57	17.23	60/190	0.4947	0.3775	0.3855	0.3728	0.4247	0.3855		0.3880	0.3764		0.3765
23	2188.00	32.20	60/190	0.1568	0.1546	0.1546	0.1542	0.1563	0.1546		0.1545	0.1538		0.1548
24	2253.60	31.40	60/190	0.1519	0.1515	0.1515	0.1512	0.1525	0.1515		0.1512	0.1513		0.1513
25	2754.00	31.51	64/190	0.3112	0.3064	0.3106	0.3012	0.3096	0.3108		0.3068	0.3086.		0.3078
26	2797.50	10.51	64/190	0.5582	0.5383	0.5641	0.5314	0.5422	0.5646		0.5247	0.5492		0.5461
27	2860.00	20.01	11/190	0.0529	0.0529	0.0529	0.0529	0.0529	0.0528		0.0528	0.0528		0.0528
28	2916.00	36.01	11/190	0.0910	0.0891	0.0890	0.0883	0.0878	0.0863		0.0881	0.0860		0.0859
29	3011.00	57.01	11/190	0.2293	0.2157	0.2234	0.2055	0.2109	0.2233		0.1946	0.2203		0.2182
30	3105.00	35.01	11/190	0.0788	0.0787	0.0787	0.0778	0.0770	0.0787		0.0769	0.0788		0.0775
31	3164.50	22.51	11/190	0.0732	0.0732	0.0732	0.0730	0.0735	0.0732		0.0728	0.0735		0.0738
32	3197.00	10.01	11/190	0.0815	0.0815	0.0815	0.0812	0.0774	0.0815		0.0765	0.0818		0.0802
33	3985.88	34.88	5/190	0.2806	0.2620	0.2641	0.2506		0.2261		0.2317	0.2198		0.2196
34	4029.75	8.99	5/190	0.4949	0.4542	0.4429	0.4183		0.3149		0.3903	0.3058.		0.3065
35	4640.00	35.01	5/190	0.2697	0.2689	0.2705	0.2688		0.2705		0.2678	0.2662		0.2662
36	4888.85	33.35	6/190	0.3990	0.3995	0.3962	0.3642		0.3961		0.3996	0.3543		0.3543
37	4927.35	5.18	6/190	0.4353	0.4271	0.4199	0.3837		0.4199		0.4208	0.3951		0.3951
Mean RMS over windows:				**0.3234**	**0.3130**	**0.3146**	**0.3079**		**0.3100**		**0.3104**	**0.3049**		**0.3044**

The four right-most columns are the new, post-July 2020 linelists.

Blue values denote the lowest RMS in that row; red the highest.

Overall, smpo20d is best, and HIT12 is the worst.

VMR Scale Factors (VSF) from fits to Kitt Peak lab spectra

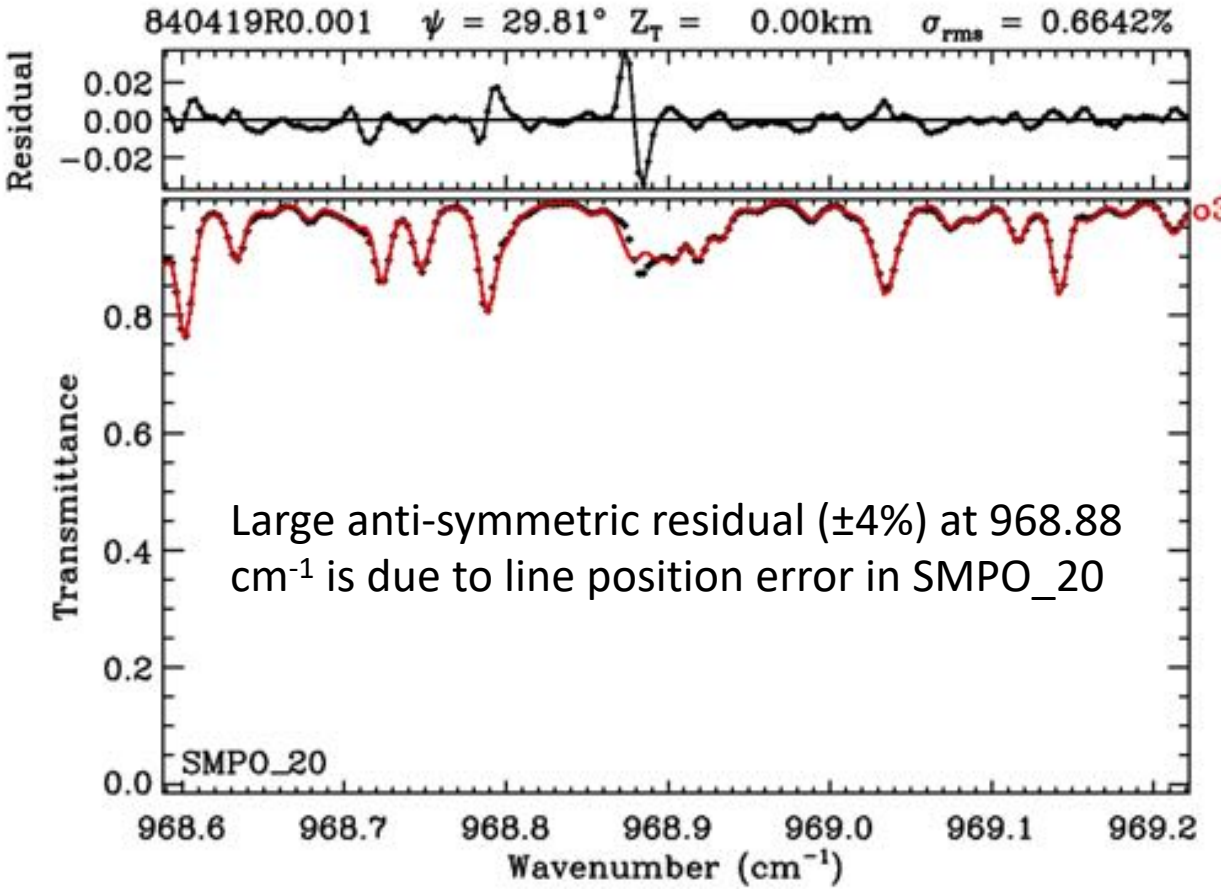
iwin	fcen	H-Wid	Nrow Npp	hit12	atm16	hit16	hit16d	ten18b	hit20a	birk19	tenn20	smpo20	birk20	smpo20d
1	648.65	18.06	105/190	0.9872	0.9873	0.9873	0.9872	0.9254	0.9875	0.9739	0.9336	0.9576	0.9740	0.9402
2	684.45	16.51	105/190	0.9923	0.9923	0.9923	0.9919	0.9197	0.9924	0.9790	0.9274	0.9472	0.9790	0.9445
3	752.40	51.41	105/190	1.0080	1.0080	1.0080	1.0080	0.9379	1.0068	0.9945	0.9425	0.9624	0.9946	0.9603
4	832.15	28.35	159/190	0.9935	0.9935	0.9935	0.9935	0.9310	0.9940	0.9773	0.9342	1.0062	0.9774	0.9466
5	1003.40	40.51	162/190	0.9995	0.9994	0.9994	0.9994	1.0045	0.9993	0.9778	0.9682	0.9710	0.9778	0.9773
6	1060.00	16.26	162/190	0.9993	0.9993	0.9993	0.9993	1.0032	0.9992	0.9774	0.9660	0.9703	0.9774	0.9738
7	1092.86	16.68	162/190	0.9966	0.9966	0.9966	0.9965	1.0442	0.9970	0.9778	1.0097	0.9829	0.9779	0.9791
8	1119.75	10.20	162/190	1.0007	1.0007	1.0007	1.0013	1.0530	1.0004	0.9809	1.0208	0.9792	0.9809	0.9816
9	1161.90	24.30	162/190	1.0052	1.0058	1.0058	1.0051	1.0602	1.0058	0.9850	1.0325	0.9797	0.9850	0.9789
10	1199.25	11.10	162/190	1.0141	1.0162	1.0162	1.0139	1.0664	1.0166		1.0433	0.9897		0.9677
11	1716.40	56.03	60/190	0.9774	0.9779	0.9774	0.9779	1.1208	0.9774		1.0623	0.9476		0.9476
12	1775.44	22.47	60/190	1.0143	1.0146	1.0143	1.0152	1.0143	1.0147		0.9985	1.0180		1.0180
13	1812.50	12.25	60/190	0.9572	0.9573	0.9572	0.9573	0.9990	0.9577		0.9791	0.9845		0.9845
14	1837.50	12.25	60/190	0.9512	0.9514	0.9512	0.9515	1.0158	0.9510		0.9981	0.9940		0.9940
15	1865.00	14.70	60/190	0.9059	0.9107	0.9059	0.9110	0.9884	0.9077		0.9709	0.9712		0.9712
16	1914.62	27.45	60/190	0.8750	0.8794	0.8795	0.9026	1.0072	0.8778		0.9760	0.9705		0.9705
17	1957.12	14.12	60/190	0.8724	0.9458	0.9458	0.9783	1.0209	0.9409		1.0220	0.9760		0.9760
18	1994.00	19.50	60/190	0.8995	1.0010	1.0008	1.0132	0.9804	1.0018		0.9896	0.9788		0.9789
19	2028.22	13.52	60/190	0.9249	1.0071	1.0070	1.0210	0.9757	1.0076		0.9865	0.9899		0.9899
20	2062.00	17.01	60/190	0.9936	1.0227	1.0228	1.0227	0.9873	1.0228		0.9738	0.9825		0.9825
21	2095.15	16.20	60/190	1.0084	1.0092	1.0091	1.0093	0.9812	1.0091		0.9595	0.9690		0.9690
22	2128.57	17.23	60/190	1.0267	1.0149	1.0147	1.0150	0.9874	1.0146		0.9638	0.9736		0.9735
23	2188.00	32.20	60/190	0.9425	1.0176	1.0176	1.0177	0.9734	1.0179		0.9682	0.9767		0.9767
24	2253.60	31.40	60/190	0.9463	1.0056	1.0056	1.0057	0.9919	1.0067		0.9737	0.9651		0.9651
25	2754.00	31.51	64/190	0.9377	0.9377	0.9377	0.9375	0.9882	0.9377		0.9378	0.9666		0.9664
26	2797.50	10.51	64/190	0.9654	0.9645	0.9664	0.9647	0.9863	0.9659		0.9384	0.9962		0.9957
27	2860.00	20.01	11/190	0.9505	0.9505	0.9510	0.9510	0.9546	0.9500		0.9580	0.9402		0.9396
28	2916.00	36.01	11/190	0.8956	0.9006	0.9009	0.9029	0.9926	0.9424		0.9626	0.9654		0.9457
29	3011.00	57.01	11/190	0.9098	0.9093	0.9095	0.9087	0.9835	0.9094		0.9440	0.9786		0.9795
30	3105.00	35.01	11/190	0.9052	0.9057	0.9057	0.9059	0.9765	0.9052		0.9367	0.9066		0.9676
31	3164.50	22.51	11/190	0.9401	0.9401	0.9401	0.9402	0.8957	0.9401		0.8829	0.9388		0.9512
32	3197.00	10.01	11/190	0.9298	0.9298	0.9298	0.9300		0.9295		0.8819	0.9286		0.9546
33	3985.88	34.88	5/190	0.9656	0.9669	0.9672	0.9688		1.0977		0.8416	0.9468		0.9468
34	4029.75	8.99	5/190	0.9377	0.9388	0.9386	0.9398		1.0918		0.8380	0.9410		0.9411
35	4640.00	35.01	5/190	0.9910	0.9925	0.9892	0.9890		0.9907		0.7980	0.9904		0.9904
36	4888.85	33.35	6/190	1.0657	1.0642	1.0668	1.0805		1.0673		0.9113	0.8940		0.8940
37	4927.35	5.18	6/190	0.9198	0.9446	0.9485	0.9699		0.9476		0.8209	0.8659		0.8659
Average VSF (over windows)				**0.9798**	**0.9942**	**0.9946**	**0.9950**	**1.0076**	**0.9965**		**0.9799**	**0.9750**		**0.9759**
RMS deviation from mean				**0.0330**	**0.0288**	**0.0285**	**0.0291**	**0.0401**	**0.0289**		**0.0366**	**0.0148**		**0.0106**

VSF is the ratio of the retrieved O_3 amounts to the nominal amount from cell length, pressure, etc. VSFs should all be 1.0

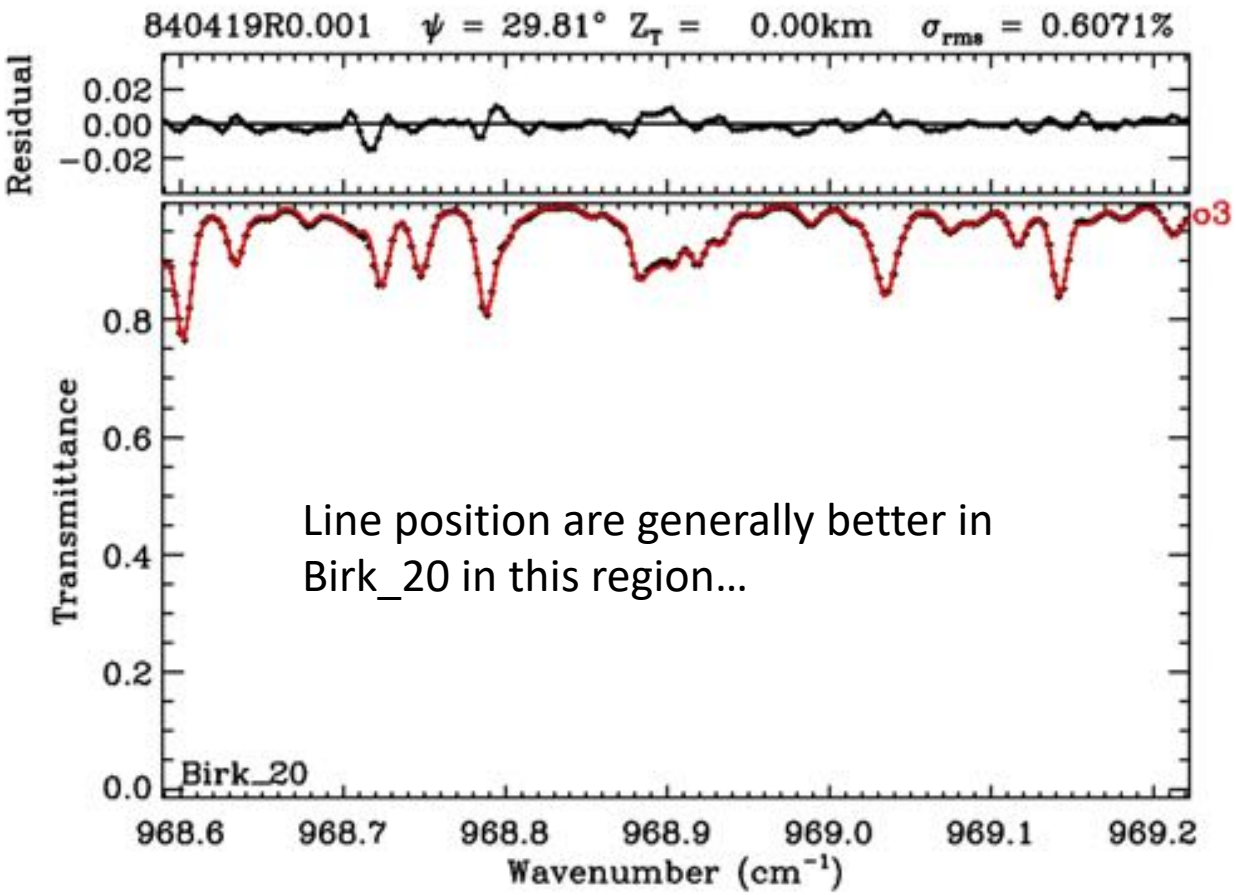
smpo20d linelist gives the smallest window-to-window VSF deviations (1.06%), but retrievals are biased low by 2-3%.

Retrievals in the 4888 and 4927 cm^{-1} windows are biased low by 10+%.

Example of fit to Kitt Peak lab spectrum -- 24 Torr of pure O_3 at 296K

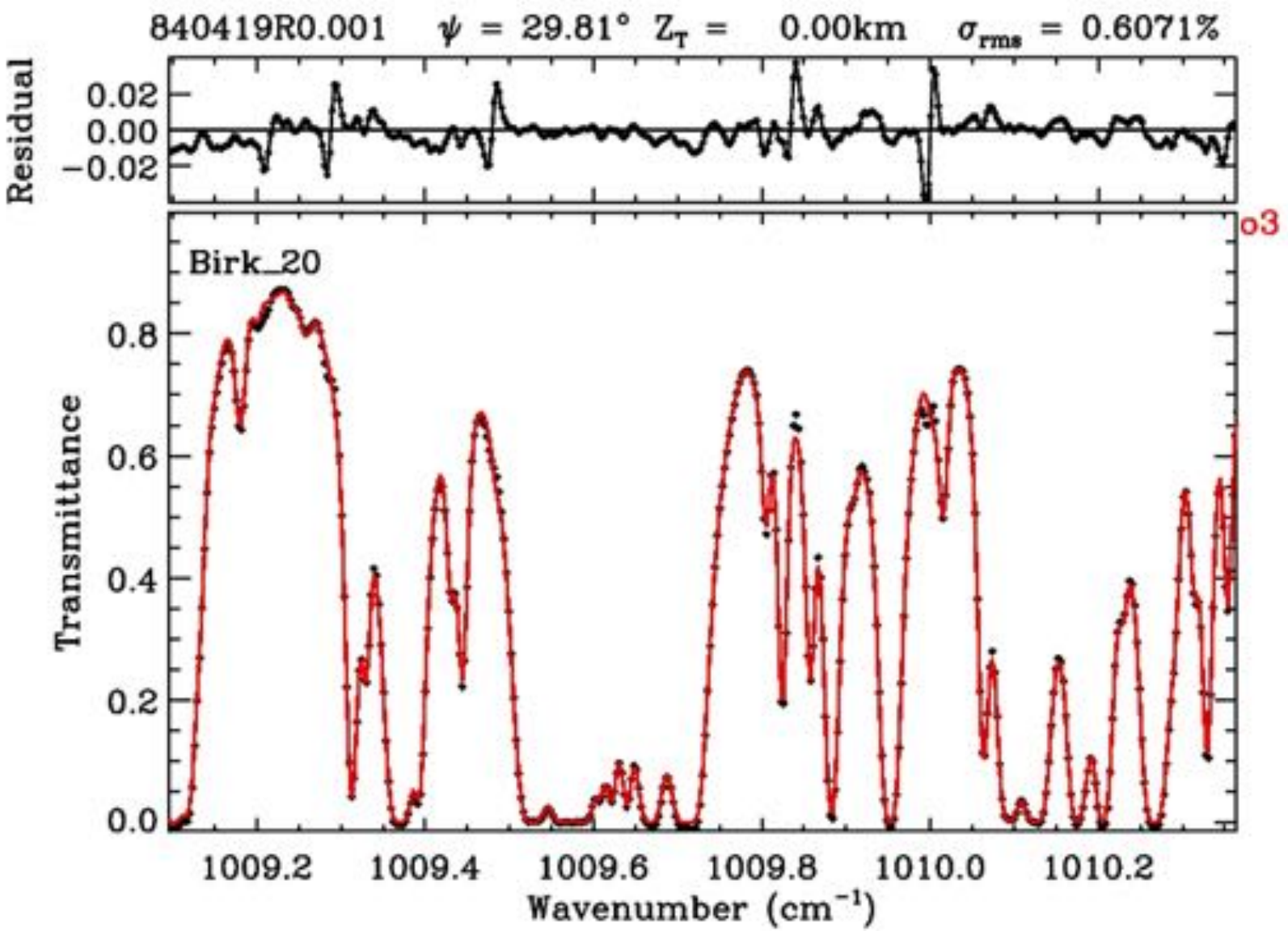


Large anti-symmetric residual (±4%) at 968.88 cm^{-1} is due to line position error in SMPO_20

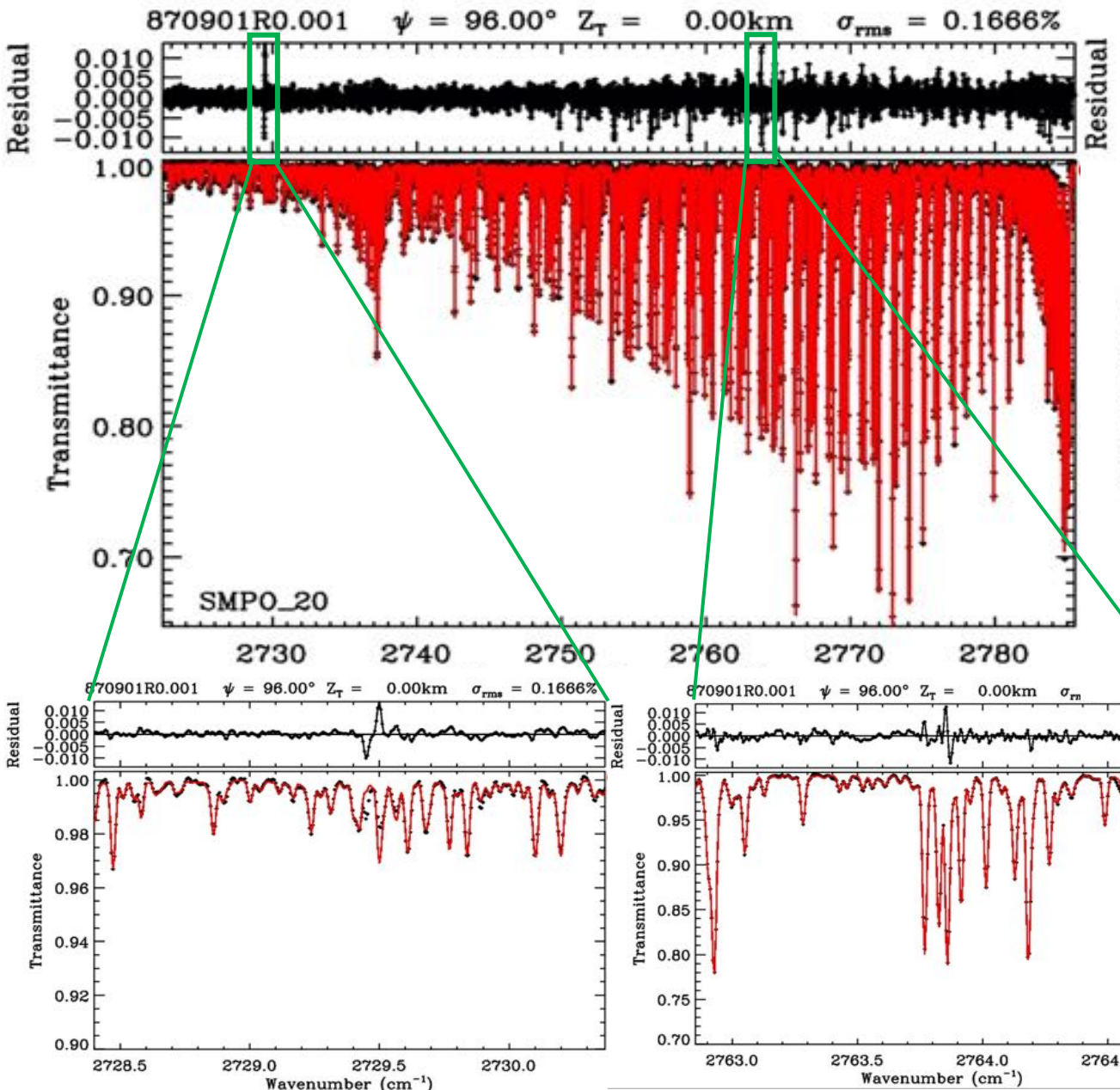


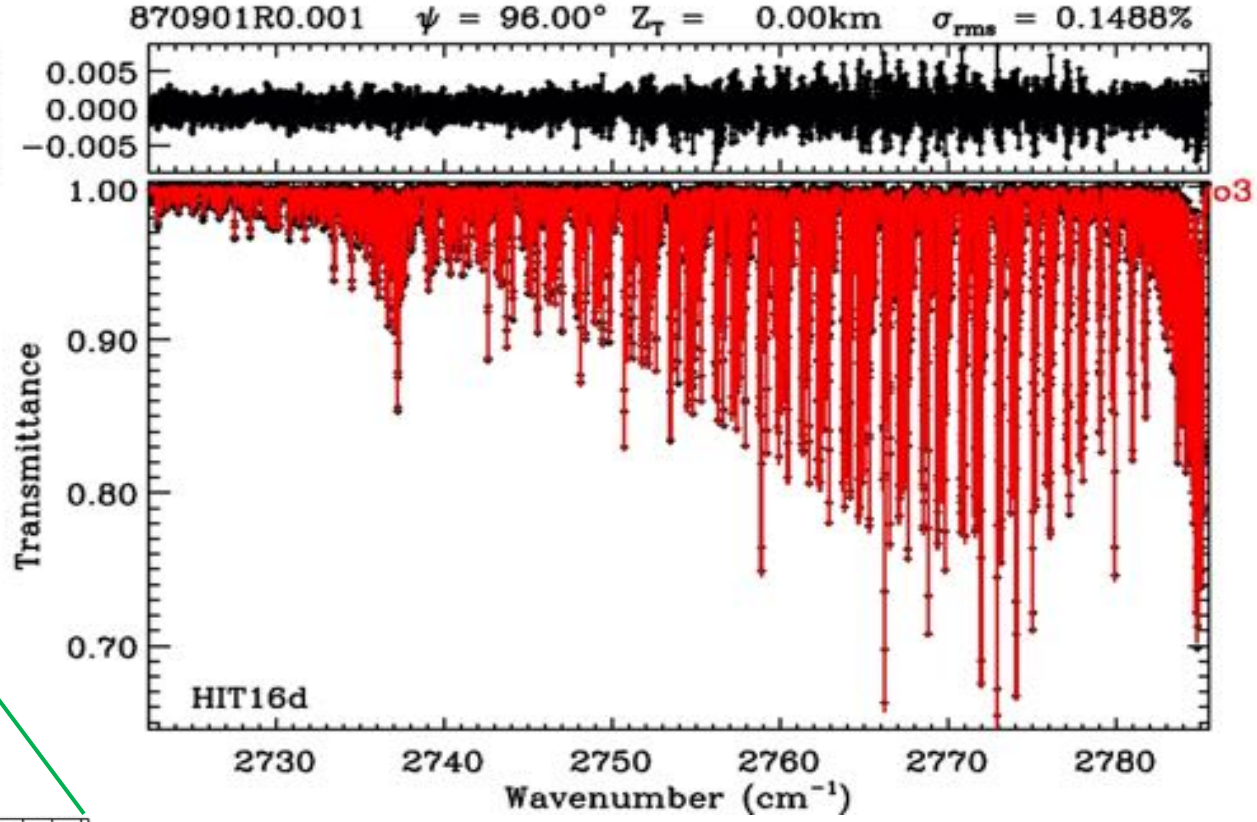
Line position are generally better in Birk_20 in this region…

…but there's still plenty of scope for improvement



In the 2700-2900 cm^{-1} region the HIT16d linelist provides the best fits





Residuals due to line position errors seen in fits to KP lab spectra using SMPO_20 linelist (left-hand panels); the two worst residuals are zoomed (lower-left).

In the HIT16d linelist such errors have already been empirically fixed, so fits (upper-right) are better. Note scale change in Residuals.

RMS fitting residuals to MKIV balloon spectra

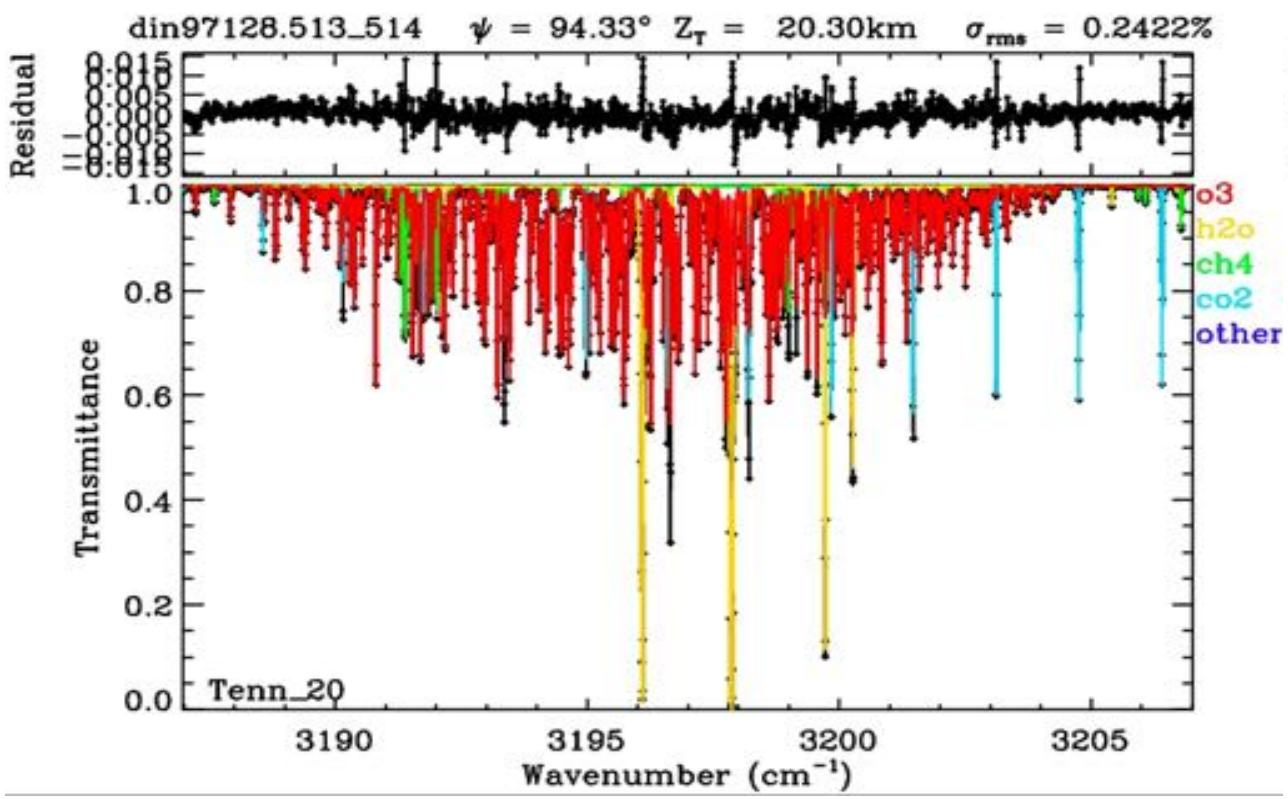
iwin	fcen	hwid	Nrow/Npp	hit12	atm16	hit16	hit16d	ten18b	hit20a	birk19	tenn20	smpo20	birk20	smpo20d
2	684.00	17.01	17/17	0.9789	0.9779	0.9779	0.9788	0.9792	0.9779	0.9796	0.9789	0.9796	0.9790	0.9790
3	752.40	51.41	17/17	1.1136	1.1135	1.1135	1.1135	1.1150	1.1135	1.1134	1.1139	1.1109	1.1135	1.1138
4	832.15	28.35	17/17	0.5059	0.5059	0.5059	0.5059	0.5061	0.5059	0.5062	0.5060	0.5052	0.5062	0.5059
5	1003.40	40.51	17/17	0.5308	0.5213	0.5220	0.5209	0.5076	0.5220	0.5095	0.5020	0.5360	0.4901	0.5218
6	1059.40	16.30	17/17	0.3588	0.3586	0.3591	0.3429	0.4266	0.3591	0.3500	0.4536	0.3779	0.3385	0.3698
7	1092.86	16.68	17/17	0.3379	0.3379	0.3379	0.3375	0.6138	0.3379	0.3335	0.6673	0.3502	0.3328	0.3554
8	1122.58	13.04	17/17	0.3784	0.3787	0.3787	0.3778	0.6132	0.3787	0.3790	0.6765	0.3797	0.3788	0.3895
9	1161.90	24.31	17/17	0.3230	0.3569	0.3569	0.3201	0.4124	0.3569	0.3220	0.4445	0.3189	0.3220	0.3499
10	1199.25	11.10	17/17	0.2798	0.2828	0.2828	0.2785	0.2866	0.2828		0.2883	0.2766		0.2814
11	1706.90	46.53	17/17	1.4252	1.4244	1.4252	1.4244	1.4243	1.4252		1.4230	1.4165		1.4165
12	1775.44	22.47	17/17	0.8966	0.8963	0.8966	0.8963	0.8896	0.8966		0.8895	0.8904		0.8904
13	1812.50	12.25	17/17	0.6642	0.6632	0.6642	0.6625	0.6650	0.6642		0.6628	0.6621		0.6621
14	1837.50	12.25	17/17	0.8663	0.8550	0.8663	0.8548	0.8653	0.8663		0.8651	0.8641		0.8541
15	1865.00	14.70	17/17	0.6707	0.6682	0.6707	0.6681	0.6702	0.6707		0.6699	0.6669		0.6669
16	1905.82	25.25	17/17	0.6170	0.6169	0.6169	0.6166	0.6166	0.6169		0.6169	0.6169		0.6169
17	1953.12	18.12	17/17	0.5485	0.5476	0.5476	0.5468	0.5472	0.5476		0.5472	0.5468		0.5468
18	1992.00	20.50	17/17	0.5426	0.5326	0.5328	0.5303	0.5327	0.5328		0.5323	0.5091		0.5090
19	2027.22	14.52	17/17	0.6281	0.6540	0.6568	0.6108	0.6047	0.6568		0.6125	0.5469		0.5462
20	2059.00	17.01	17/17	0.6609	0.6202	0.6404	0.6137	0.5627	0.6404		0.5355	0.5670		0.5650
21	2095.15	16.20	17/17	0.6628	0.5861	0.5922	0.5805	0.5403	0.5922		0.5274	0.5672		0.5666
22	2128.57	17.23	17/17	0.9359	0.5678	0.5728	0.5673	0.6084	0.5728		0.5784	0.5748		0.5748
23	2183.00	37.20	17/17	0.5109	0.5026	0.5027	0.5027	0.5066	0.5027		0.5019	0.5003		0.5002
24	2252.60	32.40	17/17	0.5265	0.5253	0.5253	0.5252	0.5251	0.5253		0.5227	0.5251		0.5251
25	2754.00	31.51	17/17	0.2707	0.2528	0.2734	0.2514	0.2786	0.2734		0.2701	0.2598		0.2600
26	2796.30	10.51	17/17	0.3295	0.2872	0.3290	0.2864	0.3303	0.3290		0.3116	0.2999		0.3012
27	2860.00	20.01	17/17	0.5246	0.5246	0.5246	0.5246	0.5251	0.5246		0.5247	0.5245		0.5245
28	2916.00	36.01	17/17	0.8247	0.8235	0.8234	0.8233	0.8273	0.8258		0.8260	0.8257		0.8257
29	3011.00	59.01	17/17	0.5833	0.5169	0.5475	0.4927	0.5540	0.5473		0.5407	0.5423		0.5378
30	3104.50	34.51	17/17	0.4498	0.4495	0.4495	0.4494	0.4468	0.4495		0.4463	0.4502		0.4481
31	3164.50	22.51	17/17	0.3178	0.3178	0.3178	0.3176	0.3178	0.3178		0.3159	0.3192		0.3192
32	3197.00	10.01	17/17	0.2236	0.2236	0.2236	0.2227	0.1980	0.2236		0.1866	0.2290		0.2166
33	3985.88	34.88	17/17	0.4084	0.3940	0.3979	0.3845		0.3593		0.3565	0.3555		0.3553
34	4029.75	8.99	17/17	0.6047	0.5574	0.5557	0.5291		0.4255		0.4996	0.4194		0.4186
35	4640.00	35.01	17/17	0.2731	0.2645	0.2658	0.2629		0.2658		0.2627	0.2580		0.2580
36	4888.85	33.35	17/17	0.4407	0.4394	0.4389	0.4371		0.4389		0.4397	0.4380		0.4380
37	4927.35	5.18	17/17	0.4055	0.3896	0.3857	0.3820		0.3857		0.3870	0.3808		0.3808
Mean RMS over windows:				**0.5573**	**0.5388**	**0.5426**	**0.5335**		**0.5381**		**0.5536**	**0.5292**		**0.5295**

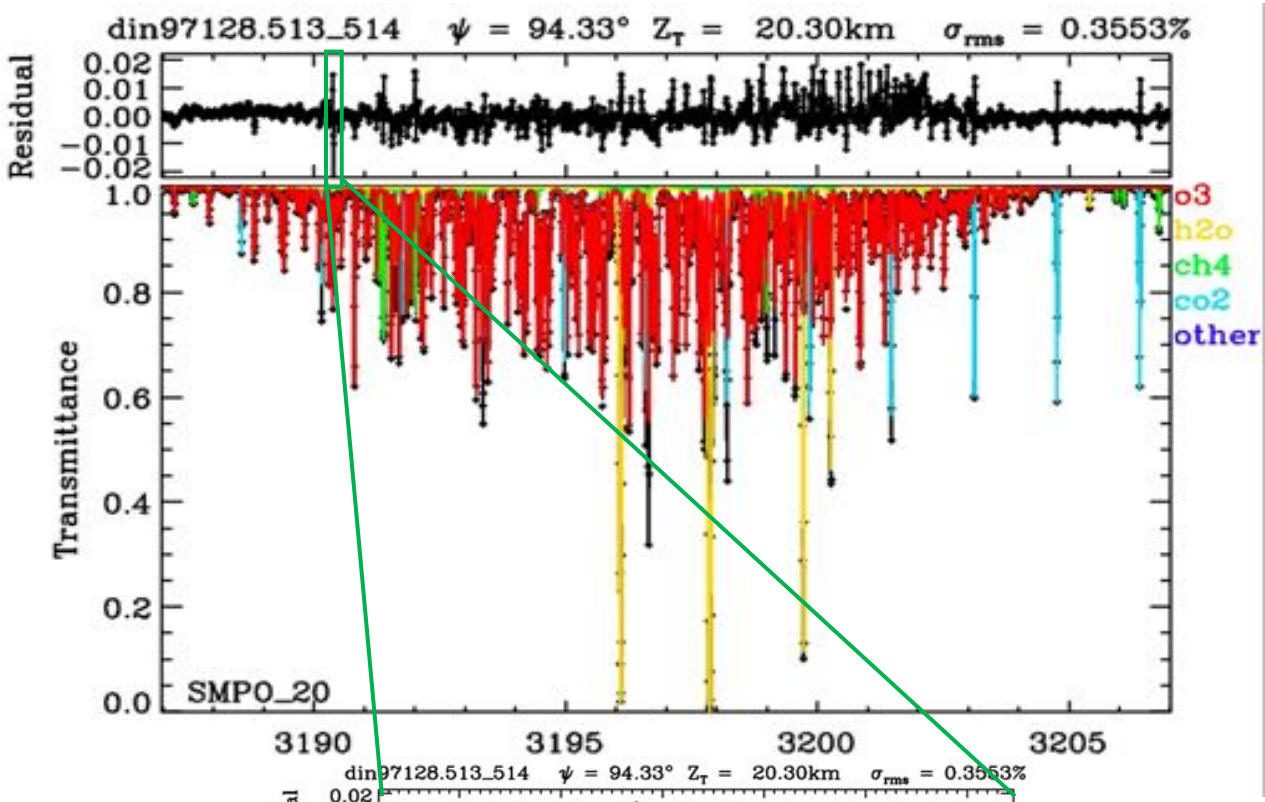
Blue denotes the lowest RMS in that row; Red denotes the highest.

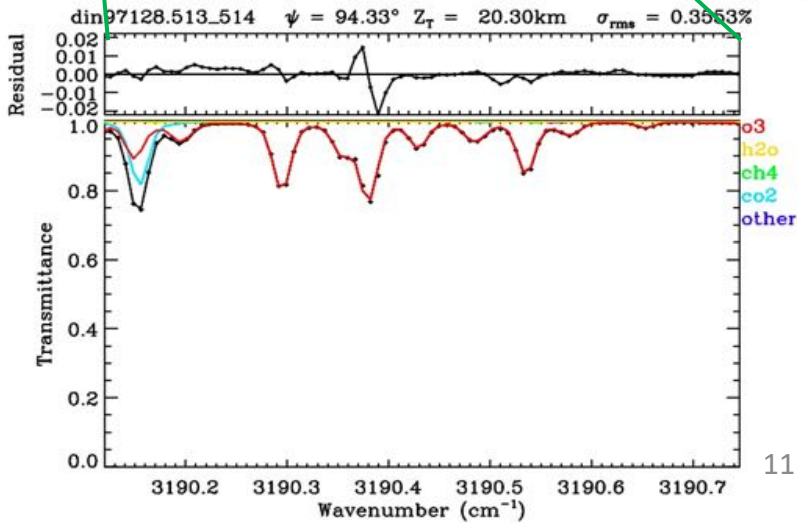
Overall, smpo20 best, HIT12 is the worst.

Window #1 is omitted; too blacked out in balloon spectra.

Fits to the 3197 cm^{-1} window in MkIV balloon spectrum (20 km tangent altitude)







Tenn_20 linelist (left) produces much better fits than SMPO_20 (right). In left-hand panel, residuals are dominated by inconsistency between H_2O, CH_4, and CO_2 line positions. In right-hand panel, residuals are mainly due to O_3. Biggest residual is due to a line position error in line at 3190.38 cm^{-1} in SMPO_20 (zoomed lower right).

VMR Scale Factors (VSF) from fits to MkIV balloon spectra

iwin	fcen	hwid	Nrow Npp	hit12	atm16	hit16	hit16d	ten18b	hit20a	birk19	tenn20	smpo20	birk20	smpo20d
2	684.00	17.01	17/17	1.2013	1.2013	1.2013	1.2008	1.1138	1.2013	1.1862	1.1214	1.1428	1.1862	1.1439
3	752.40	51.41	17/17	1.1078	1.1078	1.1078	1.1078	1.0299	1.1078	1.0931	1.0355	1.0695	1.0931	1.0552
4	832.15	28.35	17/17	1.0404	1.0404	1.0404	1.0404	0.9746	1.0404	1.0288	0.9781	1.0587	1.0288	0.9912
5	1003.40	40.51	17/17	1.0433	1.0416	1.0413	1.0420	1.0518	1.0413	1.0234	1.0199	1.0188	1.0283	1.0226
6	1059.40	16.30	17/17	1.0462	1.0463	1.0461	1.0466	1.0665	1.0461	1.0263	1.0280	1.0237	1.0252	1.0212
7	1092.86	16.68	17/17	1.0791	1.0791	1.0791	1.0794	1.1325	1.0791	1.0567	1.0979	1.0625	1.0571	1.0614
8	1122.58	13.04	17/17	1.0925	1.0925	1.0925	1.0914	1.1755	1.0925	1.0676	1.1478	1.0681	1.0677	1.0703
9	1161.90	24.31	17/17	1.0784	1.0825	1.0825	1.0788	1.1444	1.0825	1.0541	1.1176	1.0509	1.0542	1.0439
10	1199.25	11.10	17/17	1.0555	1.0567	1.0567	1.0555	1.1118	1.0567		1.0879	1.0312		1.0087
11	1706.90	46.53	17/17	1.0307	1.0308	1.0307	1.0308	1.1666	1.0307		1.1055	0.9994		0.9994
12	1775.44	22.47	17/17	1.0305	1.0305	1.0305	1.0305	1.0295	1.0305		1.0138	1.0329		1.0329
13	1812.50	12.25	17/17	0.9906	0.9907	0.9906	0.9906	1.0316	0.9906		1.0132	1.0175		1.0175
14	1837.50	12.25	17/17	0.9611	0.9609	0.9611	0.9610	1.0252	0.9611		1.0079	1.0032		1.0032
15	1865.00	14.70	17/17	0.9139	0.9149	0.9139	0.9148	0.9960	0.9139		0.9788	0.9711		0.9711
16	1905.82	25.25	17/17	0.8911	0.8915	0.8915	0.8937	0.9922	0.8915		0.9737	0.9664		0.9664
17	1953.12	18.12	17/17	0.8371	0.9226	0.9225	0.9400	0.9512	0.9225		0.9740	0.9169		0.9169
18	1992.00	20.50	17/17	0.9152	1.0287	1.0286	1.0304	0.9861	1.0286		1.0057	0.9892		0.9893
19	2027.22	14.52	17/17	0.9527	1.0433	1.0428	1.0512	1.0030	1.0428		1.0142	1.0136		1.1038
20	2059.00	17.01	17/17	0.9826	1.0377	1.0376	1.0378	1.0125	1.0376		1.0062	1.0049		1.0046
21	2095.15	16.20	17/17	1.0536	1.0694	1.0701	1.0696	1.0469	1.0701		1.0272	1.0312		1.0315
22	2128.57	17.23	17/17	1.0531	1.0585	1.0582	1.0585	1.0309	1.0582		1.0065	1.0149		1.0149
23	2183.00	37.20	17/17	0.9588	1.0384	1.0384	1.0385	0.9944	1.0384		0.9896	0.9966		0.9966
24	2252.60	32.40	17/17	1.0041	1.0687	1.0687	1.0688	1.0510	1.0687		1.0313	1.0257		1.0257
25	2754.00	31.51	17/17	0.9653	0.9642	0.9655	0.9638	1.0158	0.9655		0.9643	0.9943		0.9941
26	2796.30	10.51	17/17	0.9992	0.9974	1.0002	0.9971	1.0211	1.0002		0.9703	1.0305		1.0295
27	2860.00	20.01	17/17	0.9376	0.9376	0.9376	0.9376	0.9422	0.9376		0.9461	0.9375		0.9382
28	2916.00	36.01	17/17	1.0010	1.0120	1.0119	1.0132	1.0536	1.0129		1.0189	1.0278		1.0126
29	3011.00	59.01	17/17	0.9479	0.9477	0.9477	0.9451	1.0230	0.9477		0.9807	1.0175		1.0196
30	3104.50	34.51	17/17	0.9486	0.9487	0.9487	0.9481	1.0113	0.9487		0.9690	0.9485		1.0068
31	3164.50	22.51	17/17	0.9813	0.9813	0.9813	0.9813	0.9289	0.9813		0.9164	0.9801		0.9905
32	3197.00	10.01	17/17	0.9682	0.9682	0.9682	0.9681	0.9210	0.9682		0.9125	0.9674		0.9934
33	3985.88	34.88	17/17	1.0345	1.0341	1.0347	1.0353		1.1681		0.8921	1.0081		1.0081
34	4029.75	8.99	17/17	1.0061	1.0056	1.0053	1.0064		1.1615		0.8963	1.0036		1.0038
35	4640.00	35.01	17/17	1.0286	1.0364	1.0363	1.0351		1.0363		0.8241	1.0439		1.0439
36	4888.85	33.35	17/17	1.0516	1.0607	1.0638	1.0788		1.0638		0.8807	0.8698		0.8698
37	4927.35	5.18	17/17	0.9583	0.9982	1.0044	1.0206		1.0044		0.8516	0.9148		0.9148
Average VSF (over windows)				**1.0160**	**1.0206**	**1.0227**	**1.0211**		**1.0366**		**0.9878**	**1.0162**		**1.0158**
RMS deviation from mean				**0.0521**	**0.0486**	**0.0486**	**0.0484**		**0.0637**		**0.0716**	**0.0325**		**0.0258**

Windows # 1 is omitted; too blacked out in atmospheric balloon spectra to derive useful VSFs.

Absolute VSF values are meaningless since we don't know the true atmospheric O_3.

SMPO20d linelist has the smallest/best window-to-window biases (2.58% RMS), although Birk20 is very good below 1180 cm^{-1}.

MkIV ground-based atmospheric spectra: RMS fitting residuals (%)

iwin	fcen	H-Wid	Nrow/Npp	hit12	atm16	hit16	hit16d	ten18b	hit20a	birk19	tenn20	smpo20	birk20	smpo20d
3	752.40	51.41	78/78	1.2551	1.2551	1.2551	1.2551	1.2555	1.2551	1.2551	1.2552	1.2569	1.2551	1.2551
4	832.15	28.35	78/78	0.5306	0.5306	0.5306	0.5306	0.5306	0.5306	0.5306	0.5306	0.5307	0.5306	0.5306
5	1003.40	40.51	78/78	0.4675	0.4647	0.4649	0.4648	0.4827	0.4649	0.4600	0.4701	0.4711	0.4569	0.4612
6	1059.40	16.30	78/78	0.4375	0.4375	0.4376	0.4374	0.5074	0.4376	0.4471	0.5106	0.4458	0.4399	0.4451
7	1092.86	16.68	78/78	0.3391	0.3392	0.3392	0.3387	0.4564	0.3392	0.3385	0.4796	0.3418	0.3388	0.3435
8	1122.68	13.14	78/78	0.3630	0.3630	0.3630	0.3626	0.4624	0.3630	0.3607	0.4707	0.3635	0.3607	0.3635
9	1161.90	24.31	78/78	0.4423	0.4429	0.4429	0.4420	0.4545	0.4429	0.4415	0.4567	0.4407	0.4415	0.4428
10	1199.25	11.10	78/78	0.7204	0.7204	0.7204	0.7203	0.7206	0.7204		0.7205	0.7200		0.7200
11	1706.90	46.53	78/78	0.1208	0.1210	0.1208	0.1209	0.1215	0.1208		0.1210	0.1210		0.1210
12	1775.44	22.47	78/78	0.2437	0.2437	0.2437	0.2437	0.2437	0.2437		0.2444	0.2429		0.2429
13	1812.50	12.25	62/78	0.2471	0.2447	0.2471	0.2426	0.2472	0.2471		0.2460	0.2513		0.2513
14	1837.50	12.25	62/78	0.1343	0.1320	0.1343	0.1332	0.1387	0.1343		0.1358	0.1317		0.1317
15	1865.00	14.70	78/78	0.3740	0.3740	0.3740	0.3740	0.3742	0.3740		0.3742	0.3758		0.3758
16	1905.82	25.25	78/78	0.4074	0.4074	0.4074	0.4074	0.4074	0.4074		0.4074	0.4074		0.4074
17	1953.12	18.12	78/78	0.5118	0.5114	0.5098	0.5107	0.5117	0.5098		0.5110	0.5105		0.5108
18	1992.00	20.50	78/78	0.5280	0.5280	0.5280	0.5280	0.5280	0.5280		0.5280	0.5277		0.5277
19	2027.22	14.52	78/78	0.4972	0.4971	0.4972	0.4968	0.4973	0.4972		0.4971	0.4965		0.4965
20	2059.00	17.01	78/78	0.5161	0.5161	0.5164	0.5157	0.5219	0.5164		0.5173	0.5165		0.5165
21	2095.15	16.20	78/78	0.7542	0.7312	0.7318	0.7303	0.7477	0.7318		0.7336	0.7345		0.7344
22	2128.57	17.23	78/78	0.8356	0.7996	0.8003	0.7991	0.8252	0.8003		0.8016	0.8006		0.8006
23	2183.00	37.20	78/78	0.3302	0.3303	0.3304	0.3304	0.3305	0.3304		0.3304	0.3303		0.3303
24	2252.60	32.40	78/78	0.1481	0.1481	0.1481	0.1481	0.1482	0.1481		0.1481	0.1481		0.1481
25	2754.00	31.51	78/78	0.3625	0.3616	0.3633	0.3611	0.3633	0.3633		0.3629	0.3623		0.3624
26	2796.30	10.51	78/78	0.4314	0.4299	0.4306	0.4296	0.4299	0.4306		0.4302	0.4303		0.4307
27	2860.00	20.01	78/78	0.7141	0.7141	0.7141	0.7141	0.7141	0.7141		0.7141	0.7141		0.7141
28	2916.00	36.01	78/78	1.2027	1.2027	1.2027	1.2027	1.2027	1.2027		1.2027	1.2027		1.2027
29	3011.00	59.01	78/78	0.5750	0.5736	0.5744	0.5734	0.5761	0.5744		0.5744	0.5748		0.5748
30	3104.50	34.51	78/78	0.4929	0.4929	0.4929	0.4929	0.4929	0.4929		0.4930	0.4930		0.4931
31	3164.50	22.51	78/78	0.9608	0.9608	0.9608	0.9608	0.9608	0.9608		0.9608	0.9607		0.9608
32	3197.00	10.01	78/78	0.5346	0.5346	0.5346	0.5346	0.5347	0.5346		0.5346	0.5347		0.5347
33	3985.88	34.88	78/78	0.3530	0.3529	0.3530	0.3532		0.3520		0.3511	0.3517		0.3514
34	4029.75	8.99	78/78	0.4853	0.4847	0.4849	0.4844		0.4834		0.4848	0.4833		0.4833
35	4640.00	35.01	78/78	0.3167	0.3164	0.3164	0.3163		0.3164		0.3164	0.3161		0.3161
36	4888.85	33.35	78/78	0.6193	0.6192	0.6192	0.6192		0.6192		0.6193	0.6191		0.6191
37	4927.35	5.18	78/78	0.5209	0.5207	0.5207	0.5206		0.5207		0.5207	0.5207		0.5207
Mean % fits over windows:				**0.4923**	**0.4903**	**0.4906**	**0.4903**		**0.4905**		**0.4999**	**0.4910**		**0.4909**

Ground-based spectral fits are sensitive to line shape (i.e. widths and shifts).

Windows # 1 and 2 are omitted; too blacked out in ground-based spectra.

Blue values denote the lowest RMS in that row; red the highest.

Overall hit16d is best, closely followed by smpo20d.

VSF values retrieved from MKIV ground-based spectra

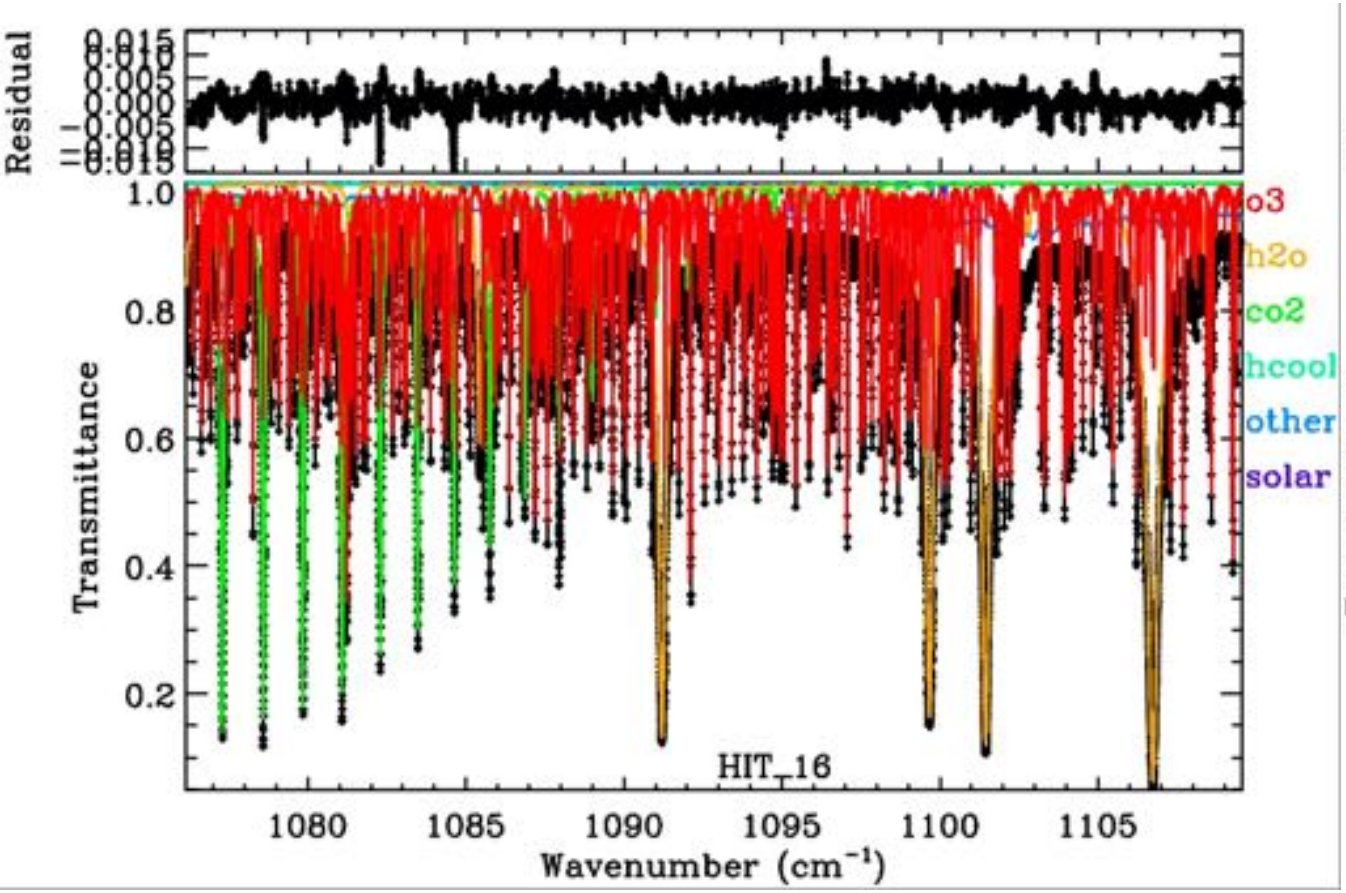
iwin	fcen	H-Wid	Nrow/Npp	hit12	atm16	hit16	hit16d	ten18b	hit20a	birk19	tenn20	smpo20	birk20	smpo20d
3	752.40	51.41	78/78	1.0146	1.0147	1.0147	1.0147	0.9471	1.0147	1.0009	0.9516	0.9852	1.0009	0.9665
4	832.15	28.35	78/78	1.0285	1.0285	1.0285	1.0285	0.9613	1.0285	1.0092	0.9653	1.0378	1.0092	0.9796
5	1003.40	40.51	78/78	1.0196	1.0189	1.0189	1.0189	1.0255	1.0189	0.9942	0.9899	0.9921	0.9960	0.9973
6	1059.40	16.30	78/78	1.0238	1.0238	1.0238	1.0239	1.0413	1.0238	1.0005	1.0045	0.9983	1.0006	0.9999
7	1092.86	16.68	78/78	1.0079	1.0079	1.0079	1.0079	1.0645	1.0079	0.9879	1.0308	0.9924	0.9879	0.9912
8	1122.68	13.14	78/78	1.0103	1.0103	1.0103	1.0100	1.0738	1.0103	0.9892	1.0459	0.9880	0.9892	0.9909
9	1161.90	24.31	78/78	1.0186	1.0188	1.0188	1.0185	1.0797	1.0188	0.9970	1.0531	0.9926	0.9970	0.9911
10	1199.25	11.10	78/78	1.0074	1.0077	1.0077	1.0071	1.0619	1.0077		1.0402	0.9841		0.9592
11	1706.90	46.53	78/78											
12	1775.44	22.47	78/78											
13	1812.50	12.25	62/78	0.9173	0.9172	0.9173	0.9178	0.9589	0.9173		0.9391	0.9451		0.9451
14	1837.50	12.25	62/78	0.8083	0.8071	0.8083	0.8073	0.8662	0.8083		0.8517	0.8415		0.8415
15	1865.00	14.70	78/78	0.8493	0.8499	0.8493	0.8494	0.9259	0.8493		0.9104	0.9026		0.9026
16	1905.82	25.25	78/78											
17	1953.12	18.12	78/78											
18	1992.00	20.50	78/78	0.8829	0.9934	0.9934	0.9937	0.9445	0.9934		0.9669	0.9536		0.9536
19	2027.22	14.52	78/78	0.9409	1.0362	1.0361	1.0387	0.9797	1.0361		0.9988	0.9997		0.9996
20	2059.00	17.01	78/78	0.9740	1.0184	1.0185	1.0183	0.9784	1.0185		0.9721	0.9787		0.9787
21	2095.15	16.20	78/78	1.0088	1.0121	1.0121	1.0122	0.9840	1.0121		0.9623	0.9719		0.9719
22	2128.57	17.23	78/78	1.0193	1.0102	1.0102	1.0102	0.9833	1.0102		0.9594	0.9697		0.9697
23	2183.00	37.20	78/78	0.9405	1.0180	1.0180	1.0178	0.9745	1.0180		0.9693	0.9767		0.9767
24	2252.60	32.40	78/78	0.9313	0.9951	0.9951	0.9951	0.9934	0.9951		0.9646	0.9552		0.9552
25	2754.00	31.51	78/78	0.9422	0.9426	0.9421	0.9425	0.9944	0.9421		0.9436	0.9719		0.9717
26	2796.30	10.51	78/78	0.9654	0.9658	0.9656	0.9661	0.9935	0.9656		0.9438	0.9966		0.9959
27	2860.00	20.01	78/78											
28	2916.00	36.01	78/78											
29	3011.00	59.01	78/78	0.9000	0.9003	0.9001	0.9002	0.9733	0.9001		0.9338	0.9679		0.9687
30	3104.50	34.51	78/78	1.0233	1.0234	1.0234	1.0240	1.0760	1.0234		1.0284	1.0177		1.0677
31	3164.50	22.51	78/78	0.8919	0.8919	0.8919	0.8918	0.8484	0.8919		0.8367	0.8916		0.9012
32	3197.00	10.01	78/78	0.9733	0.9733	0.9733	0.9735		0.9733		0.9089	0.9713		0.9866
33	3985.88	34.88	78/78	1.0064	1.0070	1.0072	1.0089		1.1545		0.8674	0.9945		0.9945
34	4029.75	8.99	78/78											
35	4640.00	35.01	78/78											
36	4888.85	33.35	78/78											
37	4927.35	5.18	78/78											
Average VSF (over windows)				**1.0003**	**1.0044**	**1.0045**	**1.0044**	**1.0314**	**1.0050**		**0.9992**	**0.9883**		**0.9878**
RMS deviation from mean				**0.0311**	**0.0281**	**0.0281**	**0.0281**	**0.0418**	**0.0290**		**0.0439**	**0.0138**		**0.0133**

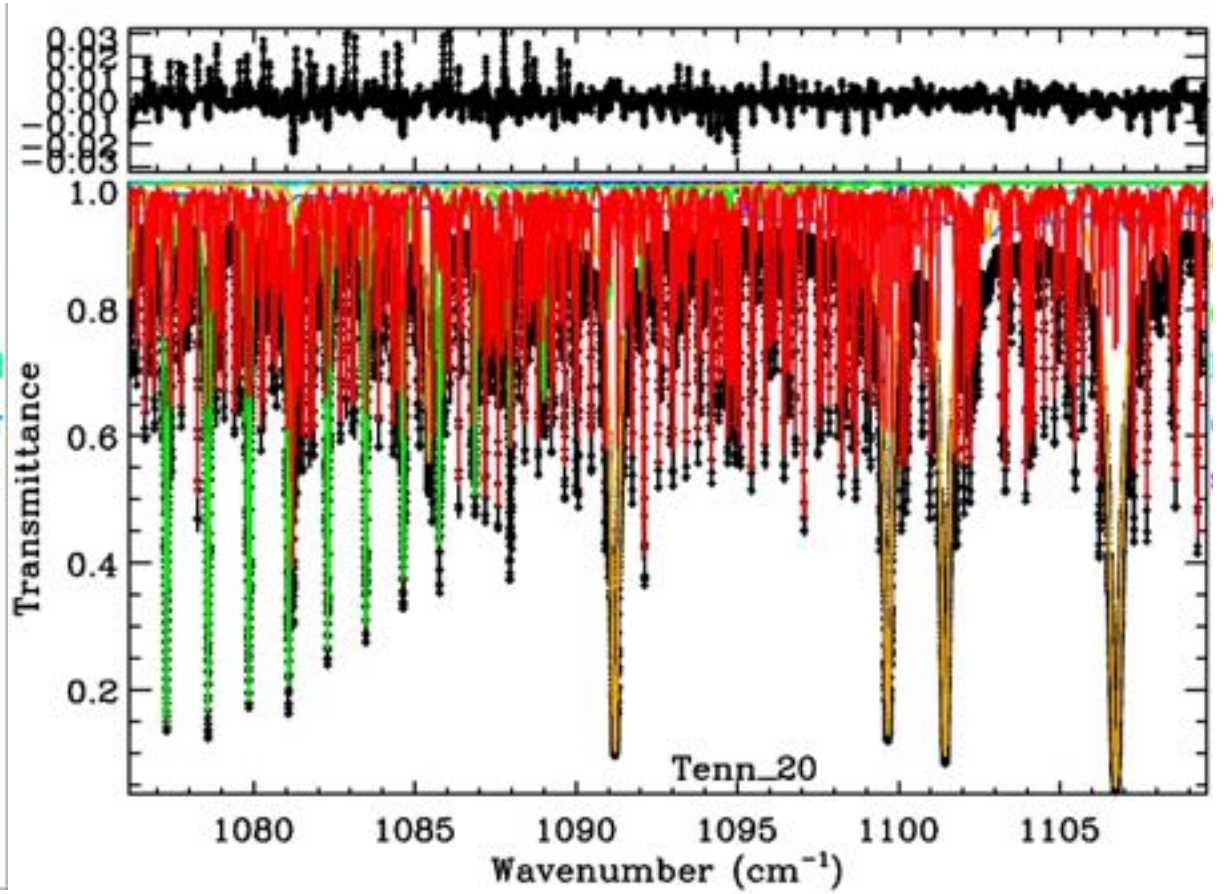
Windows # 1, 2, 11, 12 are too blacked out in ground-based spectra to determine useful VSFs

In windows #16, 17, 27, 28, 35, 36, and 37, O_3 lines are too weak in ground-based spectra to ascertain useful VSFs.

SMPO20d linelist has the smallest window-to-window biases (1.33%), although Birk20 is also good below 1185 cm^{-1}.

Example of Fits to MkIV ground-based spectra in 1092 cm^{-1} window





HIT_16 (left) has peak residuals of 1.5% and a RMS of 0.34%. Tenn_20 (right) has peak residuals of 3% and a RMS of 0.48%. Note the factor 2 scale change between the two residuals panels. In Tenn_20 a subset of lines below 1090 cm^{-1} seem inconsistent (too strong) compared with the other lines in the window. For example, the intensity of the following line in HIT16

31 1082.87766 2.895E-22 286.5665 .0698 .1010 .79 -.001 1 0 0 0 0 0 25 1 25 26 0 26 0065501412 4 2 2 1 51.0 53.0

became 3.300E-22 in Tenn_20, which is 14% stronger, causing a large upward residual. Other examples can be seen.

Conclusions

Based on the results of fitting KP lab spectra, plus MkIV balloon & ground-based atmospheric spectra, using 10 linelists:

- HIT_12 has the worst RMS fitting residuals, which are indicative of position errors and inconsistent intensities
- Birk_20 produces better RMS fits than Birk_19, especially in windows # 5 and 6.
- Birk_20 is the best linelist below 1135 cm^{-1}, in terms of RMS fitting residuals, and probably absolute intensities.
- SMPO_20d is, in general, the best linelist above 1135 cm^{-1}, except for window # 31.
- Tenn_20 is worse than Ten_18b in windows # 7, 8, 9, but is generally better elsewhere.
- There are still several windows (e.g. 2040-3070 cm^{-1}) where the HIT16d O_3 linelist has the smallest fitting residuals. (HIT16d is an empirically modified version of the HIT16)
- Would be nice for HITRAN_2024 to have linelists for the doubly-substituted isotopologs (e.g. 688, 868) in order to better analyze ^{18}O-enriched lab spectra in the ν_3 band.

Supplemental Material – Focus on 2975-3205 cm^{-1} region

This is an important region for atmospheric trace gas measurements (e.g. NDACC, ATMOS, MkIV, ACE) since several gases have their best or strongest absorption bands here (CH4, HCl, C2H2, C2H4, C2H6, C3H8, CH3Cl, HCN etc.)

So I was trying to figure out what was the main limitation to the O_3 spectroscopy in this region. Specifically, why the SMPO linelist RMSs were poor in windows # 30, 31 & 32, relative to the other windows. And why the Tenn_20 linelist was relatively better here. And why they both give low retrieved O_3 amounts. I didn't get to the bottom of the problem, but the next 6 slides summarize what I found regarding the 2975-3205 cm^{-1} region.

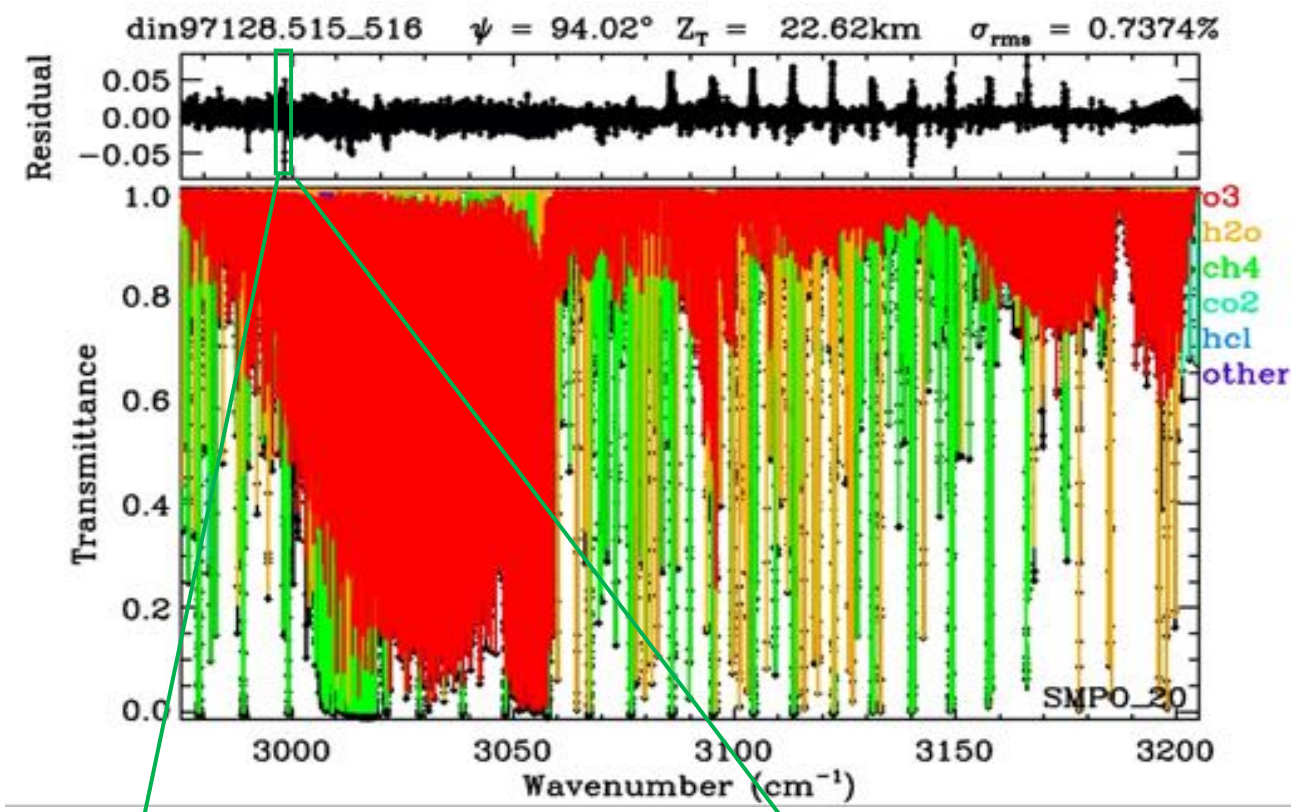
I first tried to fit the entire 2975-3005 cm^{-1} region simultaneously using the SMPO_20 linelist to see which, if any, O_3 lines stood out as being too strong (because the retrieved O_3 is too low here). There were lots in the R-branch of the O_3 band centered at 3187 cm^{-1}. But not all lines in this branch were too strong, only a subset, so I'm not sure how to fix it.

The MkIV balloon spectra were measuring O_3 that was quite cold (220K), so I couldn't rule out an error in the E" or the TDPBHW playing a role. But since the 296K Kitt Peak lab spectra saw similar residuals and they were mostly symmetrical about line centers, this suggests inconsistencies in the line intensities as being dominant cause of the residuals.

Also, I found a single O_3 line with a (position?) problem at 2998.2 cm^{-1}, both in MkIV balloon and in KP lab spectra. This problem iss present in both SMPO_20 and Tenn_20 linelists.

Tenn_20 produces better RMS residuals than SMPO_20. But what surprises me most is how similar the spectral fits are with the two linelists: SMPO_20 and Tenn_20. They obviously share some ancestry. But both fall far short of perfection.

This region needs more work. It isn't obvious what needs to be done to improve the fits or the window-to-window consistency of the retrieved O_3 amounts.

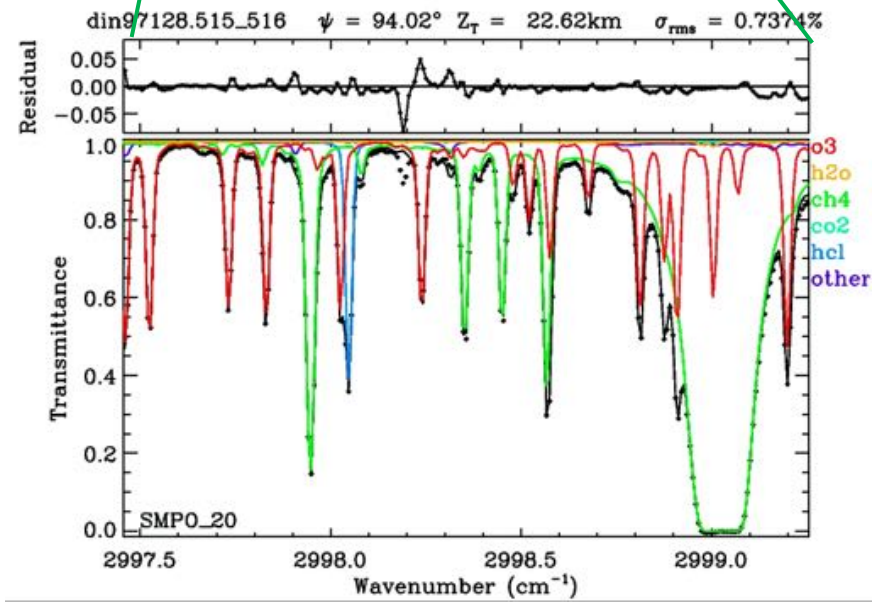


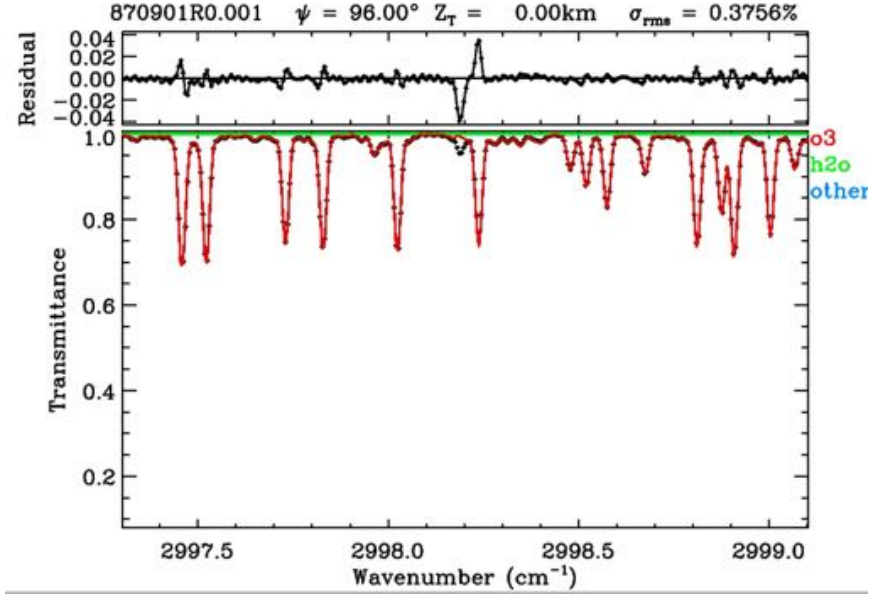
Fits using SMPO_20 linelist

Upper Left: Fit to MkIV balloon spectrum at 22.6 km tangent altitude over 2975-3205 cm^{-1}. Large residuals are due to neglect of CH_4 line-mixing. Tendency for positive residuals above 3187 cm^{-1} associated with O_3. If these lines were reduced in strength, this would improve RMS fits and band-to-band consistency.

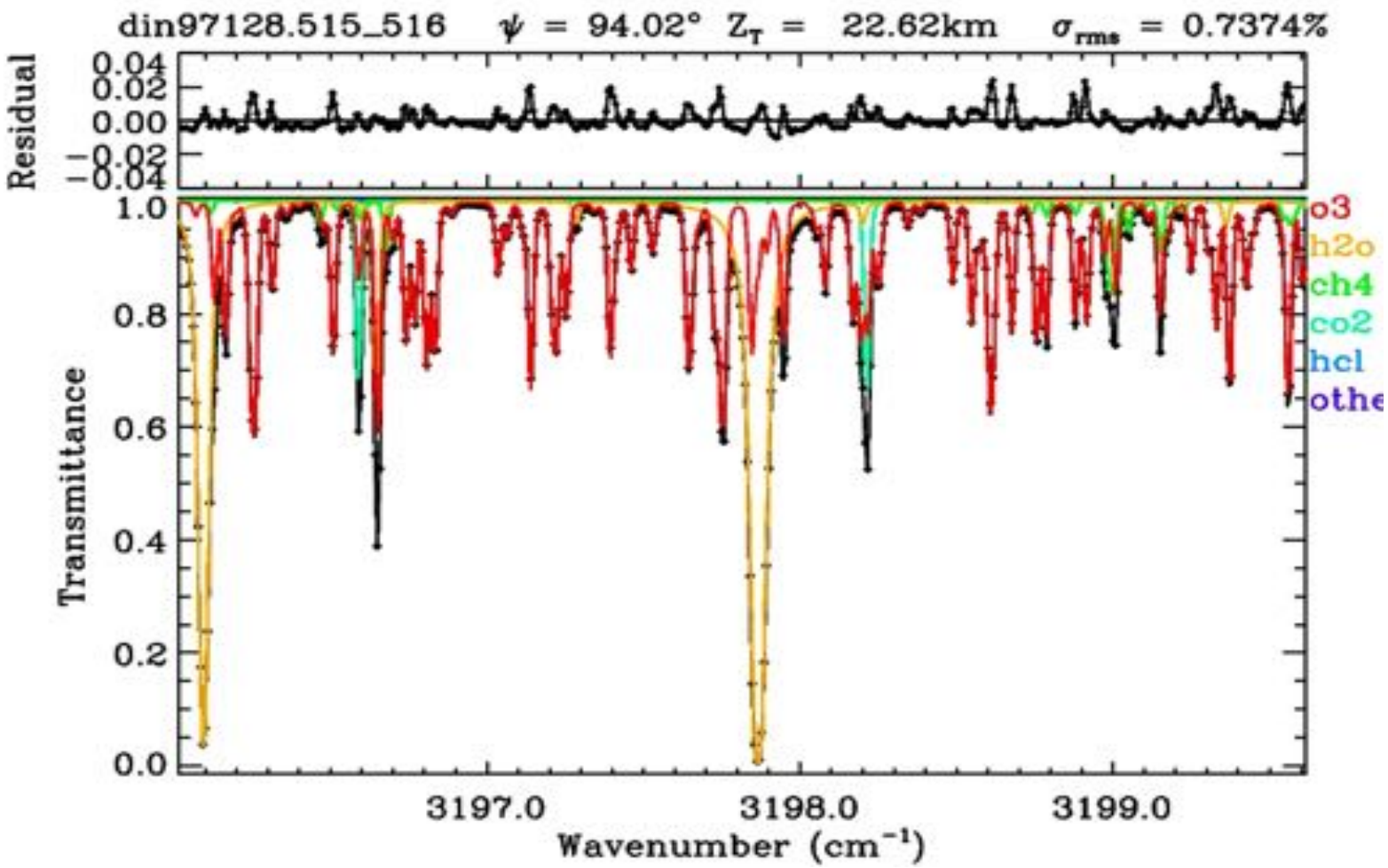
Lower-Left: Zoom into MkIV residuals around 2998.2 cm^{-1}.

Lower-Right: Similar region fitted in Kitt Peak lab O_3 spectrum shows same problem.





Fits to MKIV Balloon spectra using SMPO_20 linelist



Showing a small portion of the fit to MkIV balloon spectrum at 23 km tangent altitude over 2975-3205 cm^{-1}. O_3 is at ~220K.

In this narrow region, all the positive residuals correspond to O_3 lines. But not all O_3 lines produce a positive residuals.

For example, the pair of lines at 3198.754 and 3198.785 cm^{-1} seem to have the correct intensity, at least compared with other O_3 lines in the 2975-3005 cm^{-1} region.

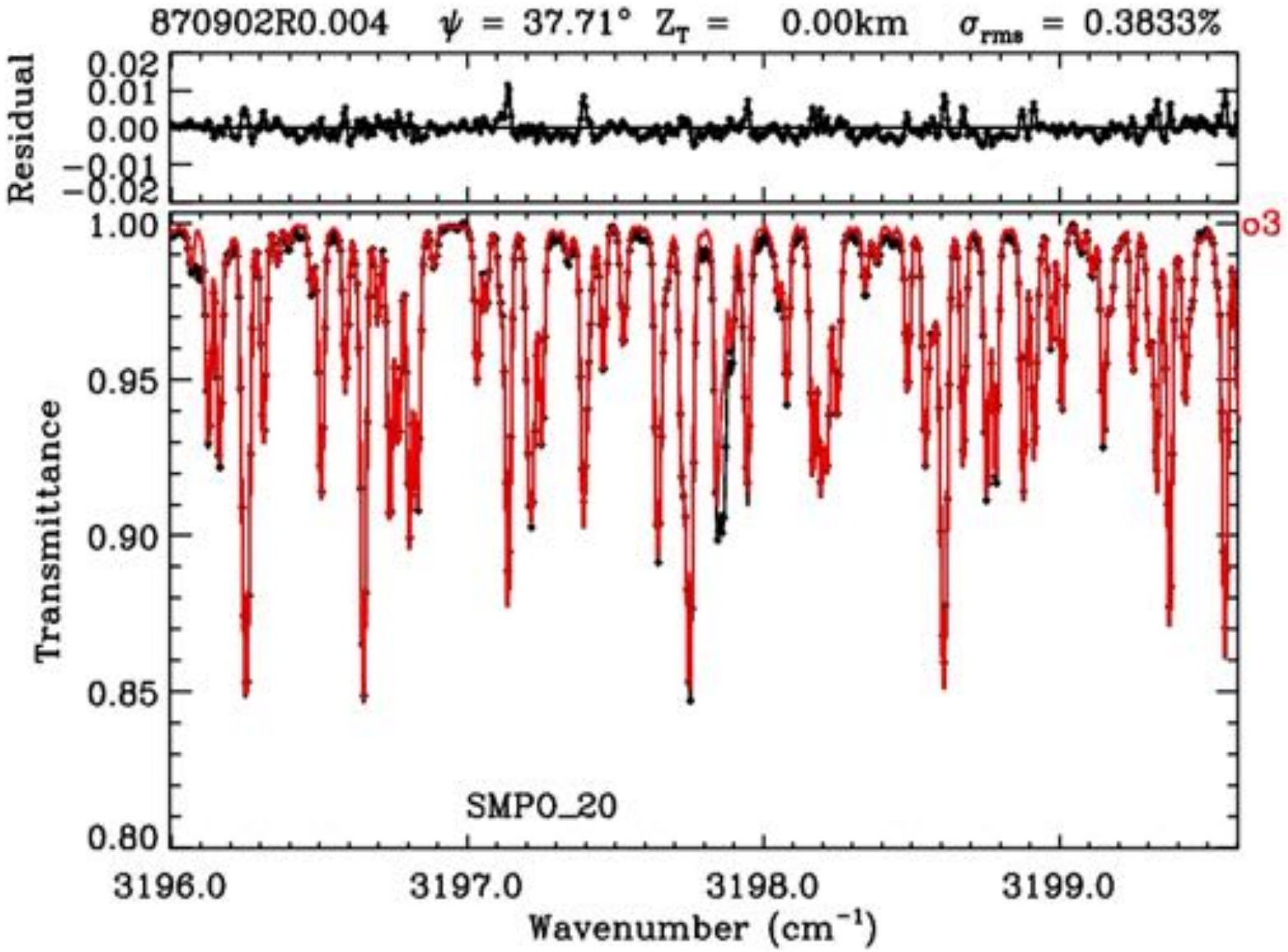
In contrast, the pair of lines at 3198.877 and 3198.914 cm^{-1} are too strong.

A subset of the O_3 lines here seem too strong, perhaps by 5-10%. Line positions seem good; residuals are symmetric about line centers.

```
31 3198.754400 2.055E-23 2.949E-02 0.0765.1034  150.19000.720.000000    2 0 1    0 0 0 19  1 18    18  1 17    445550 2 2 5 2 3 0   39.0  37.0
31 3198.785400 1.995E-23 2.976E-02 0.0768.1030  158.16530.720.000000    2 0 1    0 0 0 19  2 17    18  2 16    445550 2 2 5 2 3 0   39.0  37.0

31 3198.877400 1.212E-23 2.861E-02 0.0749.0988  290.94150.730.000000    2 0 1    0 0 0 23  5 18    22  5 17    445550 2 2 5 2 3 0   47.0  45.0
31 3198.914200 1.813E-23 2.739E-02 0.0723.1025  190.21250.730.000000    2 0 1    0 0 0 22  1 22    21  1 21    445550 2 2 5 2 3 0   45.0  43.0
```

Fits to a Kitt Peak lab spectrum using SMPO_20 linelist



Showing a small portion of the fit to KP lab spectrum (15.7 Torr at 296 K) over same interval as previous slide.

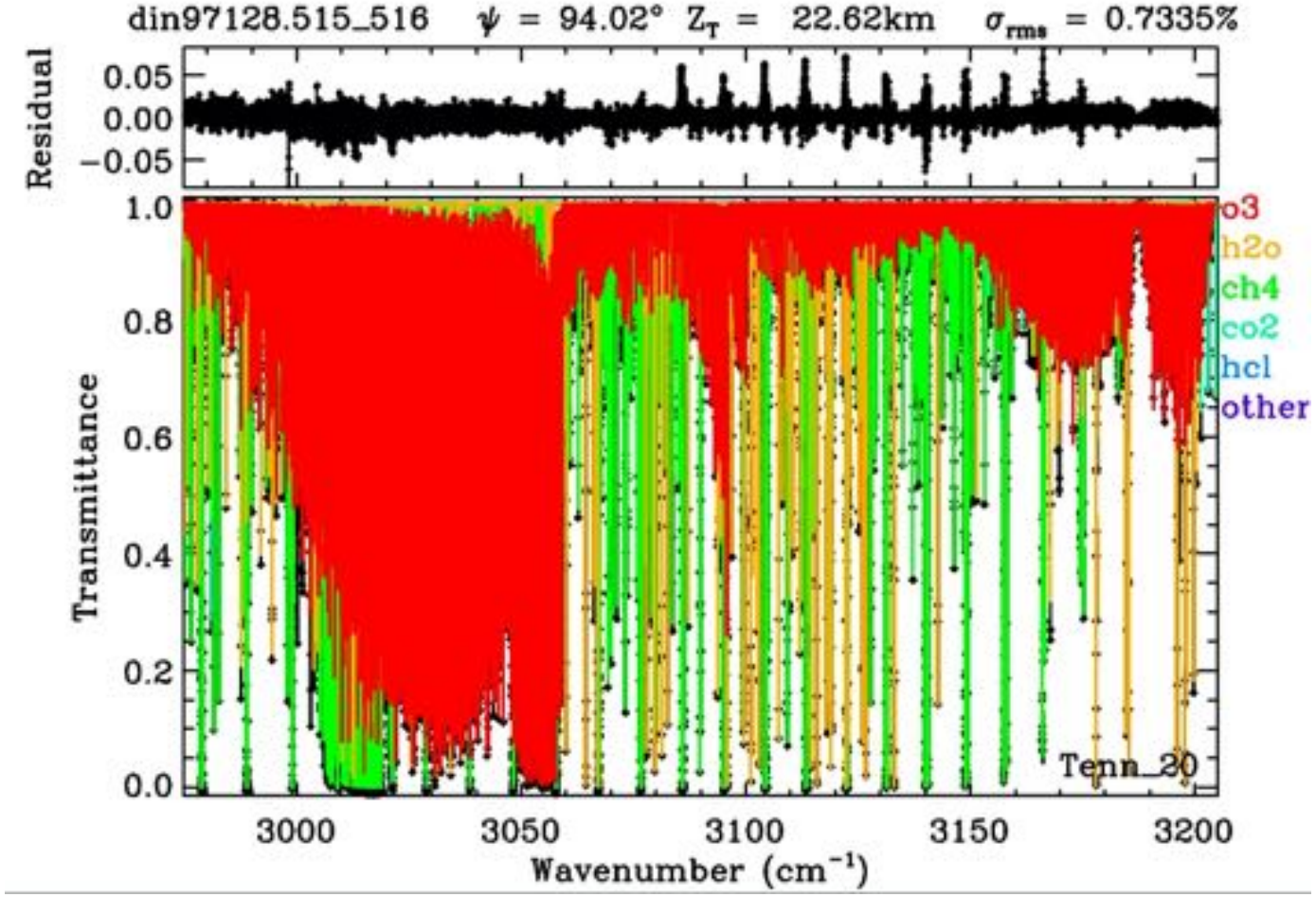
Residual pattern is similar to that seen in MkIV balloon spectral fit in previous slide. Likely caused by inconsistent intensities.

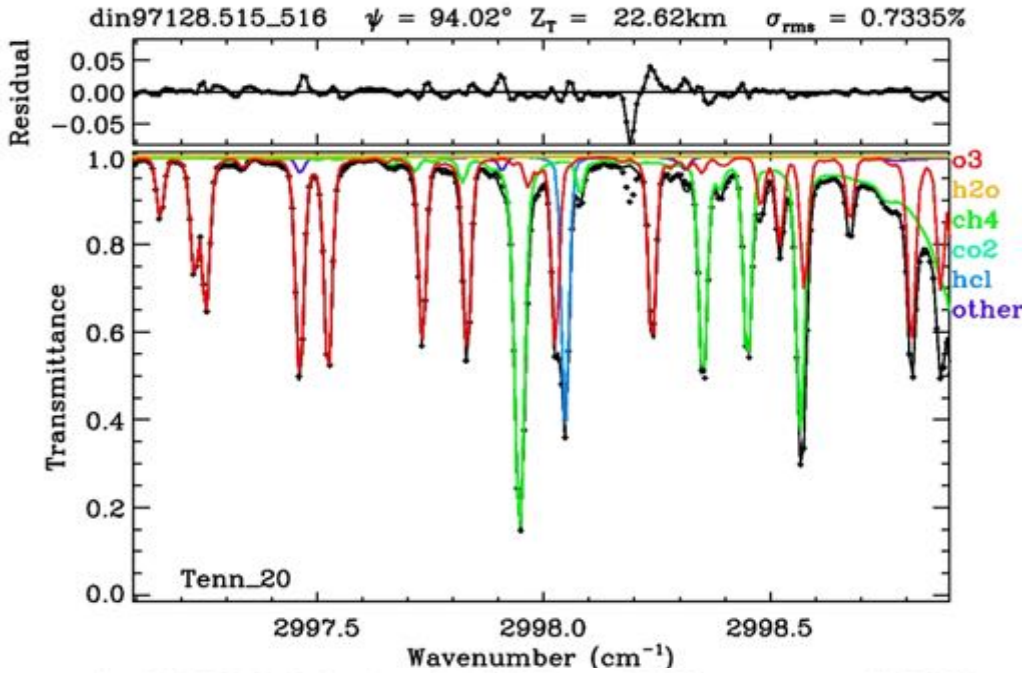
For example, the pair of lines at 3198.754 and 3198.785 cm^{-1} seem to have the correct intensity, at least compared with other O_3 lines in the 2975-3005 cm^{-1} region.

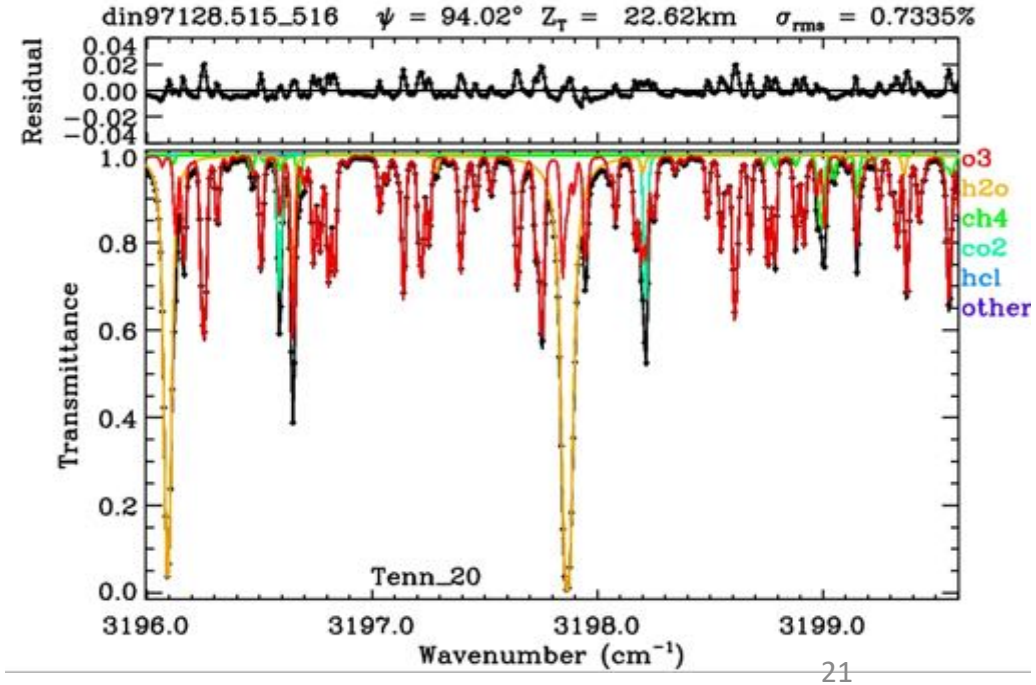
In contrast, the pair of lines at 3198.877 and 3198.914 cm^{-1} are too strong.

Looks like a subset of the O_3 lines here are too strong, perhaps by 5-10%.

Fits to a MkIV balloon spectrum 2975-3005 cm^{-1} using Tenn_20 linelist

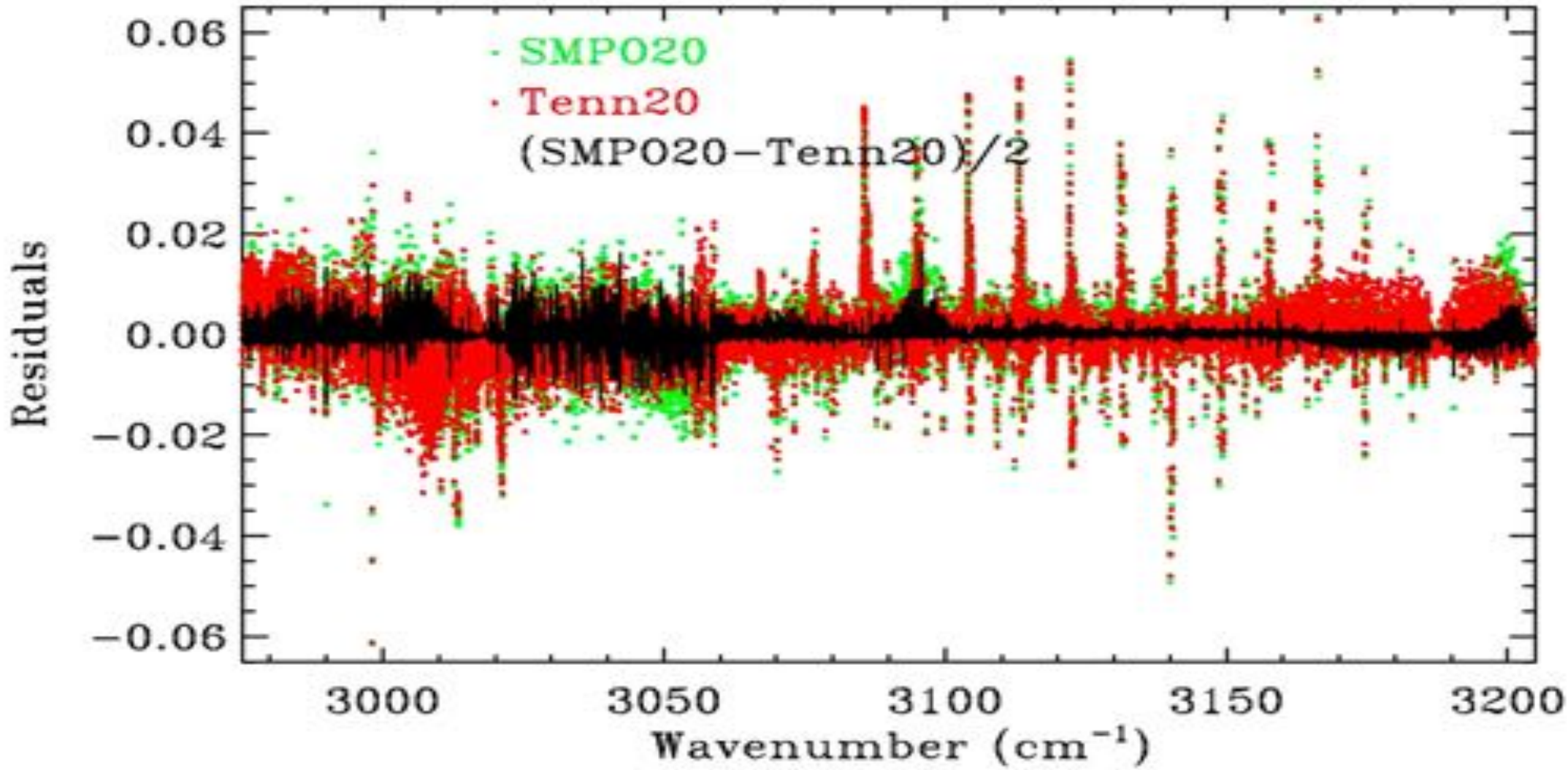






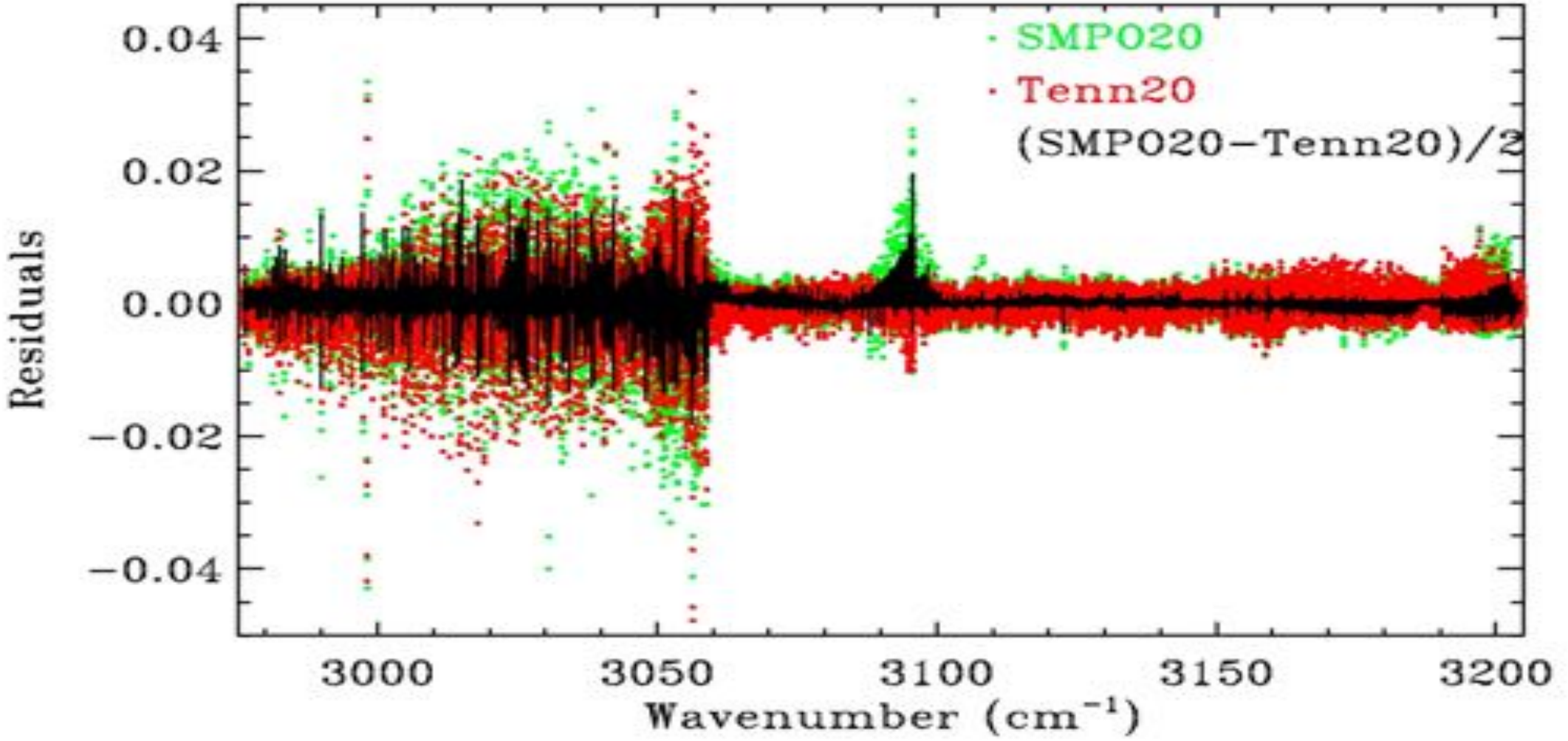
Compare these plots with fits using SMPO_20 in three previous slides. Fits with Tenn_20 look surprisingly (to me) similar to SMPO_20, even the problem at 2998.2 cm^{-1}, but Tenn_20 achieves smaller RMS residuals.

Comparing residuals obtained fitting 22.6km MkIV balloon spectrum



Largest residuals (Measured-Calculated) are due to neglect of CH_4 line-mixing, but these are the same between the two linelists. Tenn_20 linelist (red) clearly produces smaller residuals than SMPO_20 (green) in 3050 and 3200 cm^{-1} regions. Similarities in residuals are evident, e.g. at 2998.2 cm^{-1} and in O_3 band centered at 3187 cm^{-1}. Black line is difference of resids.

Comparing residuals obtained fitting 296K Kitt Peak lab spectrum



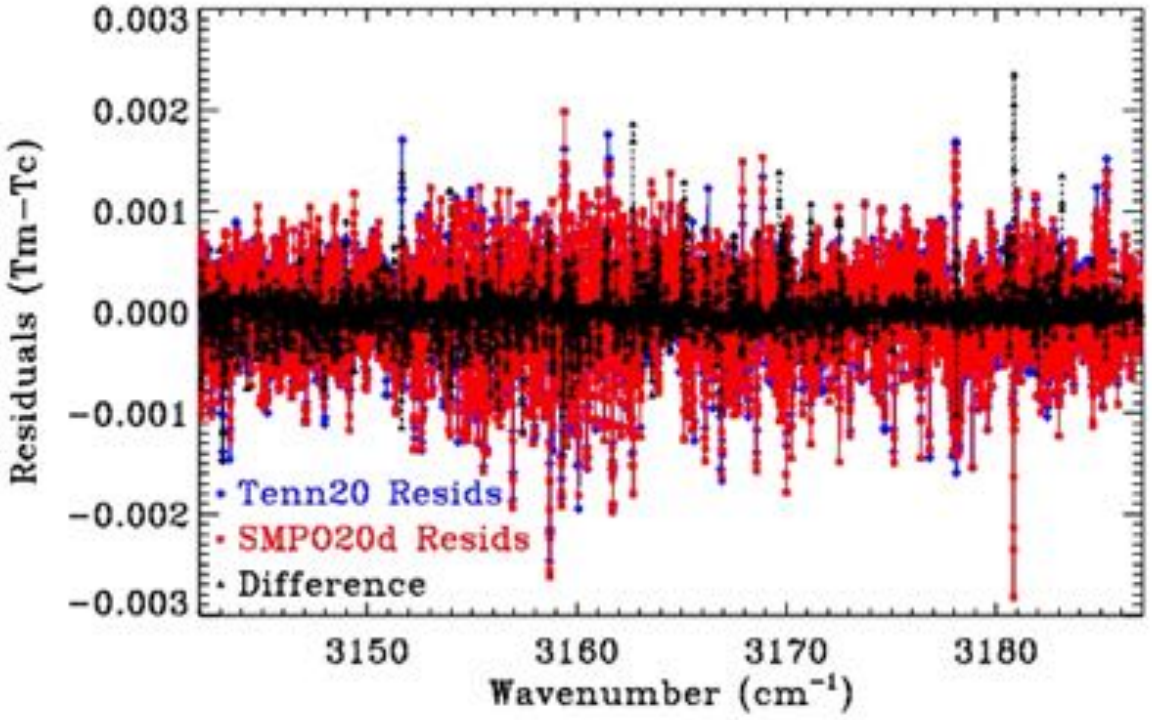
Same as previous slide, but for a 296K Kitt Peak lab spectrum (870902R0.004). Tenn_20 linelist (red) produces smaller residuals than SMPO_20 (green) in most of this region. Similarities in residuals are evident, e.g. at 2998.2 cm^{-1}. SMPO linelist produces mainly positive residuals 3090-3100 cm^{-1}, suggesting lines are too strong here, and mainly negative residuals 3050-3060 cm^{-1}, suggesting lines are too weak here, relative to other O_3 lines in region.

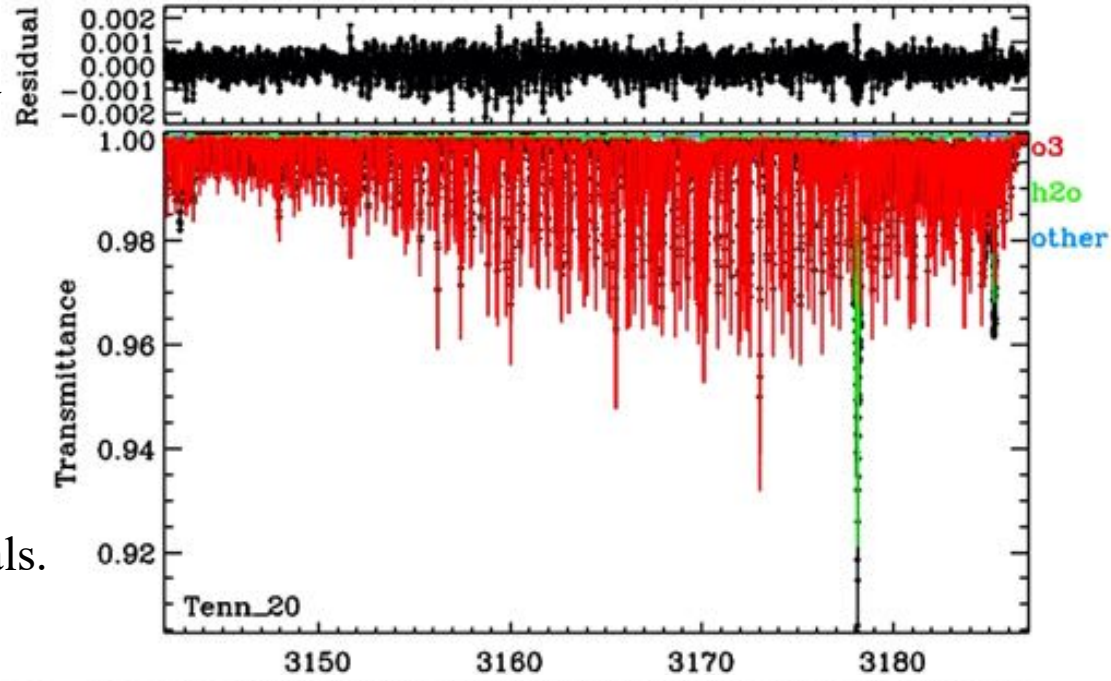
Fitting Residuals in Window #31: Tenn20 vs SMPO20d

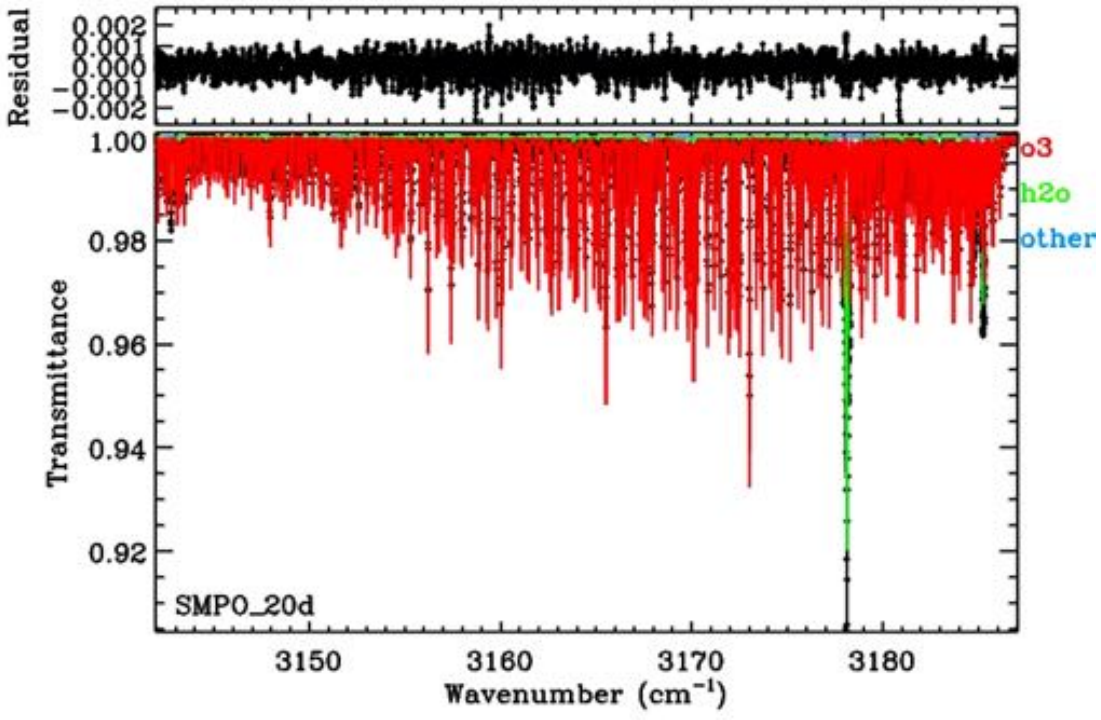
Upper Right: Fit to Kitt Peak Lab spectra using Tenn_20 linelist.
Peak residuals are 0.23% and RMS residual is 0.0728%

Lower Right: Fit to Kitt Peak Lab spectra using SMPO_20d linelist.
Peak residuals are 0.27% and RMS residual is 0.0738%.

Lower Left: Direct comparison of the Tenn_20 and SMPO_20d residuals.
The largest SMPO_20d residual occurs at 3180.85 cm^{-1}. See next slide.

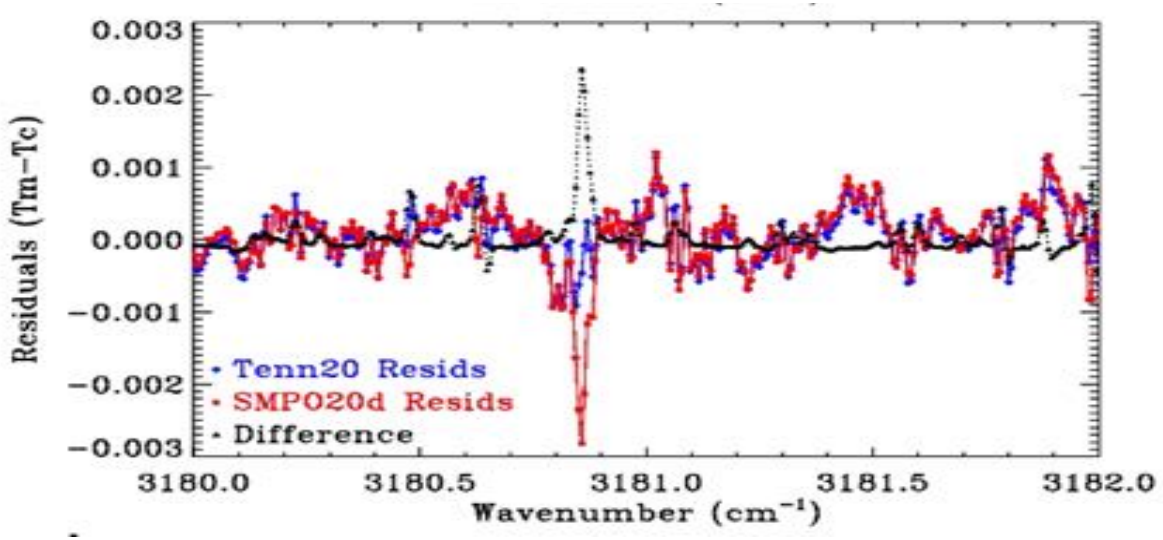






Fitting Residuals 3180-3182 cm^{-1}: Tenn20 vs SMPO20d

Upper Right: Fit to Kitt Peak Lab spectra using Tenn_20 linelist.
Lower Right: Fit to Kitt Peak Lab spectra using SMPO_20d linelist.
Large dip in residuals is seen at 3180.85 cm^{-1}
Below: Direct comparison of the Tenn20 and SMPO20d residuals.
The largest SMPO_20d residual at 3180.85 cm^{-1} is not present in fits using the Tenn_20 linelist. Excerpts from two linelists is further below:



Tenn_20:

```
31 3180.827600 1.871E-24 3.702E-03.07670.100  254.76280.720.000000
31 3180.829200 1.235E-23 3.202E-02.08600.105   30.20950.710.000000
31 3180.861200 1.096E-23 5.451E-02.07940.094  298.67220.710.000000
31 3180.871100 1.401E-23 3.509E-02.08500.106   21.29440.710.000000
```

SMPO_20d:

```
31 3180.827600 1.646E-24 3.693E-03.0767.0998  254.76280.720.000000
31 3180.829200 1.138E-23 3.195E-02.0860.1055   30.20950.710.000000
31 3180.862300 9.127E-24 4.950E-02.0794.0942  298.67210.710.000000
31 3180.871100 1.185E-23 3.186E-02.0850.1059   21.29440.710.000000
```