# HFC-23 (CHF$_3$) PSEUDO-LINELIST

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INTRODUCTION.

A CHF$_3$ pseudo-linelist has been created, based on laboratory absorption cross-section spectra measured by Chung [2006] covering 1100-1280 cm^{-1}. These spectra were re-normalized by Jeremy Harrison and Nick Allen at University of York, UK, to match the integrated band strengths of PNNL. This re-normalization involved adjustments by up to a factor 3!!

Figure 1 (below) shows a fit to the 266K spectrum. The strongest of the 6 fundamental vibrational modes have frequencies around 1150 cm^{-1}.

Figure 1: Example of fit to a CHF$_3$ lab spectrum from Chung [2006]
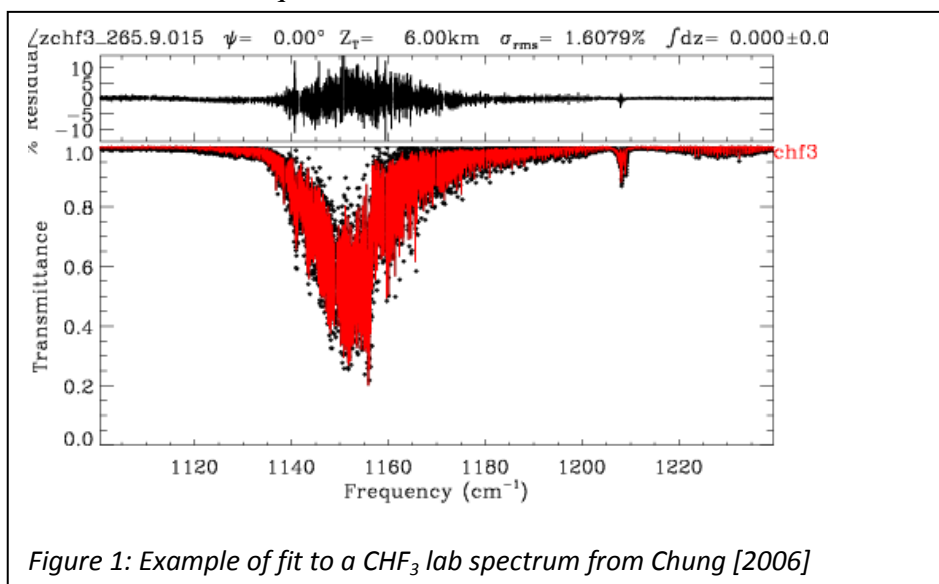
LABORATORY MEASUREMENTS

The measurements were performed in the lab of Varanasi at Stonybrook, where Chung was a Master's student. The assumed laboratory measurement conditions are tabulated below. Each measurement used the same cell of 9.28 cm length and a spectral resolution of 0.020 cm^{-1}. The air-broadened spectra cover the region between 1100 and 1280 cm^{-1} and have been over-sampled by a factor 8 (by Jeremy Harrison) providing a spectral point spacing of ~0.002 cm^{-1}. The pure gas spectra have a point spacing of ~0.013 cm^{-1}.

The Chung spectra cover 215 to 300K. The pure gas spectra are shown in red on the first 9 rows of Table 1 and cover pressures from 0.2 to 1.1 Torr. The air-broadened spectra, shown in green, cover pressures from 35 to 253 Torr. The last three rows (blue) represent PNNL spectra, which were not used directly in the derivation of the PLL due to their poor spectral resolution, but were included in the final analysis as a check on the integrated intensities.

Spectrum	nu_start	nu_end	npts	temp	tot_pres	p_pres	length	resn
chf3_300.4.024	1000	1250	18152	300.4	0.739	0.752	9.28	0.0200
chf3_300.1.023	1000	1250	18152	300.1	0.184	0.191	9.28	0.0200
chf3_282.7.018	1100	1240	10891	282.7	0.775	0.845	9.28	0.0200
chf3_282.9.017	1100	1240	10891	282.9	0.498	0.533	9.28	0.0200
chf3_282.7.016	1100	1240	10891	282.7	0.397	0.419	9.28	0.0200
chf3_265.9.015	1050	1250	14525	265.9	0.315	0.355	9.28	0.0200
chf3_265.9.014	1050	1250	14525	265.9	0.211	0.245	9.28	0.0200
chf3_232.2.009	1100	1280	11197	232.2	0.733	0.974	9.28	0.0200
chf3_215.9.004	1100	1280	11197	215.9	0.794	1.170	9.28	0.0200
chf3_300.2.022	1100	1280	89568	300.2	209.3	1.382	9.28	0.0200
chf3_300.1.021	1100	1280	89568	300.1	157.6	1.060	9.28	0.0200
chf3_300.1.020	1100	1280	89568	300.1	103.2	0.704	9.28	0.0200
chf3_300.1.019	1100	1280	89568	300.1	50.5	0.348	9.28	0.0200
chf3_256.4.013	1100	1280	89568	256.4	252.9	1.892	9.28	0.0200
chf3_256.4.012	1100	1280	89568	256.4	122.7	0.973	9.28	0.0200
chf3_256.4.011	1100	1280	89568	256.4	100.2	0.859	9.28	0.0200
chf3_256.4.010	1100	1280	89568	256.4	50.7	0.423	9.28	0.0200
chf3_232.4.008	1100	1280	89568	232.4	250.5	2.332	9.28	0.0200
chf3_234.9.007	1100	1280	89568	234.9	212.3	1.928	9.28	0.0200
chf3_233.3.006	1100	1280	89568	233.3	128.7	1.145	9.28	0.0200
chf3_233.8.005	1100	1280	89568	233.8	80.6	0.717	9.28	0.0200
chf3_214.4.003	1100	1280	89568	214.4	171.6	1.672	9.28	0.0200
chf3_214.5.002	1100	1280	89568	214.5	81.3	0.792	9.28	0.0200
chf3_215.5.001	1100	1280	89568	215.5	35.0	0.352	9.28	0.0200
chf3_pnnl_323	600	6500	97902	323.2	760.0	0.0038	19.96	0.1125
chf3_pnnl_298	600	6500	97902	298.2	760.0	0.0038	19.96	0.1125
chf3_pnnl_278	600	6500	97902	278.2	760.0	0.0038	19.96	0.1125

Table 1. Summary of laboratory measurement conditions.
Temp - Temperature in K;   P_tot - total pressure in Torr;
P_gas – CHF$_3$ partial pressure in Torr;   Length – cell length in cm

Despite the re-normalization of Harrison and Allen, large inconsistencies (up to 50%) were found to remain between the spectral absorption and the advertized measurement conditions. The absorber vmrs (but not their P/T) were therefore empirically further adjusted to bring the CHF$_3$ amounts retrieved from the Chung spectra into consistency with those from the PNNL spectra. It is therefore not clear why further adjustments were needed on top of Harrison's normalization. Perhaps when the absorption is saturated, the equivalent width method of normalization depends differently on the knowledge of the absolute pressure.

PARTITION FUNCTION.
The rotational partition function for HCFC-141b was assumed to be $(296/T)^{1.5}$. The vibrational partition function was calculated in the way it had been done for the ATMOS experiment, as described by Norton and Rinsland (1991). The following fundamental vibrational frequencies and degeneracies from Ceausu-Velcescu et al. [2003] were assumed:

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Freq.	3035	1141	700	1378	1158	508
Degen.	1	1	1	2	2	2

Table 2. Assumed CHF$_3$ fundamental vibrational frequencies and degeneracies

DESCRIPTION.
First, the cross-sections were converted back into transmittance spectra from knowledge of the cell length and gas concentrations. The resulting laboratory transmittance spectra were then simultaneously fitted (using the GFIT algorithm). At each line frequency, an effective strength

and ground-state energy were derived by simultaneous non-linear least squares fitting to the 23 spectra (chf3_256.4.013 was omitted due to poor fits), subject to the constraint that they were both positive. The ABHW, SBHW, and TDPBHW were assumed to be 0.06 cm^{-1}/atm, 0.10 cm^{-1}/atm and 0.70, respectively. Considering the 0.02 cm^{-1} resolution of the laboratory spectra, a pseudo-line spacing of 0.005 cm^{-1} was considered appropriate. The resulting pseudo-linelist consists of 28,000 lines covering the 1100-1240 cm^{-1} region.

DISCUSSION
The fits to the lab spectra (some have >4% rms) are poorer than those of any other gas that I have created pseudo-lines for. Clearly there is some inconsistency between the various Chung spectra which is preventing a single linelist from fitting them all well. I can't tell whether the inconsistency is due to the spectra themselves being of poor quality or whether it lies with the advertised P/T/VMR being wrong.

For the generation of the pseudo-linelist, I used only the 24 Chung spectra, not the PNNL (insufficiently high spectral resolution). The PNNL spectra were simply "along for the ride" in my analysis. I manually adjusted the assumed absorber amounts of each of the Chung spectra (see chf3_all.lst) in order to bring them in line with each other, and with the PNNL spectra. Some of the changes that I made were quite large, up to 50% for the cold spectra. I made no adjustment to the assumed conditions (P/T) of the PNNL spectra.

The good news is that the resulting pseudo-linelist produces vmr scale factors of 1.0046, 1.0015, and 1.0028 when I use it to fit the three PNNL spectra at 323, 298, and 278K, respectively. Of course, this wasn't an accident, I had to work quite hard fudging the Chung vmrs to achieve this. And the resulting linelist give a fair representation of the shape of the absorption seen in the Chung spectra, especially the pressure broadened ones.

The bad news is that 37% of the pseudo-lines have an E" of zero, which means that my program would have liked to have made it negative. In generating pseudo-linelists for other gases in the past, I've never had anywhere near such a high % before. It suggests that something isn't right with the Chung spectra or their advertised T/P/vmr conditions. And it calls into question the T-dependence of the resulting pseudo-lines. That said, the CHF$_3$ retrievals from the 3 PNNL spectra over the 278-323K temperature range are consistent to better than 0.2%.

FITS TO ATMOSPHERIC SPECTRA
Despite poor fits to lab spectra, I went ahead and used the CHF$_3$ pseudo-linelist to fit the MkIV balloon spectra. I fitted a window centered at 1155.0 cm^{-1} of width 37.2 cm^{-1}. Besides CHF$_3$, fitted gases include N$_2$O, O$_3$, CH$_4$, HDO, CCl$_2$F$_2$, HCFC-141b, HCFC-142b, and PAN.
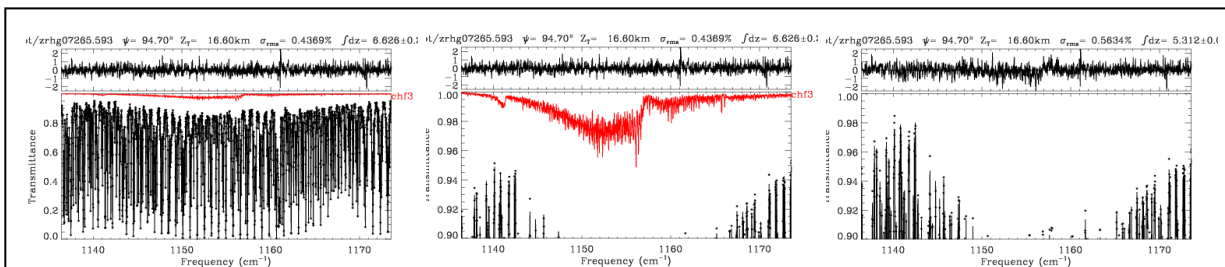
Figure 2. Fits to a MkIV atmospheric spectrum acquired in Sep 2007 at 16.6 km tangent altitude. Red trace shows CHF$_3$ contribution to the spectrum. Right panel illustrates the effect of neglecting CHF$_3$, which degrades the spectral fit from 0.437% to 0.563%.

The good news is that it definitely improves the spectra fits in the 1155 cm^{-1} region and that the retrieved CHF$_3$ vmrs are positive and increase with time from ~10 ppt in 1990 (blue) to 30 ppt in 2007 (red). There is also a tendency for large spikes in the retrieved CHF$_3$ at float altitude, which is probably contamination from the balloon or parachute.
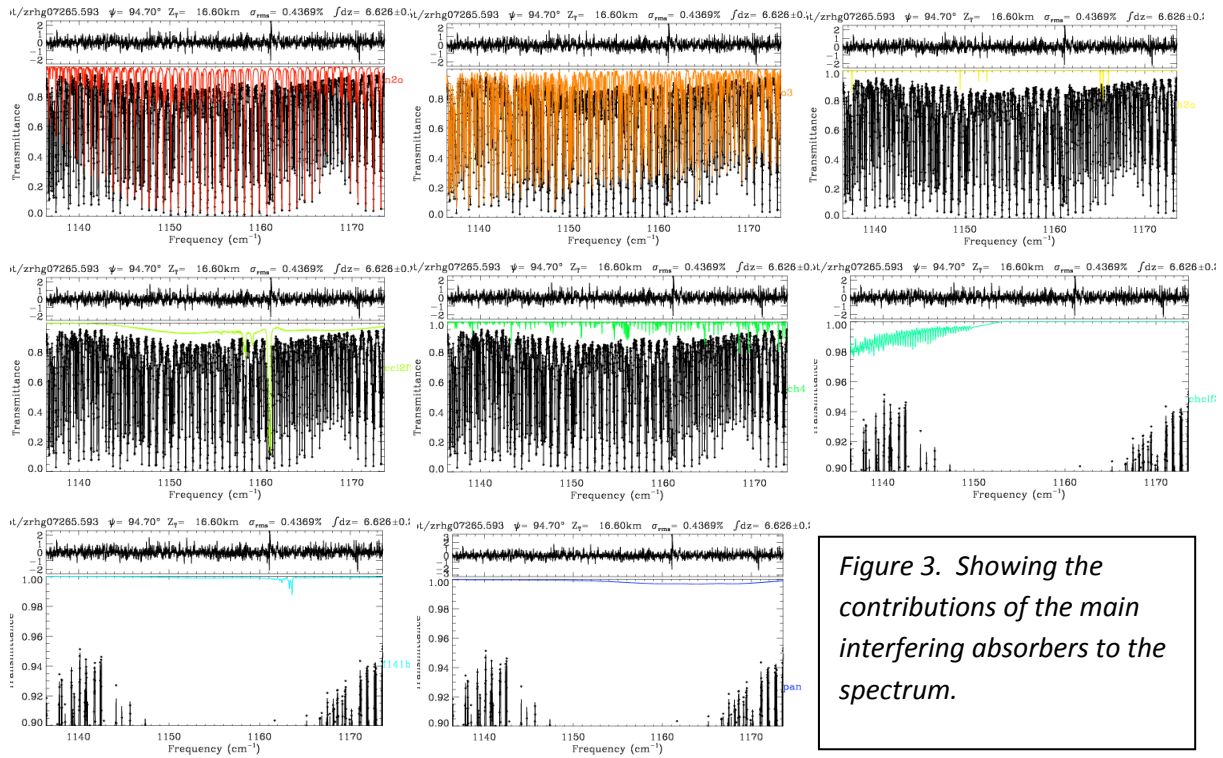

Figure 3. Showing the contributions of the main interfering absorbers to the spectrum.

CCl$_2$F$_2$ is a particularly strong absorber in this region. For example, in spectra where the CHF$_3$ absorption is strongest, at say 3-4% deep, the CCl$_2$F$_2$ absorption is 90% deep in the Q-branch and 10% deep in the P-branch. So a small error in the characterization of the CCl$_2$F$_2$ absorption will have a big impact on the retrieved CHF$_3$. This is especially true in the spectra from the 1990s when the CCl$_2$F$_2$ was higher than today, but the CHF$_3$ was much lower.
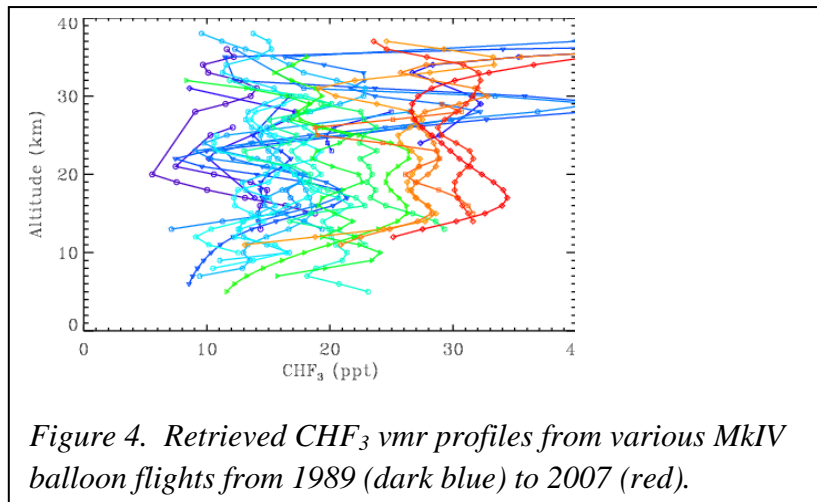

Figure 4. Retrieved CHF$_3$ vmr profiles from various MkIV balloon flights from 1989 (dark blue) to 2007 (red).

## APPENDIX – SPECTRAL FITS TO LABORATORY SPECTRA

The figures below show how well the pseudo-linelist represents the laboratory spectra. The rows represent the different temperatures (top=253K; middle=270K; bottom=287K). The columns represent the spectral windows covered by the pseudo-linelist. In fact, each interval is slightly wider than covered by the pseudo-linelist to allow estimation of the fitting error due to the truncation of the linelist. I tried to keep this $< 0.5\%$.

Due to the large adjustments that were needed to the original cross-sections, I would not trust the absolute band intensities to better than 50%. Given the large number of pseudolines with E"=0, the fidelity of the T-dependence is also highly suspect. Clearly, additional laboratory measurements are needed to more accurately quantify atmospheric CHF_3.
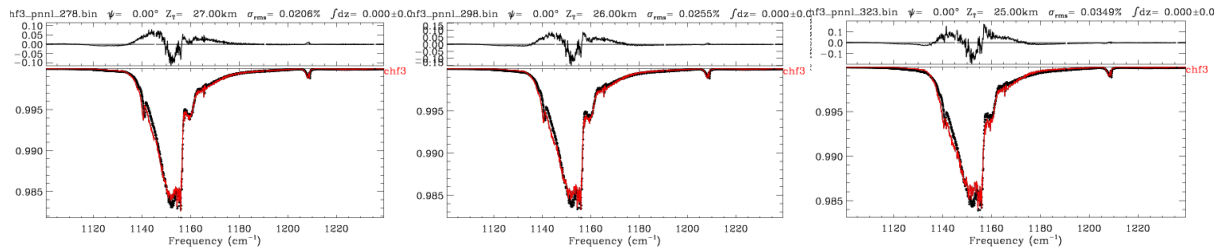
Fits to Self-Broadened Lab Spectra (low-pressure)
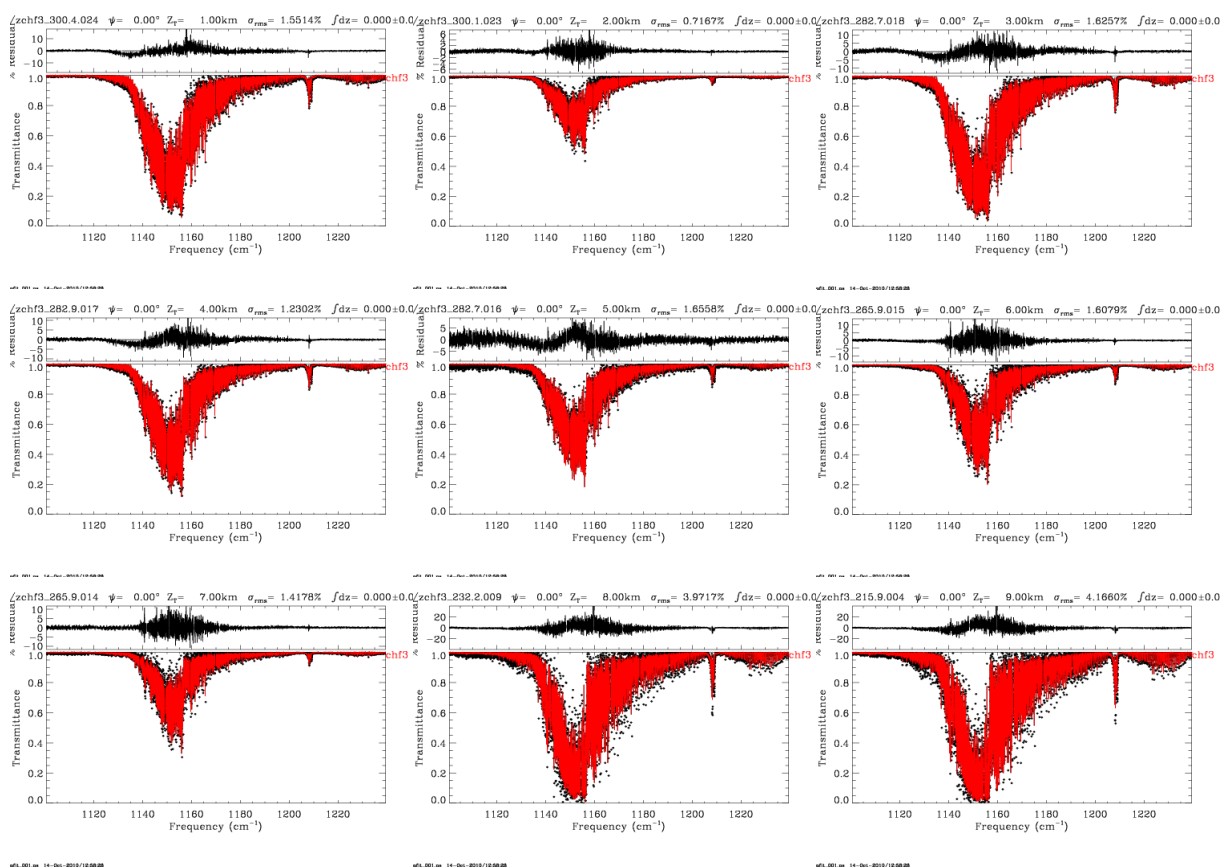
Fits to Air-Broadened Lab Spectra
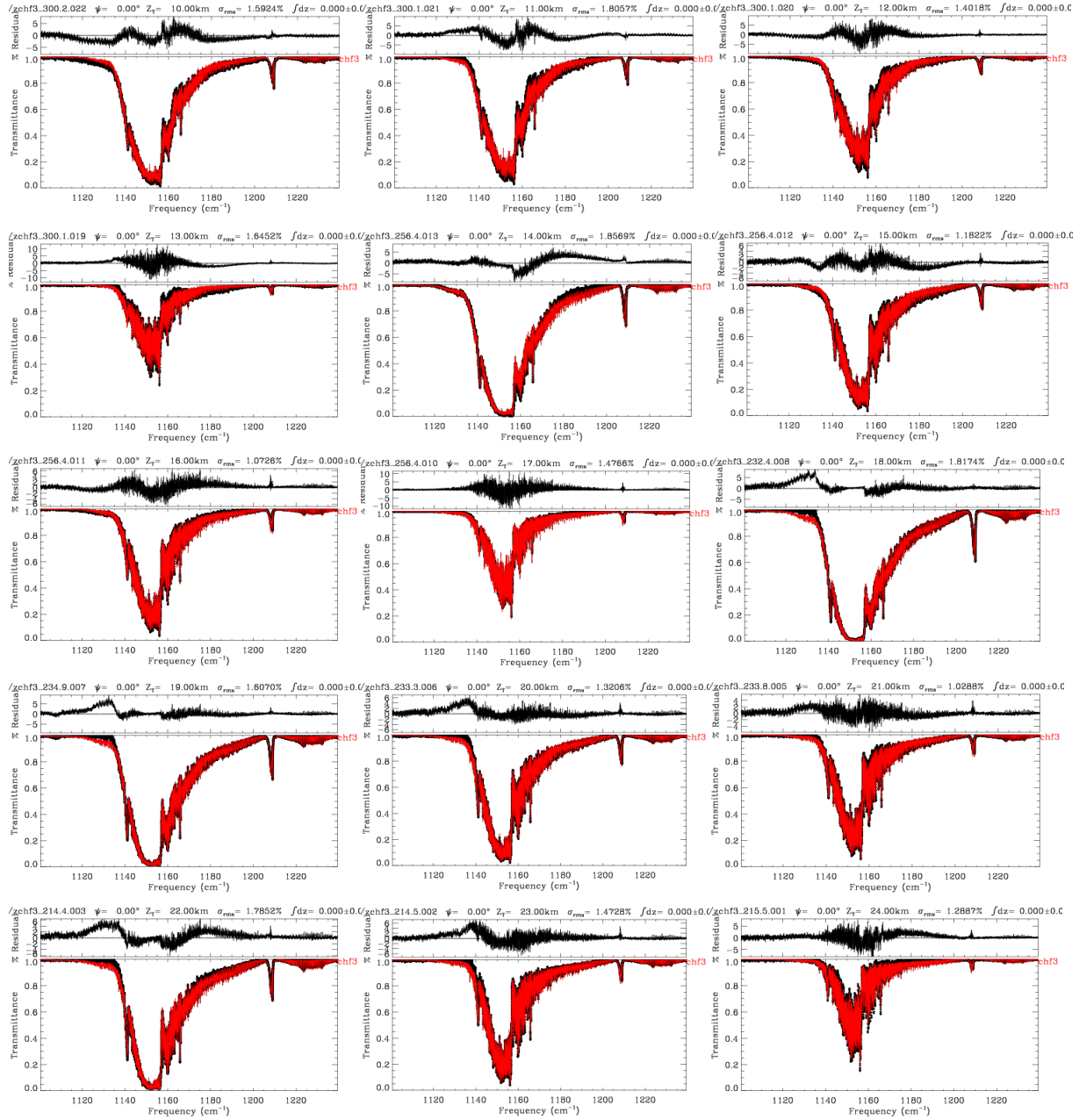
Fits to PNNL Lab Spectra (1 atm.)

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