New HCFC-22 / $CHClF_2$ Empirical Pseudo Line-List

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A new EPLL was created covering all significant absorption in the 560 to 3070 cm^{-1} range. This new EPLL was based on fits to the 99 spectra in the Supplemental folder of the HITRAN website which include:

- 3 spectra from Sharpe (2001) PNNL)
- 9 spectra from Clerbaux (1993) U Brussels
- 57 spectra from Varanasi (2000), SUNY
- 30 spectra from Harrison (2016), U Leicester

Note that although there are more Varanasi spectra, these are much narrower than Harrison's, such that overall, the number of windows fitted to Harrison's spectra exceeds the number of fitted to Varanasi spectra by a factor 3.

The majority of these spectra were measured (or became available) after the old EPLL was created in 1994. The new EPLL has:

- Extended wavenumber coverage, to include the ν_5 band centered at 596 cm^{-1} and the ν_1 band centered at 3022 cm^{-1}.
- Higher line density. In total the new EPLL has 109,300 lines as compared with 21,429 with the old EPLL
- Improved spectral fitting residuals and better band-to-band consistency of retrieved HCFC-22

HCFC-22 Empirical Pseudo Line-Lists: History

Old EPLL created in 1994 covers:

- 776 -850 cm^{-1} at line spacing of 0.00742 cm^{-1} (9977 lines) from cross-sections of McDaniel (1991) & Varanasi (1992; 1994)
- 1080-1150 cm^{-1} at line spacing of 0.010 cm^{-1} (7001 lines) from cross-sections of McDaniel (1991)
- 1290-1335 cm^{-1} at line spacing of 0.010 cm^{-1} (4501 lines) from cross-sections of McDaniel (1991)

McDaniel et al. (1991) measured three windows (780-840; 1080-1150; 1290-1335 cm^{-1}) at 0.03 cm^{-1} resolution at six temperatures $203 < T < 293$ K, so 18 spectra. Note: they mis-named HCFC-22 as "CFC-22" in the title of their paper.

Varanasi (1992) measured 8 spectra at $216 < T < 292$K with $53.4 < P < 1011.5$ mbar (cfc22-old)

Varanasi et al. (1994) measured 7 spectra at $216 < T < 294$K with $41 < P < 760$ Torr. (cfc22-new)

For some forgotten reason, when making the PLL in 1994 we did not use the measurements of Clerbaux et al. (1993), who measured spectra at T = 253, 273, & 287 K, all P=0. These spectra each covered the 765-855, 1060-1210, and 1275-1380 cm^{-1} regions at a spectral resolution of 0.03 cm^{-1}. These data are in 3 spectra x 3 temperatures = 9 files.

Since then, Harrison measured 30 lab spectra each covering $730 < \nu < 1380$ cm^{-1} with $191 < T < 294$ K and $7.5 < P < 762$ Torr.

Also, 57 Varanasi spectra are now available from the HITRAN website (not sure how these relate to the 1992 & 1994 spectra).

Only the Harrison (2016) and the Clerbaux (1993) cross-section spectra are available on the HITRAN website (Main folder).

The HITRAN Supplemental folder, however, also contains the Varanasi x-sections (57 files covering 2 windows) and the three PNNL spectra). So, everything except McDaniel.

HCFC-22 Spectral Cross-Sections: HITRAN Supplemental folder

The HITRAN website (Main folder) hosts the 30 Harrison (2016) cross-section spectra, each covering the entire 730-1380 cm^{-1} region, and 9 Clerbaux (1993) cross-section spectra covering the three strongest bands over 765-1380 cm^{-1} at 253, 270, 287K.

The HITRAN Supplemental folder, however, also hosts the Varanasi x-sections: 57 files covering 2 windows (760-850 & 1070-1195 cm^{-1}) at a variety of temperature and pressures. It also host the three PNNL spectra (each covering 550-6500 cm^{-1}) T=278, 296, 323K. This gives a total of 99 spectra (3 Sharpe, 9 Clerbaux, 30 Harrison, 57 Varanasi). So, everything except McDaniel.

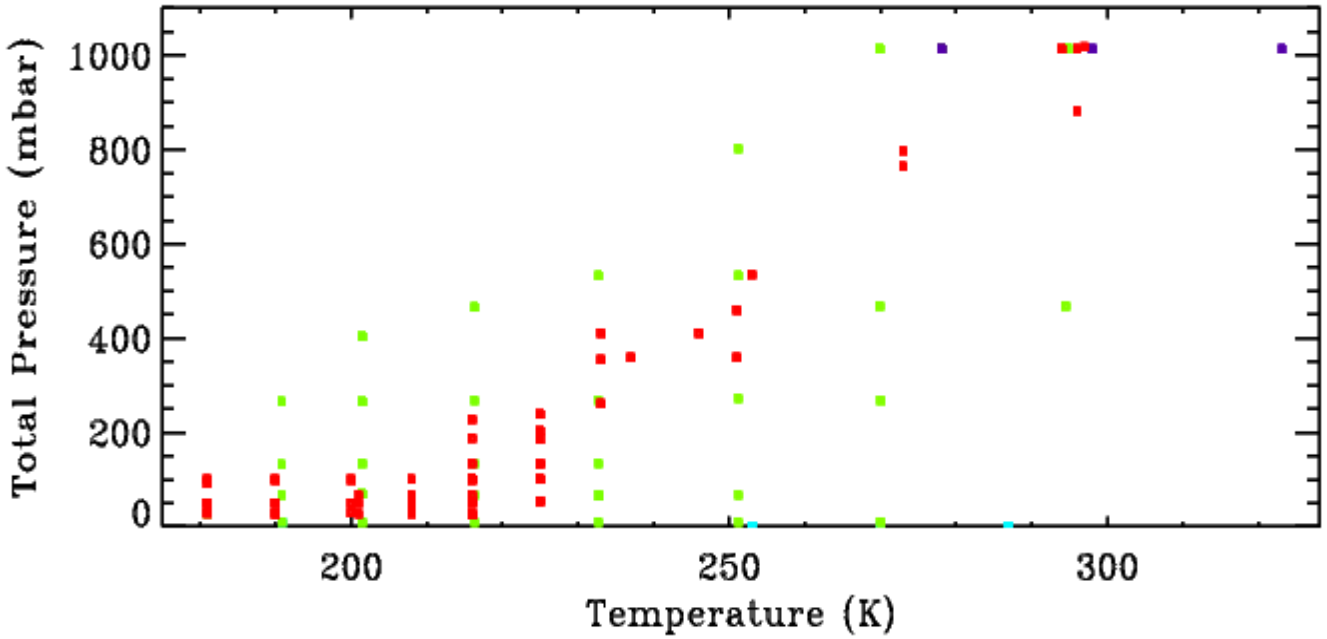
These data are all in a 2-column (wavenumber, cross-sec) asci file, with the measurement conditions (wavenumber range, temp, pres, resn, broadener) embedded into the file name. e.g., "CHClF2_216.3K-50.8Torr_730.0-1380.0_0.01_air_87_57.txt".

Unclear why there are now additional Varanasi spectra. These are labeled "private comm 2000" on the HITRAN website, which is later than the spectra that JPL received from Varanasi in the mid-1990s.

Figure (right) shows the T,P conditions for the four lab data-sets used in this analysis:

- Sharpe/PNNL spectra are purple
- Clerbaux spectra are cyan
- Harrison spectra are lime green
- Varanasi spectra are red

The Harrison spectra cover the most territory in P-T space, but not all atmospheric conditions are represented. For example, P=1 atm with T < 240K are common in the boreal winter. Conversely, conditions never encountered in the atmosphere (270 K, 7.5 Torr) were measured in lab.



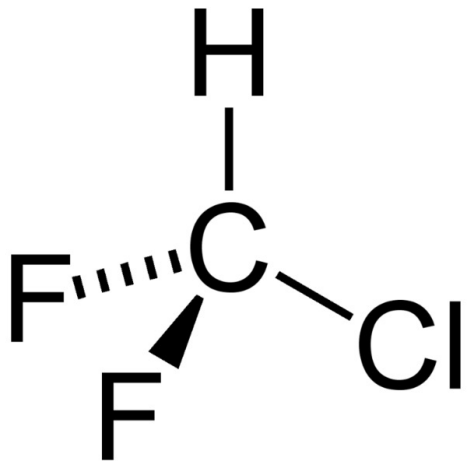
$CHClF_2$ Fundamental Modes and Partition Function

Has 5 atoms and therefore 3N-6 = 9 fundamental vibrational modes all with a degeneracy of 1.

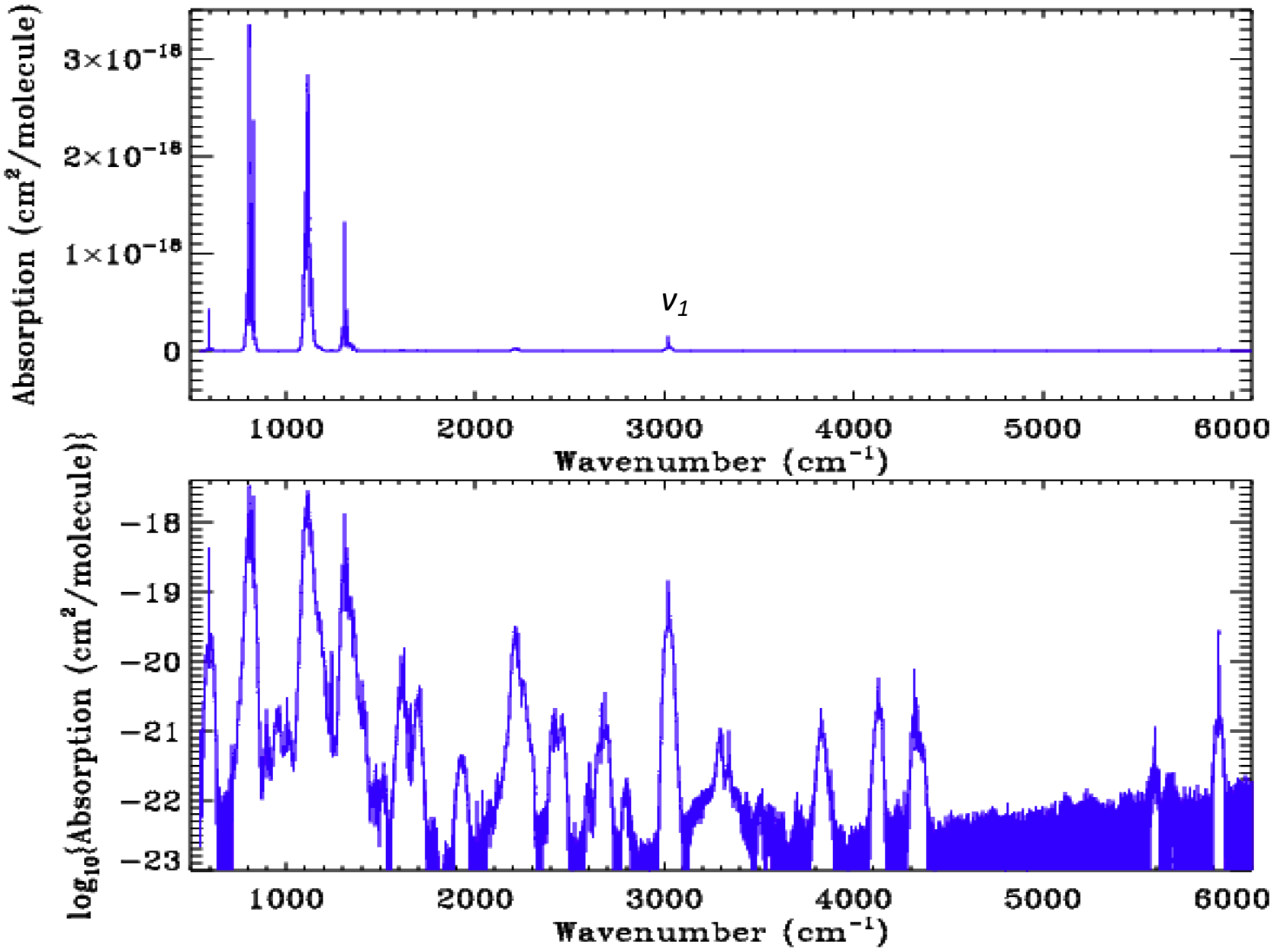
The rotational partition function is assumed to be $(296/T)^{1.5}$

The vibrational partition function was computed from the following 9 fundamental frequencies.

ν_1 3022 cm^{-1}
ν_2 1313 cm^{-1}
ν_3 1109 cm^{-1}
ν_4 809 cm^{-1}
ν_5 596 cm^{-1}
ν_6 413 cm^{-1}
ν_7 1352 cm^{-1}
ν_8 1127 cm^{-1}
ν_9 366 cm^{-1}



Sharpe (PNNL) $CHClF_2$ Absorption Spectrum at 278K and 1 atm: 500-6100 cm^{-1}



These figures provide an overview of the $CHClF_2$ spectrum.

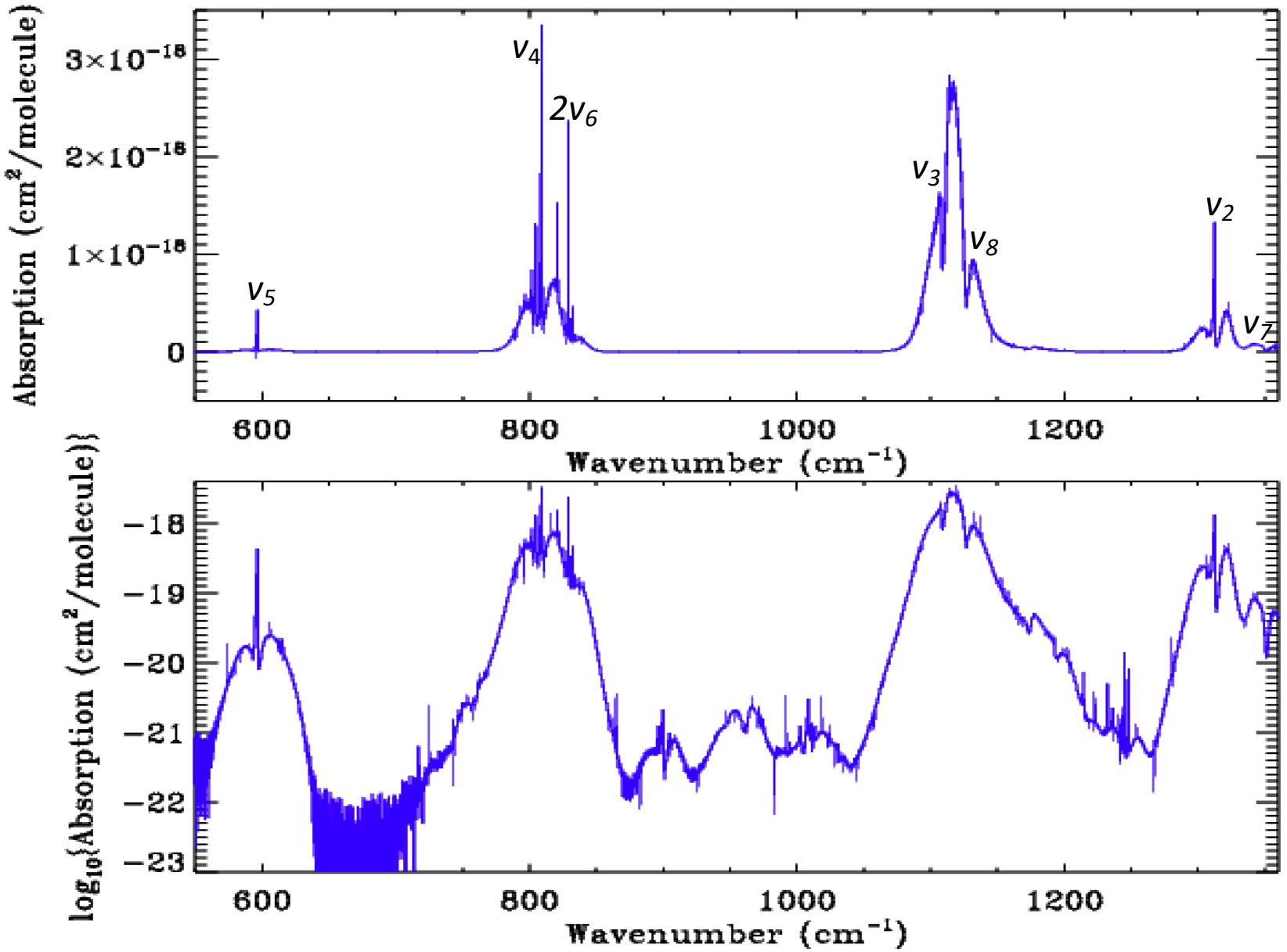
Upper panel: absorption on linear scale.

Lower panel: absorption on log scale.

The strongest bands lie between 800 and 1350 cm^{-1}.

The $\mathbf{v}_1$ band (C-H stretch) near 3000 cm^{-1} is quite weak.

Sharpe (PNNL) $CHClF_2$ Absorption Spectrum at 278K and 1 atm: 550-1360 cm^{-1}



Zooms into the low wavenumber regions where the strongest bands are located.

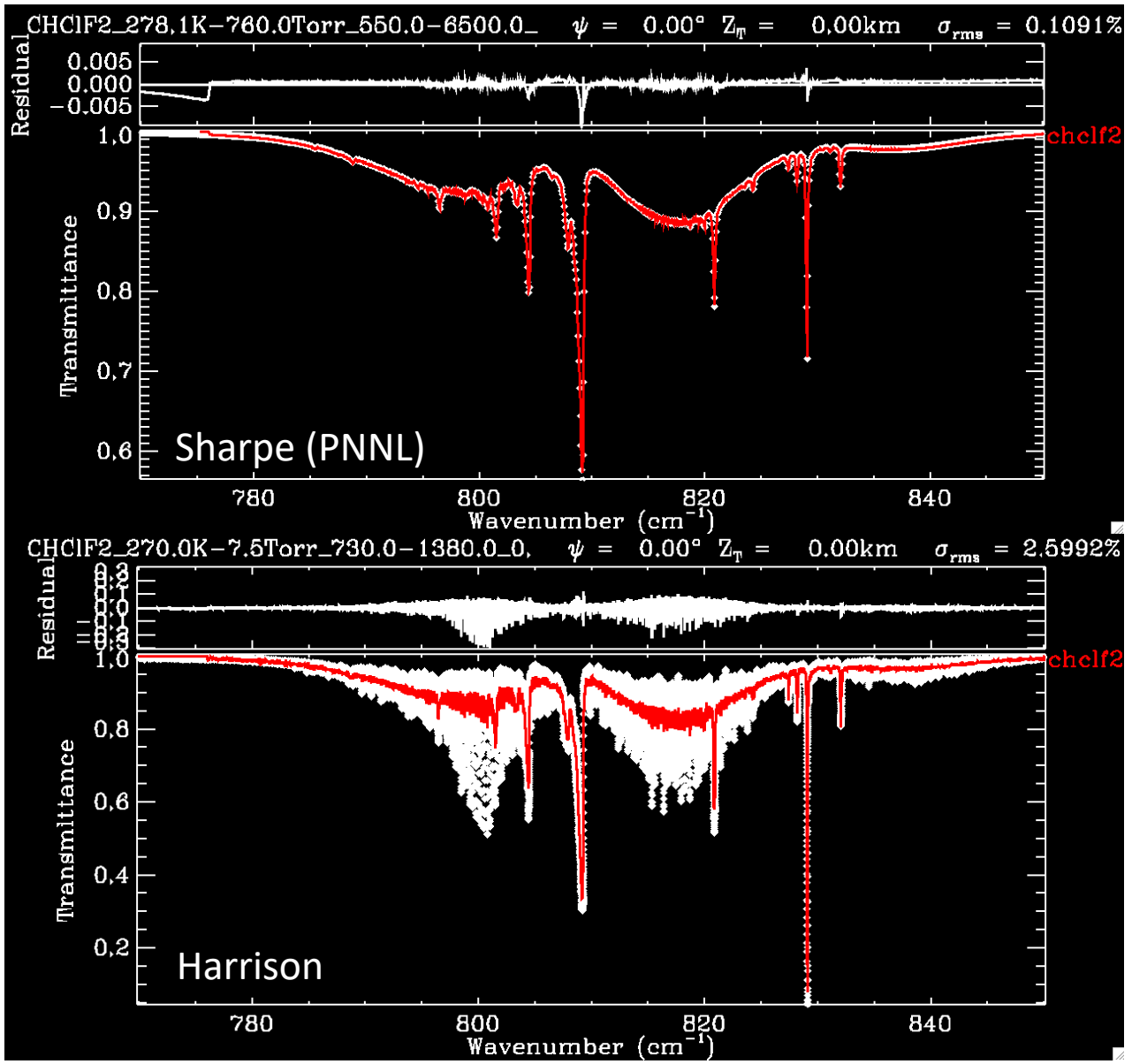
Upper panel: absorption on linear scale.

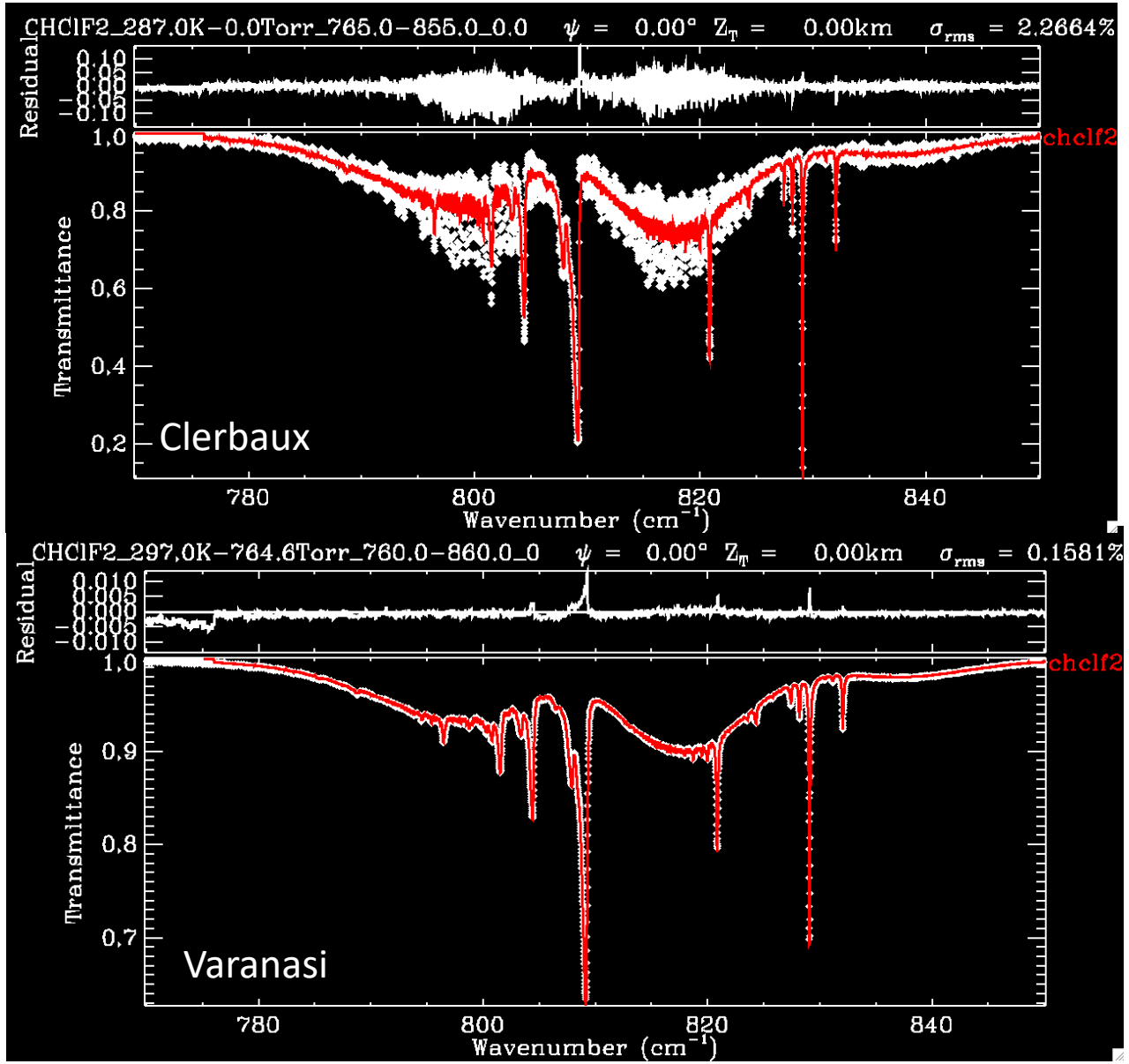
Lower panel: absorption on log scale.

The overlapping ν_3 and ν_8 bands around 1100 cm^{-1} have the strongest integrated absorption, but few sharp features, even at lower pressures.

The ν_4 and $2\nu_6$ bands have the deepest and narrowest absorption features and therefore provide the best opportunity for accurate atmospheric measurements.

Examples of Fits to Lab spectra using old 1994 HCFC-22 EPLL





Old EPPL did nice representation of Q-branches, but smoothed the P- and R-branch structure present at low pressure.

Also, old EPLL had no lines below 775 cm^{-1} and therefore missed the low wavenumber far-wing contribution (see left panels).

Retrieved Frequency Shifts: 797-830 cm^{-1} window

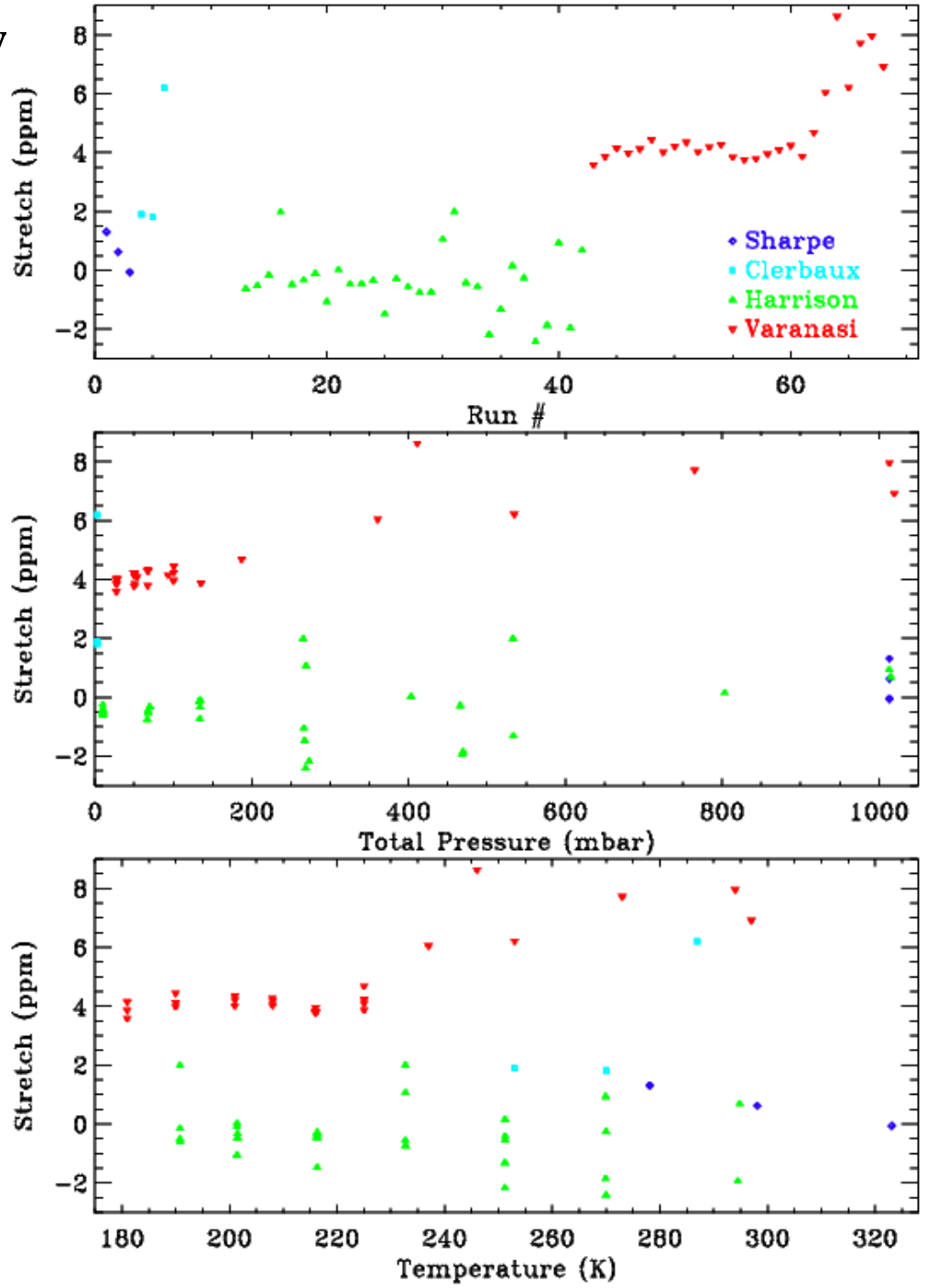
Frequency shifts were computed to look for systematic differences between the spectral calibration of the datasets. Uncorrected, such inconsistencies would broaden the spectral features in an EPLL derived using all spectra.

The 797 to 801 cm^{-1} and 1143-1145 cm^{-1} regions have sharp symmetrical spectral features with 0.26 cm^{-1} spacing. These are good for evaluating the relative spectral calibration, at least for the lower pressures. The Q-branches should be avoided because they are asymmetrical and their shape is T-dependent, depends on the assumed E", and is affected by line-mixing. That said, in the high-P spectra individual lines are smoothed out and only the Q-branches contain spectral structure.

In the figures shown on right:

- PNNL spectra are purple (runs 1-3)
- Clerbaux spectra are cyan (runs 4-6; 7-9, 10-12)
- Harrison spectra are lime-green (runs 13-42)
- Varanasi spectra are red: 760 - 860 cm^{-1} (runs 43-68)
  1070 - 1195 cm^{-1} (runs 69-99)

The three panels plot the retrieved stretches versus an arbitrary run #, the pressure of the lab measurement, and their temperature.



Retrieved Frequency Shifts: 797-830 cm^{-1} window

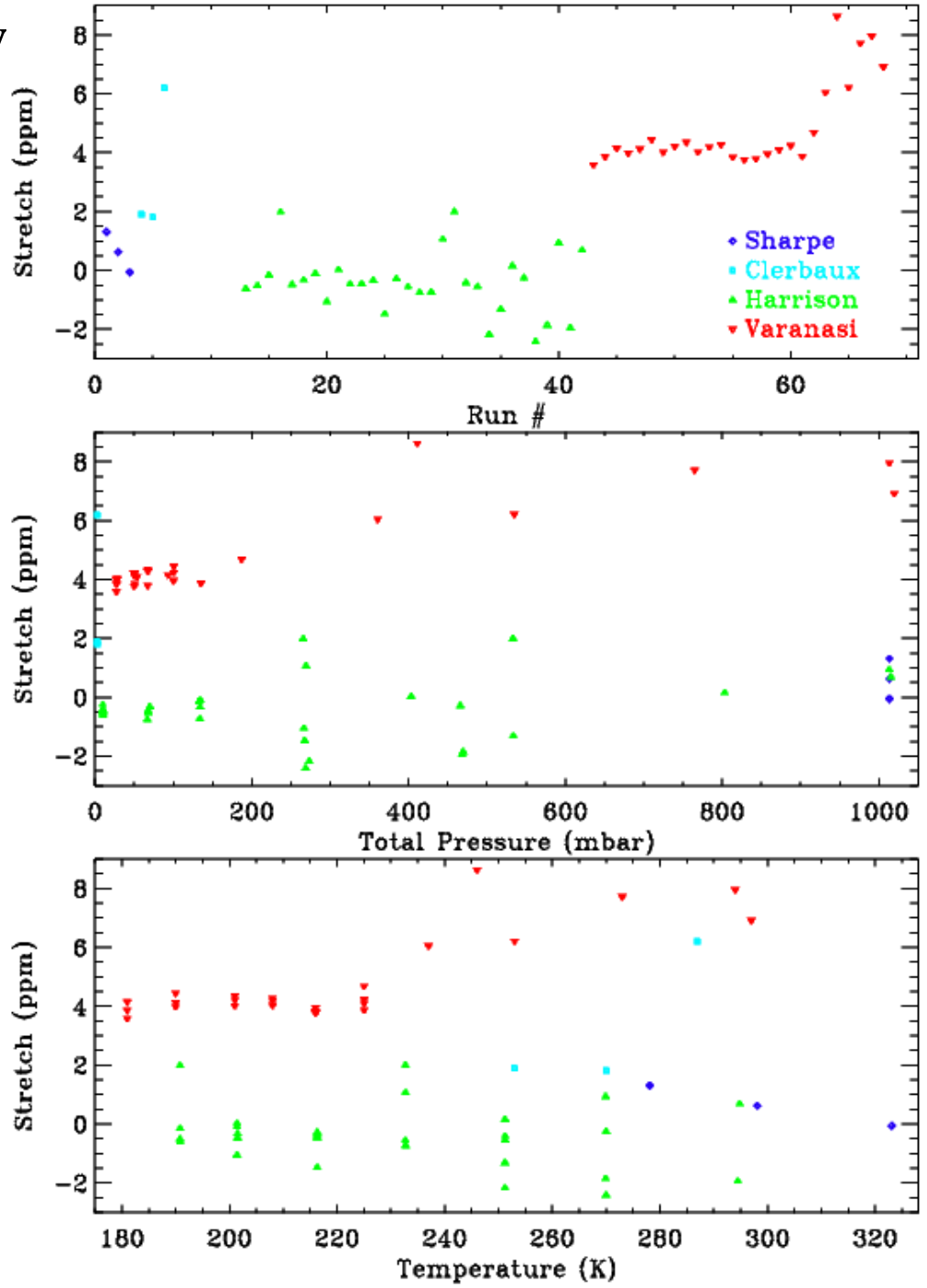
The Varanasi spectra have stretches of about +4 ppm for the low-P spectra increasing to +8 ppm for the high-P spectra.

The Harrison spectral stretches range from -2 to +2 ppm with no P-dependence, suggesting that the assumed pressure shifts, -0.0011 cm^{-1}/atm, in this region, are okay.

No obvious T-dependence to the shifts suggesting that derived E"s are OK.

We cannot say that the datasets with shifts closest to zero have the best spectral calibration. We cannot say anything about the absolute spectral calibrations from these lab data because there are no lines in the spectra whose positions we know accurately.

Harrison (2016) claim that their spectral calibration was verified using a low-P N_2O cell recording lines at around 1200 cm^{-1}, interspersed with the $CHClF_2$ measurements, so that their absolute spectral calibration is good (or as good as the N_2O lines) and that the discrepancy is entirely Varanasi's fault, which I can believe. This does not explain the large scatter of the shifts retrieved from the Harrison spectra (neglect of LM in my analysis?).



Pseudo-Line Spectroscopic Parameters

The pseudo-line intensities and E" values were adjusted based on the spectral fitting residuals, and their T-dependence. For each pseudo-line, the fractional fitting residual at the center wavenumber was plotted versus x=1/T for all 99 spectra and a straight line was fitted. The intercept at x=1/296K gives the fractional adjustment to the line intensity, and the gradient gives the adjustment to the E". The 99 lab spectra (or those available in a given window) were then refitted by GFIT using the adjusted EPLL. This procedure was iterated until the improvement to the RMS spectral fits became negligible.

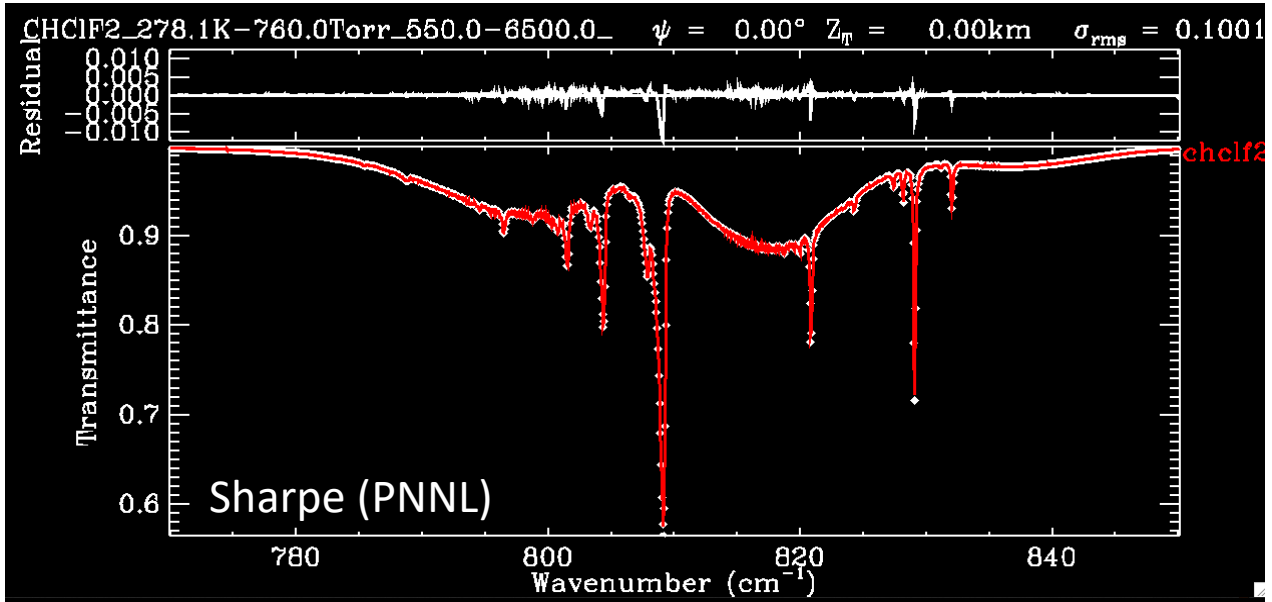
Air-broadened widths were determined from the narrow P-branch lines of the ν_4 band around 800 cm^{-1} and also from the R-branch lines of the ν_8 band around 1144 cm^{-1}. These are the narrowest features in the entire spectrum. An air-broadened width of 0.07 cm^{-1}/atm was found to give the best fits in these places and was adopted throughout. In regions without narrow lines, the adopted widths don't matter (provided the line intensities are re-determined after the widths are chosen).

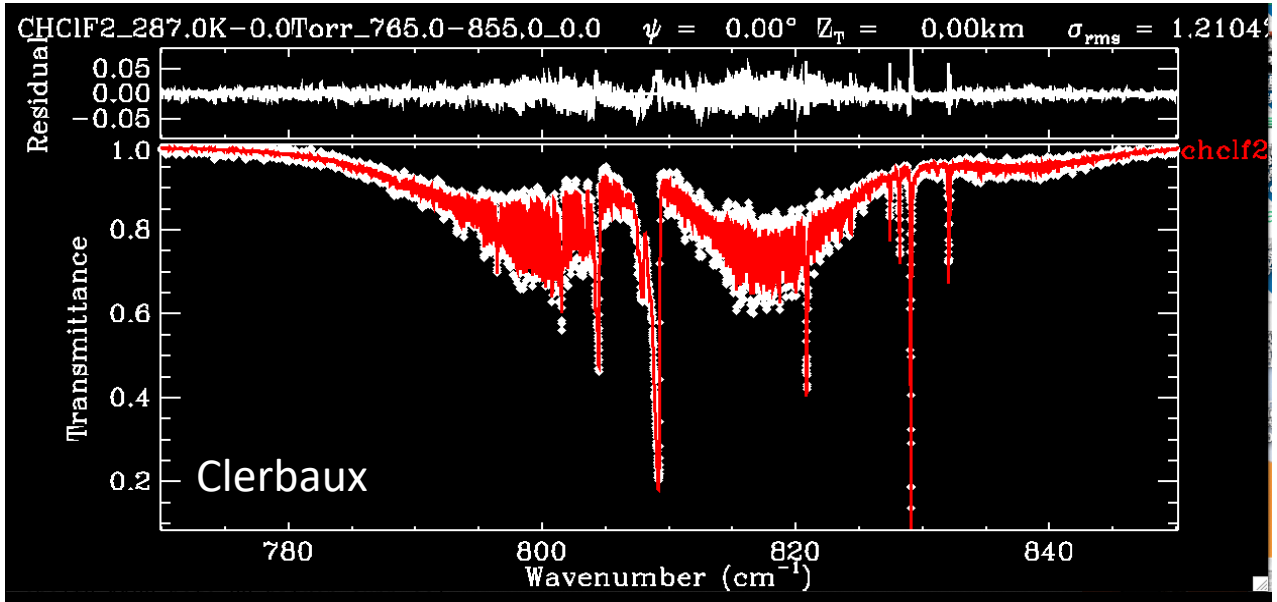
It was seen that this choice of width caused a dip in the high-pressure residuals centered on each Q-branch, presumably due to the neglect of $CHClF_2$ line-mixing in the GFIT forward model. This effect was particularly pronounced in the $2\nu_6$ Q-branch at 829.05 cm^{-1}, the deepest feature in the infrared, which is used in atmospheric retrievals. To mitigate this effect, the widths were reduced by up to 40% in the centers of the six Q-branches and then the intensities and E" values were re-determined.

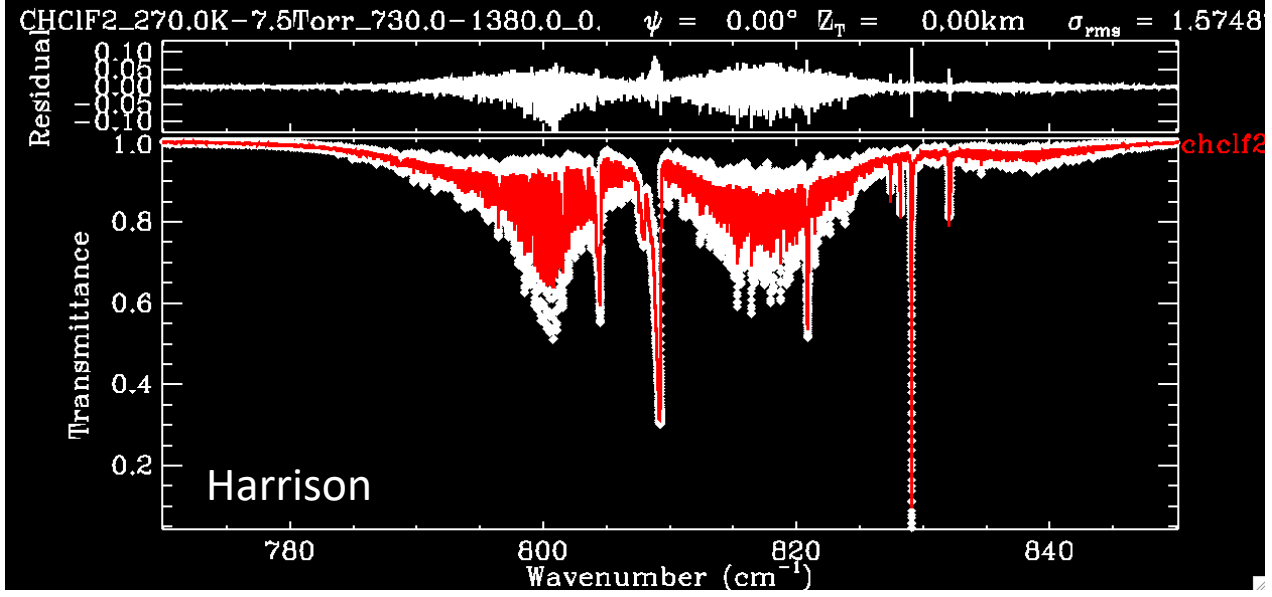
There is no information about self-broadened widths in these datasets (no pure gas spectra at higher pressures) so an arbitrary value of 0.075 cm^{-1}/atm was adopted.

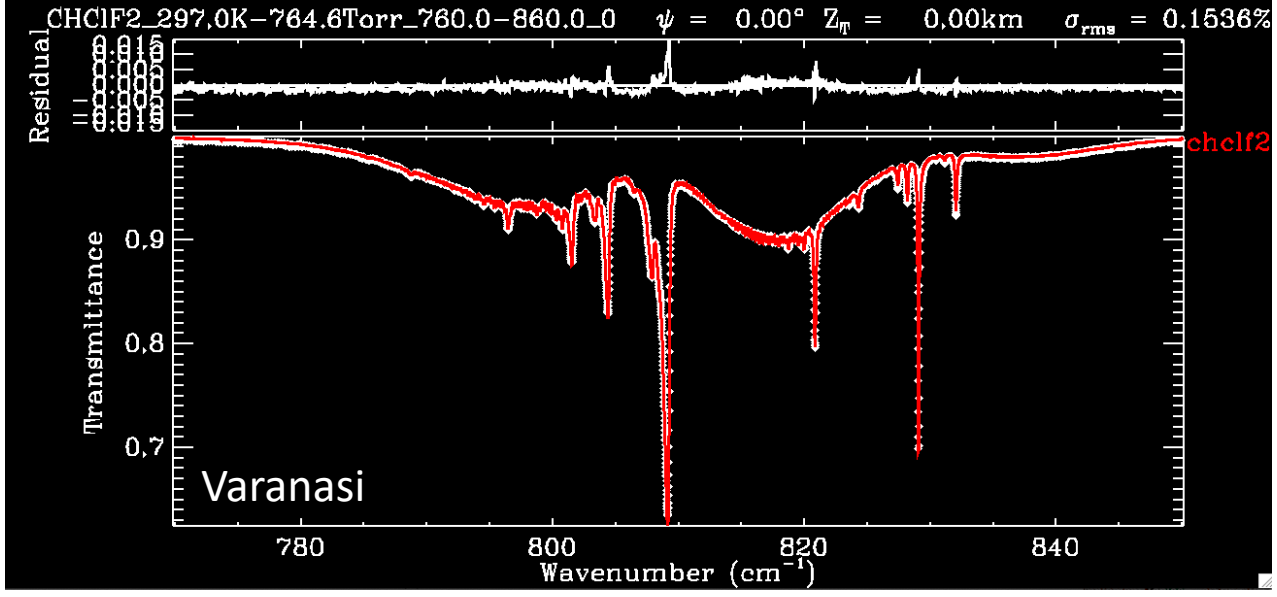
A pressure shift of -0.0011 cm^{-1}/atm was adopted for ν<1500 cm^{-1}, and -0.0040 cm^{-1}/atm for the ν>3000 cm^{-1}.

Examples of Fits to Lab spectra using new HCFC-22 EPLL





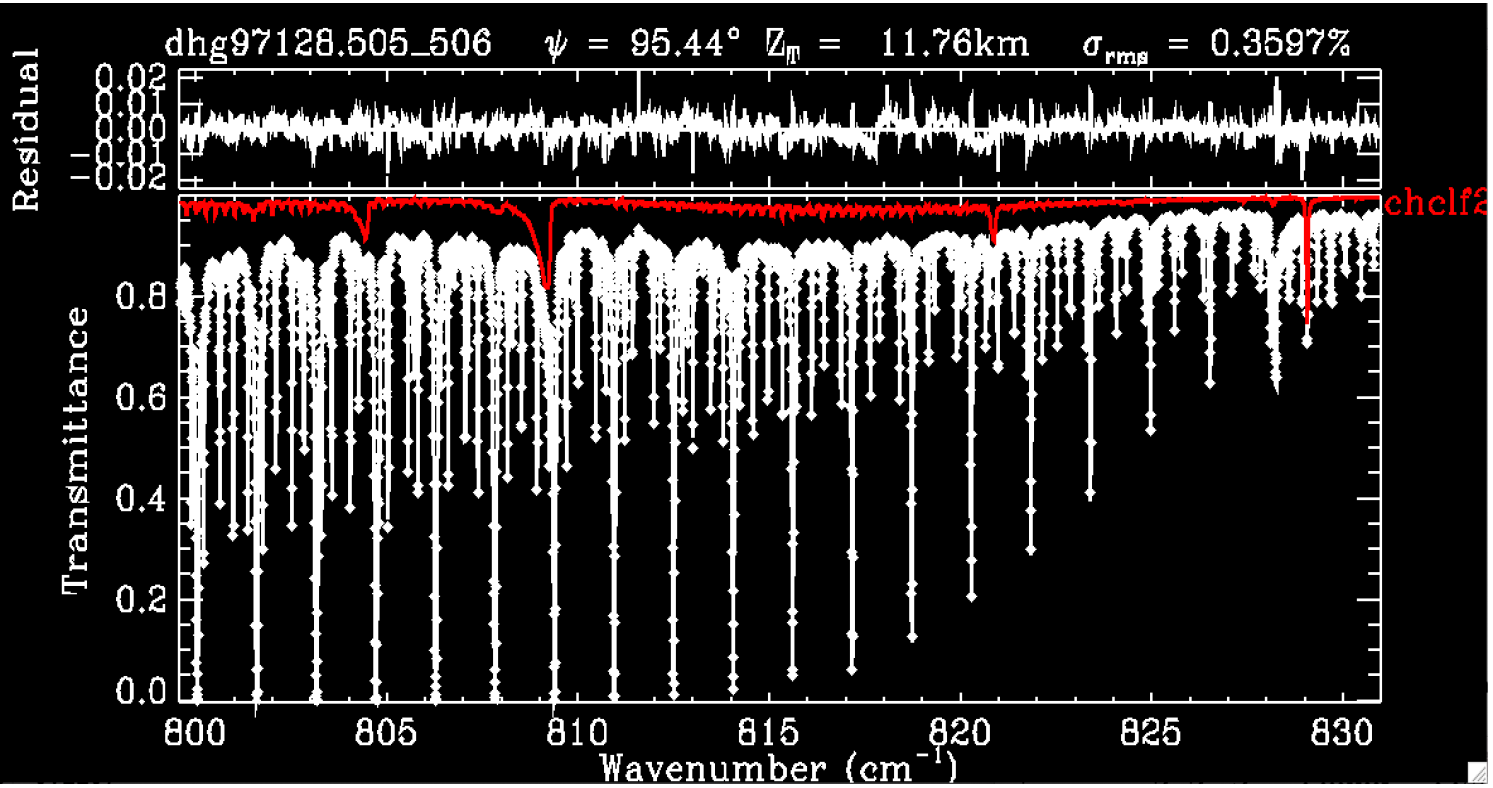


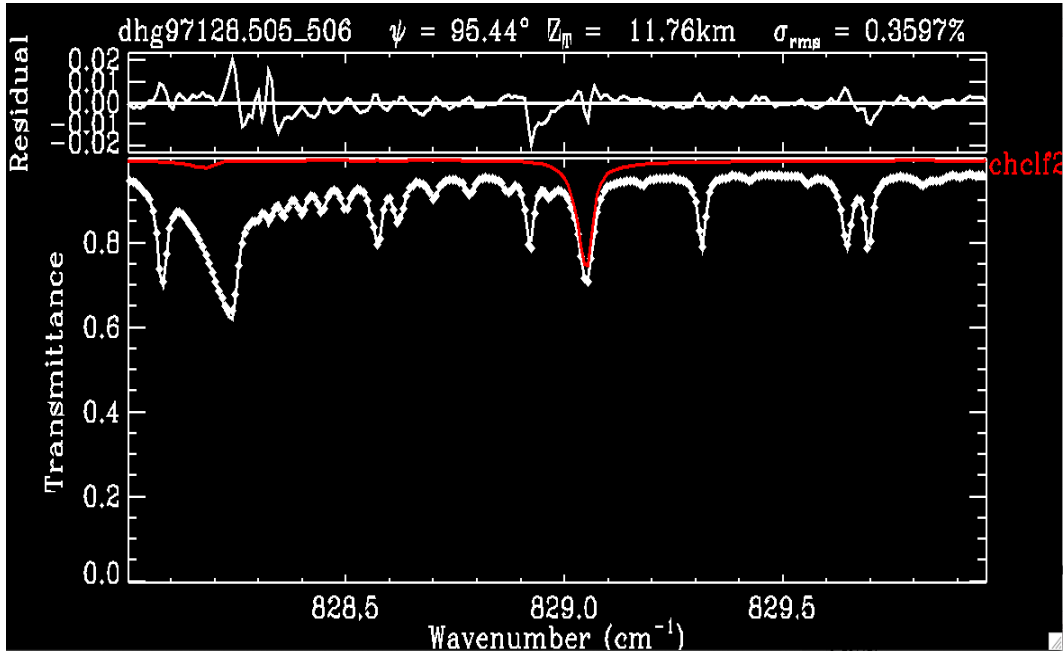


New EPLL provides smaller residuals for each of these four example cases, and overall.

Fits to MKIV Atmospheric Balloon Spectra

MkIV balloon spectra have absorption features from CO_2, O_3, H_2O in addition to those from $CHClF_2$. These provide a check the spectral calibration of the derived EPLL. Spectral fits with the new EPLL show slightly better residuals than those using the old EPLL. In the example below, the new EPLL obtains a rms fit of 0.3597% to a balloon spectrum measured at 11.76 km tangent altitude. The old linelist produced a rms residual of 0.3733%. Averaged over the entire occultation, the new EPLL produces rms fitting residuals of 0.2927% as compared with 0.2972% for the old EPLL. Although this isn't much better, the largest residuals are due to neglect of CO_2 line mixing or O_3 lines. The inset zooms into the 829 cm^{-1} Q-branch.

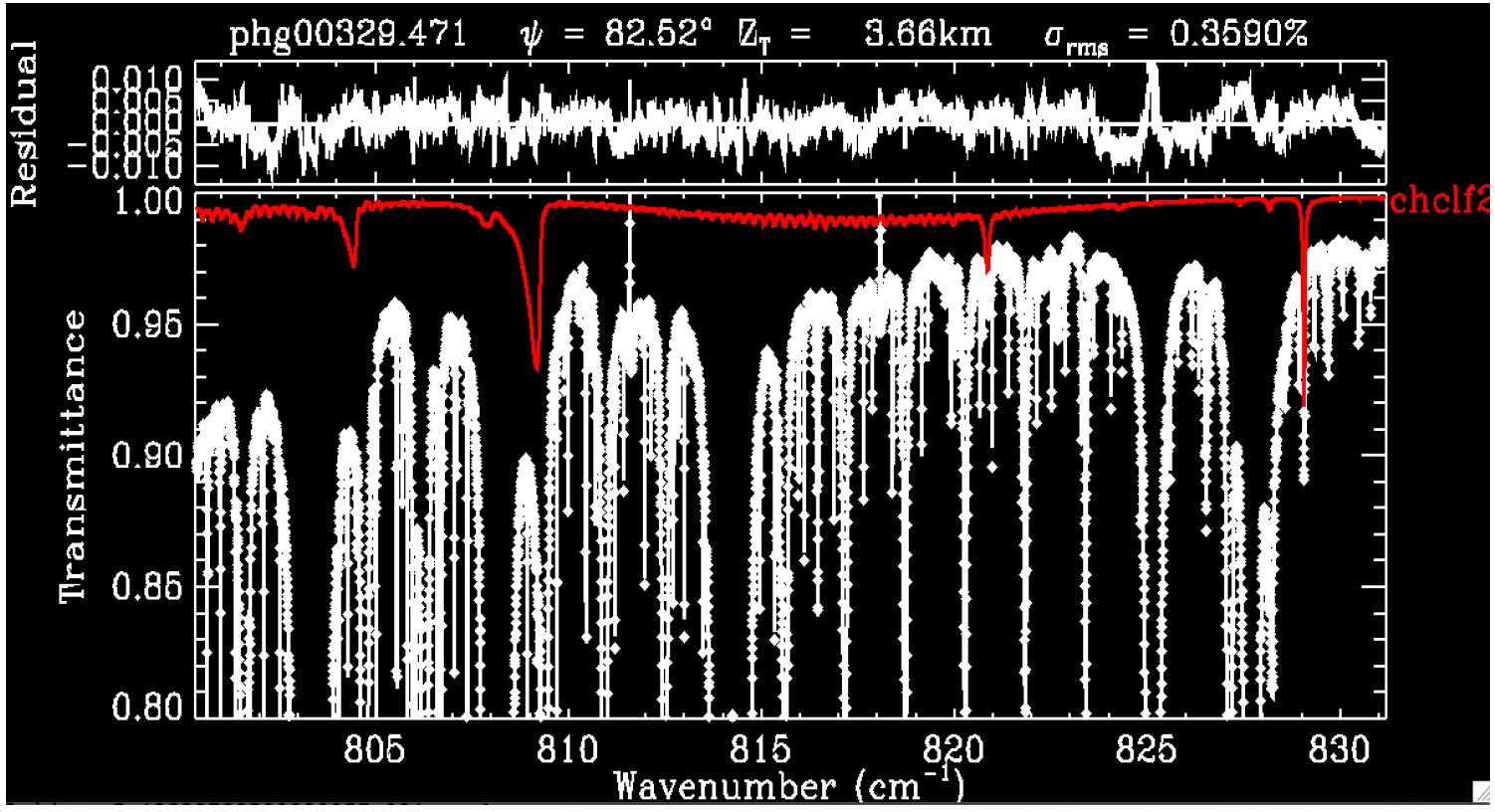


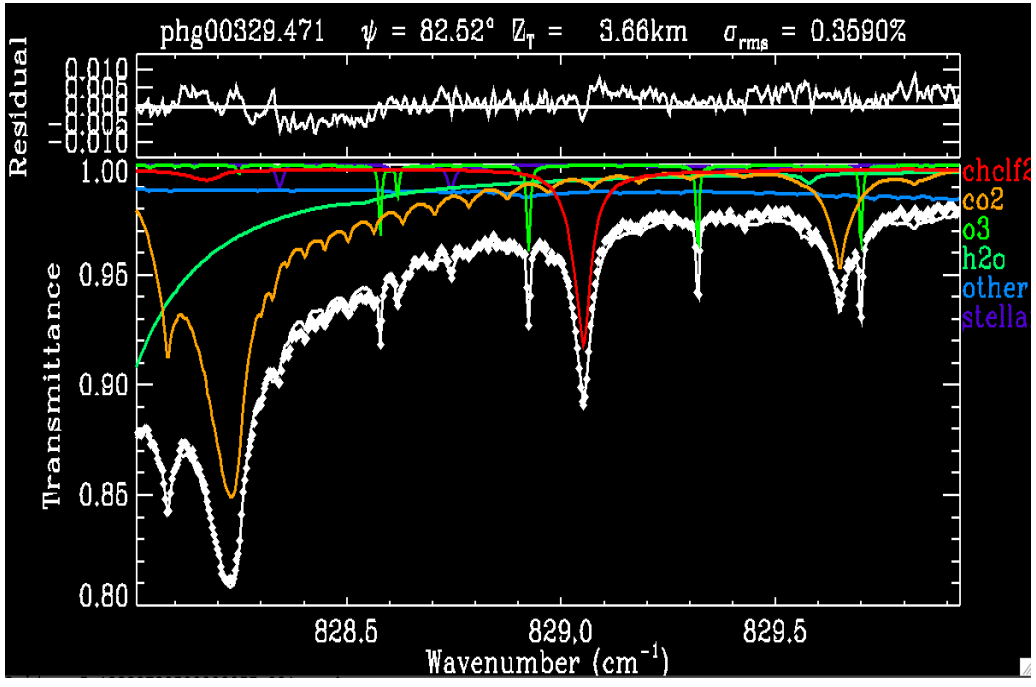


Fits to MkIV Atmospheric Ground-based Spectra

A subset of 78 MkIV ground-based spectra were fitted in the 800-830 cm^{-1} region where the strongest and sharpest $CHClF_2$ features occur. The old (1994) EPLL produced an average rms residual of 0.4633% whereas the new EPLL produced 0.4629%.

The example below shows a fit to a MKIV spectrum taken at 82.5° SZA from Mt Barcroft (3.8 km) in late 2000. The residuals are predominantly due to interfering H_2O lines, which are unaffected by the change to the $CHClF_2$ linelist and so the small reduction in the rms residual is a significant indicator of the improved new $CHClF_2$ spectroscopy. The smaller figure zooms into the 829 cm^{-1} Q-branch





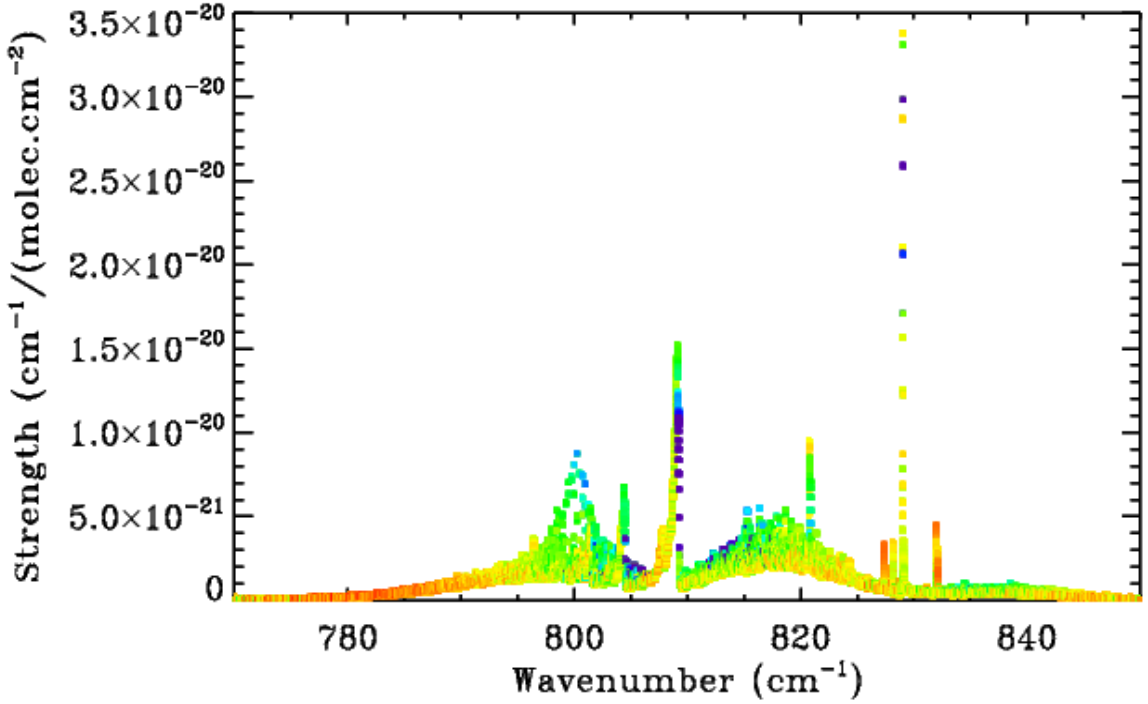
Derived EPLL Intensities (770-850 cm^{-1}) color-coded by derived E”

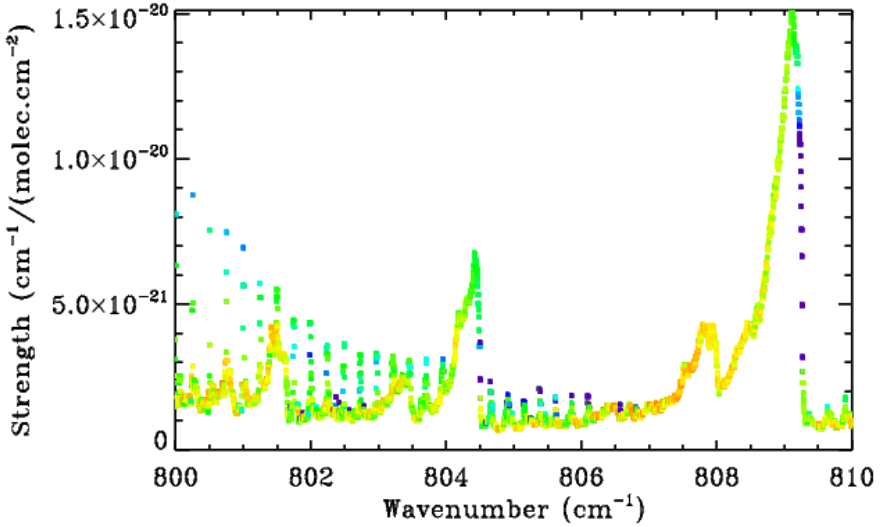
Intensities plotted versus wavenumber, color-coded by the derived E”: Blue 0 cm^{-1}; Green 300 cm^{-1}; Orange 600 cm^{-1}; Red >900 cm^{-1}.

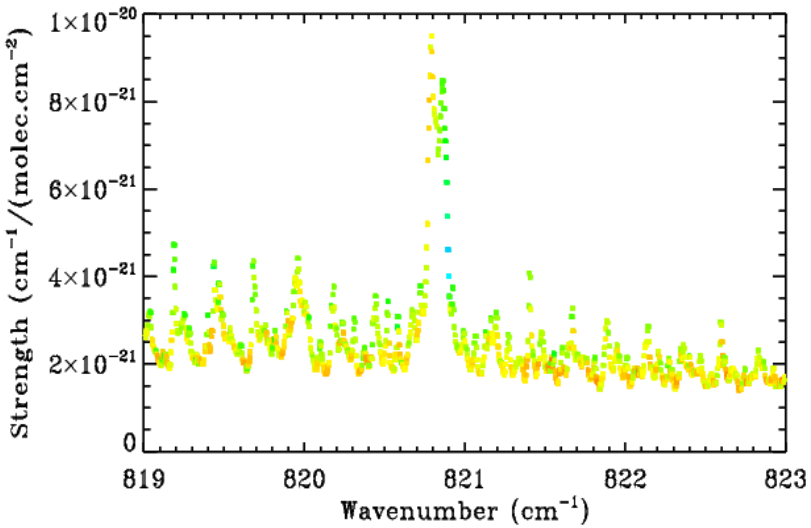
v_4 Q-branches at 804.5 (^{37}Cl) and 809.3 cm^{-1} (^{35}Cl) are asymmetrical with their lowest E”s on their steep high-wavenumber edges.

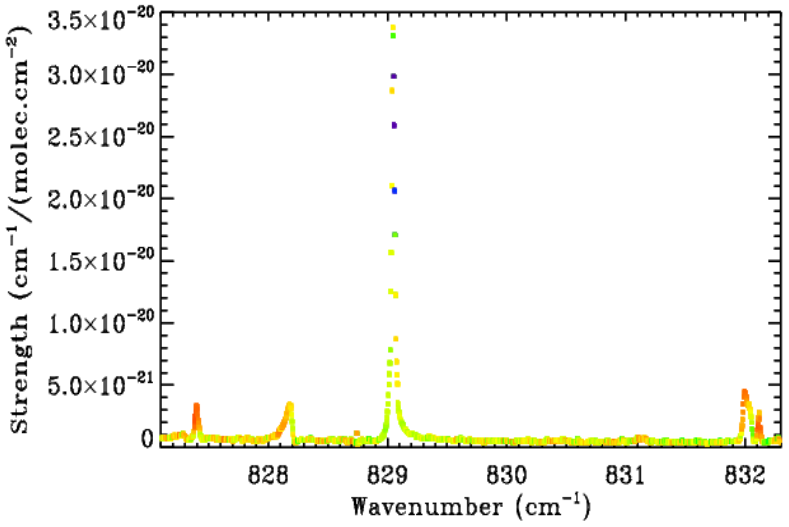
The $2v_6$ Q-branches at 820.8 (^{37}Cl) and 829.05 cm^{-1} (^{35}Cl) are narrower and more symmetrical. The lowest E”s are still slightly to the right of the strongest intensities.

In the wings of the band, below 790 and above 845 cm^{-1}, the E”s become large. The weak features at 827.4, 828.1, and 832.0 cm^{-1} also have high E”.







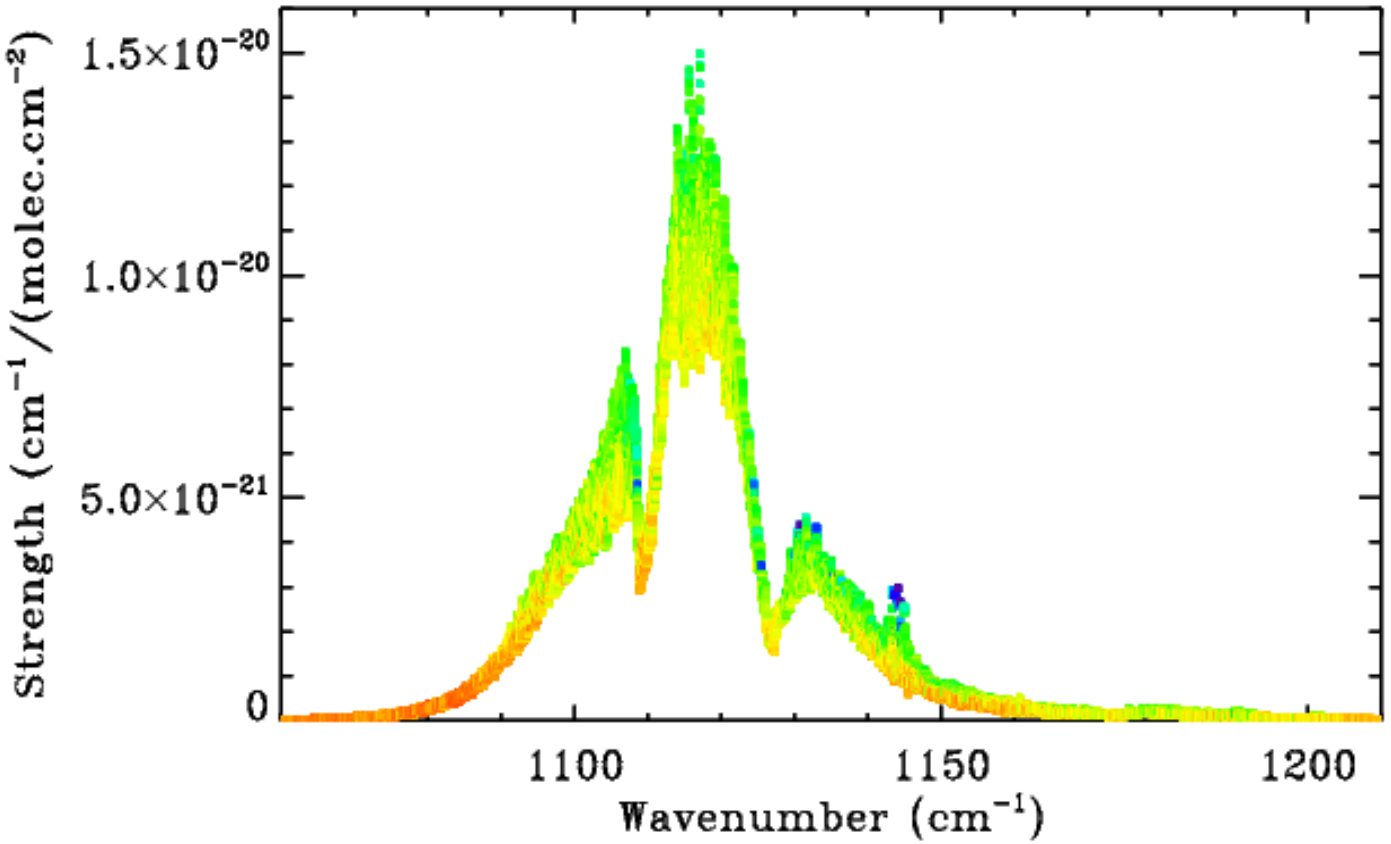


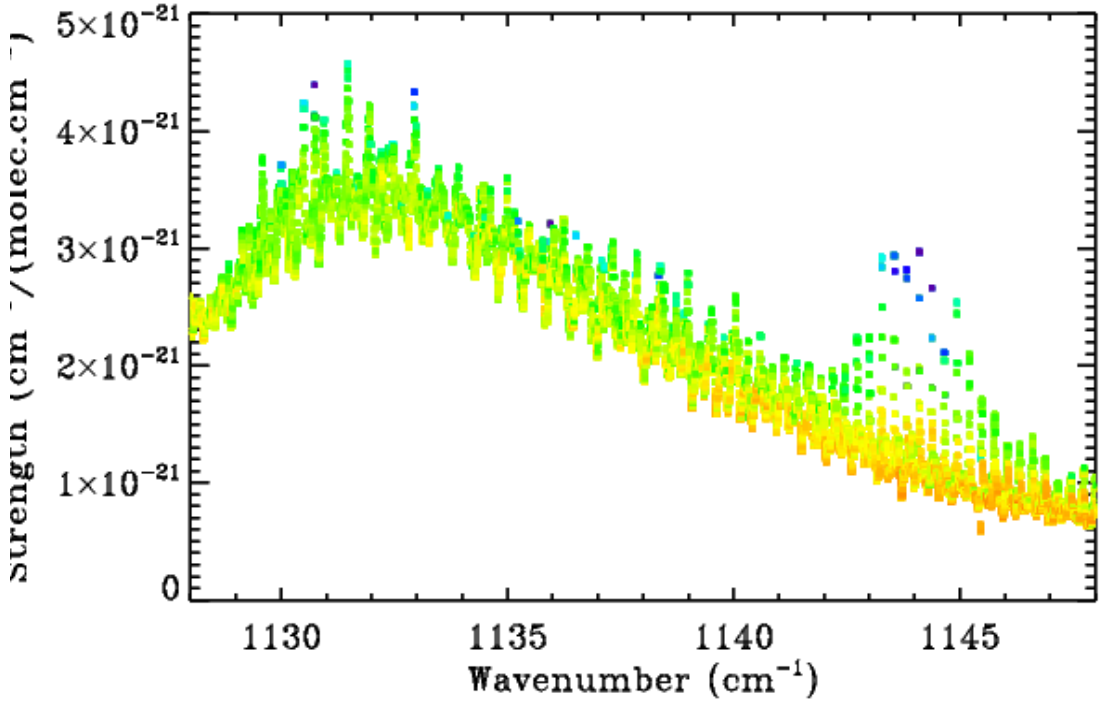
Derived EPLL Intensities (1070-1210 cm^{-1}) color-coded by derived E”

Intensities plotted vs wavenumber, color-coded by the derived E”: Blue 0 cm^{-1}; Green 300 cm^{-1}; Orange 600 cm^{-1}; Red 900+ cm^{-1}.

The ν_3 and ν_8 bands are centers at at 1105 and 1126 cm^{-1}.

In the far wings of the bands, below 1090 and above 1205 cm^{-1}, the E” values become large.





Derived EPLL Intensities (1275-1375 cm^{-1}) color-coded by derived E”

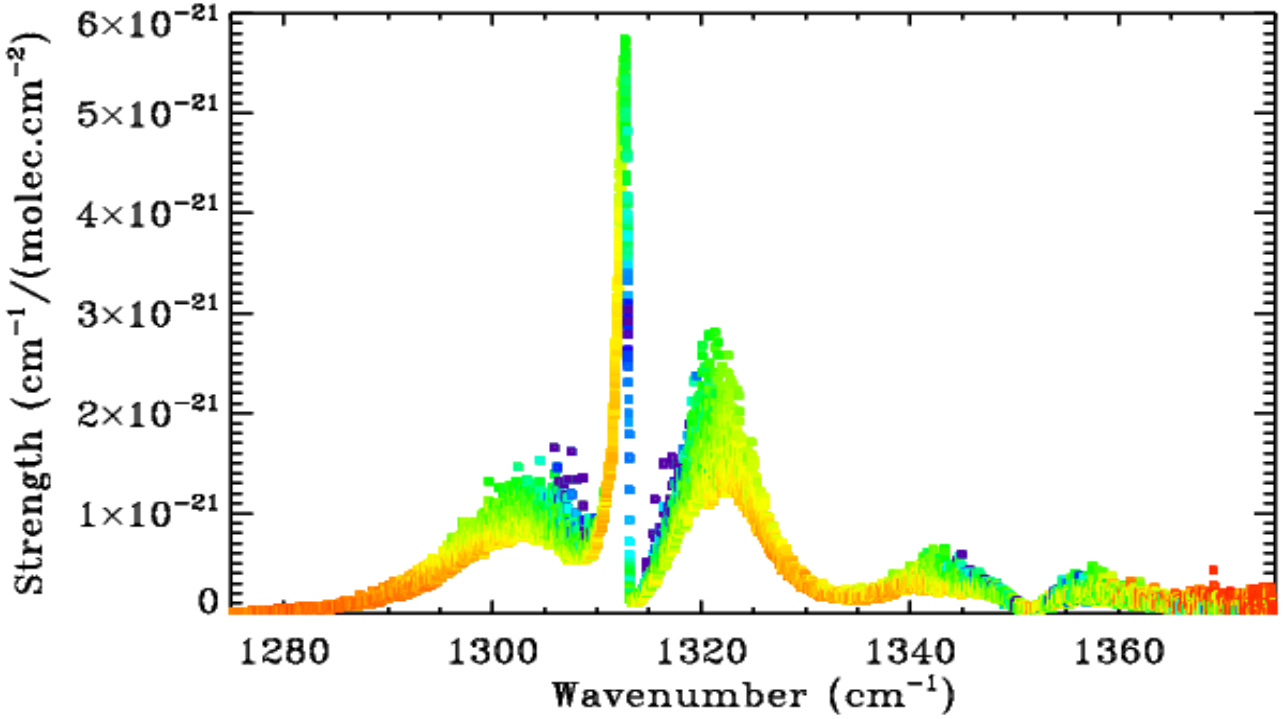
Intensities plotted vs wavenumber, color-coded by the derived E”: Blue 0 cm^{-1}; Green 300 cm^{-1}; Orange 600 cm^{-1}; Red 900+ cm^{-1}.

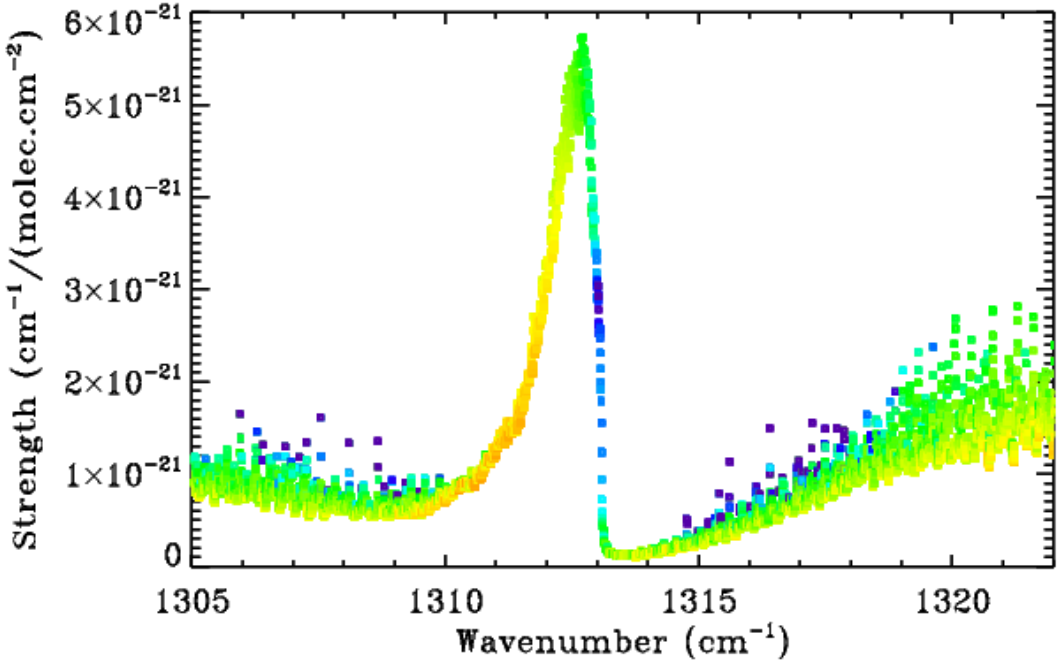
This region is covered only by the 3 PNNL and 30 Harrison spectra. The Harrison spectra become increasingly noisy above 1365 cm^{-1}, causing large uncertainty to the derived intensities and E”.

The v_2 and v_7 band centers are seen at at 1313 and 1352 cm^{-1} respectively. The former has a strong Q-branch, the latter does not.

The lowest E” values are seen on the steep high-wavenumber edge of the Q-branch at 1313 cm^{-1}.

In the far wings of the bands, below 1290 and above 1365 cm^{-1}, the E” values become large.





Summary of fitting results using the 99 lab spectra from HITRAN/Supp/

Window	#1: 596 cm^{-1} 560-632 cm^{-1}	#2: 810 cm^{-1} 770-850 cm^{-1}	#3: 829 cm^{-1} 828.8-829.3 cm^{-1}	#4: 1132 cm^{-1} 1070-1195 cm^{-1}	#5: 1135 cm^{-1} 1060-1210 cm^{-1}	#6: 1325 cm^{-1} 1275-1375 cm^{-1}	#7: 3025 cm^{-1} 2980-3070 cm^{-1}
# spectra	3/99	62/99	62/99	67/99	35/99	33/99	3/99
Integrated Intensity	0.0 0.97E-18	22.5E-18 22.5E-18	0.418E-18 0.427E-18	55.8E-18 67.5E-18	55.9E-18 68.1E-18	7.42E-18 11.0-18	0.0 1.70E-18
Average RMS Fit	0.4080% 0.0155%	0.4811% 0.3043%	1.0716% 0.9466%	1.7546% 0.3027%	1.8385% 0.2405%	1.2087% 0.1667%	0.4426% 0.0104%
Average VMR SF	N/A 0.993±0.035	1.006±0.011 0.996±0.009	1.007±0.058 1.005±0.048	1.220±0.046 0.994±0.008	1.226±0.065 1.001±0.009	1.228±0.052 1.000±0.008	N/A 0.997±0.028

Green represents the 1994 EPLL. Red represents the 2022 EPLL

Spectral fits are improved using the 2022 EPLL, which they should be because it was generated from these same 99 spectra. The intercomparison is unfair because the defined windows are wider than the 1994 EPLL limits in several cases. For example, the ν_7 band centered at 1352 cm^{-1} is fully covered by window #5 and by the new EPLL but only partially by the 1994 EPLL.

VSF factors using the 2022 EPLL are much closer to 1 for windows #4-6, which previously over-estimated $CHClF_2$ by 22%.

The two middle windows (#4 and #5) overlap. This is because the Varanasi spectra cover only 1070-1195 cm^{-1}, so the slightly narrower window #4 captures 67/99 spectra, whereas the slightly wider window #5, needed to fully capture all the absorption in the wings of the ν_3 and ν_8 bands, captures only 35/99 spectra since the Varanasi spectra are not wide enough.

Windows #1 and #7 were not covered by the 1994 EPLL. These windows are captured only by the PNNL spectra (278-323K). So the absorptions computed from the EPLL are likely to be unreliable at lower temperatures and pressures in these windows.

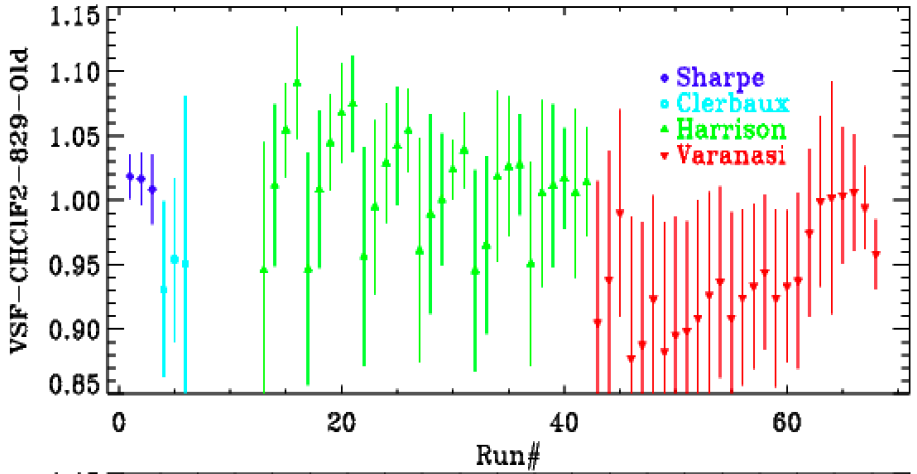
VSF retrieved from 829 cm^{-1} window

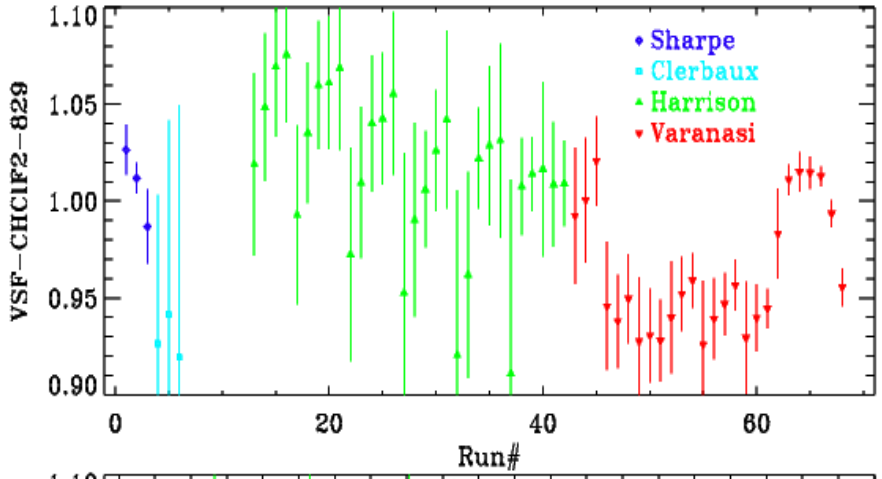
Old EPLL (left):
RMS = 1.0716%
VSF = 1.007±0.0417

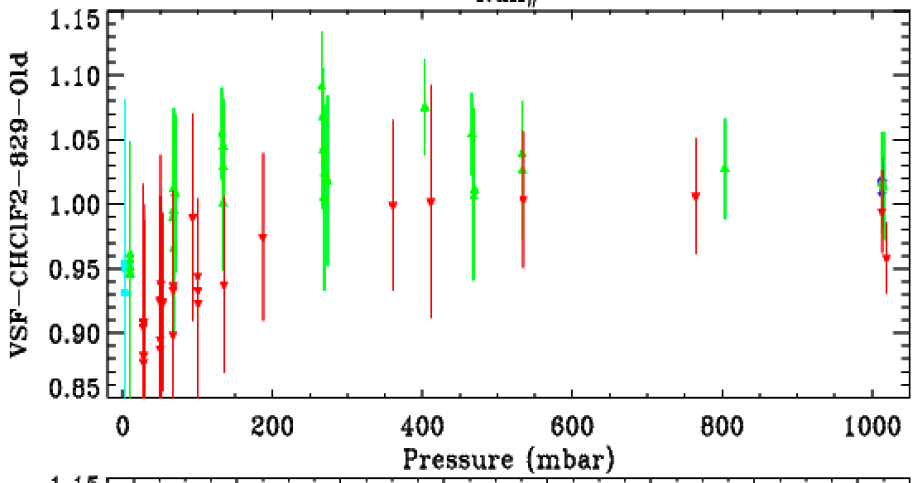
New EPLL (right):
RMS: 0.9466%
VSF = 1.005±0.0293

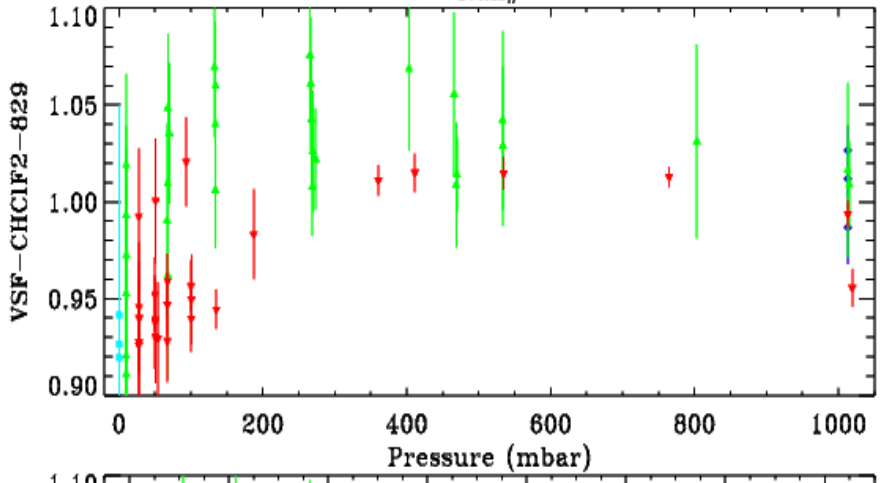
Sharpe's spectra have the smallest error bars, because the fits are really good due to the absence of spectral structure at 1 atm.

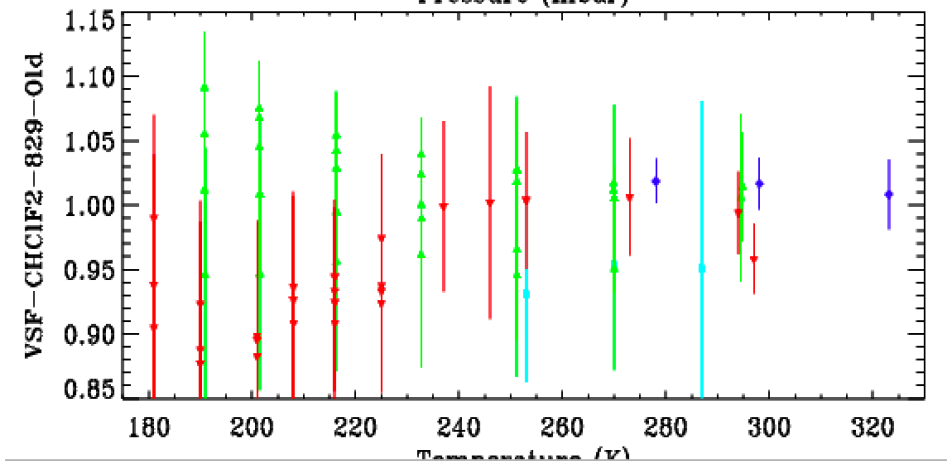
The 7.5 Torr Harrison spectra consistently yield lower VSFs than the higher pressure spectra, for both old and new linelists. Not sure why.

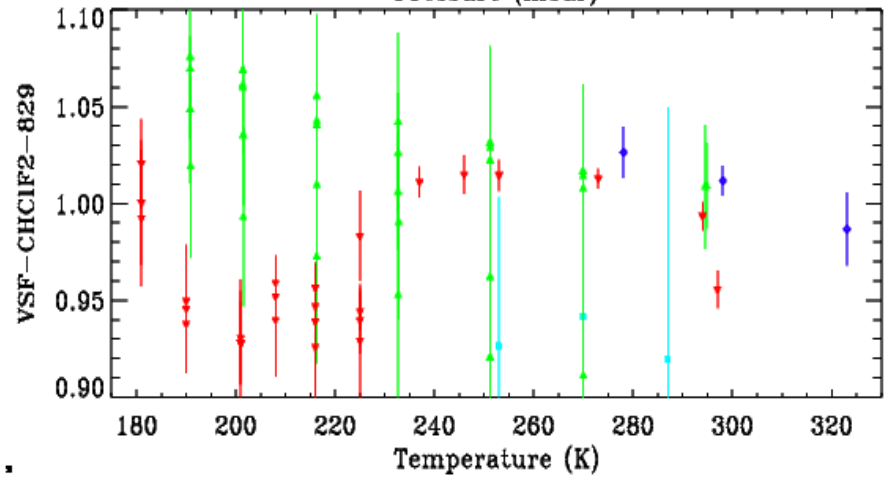












Summary and Conclusions

A new EPLL has been generated for $CHClF_2$ that supersedes the old one generated in 1994.

In general terms the new EPLL is a big improvement over the old one, covering a broader region and with better spectral fits and more consistent retrieved gas amounts.

In the $2\nu_6$ Q-branch at 829 cm^{-1}, the improvement was modest. The old EPLL seems to have done a good job here, despite being based only on a few Varanasi & McDaniel spectra. The Clerbaux and Harrison datasets, plus additional Varanasi spectra, didn't improve things much at 829 cm^{-1}.

The new EPLL (and the old one) under-estimates the $CHClF_2$ amounts retrieved from the 829 cm^{-1} feature alone for the low-P lab spectra. This may be a limitation of the EPLL approach, or neglect of LM, or something else. The absorption is growing non-linearly with absorber amount in these lab spectra: the depth of the $2\nu_6$ Q-branch is 90-95% in most of these spectra. This would tend to amplify any errors (e.g. zero offsets, ILS, etc.). But for ground-based atmospheric retrievals it doesn't matter much because the $CHClF_2$ amounts are small for P<10 mbar.

An inconsistency was seen in the wavenumber calibration of the spectra, as was also noted by Harrison. This was corrected before the pseudo-lines were generated to prevent the pseudo-line intensities being smeared out in wavenumber.

The spectral fitting included channel fringes. As noted by Harrison, the Varanasi spectra contains channel fringes with periods of 0.37 and 0.52 cm^{-1} with amplitudes of up to 0.4%. The other datasets (Clerbaux, Sharpe, Harrison) generally had negligible channel fringe amplitudes (< 0.1% amplitude).

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Strength/Weaknesses of the EPLL approach

Why not use the cross-section data directly in the forward model, interpolating in T and P and wavenumber? This would be fine if the cross-section spectra had no systematic errors (ILS, channeling, zero offsets, contaminants, wavenumber error), covered the entire range of atmospheric T & P, and the full wavenumber ranges of interest. But if artifacts are present they will bias the retrievals. Also, what if there are multiple lab datasets with different attributes (T, P, *v* ranges, spec resolutions, etc).

Strengths:

1) The user doesn't have to choose a particular lab dataset. All available cross-section datasets are utilized.

2) Provides a physics-based extrapolation to T/P regimes not covered by the lab measurements (e.g. T=230 K, P=1 atm)

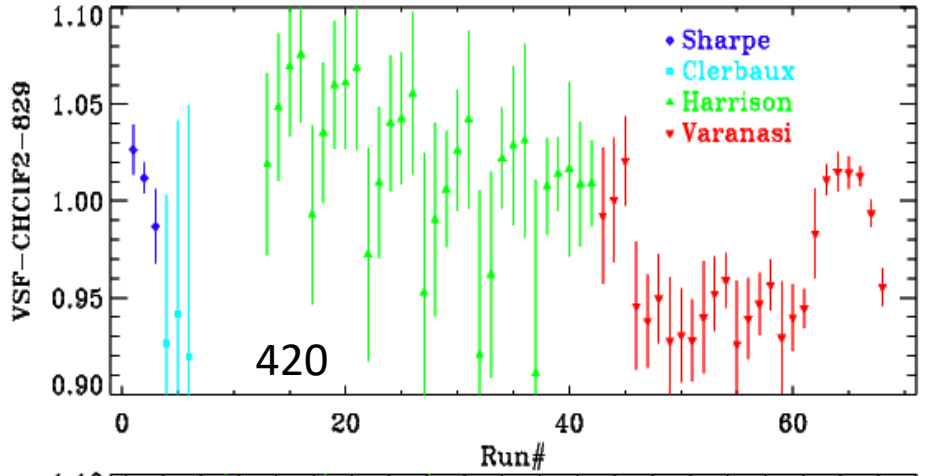
3) Fitting each lab spectrum provides an opportunity to:
   - Identify bad spectra (or spectra with incorrect P,T, vmr, *v*), or that are simply inconsistent with neighbors.
   - Identify (and perhaps correct) inconsistencies/biases between laboratory datasets, where they overlap in *v*, T, P
   - Deconvolve the ILS of the lab spectrometer, which is (hopefully only slightly) broadening sharp spectral features.
   - fit contaminating gases (e.g. H_2O, CO_2, HNO_3, CH_3OH, NH_3) in the gas cell, removing their influence on EPLL
   - Fit channel fringes in the spectra, minimizing their impact on the derived EPLL
   - Fit zero-level offsets in the spectra, which untreated would bias the stronger lines.

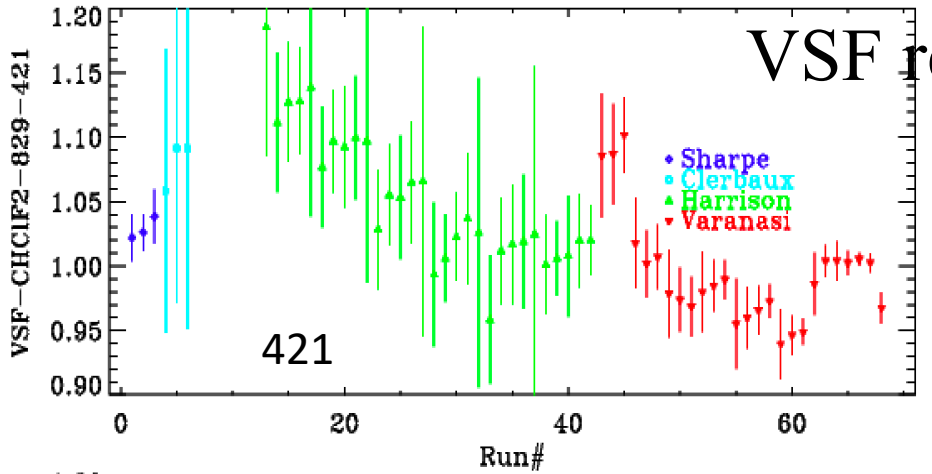
Weaknesses:

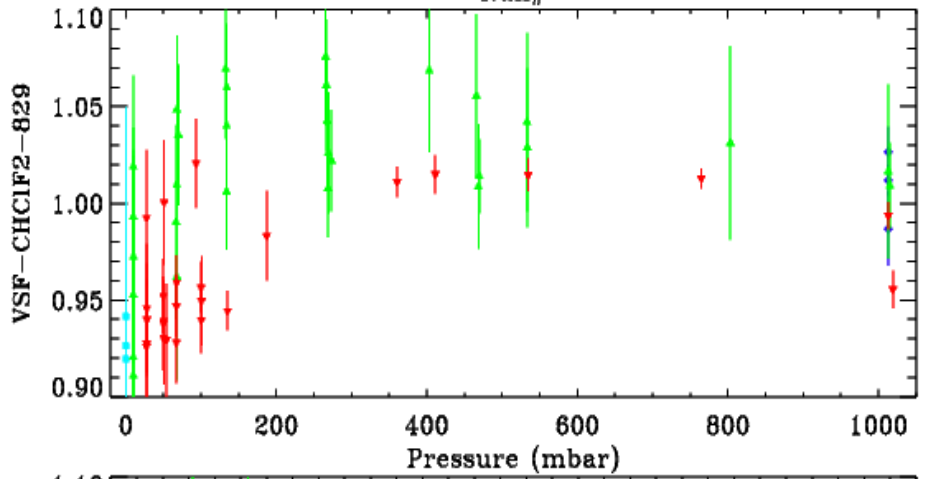
1) The pseudolines are derived assuming a Voigt lineshape, and therefore may not be able to accurately represent absorption in Q-branch regions where line-mixing is important.

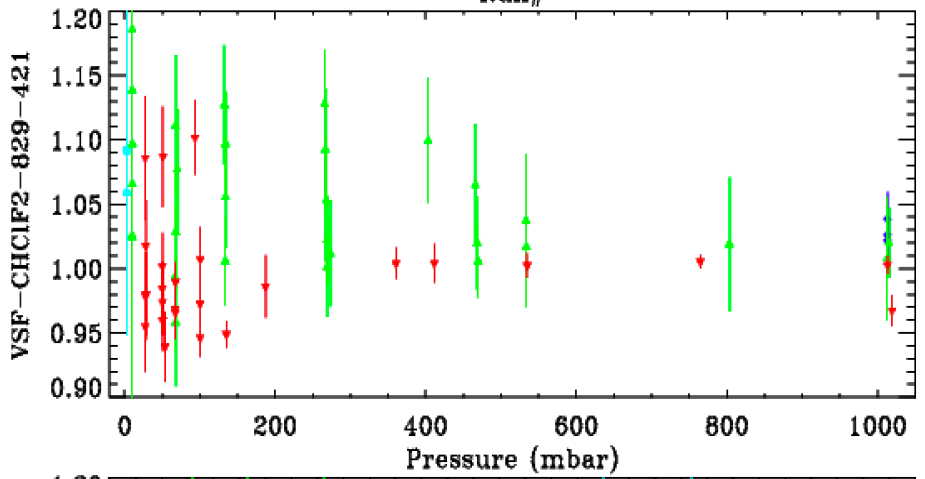
2) Overlapping low- and high-E" lines may not be accurately represented by a single medium-E" line.

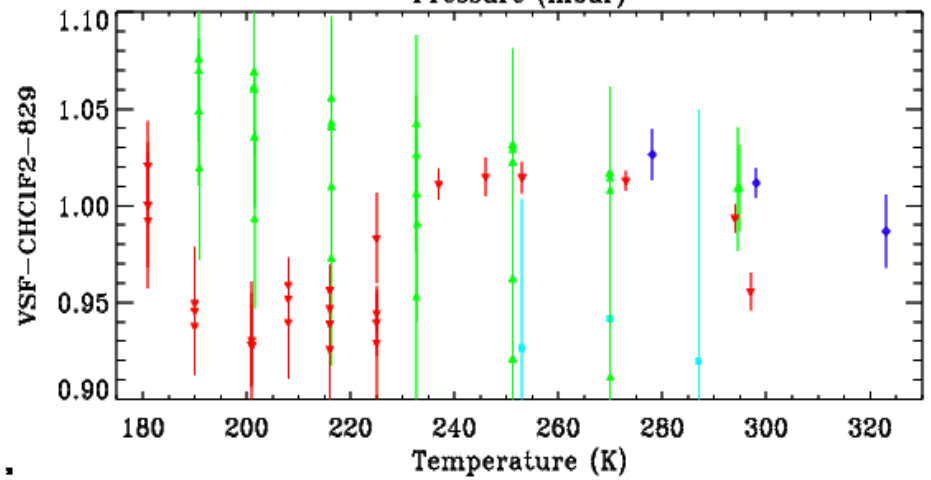
VSF retrieved @ 829 cm^{-1}

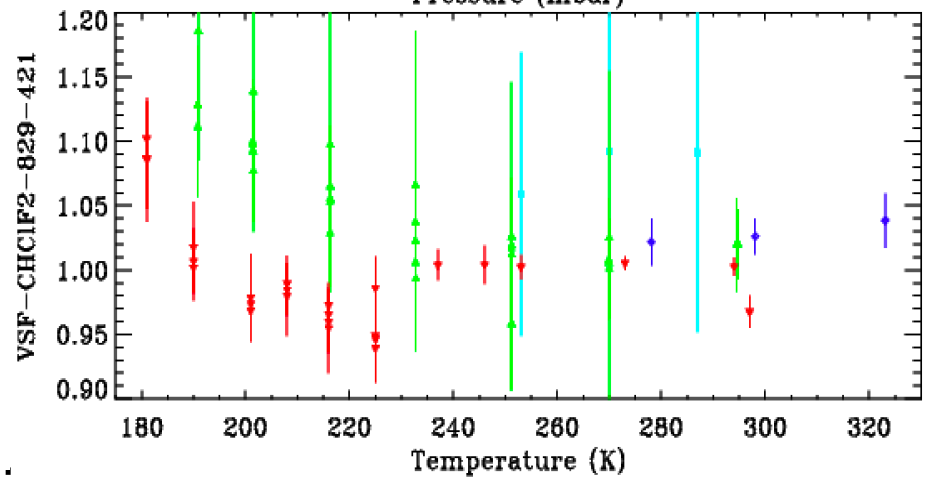












420: Doppler width is artificially set to line spacing (0.004 cm^{-1}) which is several times larger than the real Doppler width at 800 cm^{-1}.

421: Doppler width is computed normally

Retrieved VSFs are larger in 421 case, especially at low P because narrower lines are growing non-linearly, requiring more absorber to produce a given Eq Wid.

This is especially noticeable in the Clerbaux (assumed 5 Torr) and the 7.5 Torr Harrison spectra. Less noticeable in Varanasi spectra (P > 20 Torr)