CHF_3 Empirical Pseudo-Linelist Update

Geoffrey Toon
Jet Propulsion Laboratory
2020-09-22

In 2011 I created a CHF_3 (aka HFC-23, R-23, TriFluoroMethane, Fluoroform) empirical pseudo-linelist (EPPL), based on the measurements of PNNL (Sharpe et al. 2004) and SUNY (Chung, 2005), as described in:
https://mark4sun.jpl.nasa.gov/data/spec/Pseudo/Readme.chf3.pdf

Based on this EPLL, Harrison et al. (2012) retrieved atmospheric CHF_3 from solar occultation spectra of ACE and MkIV.

In 2013 Harrison made new laboratory measurements of CHF_3 which cover a broader spectral domain (Infrared absorption cross sections for trifluoromethane, *JQSRT*, 10.1016/j.jqsrt.2013.05.026, 130, 2013).

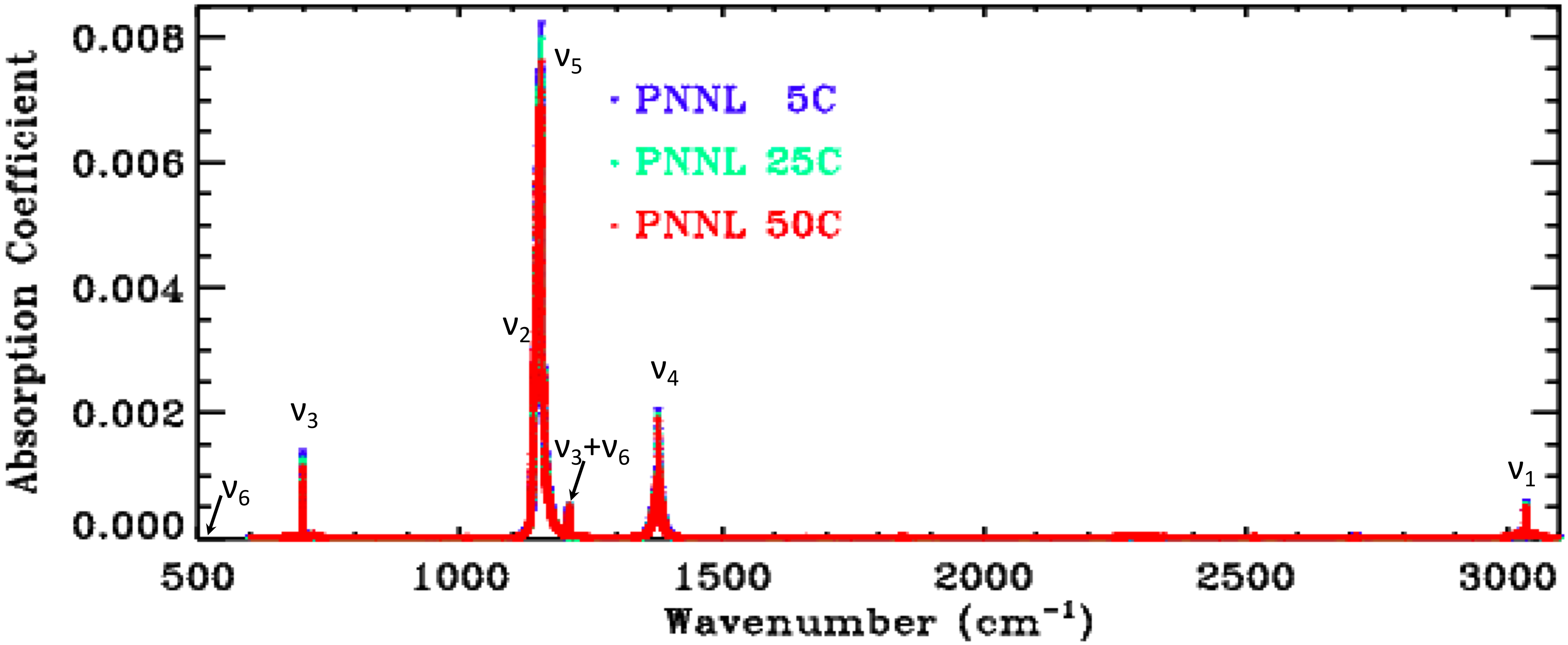
So I made made a new EPLL using four datasets (instead of two previously):

Gohar (2004):	1 spectrum covering	400 - 1499 cm^{-1}
PNNL (Sharpe et al. 2004):	3 spectra covering	650 - 6000 cm^{-1}
SUNY (Chung, 2005):	24 spectra covering	1100 – 1250 cm^{-1}
Harrison (2013):	27 spectra covering	950 – 1500 cm^{-1}

We ignore the spectrum of Highwood & Shine (2000) which covers only the v_3 band at 656-745 cm^{-1}, whose sharp Q-branch feature at 699.9 cm^{-1} is overlapped by the very strong R40 line (700.0587 cm^{-1}) of the CO_2 v_2 fundamental.

Old EPLL: covered 1100 to 1240 cm^{-1} at a line spacing of 0.005 cm^{-1} (28,000 lines)
New EPPL: covers 1104.9 to 1425 cm^{-1} at a line spacing of 0.004 cm^{-1} (80,051 lines)

CHF_3 Absorption Spectrum -- Overview (PNNL)



The v_5 bands is the strongest and fortuitously fall in the most transparent windows. PNNL spectra don't cover the v_6 band centered at 508 cm^{-1} (Gohar spectrum does). The v_3 band centered at 700 cm^{-1} is useless for atmospheric observations since its strong, sharp, Q-branch is overlapped by CO_2

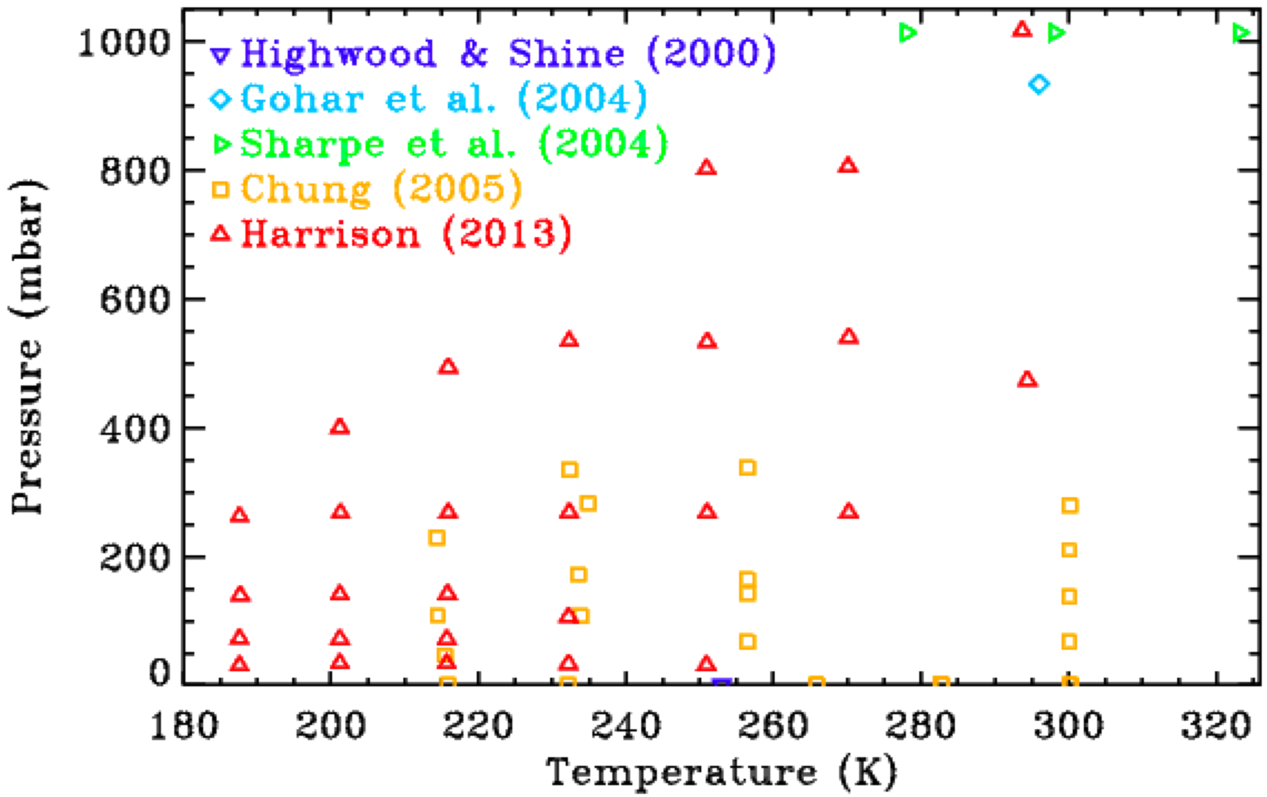
CHF_3 Lab Measurement Conditions

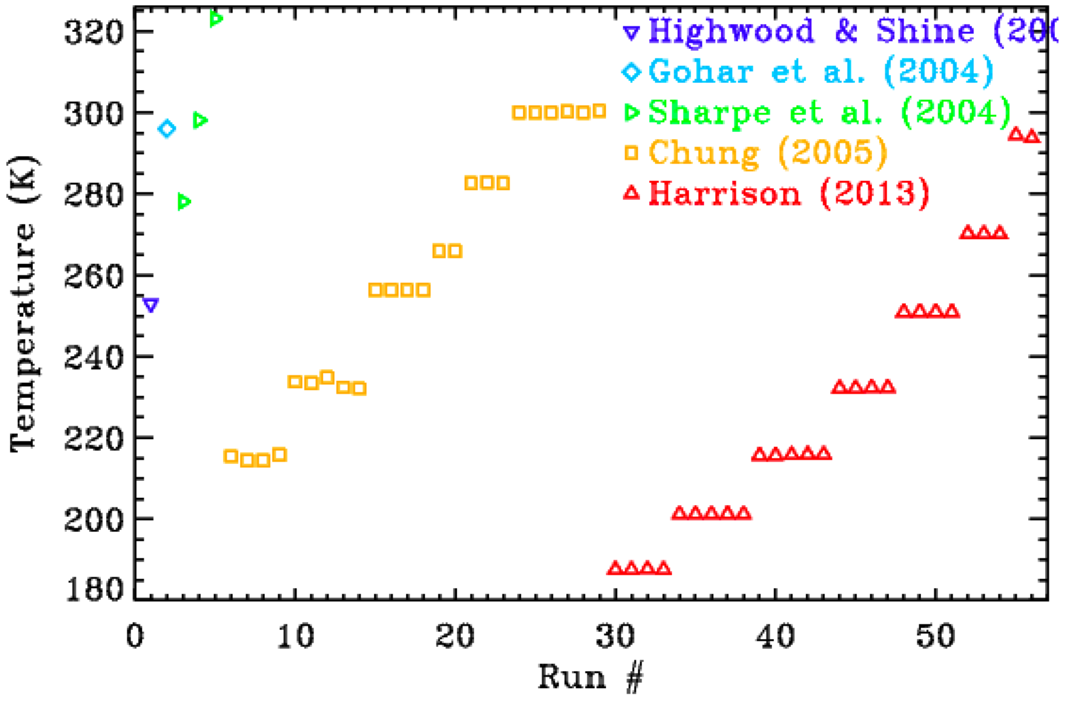
55/56 spectra fitted 1105 to 1240 cm^{-1} (1 Gohar + 3 PNNL + 24 Chung 27 Harrison)

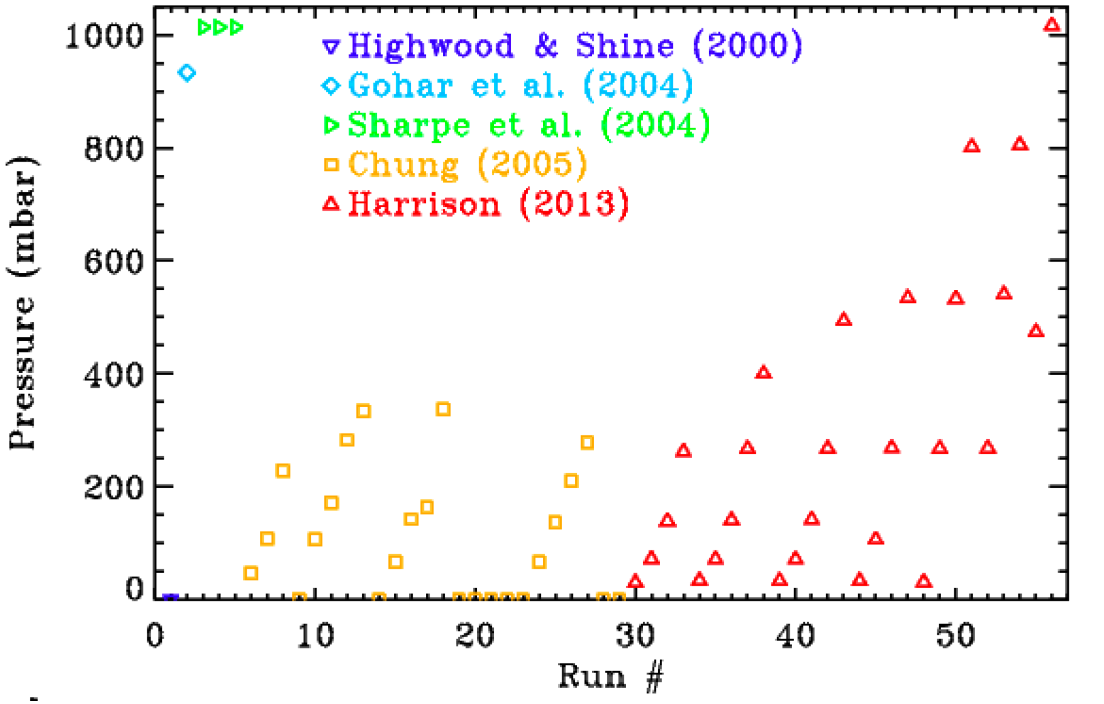
31/56 spectra fitted 1240 to 1425 cm^{-1} (1 Gohar, 3 PNNL + 27 Harrisor

Highwood & Shine spectrum, covering 555-645 cm^{-1}, was not used.

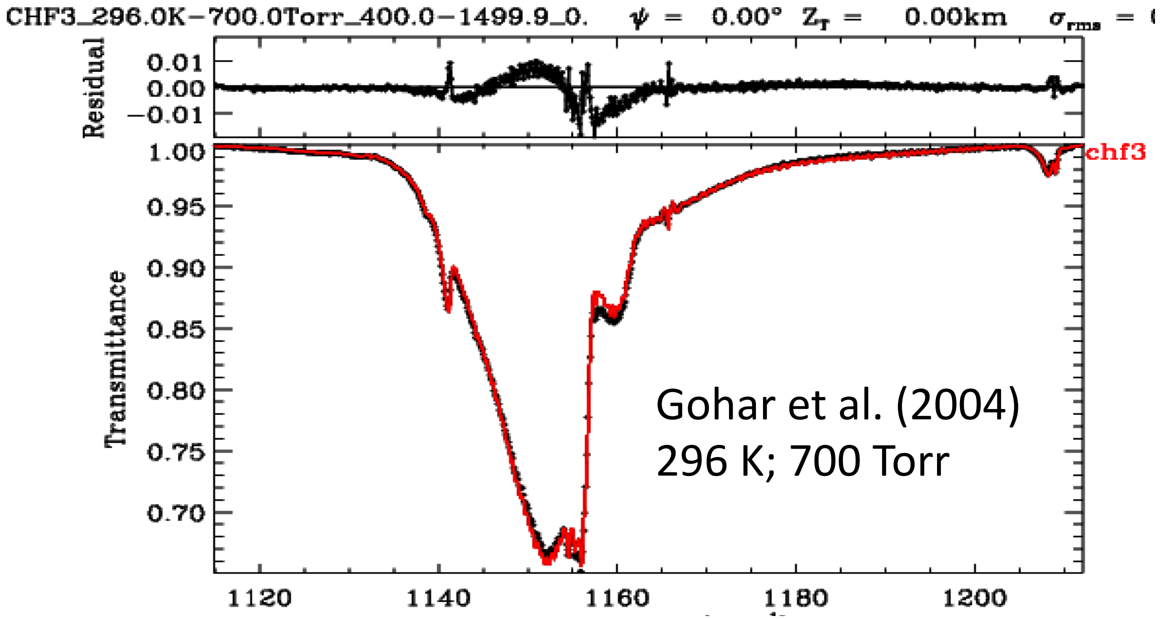
The plots show the P/T conditions for each spectrum.

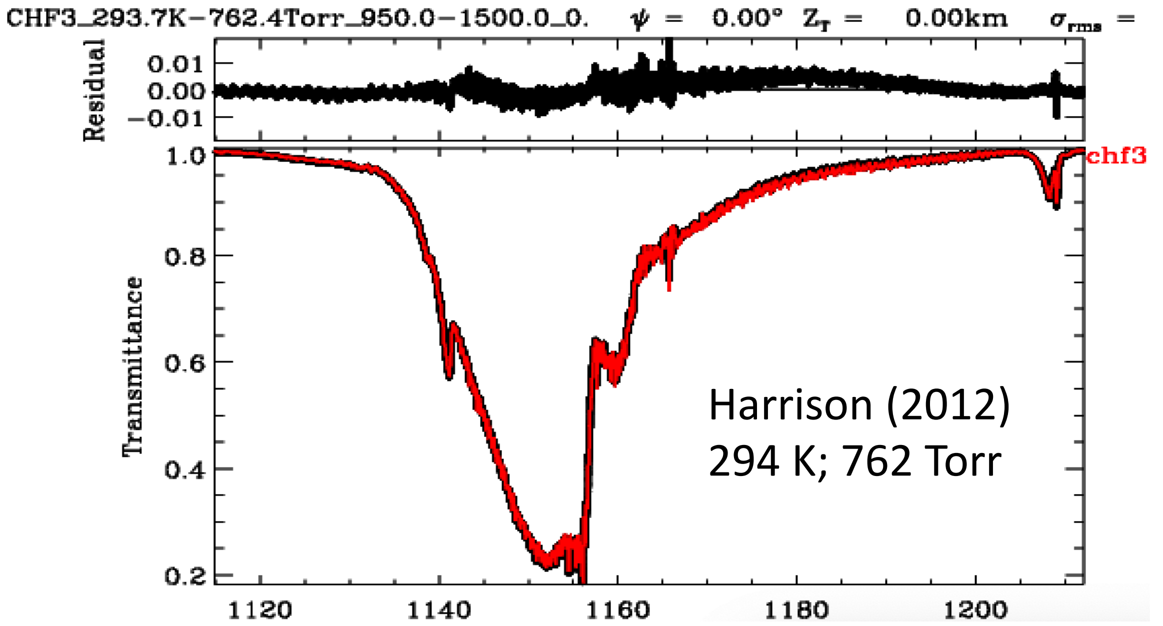


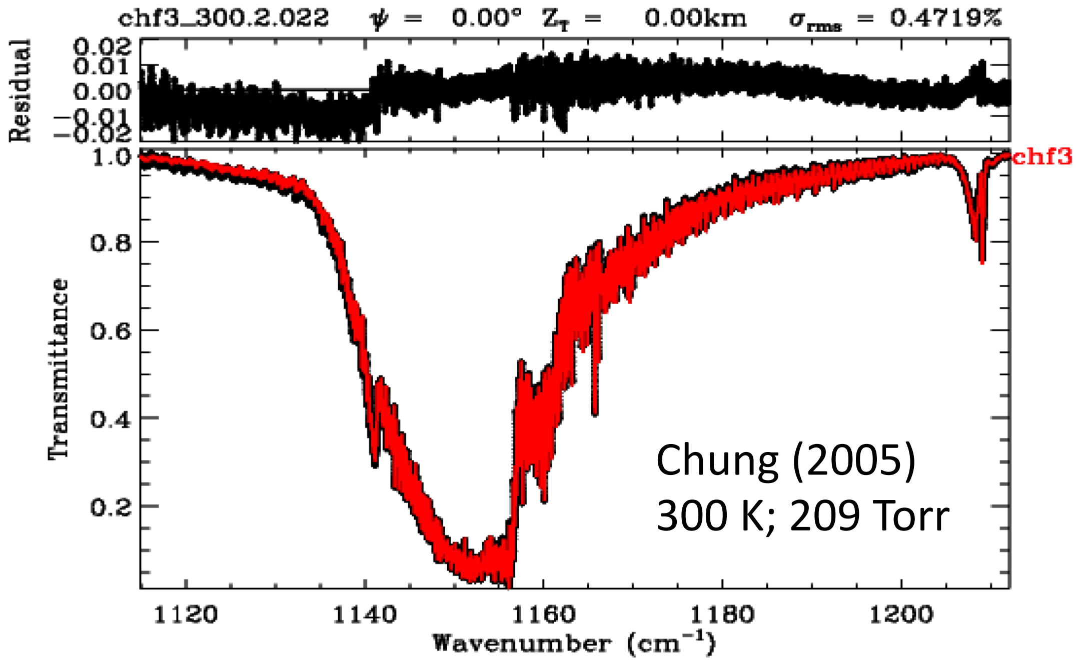


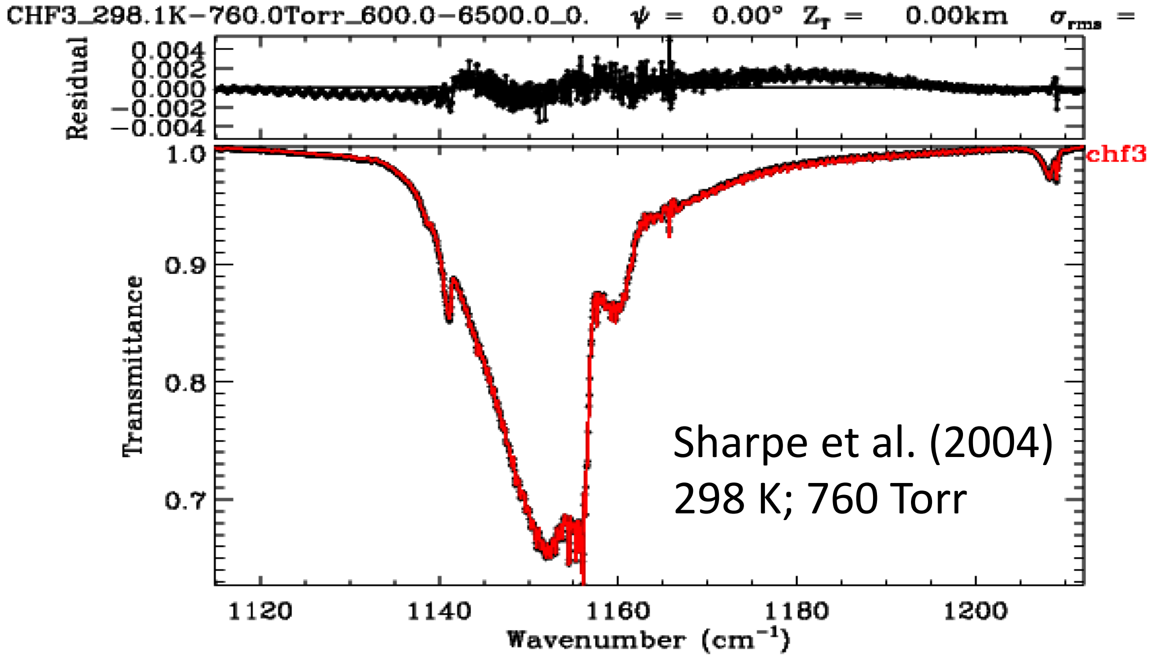


Examples of fits to CHF_3 Lab Spectra at ~300K: 1120-1212 cm^{-1}

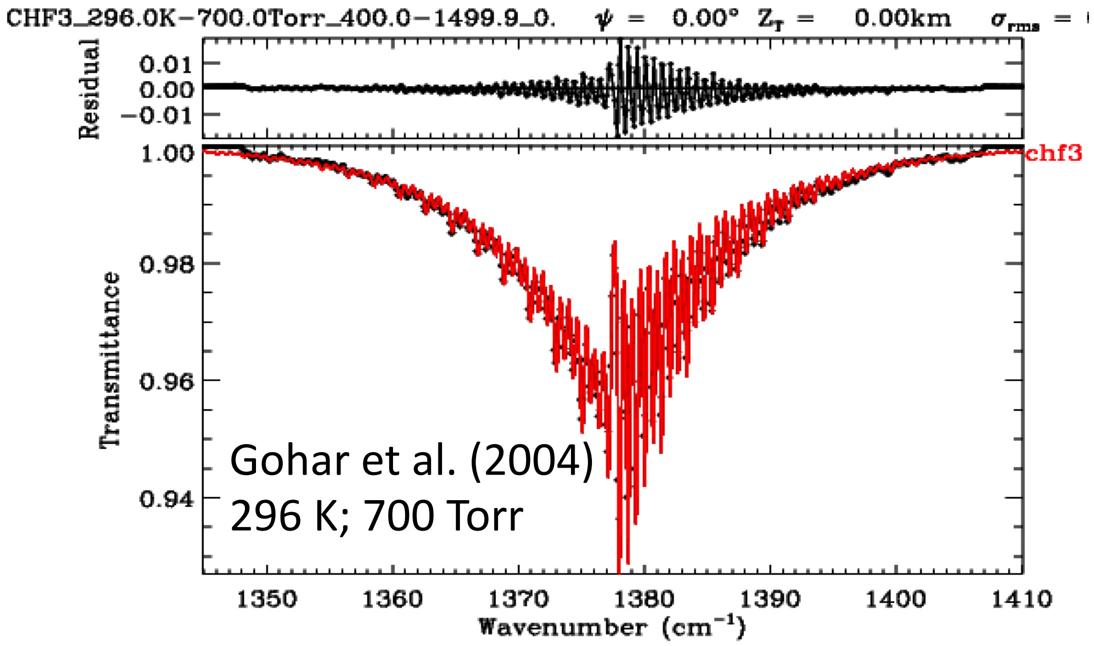


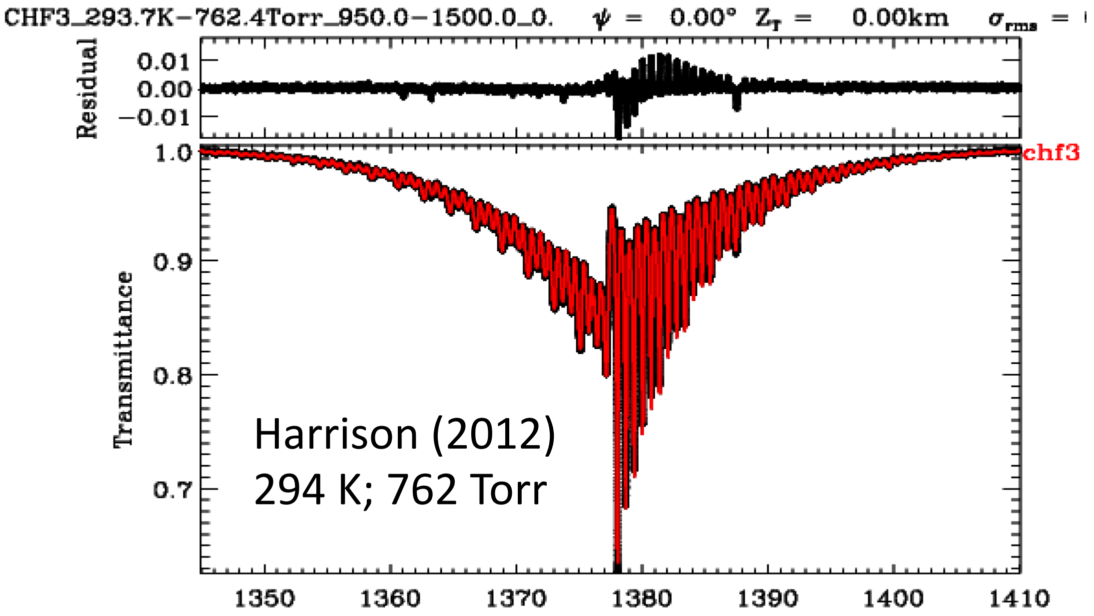


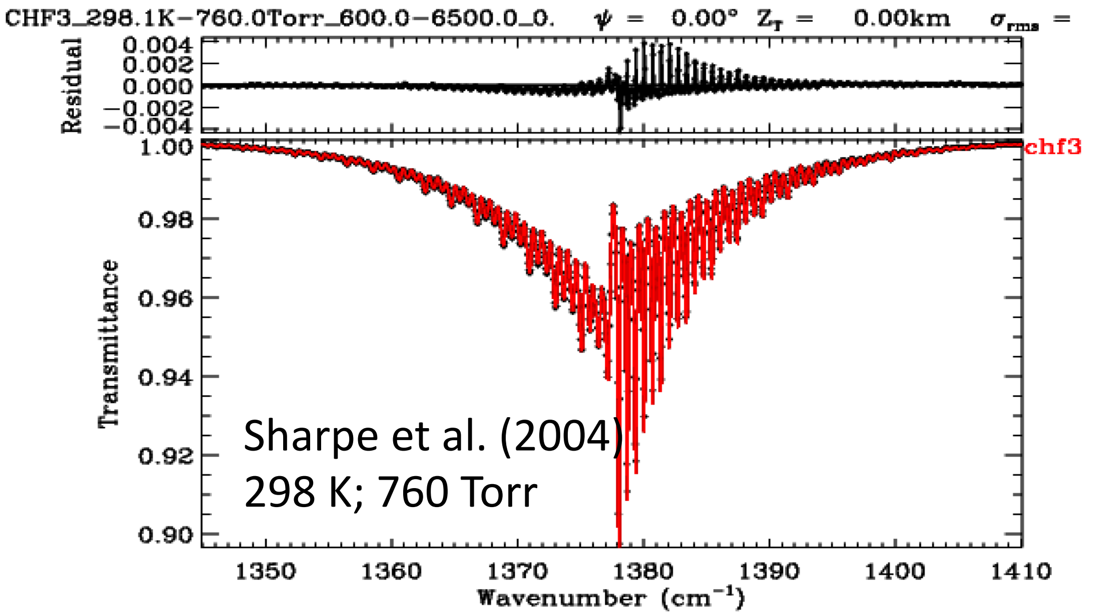




Examples of fits to CHF_3 Lab Spectra at ~300K: 1345-1410 cm^{-1}





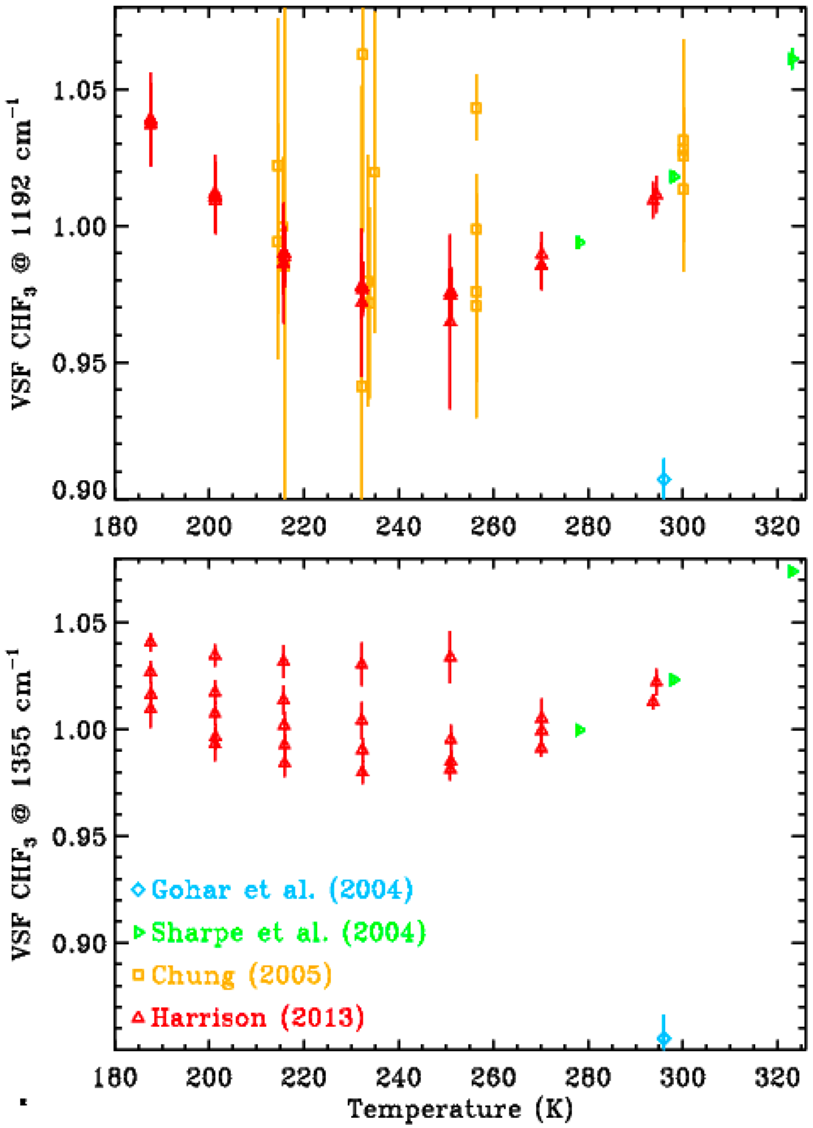


Chung spectra do not cover this region.

Even at highest pressures, this band contains substantial spectral structure and is useful in analyzing solar occultation spectra. But not ground-based spectra (this region is blacked out by H_2O).

Retrieved CHF_3 scale factors plotted versus Temperature (left) and Pressure (right)

Upper panels: results from 1105-1240 cm^{-1} region. **Lower panels:** results from 1240 to 1425 cm^{-1} region (no orange points).



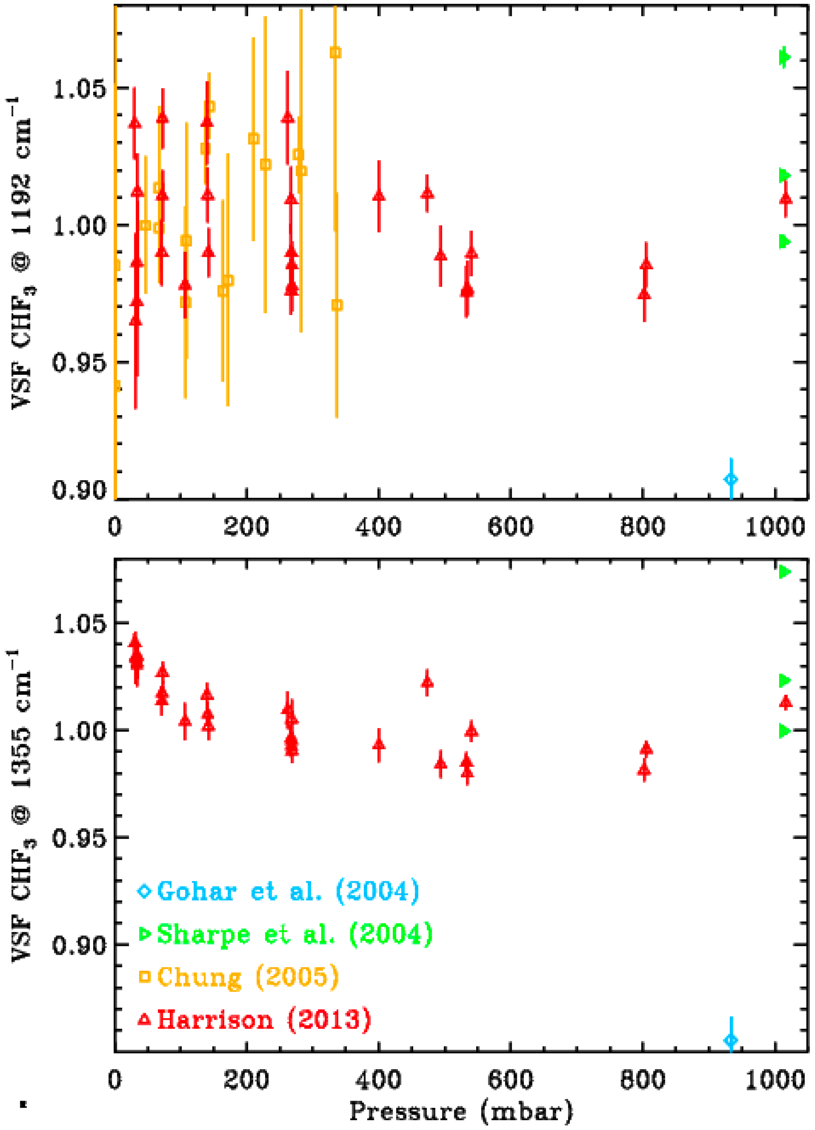
Used the final linelist to retrieve the CHF_3 VMR Scaling Factors from lab spectra. In a perfect world, these would all be 1.0.

Good consistency between Harrison's & Sharpe's (PNNL) measurements. Not only at 298K, where they were normalized into agreement, but also the T-dependence matches. There's a broad 5% dip around 240K in the Harrison's measurements, especially in 1192 cm^{-1} window.

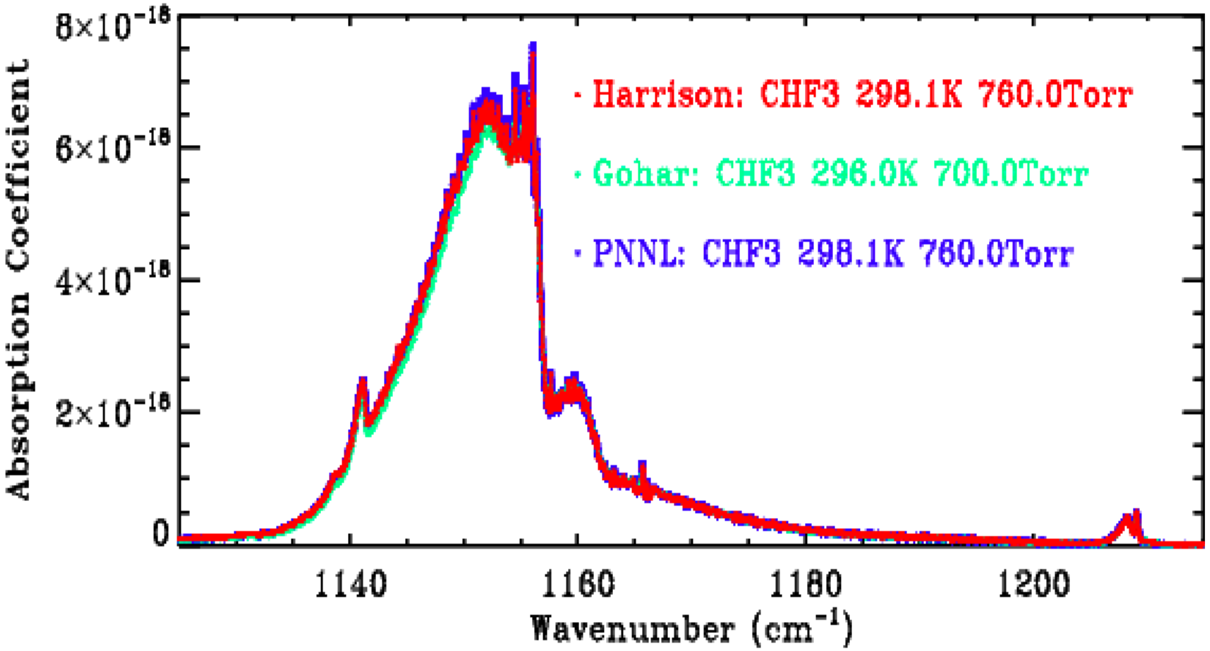
Chung's measurements have larger error bars than Harrison's, due to poorer spectral fits.

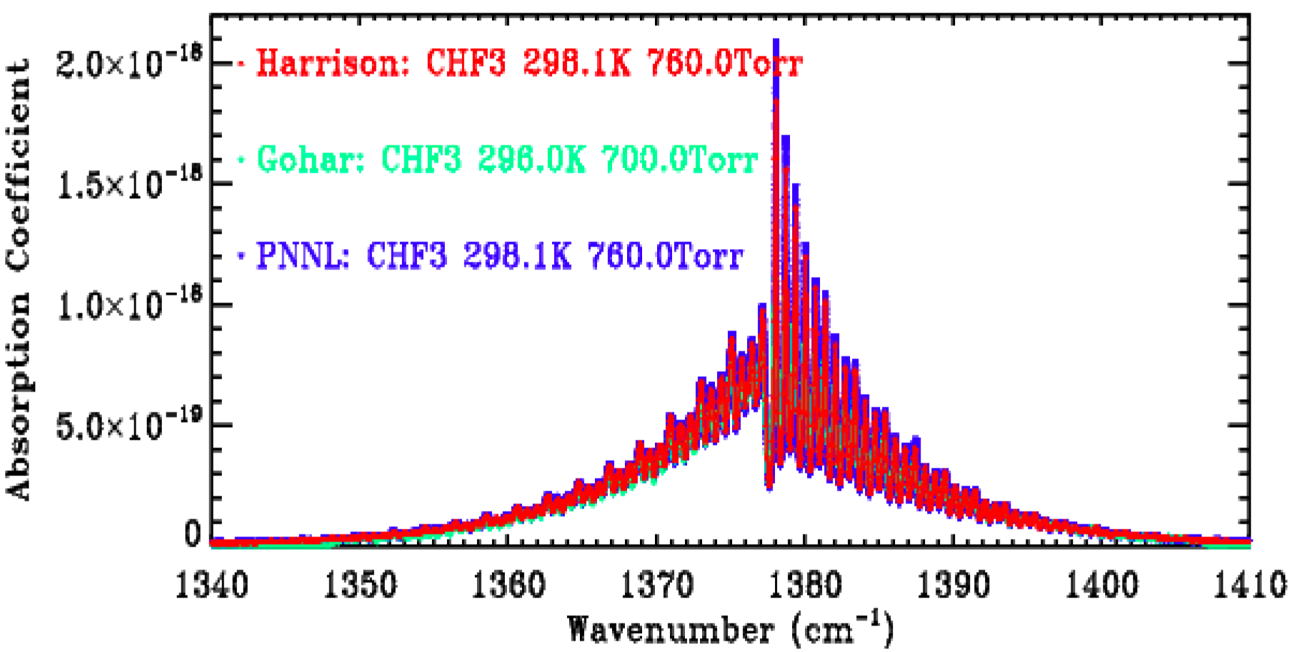
The Gohar measurements are 10-15% low, which is a mystery because their cross-sections seemed to agree well at 1192 cm^{-1}

Harrison's measurements show an increased VSF toward low pressures in the 1355 region, but not at 1192 cm^{-1}. Perhaps the assumed widths were inappropriate for the 1355 cm^{-1} region which contain multiple Q-branches, that are likely narrowed by line mixing.



Absorption Cross-Sections by different Instruments at 298K and ~1 atm

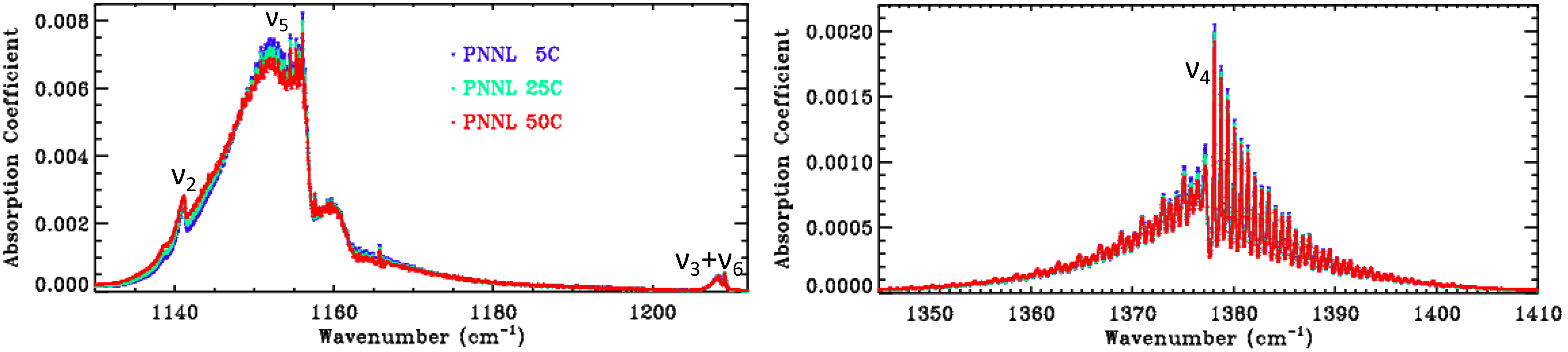




These cross-sections seem fairly consistent. The Gohar cross-section are smaller than the others below 1154 cm^{-1}, but very consistent above.

The Chung data are omitted because I only have these as transmittance spectra, not absorption cross-sections.

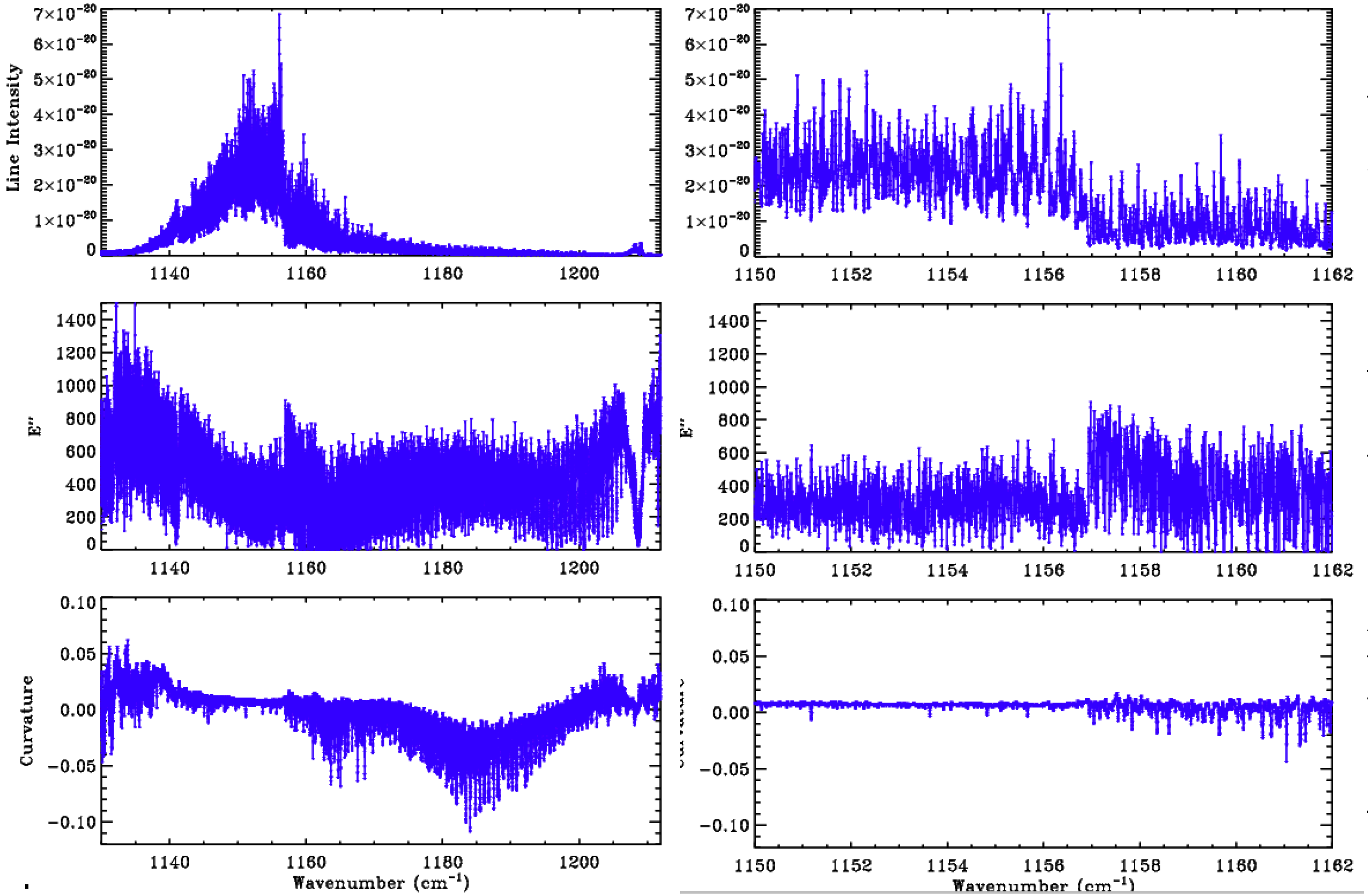
PNNL Absorption Cross-Sections at Different Temperatures



In the band center the absorption coefficient is largest at the cold temperature (blue), implying a low E”.
In the wings the absorption is largest at high temperature (red) implying high E”.

Note the factor 4 change in the Y-scale between the left- and right-hand panels

Derived PLL Intensities, E” and residual curvature: 1135-1212 cm^{-1}



Left-hand panels: derived spectroscopic parameters over 1135-1212 cm^{-1}.
Right-hand panels: same thing, zoomed into the band center.

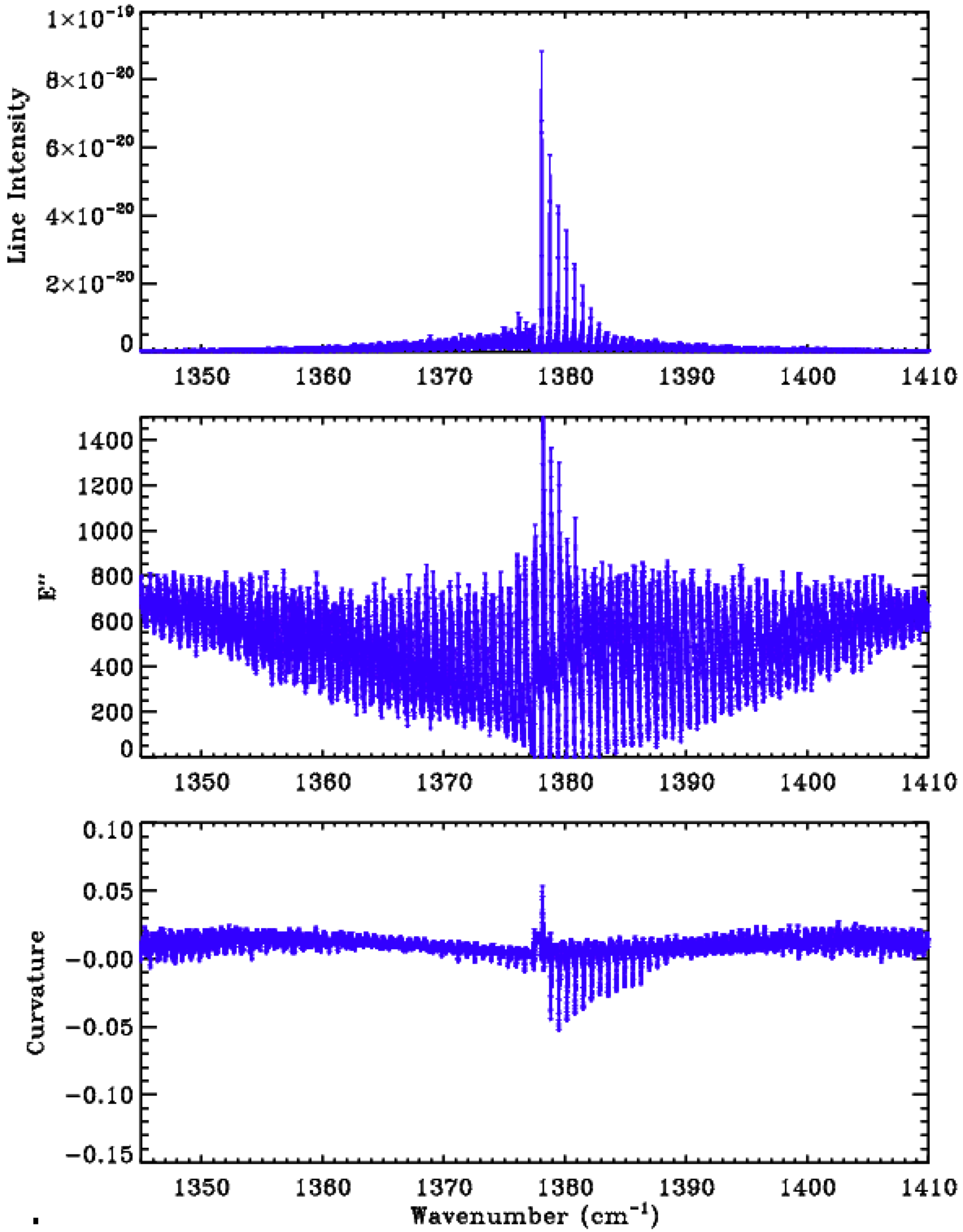
Why are the derived intensities and E” so noisy? This is not noise, this is real spectral structure that is smeared out in the near 1 atm spectral fits shown earlier.

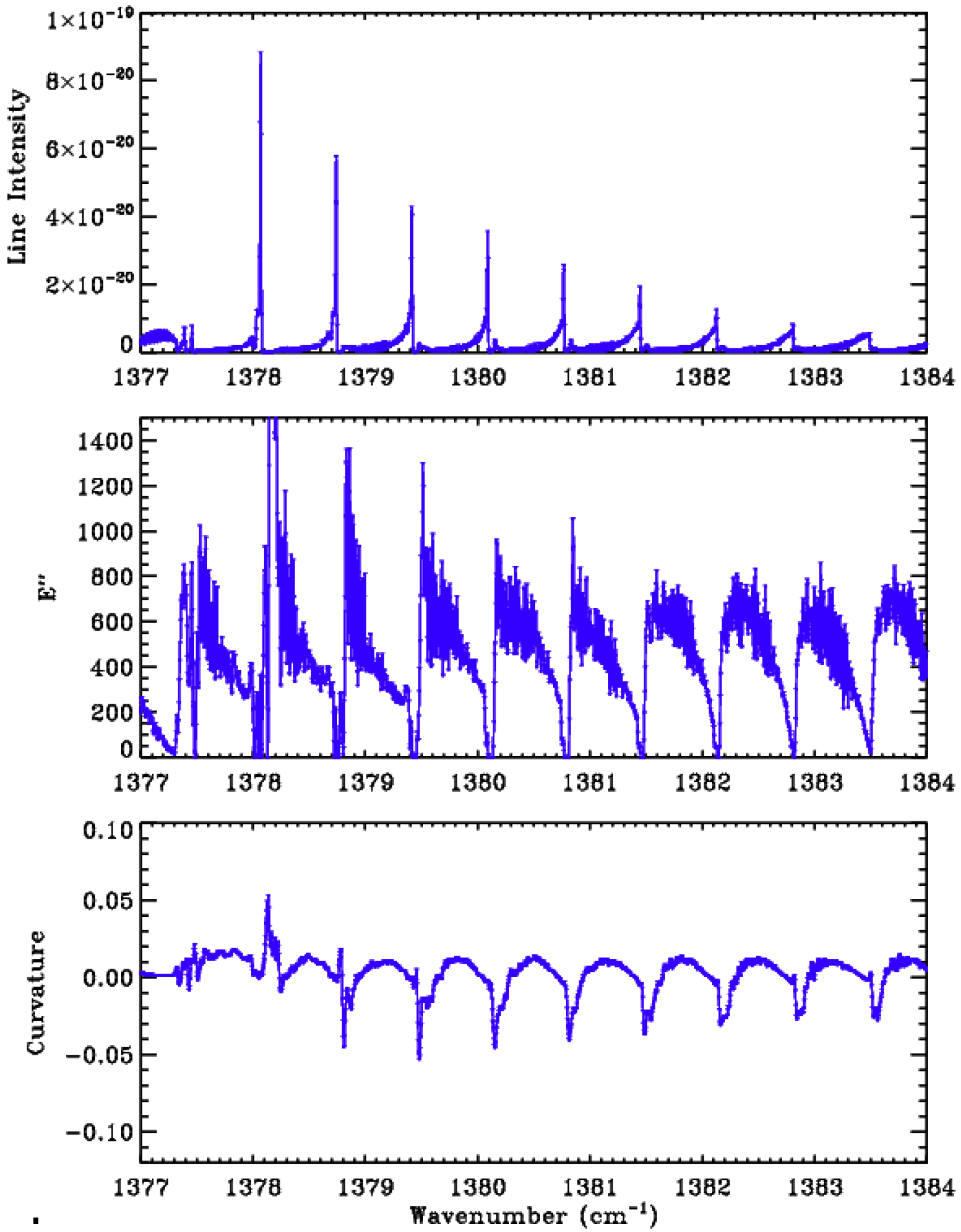
The lowest E” values are found in the 1150-1157 cm^{-1} region which also corresponds to the strongest absorption. There is an abrupt drop in absorption at 1157 cm^{-1} which looks like a band-head.

At 1157 cm^{-1} there is an abrupt increase in the E” values as if a hot-band underlying the fundamental, becomes revealed at band head.

The residual curvature is small across all parts of the band with strong absorption.

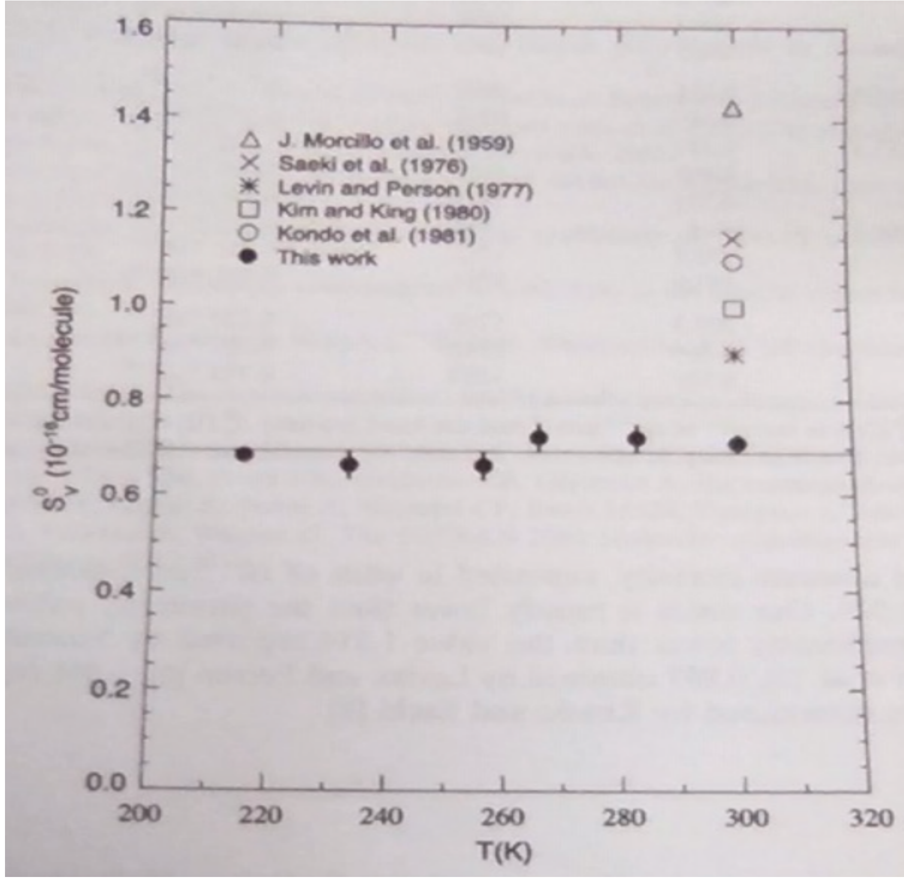
Derived PLL Intensities, E” and residual curvature





CHF_3 Integrated Band Intensity

Chung (2005) reported an integrated band intensity of 0.693±0.029 x 10^{-16} $cm^{-1}/(molec.cm^{-2})$ over the 1100-1280 cm^{-1} interval. This is considerably lower than all previous measurements at that time (see figure below) and since.



Harrison (2012) reported an an integrated band intensity of 1.228 x 10^{-16} $cm^{-1}/(molec.cm^{-2})$ over the 950-1500 cm^{-1} region. This was based on PNNL data (Sharpe et al., 2004) to which Harrison normalized his cross-sections. Over this same interval, our EPLL yields a integrated intensity of 1.20 x 10^{-16} $cm^{-1}/(molec.cm^{-2})$.

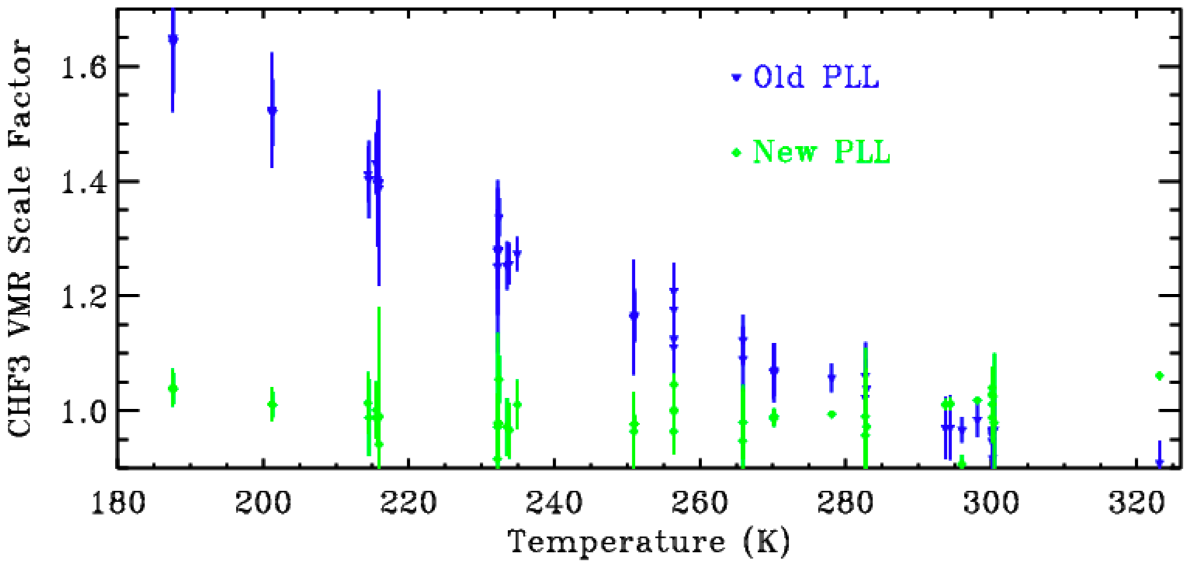
This 296K integrated intensity comparison is summarized below.

	1100-1280 cm^{-1}	950-1500 cm^{-1}
Gohar (2004)[#]	1.025x 10^{-16}	1.156 x 10^{-16} [$]
Chung (2005)	0.693 x 10^{-16}	Not Covered
PNNL (Harrison)	Not Reported	1.228 x 10^{-16}
Old EPLL (2011)	1.091 x 10^{-16}	Not Covered
New EPLL (2020)	1.067 x 10^{-16}	1.210 x 10^{-16}

[#] 256K [$] 950-1400 cm^{-1}.

Comparing Old and New PLLs: Fits to Lab spectra

Figure shows the results of fitting all lab spectra in a 38 cm^{-1} wide window centered at 1155 cm^{-1} using the old PLL (blue points) and the new PLL (green points). The green points are those shown on slide 6 (upper-left). All datasets (Harrison, Sharpe, Chung) have the same color points. At cold temperatures the old PLL causes large over-estimates of the retrieved CHF_3 amounts, by 30% at typical stratospheric temperatures (230K).



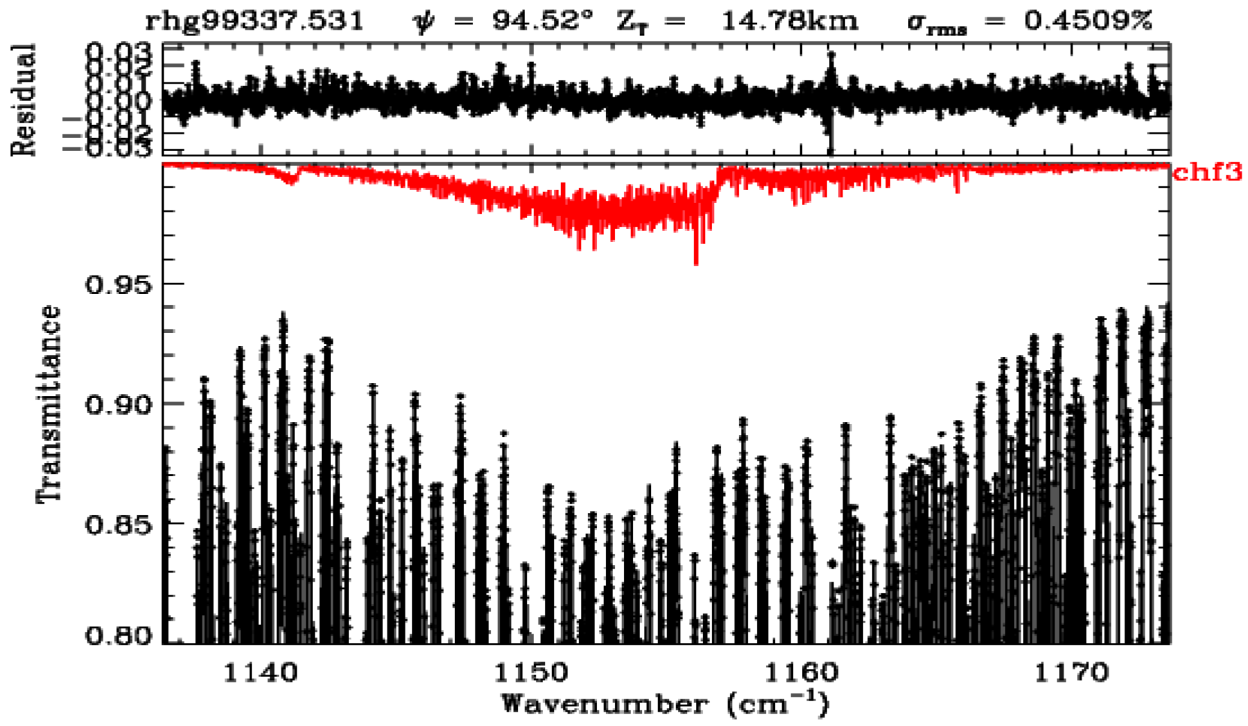
Why did the old PLL developed in 2011 do such a poor job at fitting the Chung measurements? Back in 2011 the only high-resolution lab measurements of CHF_3 were those of Chung (2008). Harrison had looked at these and compared their integrated cross-sections with the warm, low-res, measurements of Sharp (2004). Based on this, Harrison made large corrections to the Chung cross-sections – up to a factor 3 – before he gave them to me. I never saw the original Chung data.

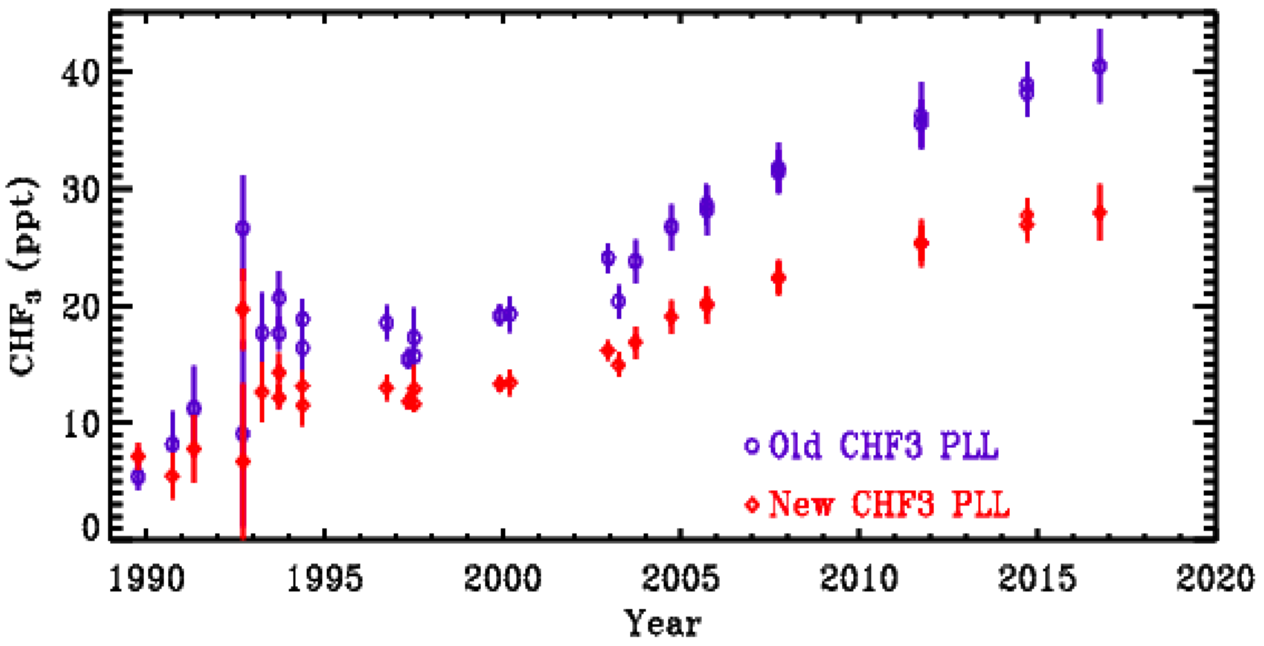
I found that in 2011 I had to make further adjustments to Chung's CHF_3 amounts to achieve consistency with warm, low-res spectra of Sharpe (2004). And many of the Chung spectra produced poor fits and hence large error bars. The Sharpe spectra, on the other hand, produced very good spectral fits and small error bars. I now think the resulting over-reliance on Sharpe spectra in 2011 was a mistake. It caused the Sharpe T-dependence from the 278-324K range being extrapolated to low temperatures. This mistake resulted in the old PLL having 37% of lines with E"=0 (negative values are not allowed) which is unphysical. In retrospect, I should have relied only on the Chung spectra to determine the T-dependence of the PLL due to its broader and more relevant range of temperatures.

In the new PLL, the results are dominated by the Harrison spectra since there are 27 of them (versus 3 from Sharpe) and they provide good spectral fits and hence small error bars. The resulting new PLL has only 0.5% of lines with E"=0, which is to be expected.

Effect on MkIV Balloon CHF_3 Retrievals

We compared the old and new CHF_3 EPLL on the MkIV balloon dataset. The figure below shows the average CHF_3 over the 12-35 km altitude range, plotted versus the year of measurement. The new EPLL produces VMRs ~ 30% smaller than previously. The change may seem rather large given the small change in the overall band intensity at 296K (see previous slide). But remember that the stratospheric temperatures are 200 to 250K which implies that there was a serious error in the E" of the old EPLL. Over the 1140-1170 cm^{-1} window, the old PLL had a weighted-mean E" of 650 cm^{-1} versus 350 cm^{-1} for the new PLL. The change to ground-based retrieved VMRs, where the CHF_3 is typically much warmer, should be smaller. The spectral fits to the balloon data also improved using the new EPLL. Lower left show a fit to a spectrum measured in late 1999 at 15 km tangent altitude, where the effective temperature was ~200K. Main interfering gases are N_2O, O_3 and CCl_2F_2.





Summary & Conclusions

From 4 laboratory data-sets containing 56 spectra, a new EPLL has been generated for CHF_3 covering 1104.9 to 1425.0 cm^{-1}. Due to this wider spectral coverage and the closer line spacing (0.004 cm^{-1}), the total number of lines is nearly 3x larger than the old EPLL.

A large improvement in the quality is the EPPL is achieved, largely a consequence of including Harrison's (2013) lab spectra (unavailable in 2011 when the old EPLL was made) which are higher resolution than Chung's or Sharpe's and cover a wider range of T/P conditions. The down-side of the Harrison cross-sections is that they were normalized to PNNL integrated intensities, and therefore perpetuate any bias therein.

Only 0.5 % of the lines in the new EPLL have E"=0, as compared with 37% in the old PLL. The 0.5% figure is consistent with the presence of noise on the measurement. Despite the large fraction of lines with E"=0, the old linelist had a mean-intensity-weighted E" values of 654 cm^{-1} in the 1155 cm^{-1} region, which caused a ~30% over-estimate in CHF_3 at stratospheric temperatures. The new EPLL has a mean E" value of 350 cm^{-1}.

The integrated band intensity of the new EPLL is similar to the old EPLL, both being constrained to match PNNL cross-sections (Sharpe et al. 2004). It is somewhat worrying that there are only 3 independent measurements of integrated band intensity, and that one of them (Chung) is 30% lower than the other two (Gohar, Sharpe).

Regarding uncertainties, for retrievals that use the strong nu_5 band I would guess a total spectroscopic error of 15%, including the band intensity and its T- and P-dependencies. The 15% value is a big improvement over the old EPLL for which I estimated an uncertainty of 40% (nu_5 band). For retrieval using weaker bands such as the nu_2 Q-branch at 1141 cm^{-1} or the nu_4 at 1378 cm^{-1} band the uncertainty will be larger, perhaps 20%.

Future Work

Figure out why the Gohar spectrum give VSFs of 0.9 and 0.85 in the two fitted windows, despite the cross-sections being similar to the others. Since there is only one such spectrum out of 54, there is probably little affect on the resulting EPLL, so not worth fixing immediately.

Investigate the effect of narrowing the prescribed ABHW/SBHW from the current 0.06/0.10 values to see if this reduces the Pressure-dependence and improves the fits.

Need more lab measurements of the absolute cross-sections (not normalized to Sharpe's PNNL measurements).

References

Gohar, L. K., G. Myhre, and K. P. Shine (2004), Updated radiative forcing estimates of four halocarbons, J. Geophys. Res.-Atmos., 109(D1).

Sharpe, Steven W., Johnson, Timothy J., Sams, Robert L., Chu, Pamela M., Rhoderick, George C., Johnson, Patricia A., Gas-Phase Databases for Quantitative Infrared Spectroscopy. Applied Spectroscopy 2004; 58:1452-1461. doi:10.1366/0003702042641281.

Chung, Y. K., (2005). Absorption Cross-sections off HFC-23 at atmospheric conditions, JQSRT, 96,2005, 281-287

Harrison, J. J., Boone, C. D., Brown, A. T., Allen, N. D. C., Toon, G. C., & Bernath, P. F. (2012). First remote sensing observations of trifluoromethane (HFC-23) in the upper troposphere and lower stratosphere. *Journal of Geophysical Research: Atmospheres, 117*(5), D05308. doi:10.1029/2011JD016423

Harrison, J. J. (2013). Infrared absorption cross sections for trifluoromethane. Journal of Quantitative Spectroscopy and Radiative Transfer 2013;130:359-364. doi:10.1016/j.jqsrt.2013.05.026.

Supplementary Material

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 109, D01107, doi:10.1029/2003JD004320, 2004

Updated radiative forcing estimates of four halocarbons

L. K. Gohar
Department of Meteorology, University of Reading, Reading, UK

G. Myhre
Department of Geosciences, University of Oslo, Oslo, Norway

K. P. Shine
Department of Meteorology, University of Reading, Reading, UK

Received 3 November 2003; accepted 14 November 2003; published 13 January 2004.

[1] There is a large discrepancy (greater than 20%) between two recently published estimates of radiative forcing of four hydrofluorocarbons (HFCs), two of which, HFC-23 and HFC-134a, are the most abundant HFCs in the atmosphere. We report an intercomparison, using two different radiative transfer methods, aimed at clarifying the forcing values for HFC-23 and HFC-134a, as well as HFC-227ea and HFC-32. The calculated global, annual mean radiative forcings differed by 12% or less and are within the expected errors in the radiative forcing estimates. *INDEX TERMS:* 1699 Global Change: General or miscellaneous; 3359 Meteorology and Atmospheric Dynamics: Radiative processes; 3399 Meteorology and Atmospheric Dynamics: General or miscellaneous; *KEYWORDS:* radiative forcing, halocarbons

Table 1. Integrated Absorption Cross Sections of the Spectra Used in the Present Work (200–2000 cm^{-1}) and Those Employed in the Work of *Sihra et al.* [2001] (450–2000 cm^{-1})[a]

Gas	Integrated Cross Section, 10^{-17} cm^2 $molecules^{-1}$ cm^{-1}	
	Ford 2003	Ford Data Given by *Sihra et al.* [2001]
HFC-134a	13.07	12.40
HFC-227ea	23.27	23.04
HFC-23	11.82	11.61
HFC-32	5.77	5.65

[a]Spectra were recorded at 296 K in 700 torr of air diluent (Ford Motor Company).