

JPL Activities (relevant to ACE)



Geoff Toon

*Jet Propulsion Laboratory
California Institute of Technology*

Developed three empirical pseudo-linelists:

- C_2H_6 based on lab measurements of Harrison et al. [2010]
- CHF_3 based on lab measurements from Chung and Varanasi
- HCFC-141b based on Clerbaux [1993] cross-sections

These are all heavy molecules – so difficult to generate complete and accurate linelists from spectroscopic first principles.

Instead use an empirical approach.

An empirical C₂H₆ Pseudo-linelist covering 2720-3100 cm⁻¹

I made a presentation at the ACE meeting 3 years ago complaining about the C₂H₆ spectroscopy in the 3000 cm⁻¹ region.

Since then the situation has improved considerably thanks to lab measurements performed at the RAL and recently published in:

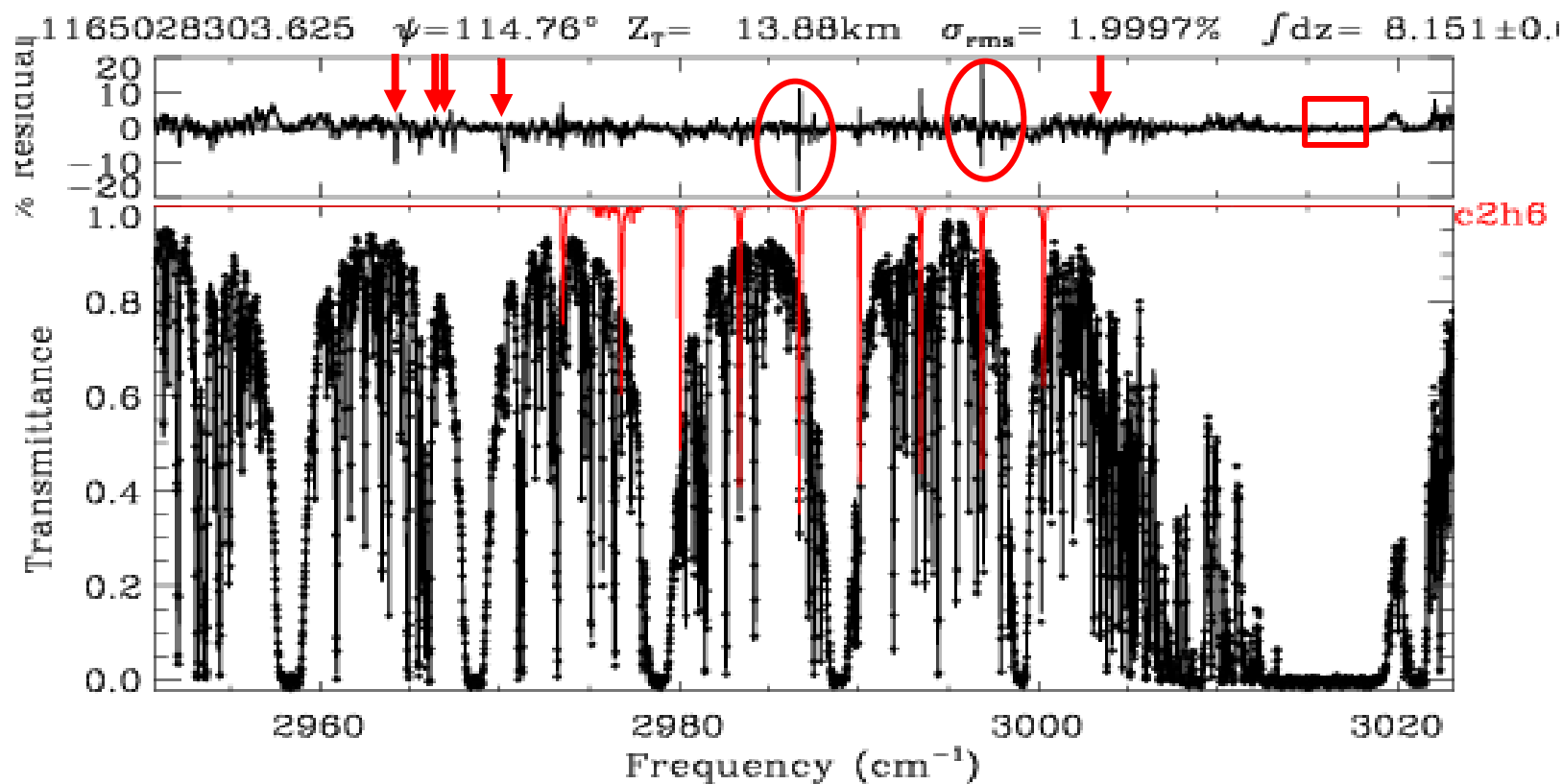
Jeremy J. Harrison, Nicholas D. C. Allen, and Peter F. Bernath,
Infrared absorption cross-sections for ethane (C₂H₆) in the 3 μm
region, JQSRT, 111, 357–363, 2010

Using 27 lab spectra of Harrison et al., covering a wide range of T/P, a pseudo-linelist covering the 2720-3100 cm⁻¹ region was developed.

In this presentation I will compare it to HITRAN_2008.

Fits to ACE Spectra – HITRAN 2008

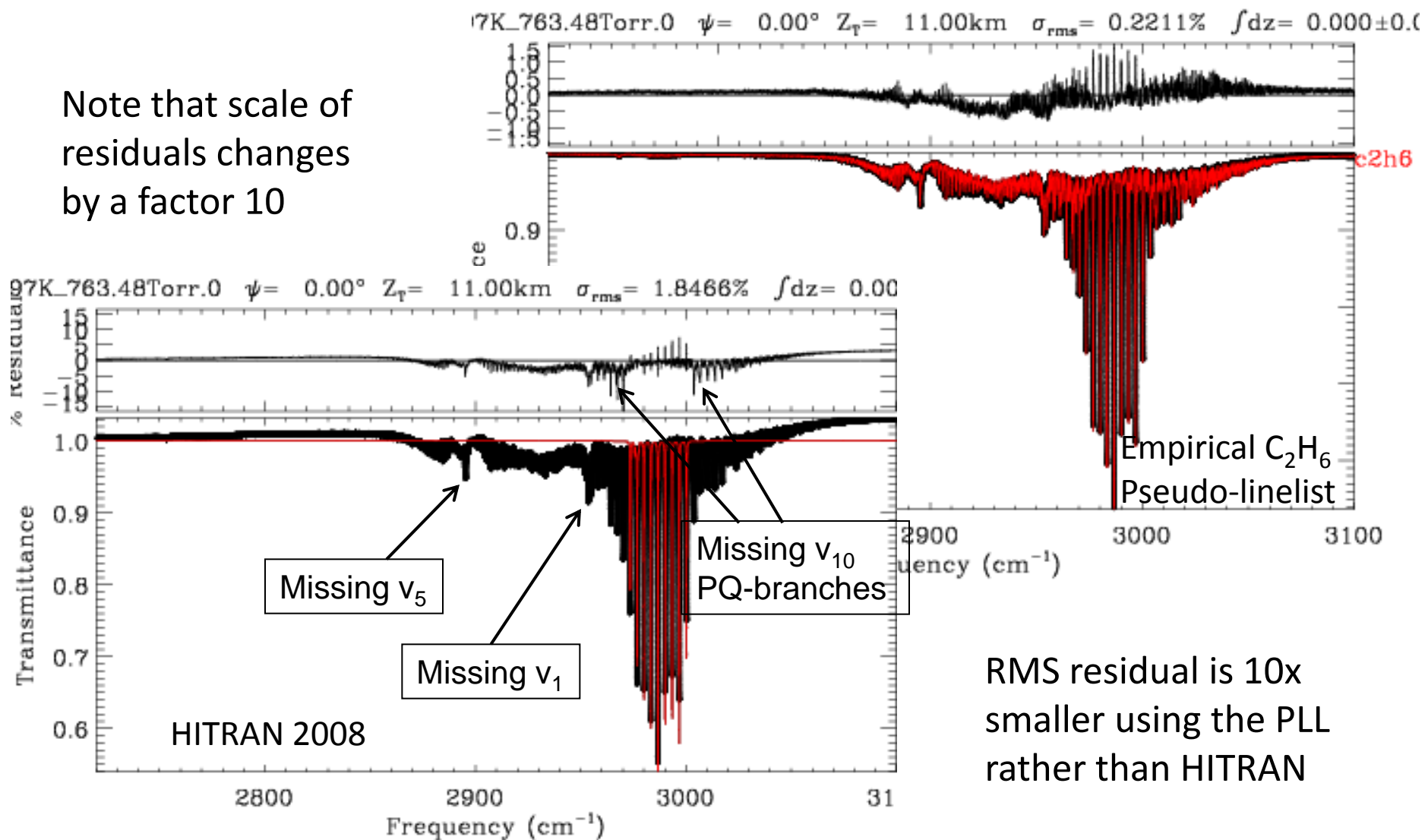
Fit to an ACE spectrum acquired at 13.88 km tangent altitude in the tropics.
Strongest absorptions due to CH_4 , H_2O , O_3 , and C_2H_6 (red).



Largest residuals due to the 2986 and 2997 cm^{-1} C_2H_6 PQ-branches (red circles)
Residuals also seen due to missing PQ-branches (Red arrows).
Noise level is about 0.3% (Red rectangle), so residuals are mainly systematic.

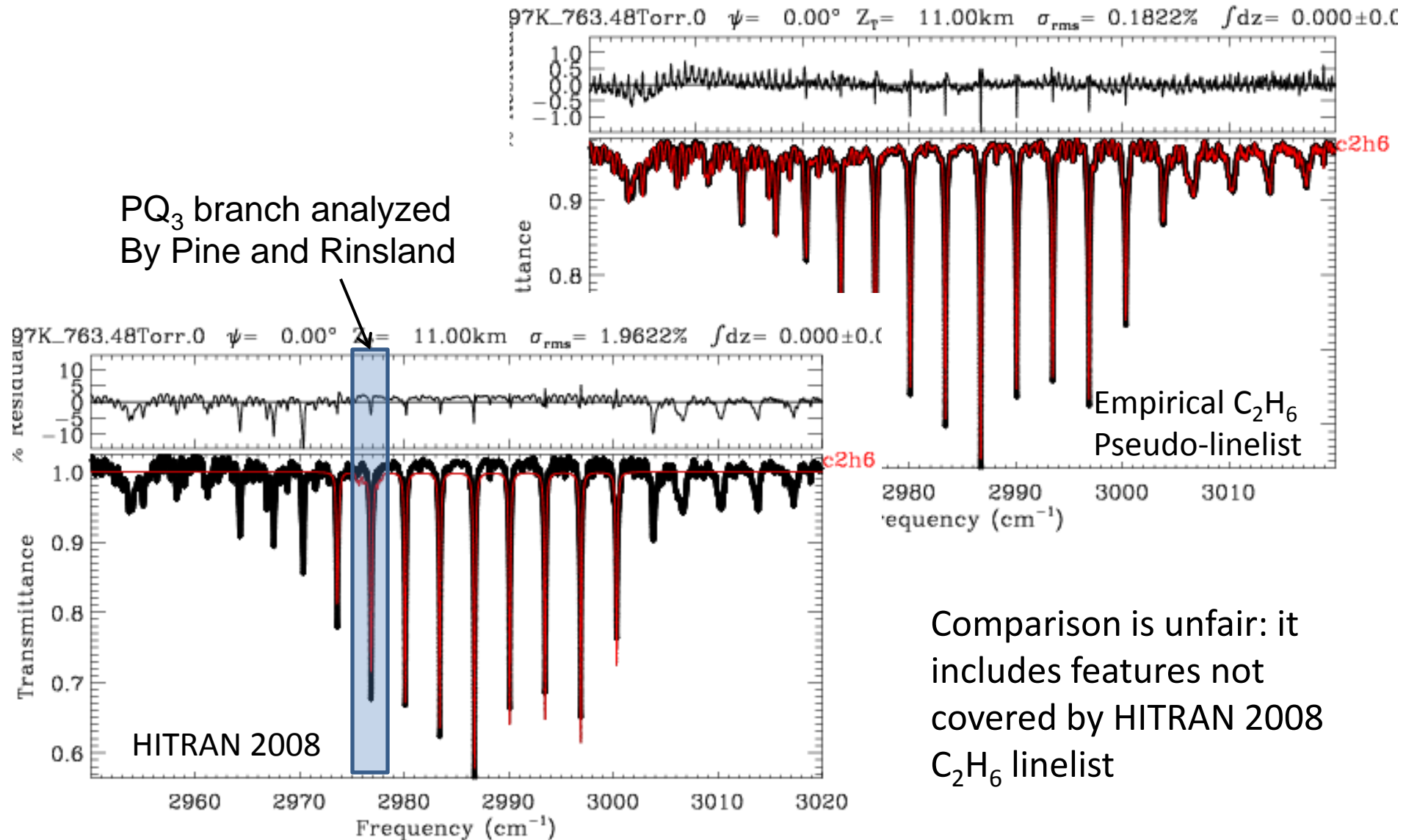
C₂H₆ lab spectrum: 1 atm, 297K

Note that scale of residuals changes by a factor 10

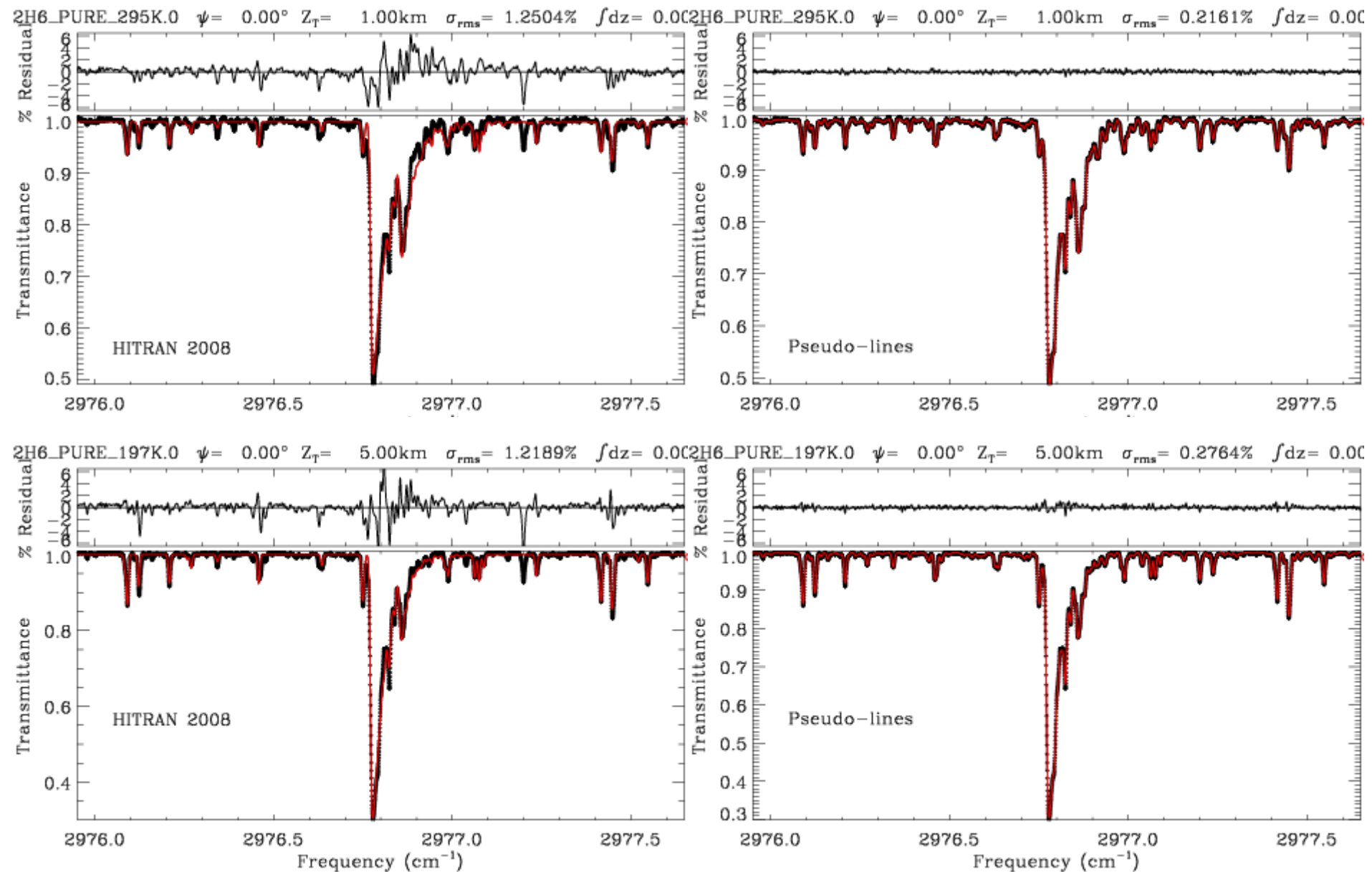


RMS residual is 10x smaller using the PLL rather than HITRAN

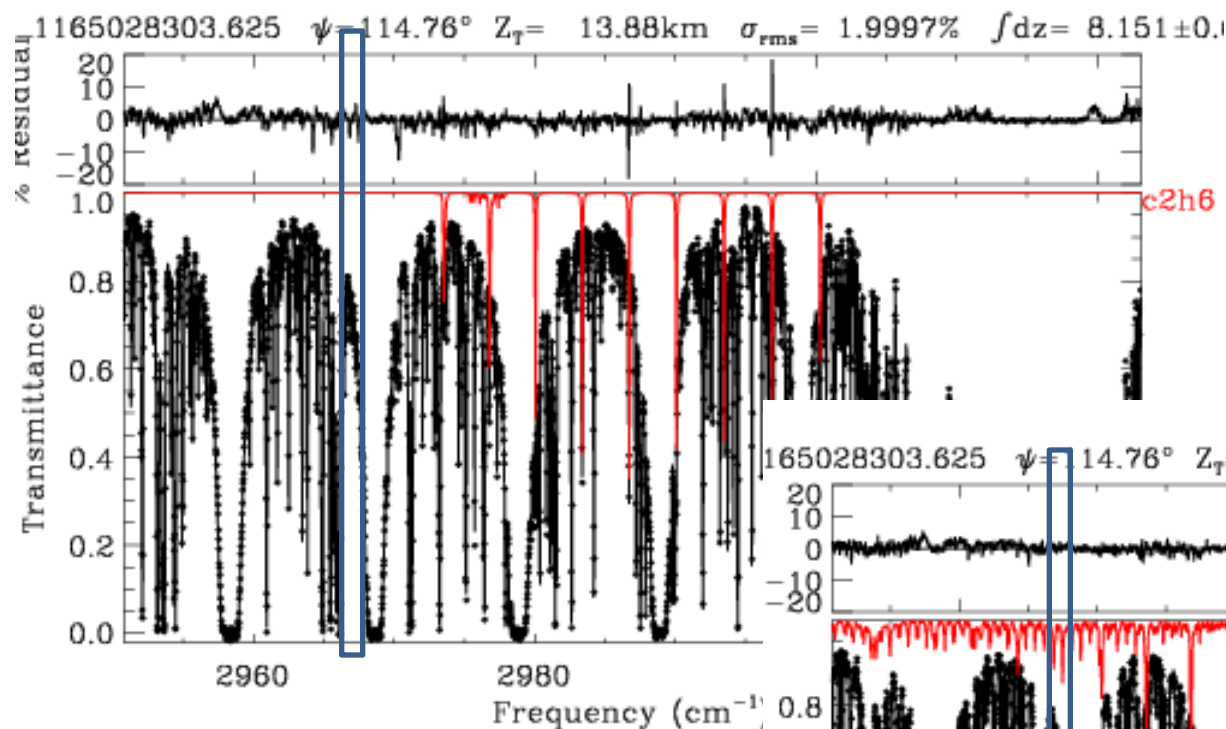
Zoom into region of PQ branches



Fits to Lab spectra of PQ₃ branch

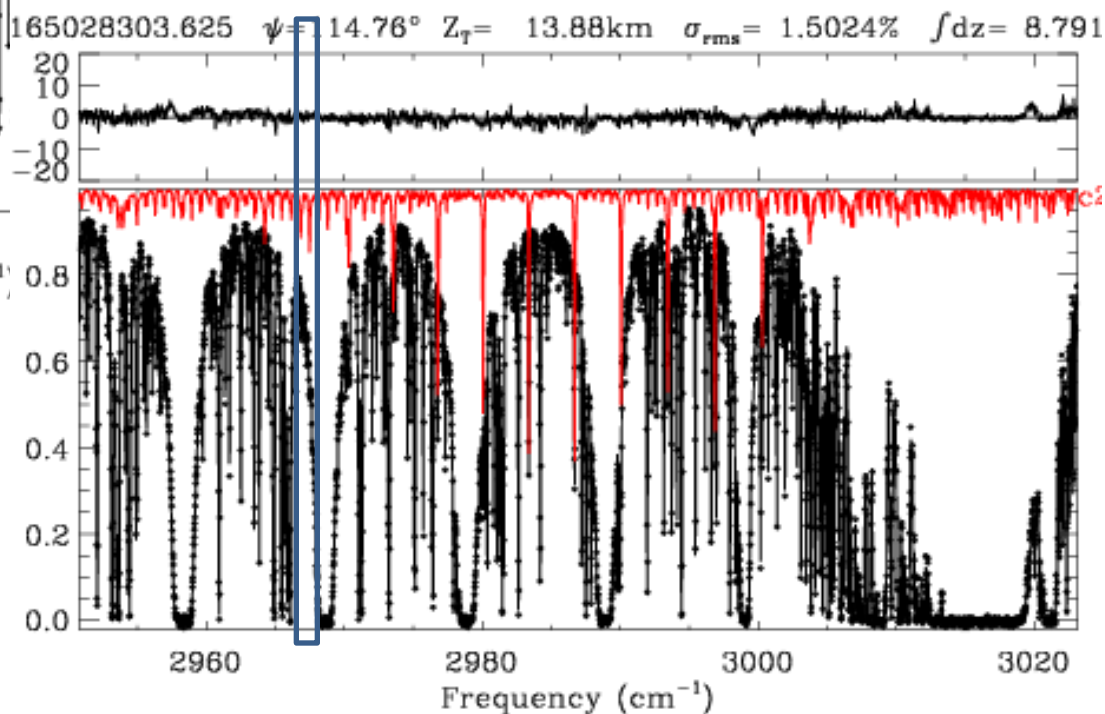


Fits to an ACE spectrum at 14 km

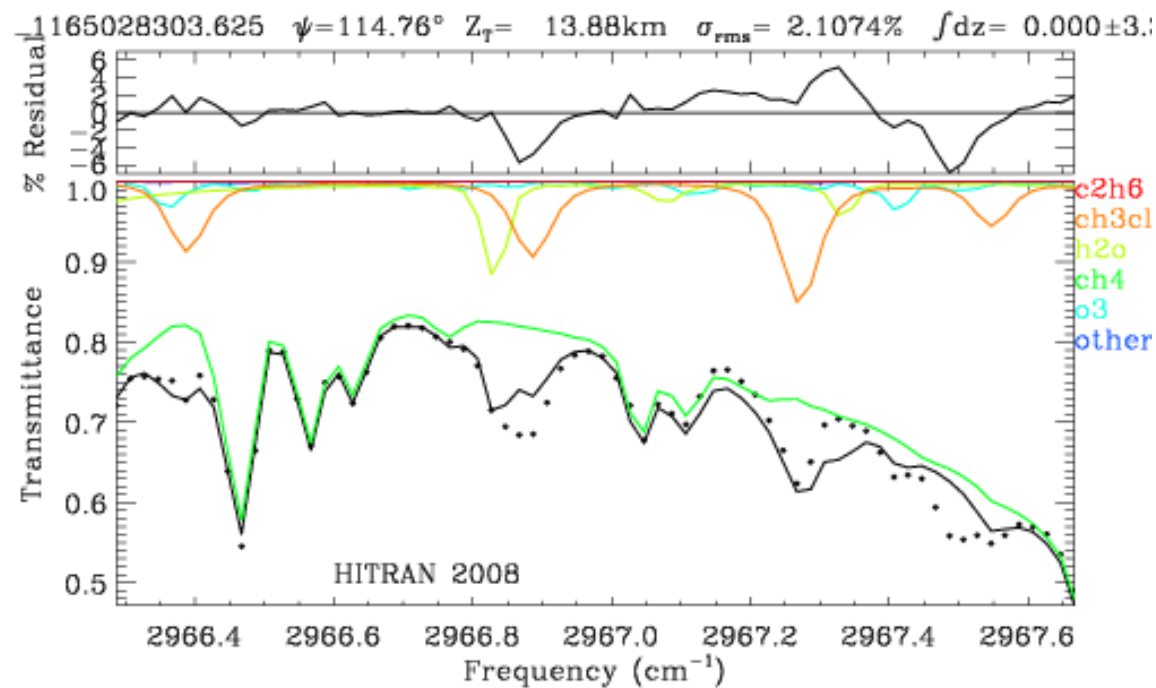


Left: HITRAN 2008

Below: Empirical
 C_2H_6 pseudo-linelist



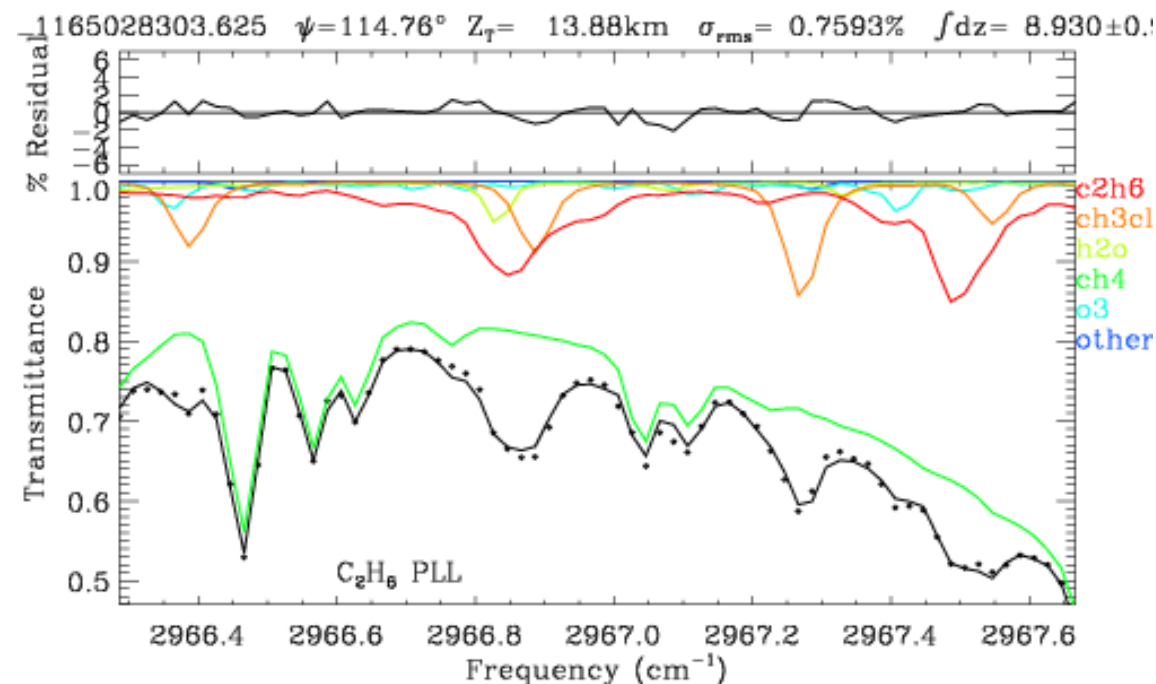
Blue rectangle denotes
window often used for
 CH_3Cl retrievals



Impact of empirical C_2H_6 pseudo-lines on ACE spectral fits of CH_3Cl

No C_2H_6 absorption lines in this interval.

Large systematic residuals due to missing C_2H_6 lines



Using empirical C_2H_6 pseudo-lines instead of HITRAN 2008 lines.

RMS residual is reduced by nearly a factor 3

C₂H₆ Summary

- In atmospheric spectra, the 2850-3050 cm⁻¹ region contains absorptions from many gases of interest (e.g. everything having a C-H stretch).
- This interval also contains the strongest infrared absorptions of C₂H₆, which can exceed 50% in depth in tropical limb spectra.
- Although the HITRAN 2008 C₂H₆ captures the 9 strongest C₂H₆ PQ-branches, it omits all of the weaker absorptions features.
- Quantum-mechanical analysis of the C₂H₆ spectrum is very difficult and therefore lacking, with the exception of the PQ₃ branch.
- As a temporary fix, an empirical C₂H₆ linelist containing 80,000 pseudo-lines has been developed based on laboratory measurements by Harrison et al. [2010].
- Use of this pseudo-linelist results in much smaller residuals to fits to lab spectra and to atmospheric spectra (e.g. ACE) and can significantly improve retrievals of other minor gases (e.g. CH₃Cl).

CHF_3 (HFC-23)

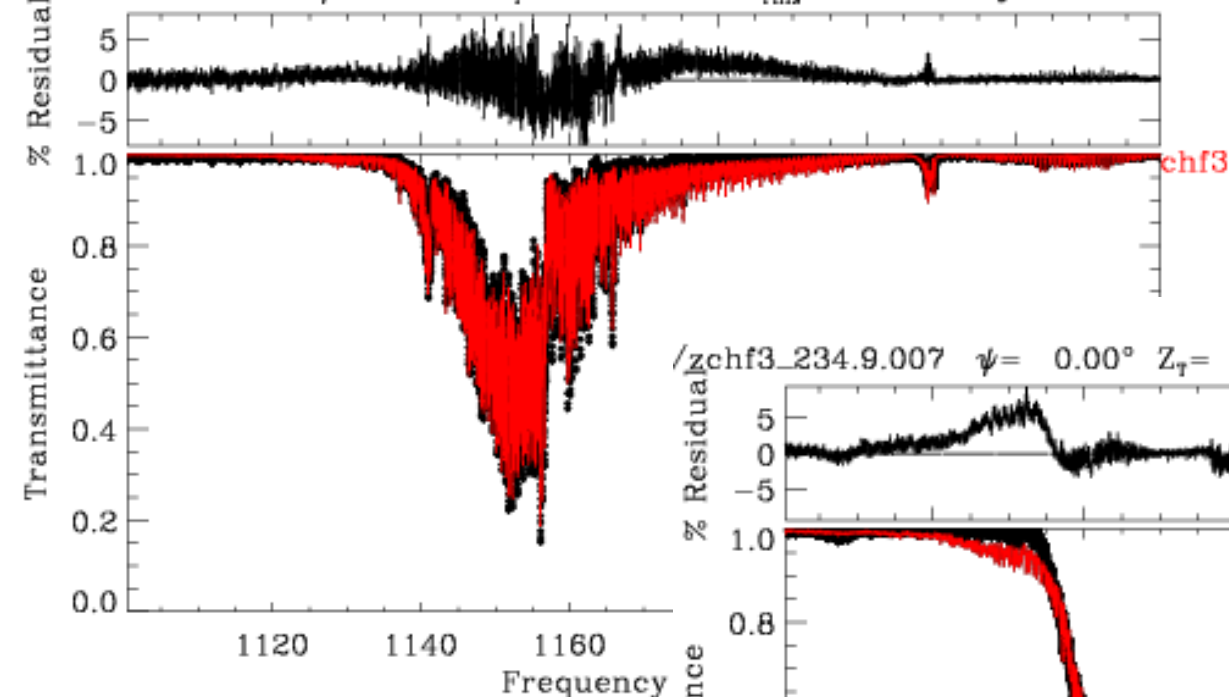
Laboratory Measurements made by Chung/Varanasi

Cross-sections were “re-normalized” by Jeremy Harrison

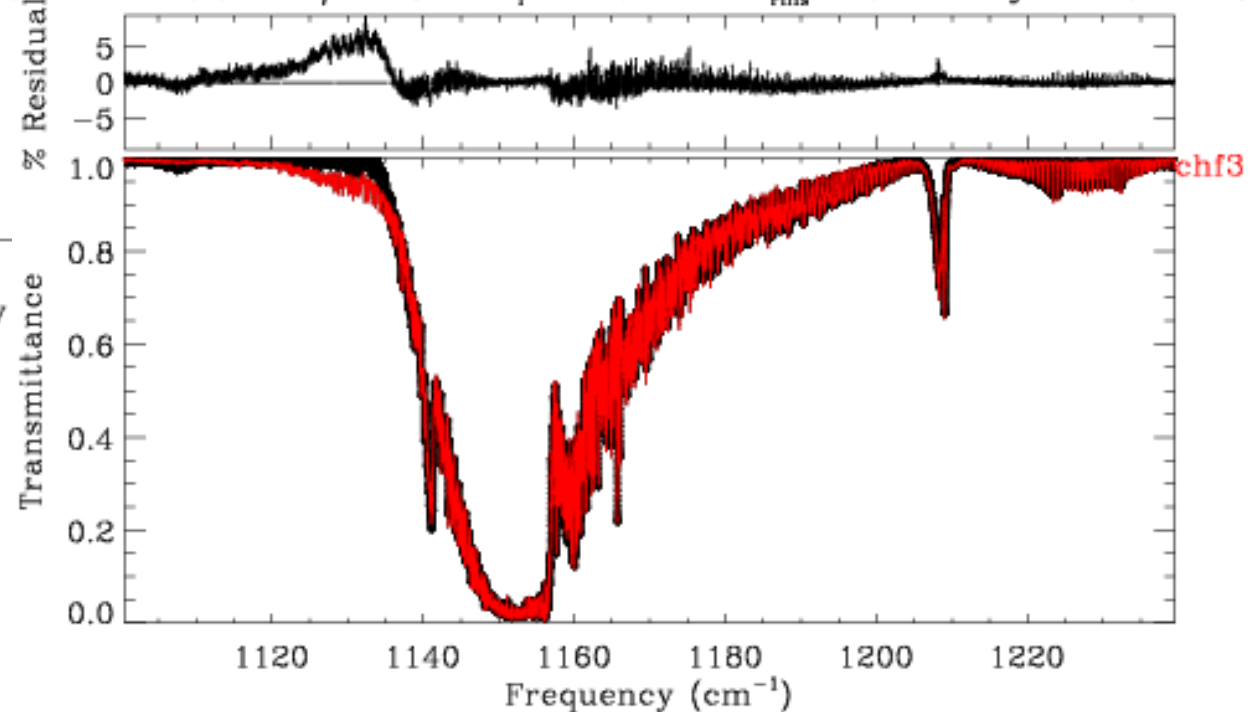
Pseudo-linelist developed by fitting these lab spectra

Fits to lab spectra using pseudo-lines

/zchf3_215.5.001 $\psi = 0.00^\circ$ $Z_T = 24.00\text{km}$ $\sigma_{\text{rms}} = 1.2887\%$ $\int dz = 0.000 \pm 0.0$

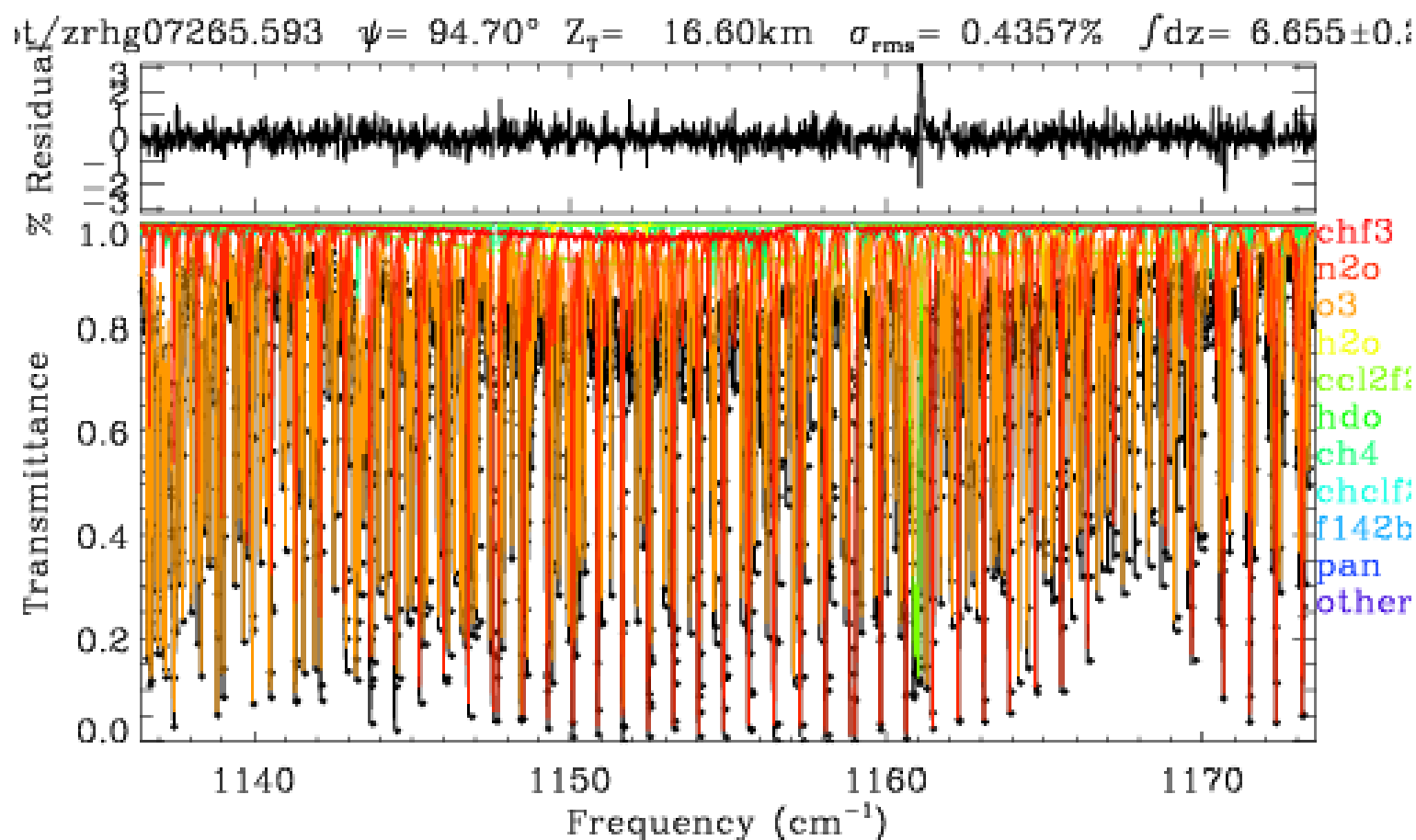


/zchf3_234.9.007 $\psi = 0.00^\circ$ $Z_T = 19.00\text{km}$ $\sigma_{\text{rms}} = 1.6070\%$ $\int dz = 0.000 \pm 0.0$

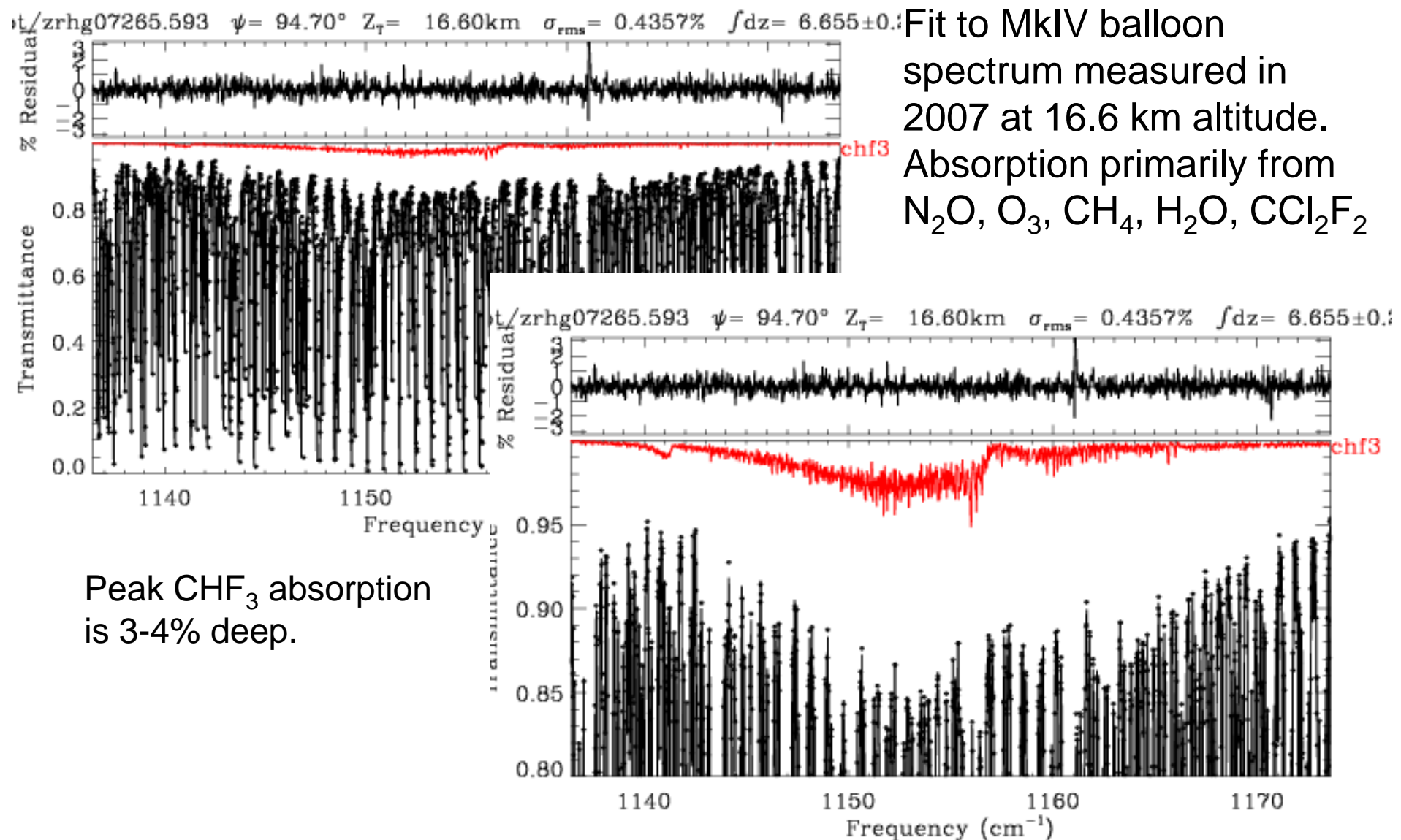


Fits to MkIV balloon spectra

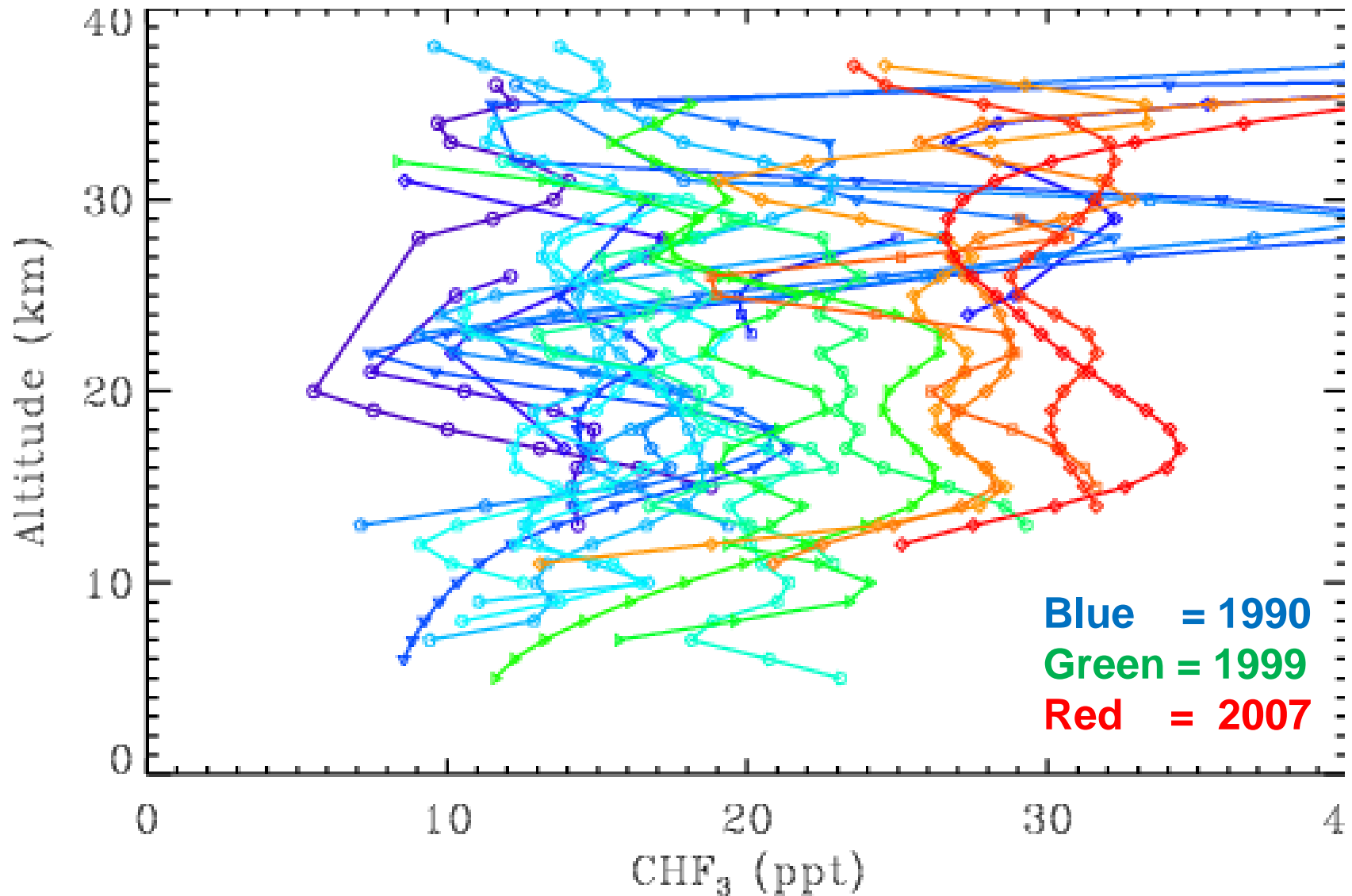
Strong interferences from N_2O , O_3 , H_2O , CCl_2F_2 , HDO , CH_4



Fits to MkIV balloon spectra



MkIV CHF₃ balloon profiles



Summary/Conclusions CHF₃

An empirical pseudo-linelist has been developed covering 1100-1240 cm⁻¹ with 14,001 lines.

It is based on unpublished lab measurements by Chung and Varanasi

Fits to lab spectra were poor (up to 4% residuals) for unknown reasons

Absorption due to CHF₃ of up to 3-4% is observable in solar occultation spectra of the atmospheric limb.

Atmospheric CHF₃ vmrs retrieved from MkIV balloon spectra strongly increase from 10 ppt in 1990 to 30 ppt in 2007.

Pseudo-Linelists - Rationale

Definition: A list of discreet lines whose intensities, E'' , (perhaps positions) have been chosen to give the best possible fit to available lab spectra. This choice is made blindly (least-squares) without any spectroscopic insight.

Why create a pseudo-linelist – why not use the cross-sections directly ?

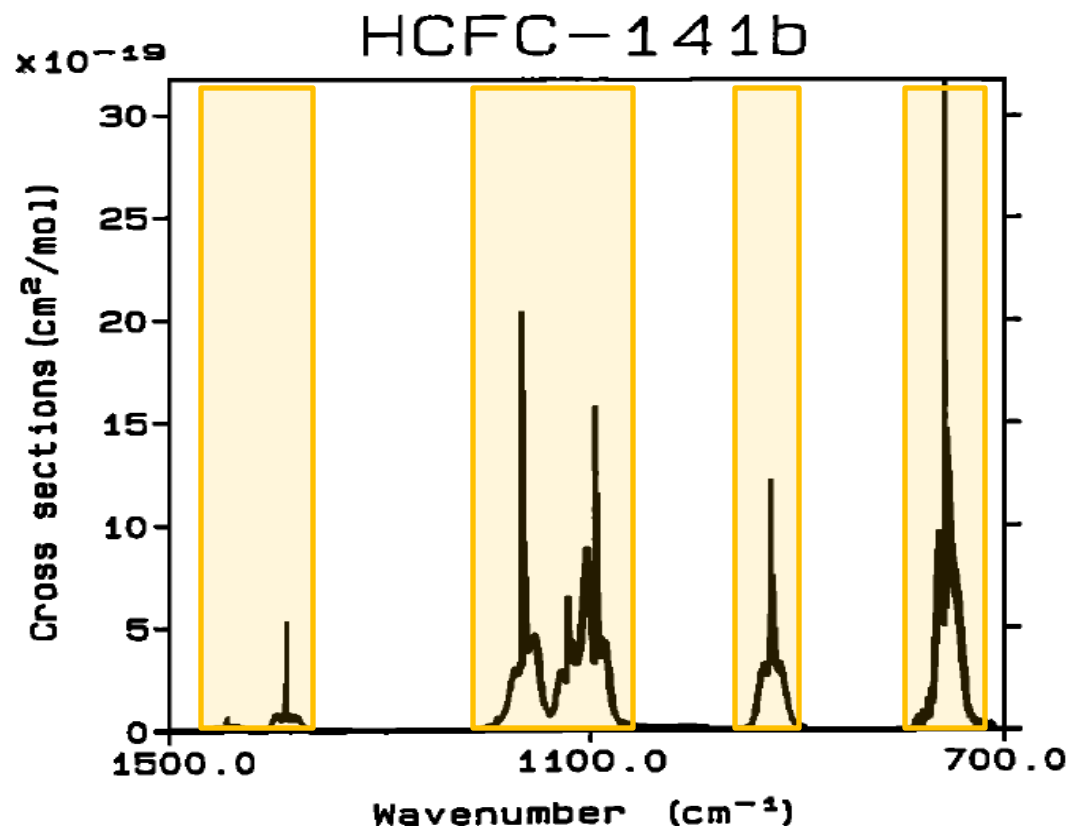
- Better interpolation/extrapolation of T and P:
 - Partition functions provide better T-dependence
 - Lab spectra are often made at low- or high-P only (e.g. PNNL)
- Allows input of multiple lab data-sets simultaneously
- Uses the same code as the HITRAN linelist
- Identification of inconsistencies between lab data (e.g. outliers)
- Opportunity for correcting systematic errors such as:
 - Contamination
 - Zero level offsets
 - Channel fringes
 - ILS of lab spectrometer

HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$)

Derived empirical pseudo-linelist for HCFC-141b from HITRAN cross-sections, which are based on the work of Clerbaux [1993]

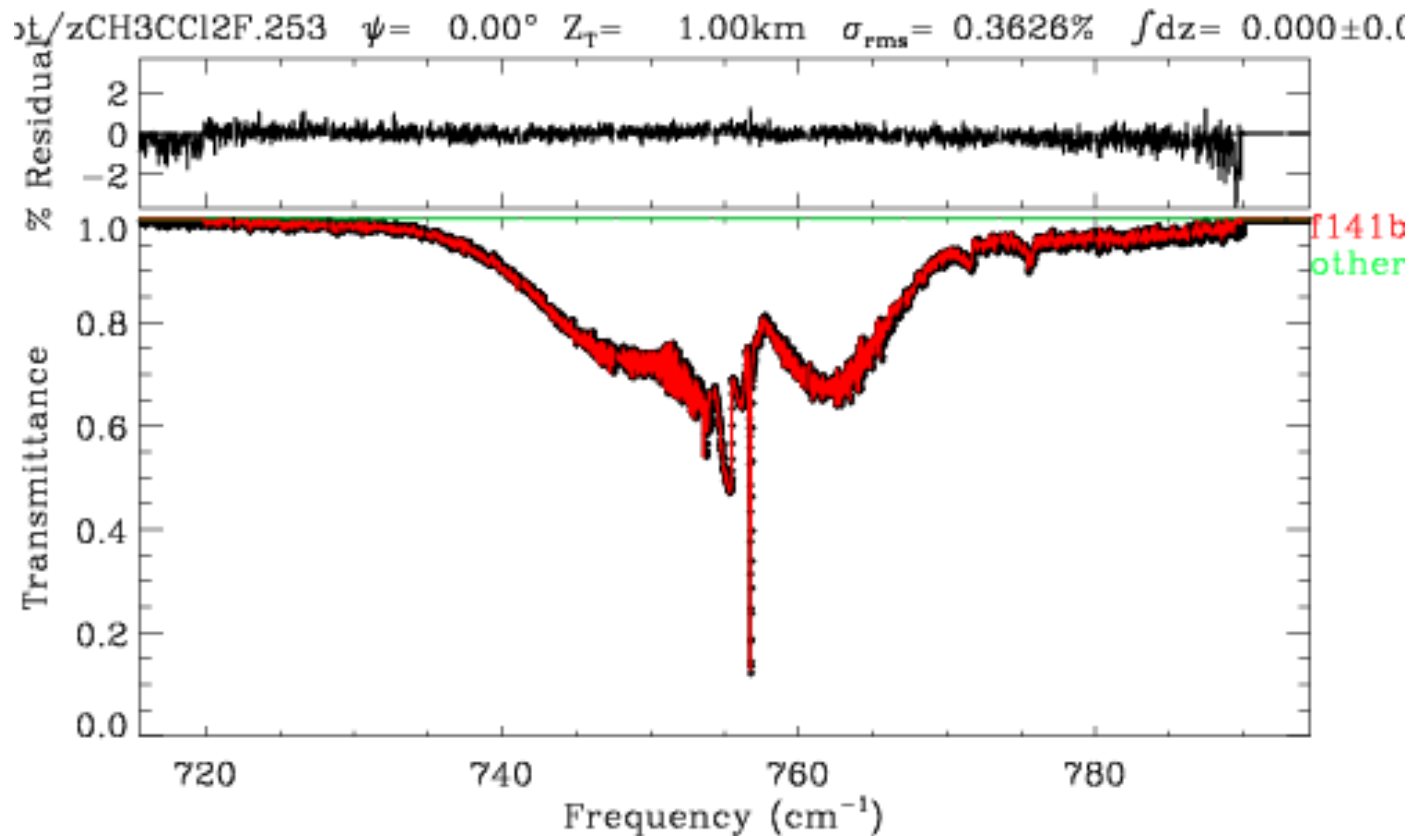
720- 790 cm^{-1}	7001 lines
900- 950 cm^{-1}	5001 lines
1055-1200 cm^{-1}	14501 lines
1365-1465 cm^{-1}	10001 lines

36004 lines total



HFC-141b

Example of fit to a 253K lab spectrum in the strongest band



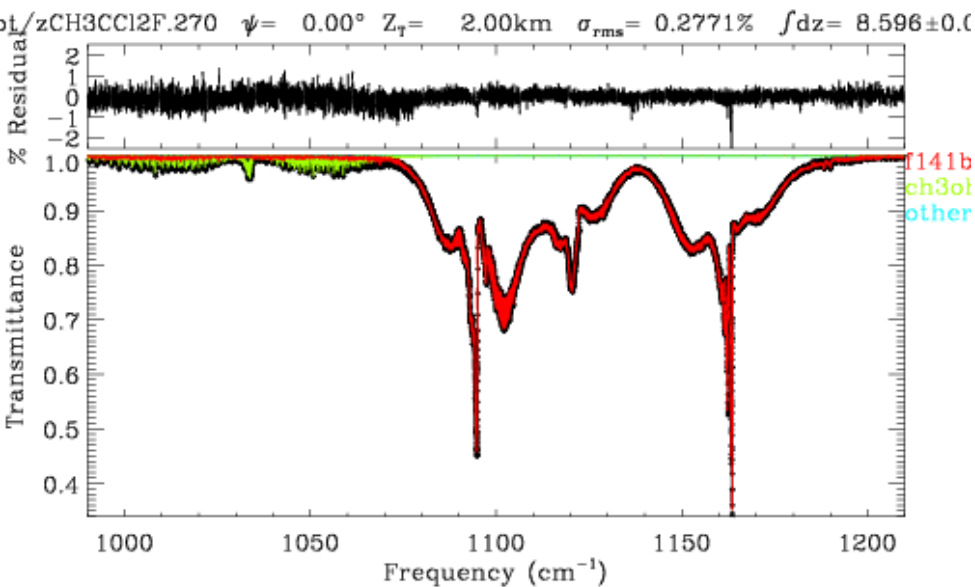
Incorrect band strength in HITRAN

TABLE 2: Integrated Cross Sections ($\text{cm molecule}^{-1} \times 10^{17}$) for HCFCs and HFCs

Molecule	Integration Limits, cm^{-1}	Integrated Cross Sections			Uncertainties
		287 K	270 K	253 K	
HCFC22 (CHClF_2)	765–855	2.36	2.32	2.25	(0.09)
	1060–1210	6.83	6.73	6.64	(0.17)
	1275–1380	1.08	1.11	1.09	(0.09)
HCFC123 (CHCl_2CF_3)	740–900	2.39	2.30	2.08	(0.14)
	1080–1450	10.49	10.26	10.09	(0.37)
HCFC124 (CHClFCF_3)	675–715	0.53	-	-	(0.04)
	790–920	1.81	-	-	(0.14)
	1035–1430	12.09	-	-	(0.52)
HCFC141b ($\text{CH}_3\text{CCl}_2\text{F}$)	710–790	2.37	2.22	2.16	(0.08)
	895–955	1.09	1.02	1.00	(0.06)
	990–1210	3.95	3.72	3.33	(0.20)
	1325–1470	0.34	0.33	0.34	(0.12)
HCFC142b (CH_3CClF_2)	650–705	0.75	0.69	0.68	(0.05)
	875–1030	2.58	2.51	2.40	(0.14)
	1075–1265	7.19	7.11	6.96	(0.20)
	1360–1475	0.61	0.64	0.78	(0.09)

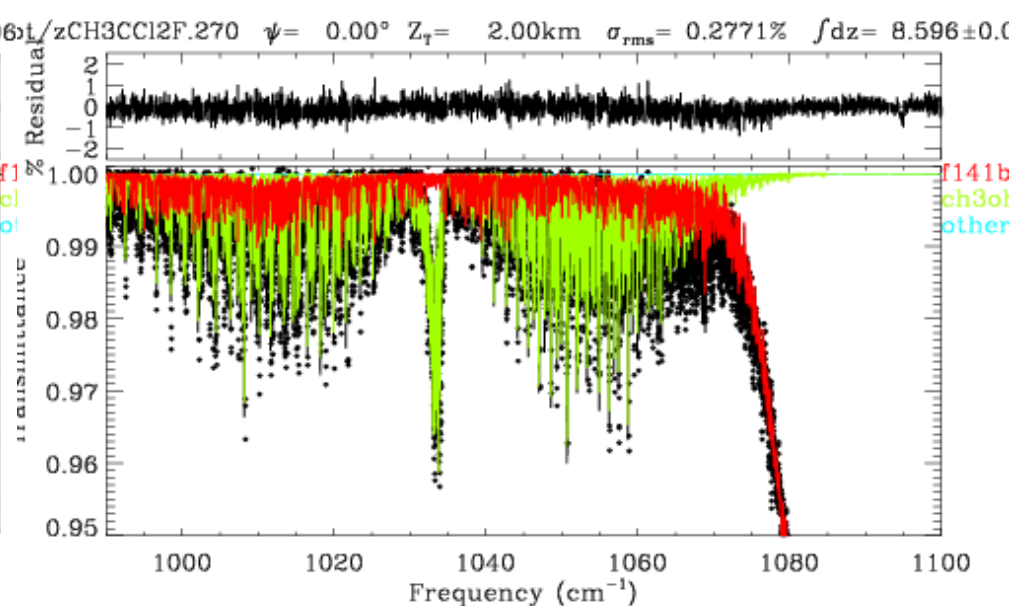
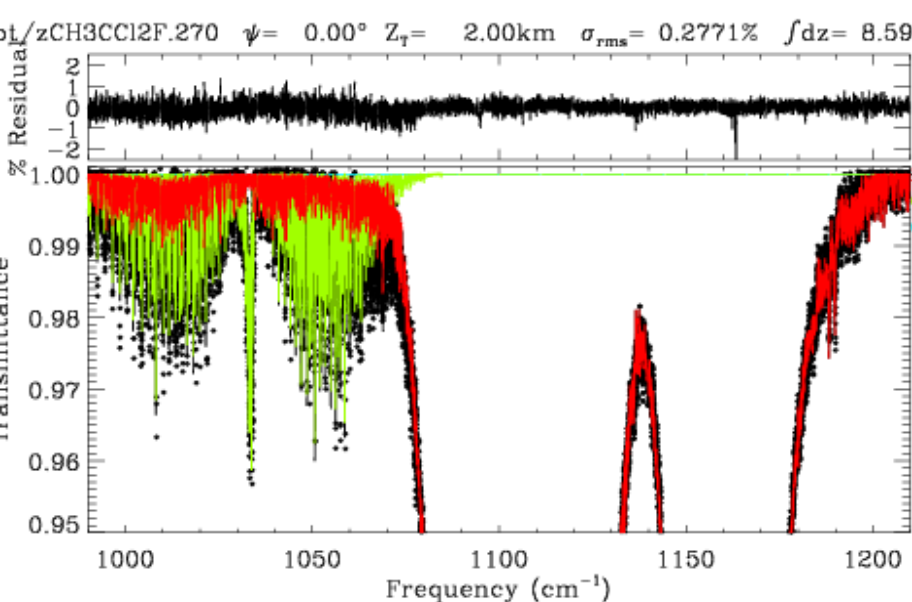
**Value = 0.18
in HITRAN**

HCFC-141b – CH₃OH contamination



270K spectrum is contaminated with ν_8 band CH₃OH (methanol), used as a coolant in the original lab studies.

Not a problem for HCFC-141b itself.
Might be a problem when fitting 1033 cm⁻¹ region for CH₃OH --absorption is incorrectly attributed to HCFC-141b.



HCFC-141b Summary

Pseudo-linelist covers all significant absorptions in 700-1500 cm^{-1} region

In deriving PLL, contamination from the ν_8 band of CH_3OH was removed

HITRAN 270K cross-sections 1325-1470 cm^{-1} were re-normalized ($\times 1.75$) to bring them back into consistency with original Clerbaux (1993) measurements.