

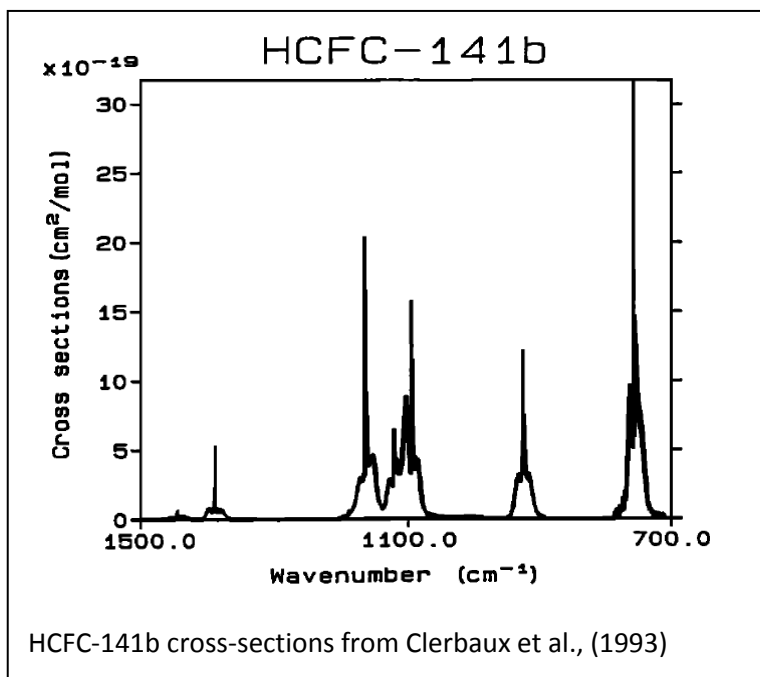
HCFC-141b (CH₃CCl₂F) PSEUDO-LINELIST

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INTRODUCTION.

A HCFC-141b pseudo-linelist has been created, based on laboratory absorption cross-section spectra described by Clerbaux et al.,(1993), which were downloaded from the HITRAN website. The original lab spectra cover 710-1470 cm⁻¹ contiguously, but the cross-section files are broken down into 3 segments:

- 710-790 cm⁻¹
- 895-1210 cm⁻¹
- 1325-1470 cm⁻¹



LABORATORY MEASUREMENTS

The assumed laboratory measurement conditions from Clerbaux et al. (1993) are tabulated below. Each measurement used the same cell of 5 cm length. Each spectrum covers a region between 600 and 1500 cm⁻¹ with an apodized spectral resolution of 0.030 cm⁻¹ (OPD=30 cm) and a spectral point spacing of 0.008 cm⁻¹.

Spectrum	nu_start	nu_end	npts	temp	Ptot	Pgas	length	resn
"CH3CCl2F.253"	709.9783	1470.0017	88280	253.	2.5	2.5	0.05	0.03
"CH3CCl2F.270"	709.9783	1470.0017	88280	270.	2.5	2.5	0.05	0.03
"CH3CCl2F.287"	709.9783	1470.0017	88280	287.	2.5	2.5	0.05	0.03

Temp - Temperature in K
P_tot - total pressure in torr
P_gas - HCFC-141b partial pressure in torr
Length – cell length in m

Norton-Beer strong apodization (N2) was assumed during the analysis. The Clerbaux paper was not explicit about the pressures that apply to each spectrum. It simply said 1-4 Torr. So an average value of 2.5 Torr was assumed in generating the transmittance spectra. This produced 60% absorption in the strongest bands, in accordance with the paper. The resolution was cited as 0.03 cm⁻¹ apodized. The max OPD was not given, so I assumed 0.9/0.03 = 30 cm.

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 3 spectra. As part of the fitting, the strengths and ground-state energies were both constrained to be positive. The ABHW, SBHW, and TDPBHW were assumed to be 0.06 cm⁻¹/atm, 0.10 cm⁻¹/atm and 0.70, respectively.

PARTITION FUNCTION.

The rotational partition function for HCFC-141b was assumed to be $(296/T)^2$, which subsumes the lowest frequency vibrational mode. 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 were assumed:

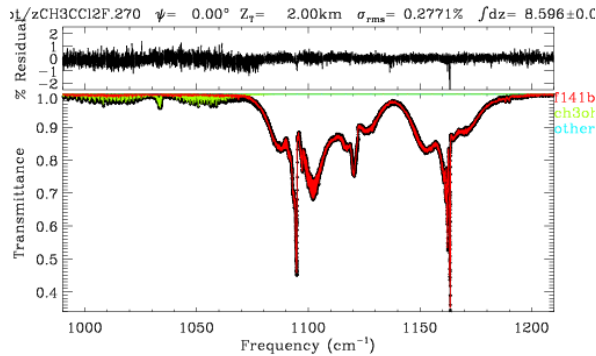
Freq.	340	681	1095	1163	2928	330	300	757	1120	1387	3013	230
Degen.	1	1	1	1	1	2	2	2	2	2	2	2

These were guesses based on f142b (CH₃CClF₂) and the observed band centers. If these are wrong it will affect the derived E'' values, but the pseudo-lines should still give a good representation of the absorption. What you must **not** do is to correct the vibrational frequencies without re-deriving the E'' values. This would cause an inconsistency leading to an incorrect T-dependence of the absorption strength.

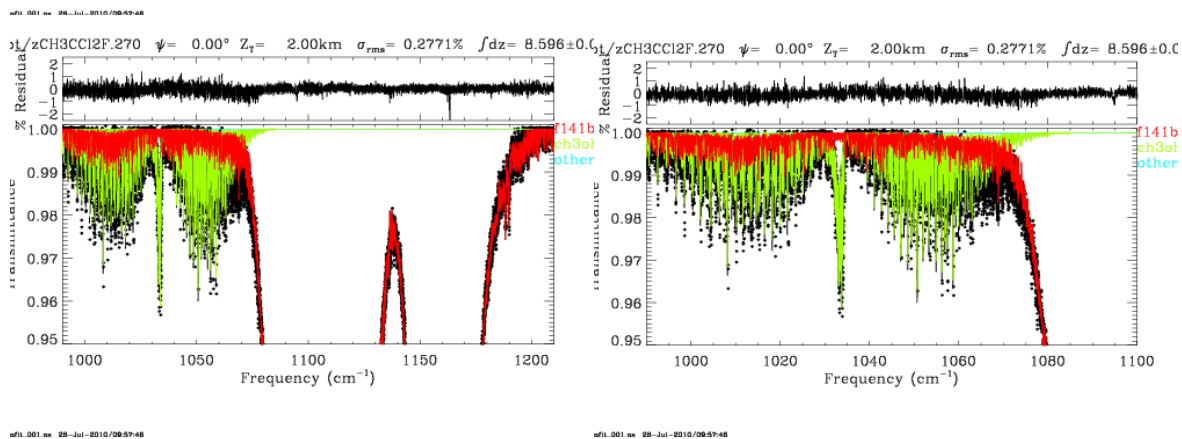
DISCUSSION

The 270K HFC-141b spectrum was found to be contaminated with methanol (CH₃OH). This is not a surprise given that the coolant fluid was methanol. It is not clear, however, why the methanol signature is so much stronger in the 270K spectrum than the other two. The following three plots show the signature of the nu₂ band of CH₃OH (green) centered at 1033 cm⁻¹ in the 270K spectrum. We know that the green absorption is CH₃OH because (i) it strongly resembles a low pressure CH₃OH spectrum and (ii) it isn't present in the 287K and 253K spectra. The

structure in the methanol spectrum indicates that it was at low pressure, so the leak occurred into the low-pressure cell.



Figures illustrating the contamination of the 270 K spectrum by methanol. The green trace clearly shows the P- Q- and R-branches of the ν_2 band of CH_3OH centered at 1033 cm^{-1} . The red trace shows the HCFC-141b absorption.



The absorption depth of the CH_3OH is much smaller than that of the HCFC-141b, and so it should not have much effect on the HCFC-141b retrievals. The danger is that when trying to fit the 1033 cm^{-1} region, the CH_3OH absorption will be attributed to HCFC-141b, resulting in a large error in the retrieved CH_3OH .

A discrepancy was noted between the HCFC-141b integrated cross sections in Table 2 of Clerbaux et al. (below) and what I calculate from the cross section files obtained from HITRAN. I agree with all 12 values except one: the integrated cross section over the $1325\text{-}1470 \text{ cm}^{-1}$ region at 270K is 0.18 and not the tabulated 0.33 ($\times 10^{17} \text{ cm} \cdot \text{molecule}^{-1}$). Since this is inconsistent with the integrated absorption at the two neighboring temperatures, since the integrated absorption is typically T-independent, it is unlikely to be a typo in the Clerbaux paper. Unlikely as it seems, there appears that a mis-normalization of the HITRAN cross-sections has occurred for the $1325\text{-}1470 \text{ cm}^{-1}$ region of the 270K spectrum only. To prevent this screwing up the derived pseudolines, I multiplied the HITRAN cross-sections covering the $1325\text{-}1470 \text{ cm}^{-1}$ region of the 270K spectrum by a factor 1.8 to correct this.

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)

PSEUDO-LINELIST

The pseudo-lines cover even narrower regions than the cross section spectra because I discarded regions in which the majority of pseudo-lines have $< 0.5\%$ absorption in the lab spectra. In any case, these weak pseudolines would have been biased anyway due to the fact that in the cross-section files downloaded from HITRAN, all the negative absorption values have been set to zero.

The resulting pseudo-linelist consists of 36504 lines with a spacing of 0.01 cm^{-1} . The regions covered are:

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

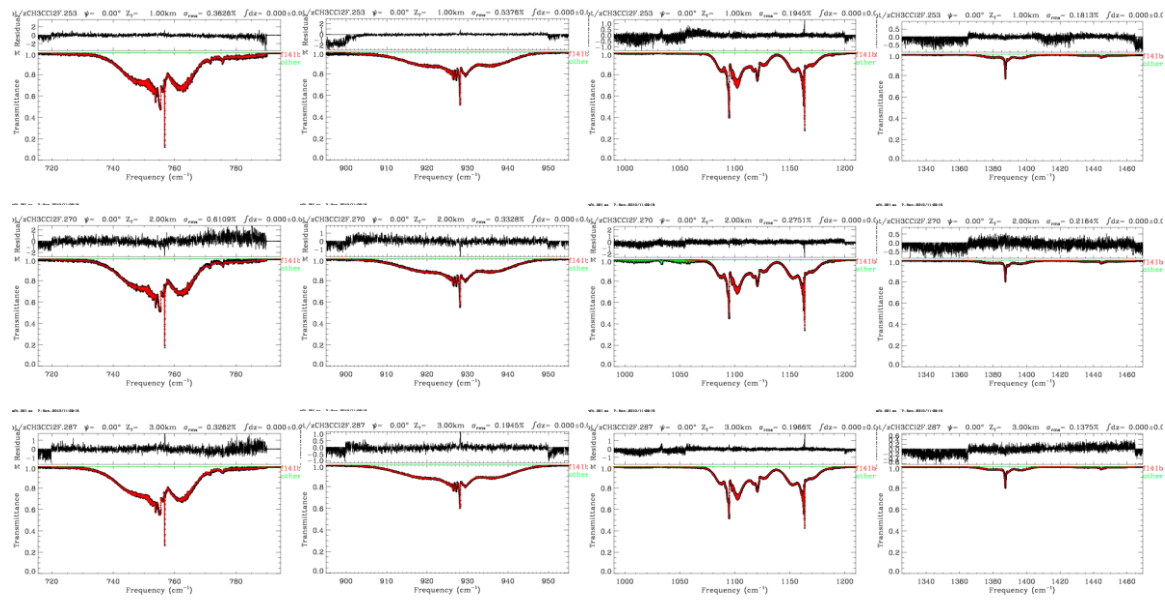
Due to the resolution of the laboratory spectra of 0.03 cm^{-1} a pseudo-line spacing of 0.01 cm^{-1} was considered to be appropriate.

ACCURACY

To estimate how well the pseudo-linelist represents the lab spectra, test retrievals were performed in which the laboratory spectra were fitted using the pseudo-linelist. The result is not a perfect fit because the problem is over-determined with 3 spectra and only 2 unknowns (S, E²). The retrieved scale factors for the HCFC-141b abundances in the different spectra are tabulated below.

Temperature	720-790 cm^{-1}	900-950 cm^{-1}	990-1210 cm^{-1}	1325-1470 cm^{-1}
253K	1.008	1.009	1.004	
270K	0.984	0.981	0.991	
287K	1.008	1.010	1.005	

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%.



REFERENCES.

Clerbaux, C., R. Colin, P. C. Simon, C. Granier, Infrared cross sections and Global Warming Potentials of 10 Alternative Hydrohalocarbons, *J Geophys. Res.* 98, 10,491-10,497, 1993

Norton, R. H. and C. P. Rinsland, ATMOS data processing and science analysis methods, *Appl. Opt.*, 30, 389-400, 1991.