HCFC-142b (CH_3CClF_2) Pseudo-Linelist

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Abstract.

A Pseudo-Line-List (PLL) has been generated by simultaneous fitting of laboratory spectra acquired by Newnham and Ballard [1995] and by Le Bris and Strong [2010]. The two sets of lab data appear consistent within 4% in terms of intensities and within 35 cm^{-1} in terms of E". This new PLL, covering 620 to 1480 cm^{-1}, replaces the one covering 870-1270 cm^{-1} developed in 1996 from the lab data of Newnham and Ballard only. The latter has been removed from the website to ensure that users download the latest and best.

Laboratory Spectra

Thirteen lab spectra were fitted: six measured at Rutherford Appleton Laboratory (RAL) by Newnham & Ballard [1995] and seven from the University of Toronto (UT) measured by Le Bris and Strong [2010]. The tables below document the measurement conditions.

RAL Spectrum	Temp	Pres	Length	Start	End	Δν	Resn
	K	mbar	cm	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
C142BNA5.DPT	295.52	2.017	5.1180	600	1500	0.015066	0.030
C142BND5.DPT	273.21	2.006	5.1167	600	1500	0.015066	0.030
C142BNH5.DPT	253.15	1.002	5.1156	600	1500	0.015066	0.030
C142BNK5.DPT	233.32	0.997	5.1145	600	1500	0.015066	0.030
C142BNN9.DPT	212.97	0.977	5.1133	600	1500	0.015066	0.030
C142BNQ7.DPT	203.52	1.027	5.1128	600	1500	0.015066	0.030

UT Spectrum	Temp	Pres	Length	Start	End	Δν	Resn
	K	Torr	cm	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
f142b_ut_283	283.0	2-12	3.17	650	1500	0.007533	0.020
f142b_ut_273	272.0	2-12	3.17	650	1500	0.007533	0.020
f142b_ut_263	263.0	2-12	3.17	650	1500	0.007533	0.020
f142b_ut_253	253.0	2-12	3.17	650	1500	0.007533	0.020
f142b_ut_243	243.0	2-12	3.17	650	1500	0.007533	0.020
f142b_ut_233	233.0	2-12	3.17	650	1500	0.007533	0.020
f142b_ut_223	223.0	2-12	3.17	650	1500	0.007533	0.020

A range of pressures was used by Le Bris and Strong to derive the UT cross-sections: high pressures to enhance weak features and low pressures to avoid saturation of the strong Q-branch features. They then averaged the cross-sections.

The UT transmittance spectra fitted were re-calculated (by me) assuming a 5 Torr pressure. This has very little influence on the derived PLL.

Motivation.

This work was done in support of efforts to quantify atmospheric HCFC-142b by remote sensing. There are two sets of absorption cross-sections. The RAL cross-sections have the advantage of a wider range of temperature (92K versus 60K) and slightly broader spectral coverage (the UT spectra slightly clip the P-branch of the 650 cm^{-1} band). On the other hand, there are more UT spectra and they are higher spectral resolution.

If one were implementing the cross-sections directly in an atmospheric radiative transfer model, one would have somehow account for the pressure broadening, since all the lab measurements are at low pressure. You would also have to choose which dataset to use (RAL or UT), since they are not consistent: they differ in spectral resolution and spacing, spectral coverage, and in absolute absorption. By fitting a PLL, you can essentially merge the two sets of cross-sections, preserving the best features of each.

Some of these spectra also have channel fringes, which were mostly removed during the iterative fitting of the lab spectra. The resulting PLL is therefore most free of the effects of the channel fringes, although in the wings of bands where the absorption is weak, residual CF are noticeable.

Partition function.

Used the harmonic oscillator approximation with the fundamental vibrational frequencies from Table 1 of Le Bris and Strong, with the exception that the 237 cm^{-1} torsional mode is dropped and the exponent of the rotational partition function was increased from 1.5 to 2.0.

Pressure Broadening

Although HCFC-142b is a tropospheric source gas and exists in highest concentrations near the surface, the lab spectra we obtained were all measured at low pressure (1-2 mbar for Newnham & Ballard; 2-12 Torr for Le Bris & Strong). The use of the PLL at tropospheric pressures is therefore an extrapolation based an assumed air-broadened half width of 0.05 cm^{-1}/atm. There is no way of validating that this is correct, except by fitting atmospheric spectra. For optically thin absorption depths that characterize atmospheric paths, an error in the assumed widths would not much affect the retrieved gas amounts.

Pseudo-Line Spacing

A uniform 0.01 cm^{-1} line spacing was adopted. Given the resolutions of the lab spectra (RAL 0.03 cm^{-1}, UT 0.02 cm^{-1}), there is no spectral structure requiring a finer spacing. So provided that the PLL is not used for situations where the lines are unresolved and strong (i.e. growing non-linearly with absorber amount), the 0.01 cm^{-1} line spacing should be adequate, even though it far exceeds the doppler width. Since HCFC-142b is found primarily at pressures > 100 mbar in the earth's

atmosphere, where the full-width pressure broadening should exceed 0.01 cm^{-1}, the PLL line spacing should not be a problem.

The initial PLL covered the contiguous 600-1500 cm^{-1} region. It was noticed, however, that in some regions between bands, the derived pseudo-lines were consistently weaker than 1.E-23 $cm^{-1}/(molec.cm^{-2})$. We therefore decided to delete lines in these regions to reduce the size of the final PLL and to speed up computation in these regions (when fitting other gases). With the strongest pseudo-lines having strengths > 4E-20, the loss of absorption by discarding these weak lines is negligible. Note that many pseudo-lines within the PLL have intensities < 1E-23 but with stronger lines in their vicinity. Table 2 shows the wavenumber coverage of the final linelist. A total of 51605 lines are used, as compared with 90001 if we had kept all.

Start (cm^{-1})	End (cm^{-1})	Number of Lines
640	720	8001
875	930	5501
937	995	5801
1079	1261	18201
1349	1490	14101

Discussion.

Figure 1 shows some example of spectral fits to the lab spectra using the final PLL. The region containing the 4 strongest bands is plotted in two RAL spectra and two UT spectra. Matching temperatures of 273K and 233 K are plotted. The fits are not perfect because it is an over-determined problem: for each pseudoline we were fitting two spectroscopic parameters (I and E") from 13 spectral values.

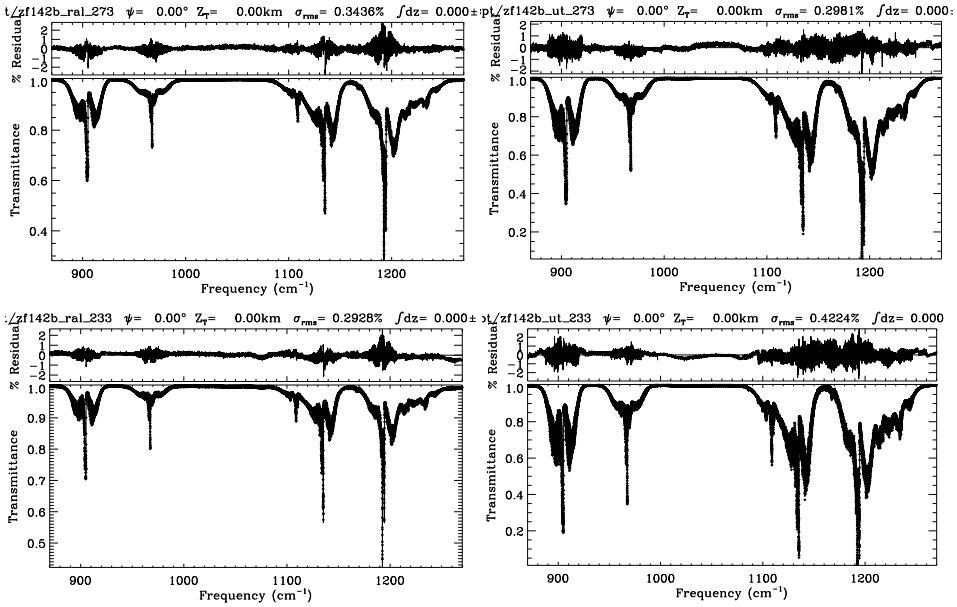

Figure 1. *Examples of spectral fits. The four panels show fits to RAL spectra (left) and UT spectra (right) measured at 273K (top) and 233K (bottom). Fits are performed over the 870-1270 cm^{-1} region containing the four strongest bands.*

A couple of peculiarities were seen in the spectral fitting. In the 650 cm^{-1} window, there was a large inconsistency in the derived frequency shifts between the RAL and UT spectra of about 6-7 mK. But in the other bands at higher wavenumbers there was good consistency between the RAL and UT frequency shifts. This tends to produce larger specttral fitting residuals and hence error bars for this band.

An upward glitch of 7% was seen at 687.90 cm^{-1} in the spectral fitting residuals of the 283K UT spectrum (see fig. 2). This is much larger than any other residual and was not present in any of the other UT spectra or the RAL spectra. This glitch was sufficiently large that a small downward glitch is seen at this wavenumber in the fitting residuals to all other spectra.

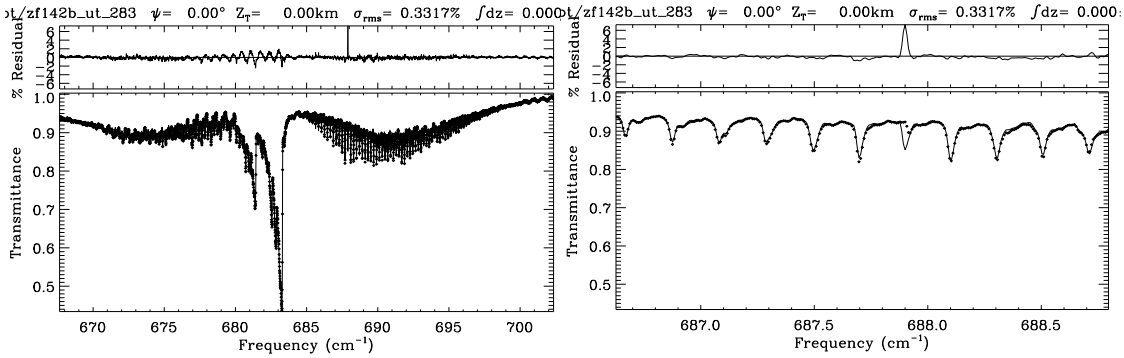

Figure 2. *Illustrating the 7% glitch in the 283K UT spectrum in the 685 cm^{-1} band.*

The VMR Scale Factors that were retrieved fitting the lab spectra in the six strongest bands using the derived PLL are plotted in fig 3. In a perfect world these VSF values would all be 1.0, but inconsistencies in the data prevented this. The RAL data are denoted by the square symbols connected by solid lines while the UT data are denoted by the diamond symbols connected by dotted lines. Colors represent the six different windows, whose central wavenumbers are included in the captions. The RAL data measured at 208K seem to be systematically high by about 15%, indicating that there was more HCFC-142b in the cell than calculated from the gas density and cell length. The fact that this 15% bias was consistent amongst all six windows suggests that it is rooted in the measurement conditions rather than the spectra themselves. The RAL measurement at 233K gives gas amounts that are all consistently 10% lower than expected. The UT data are more consistent, with VSFs ranging from 0.9 to 1.05, although they do cover a narrower temperature range. Above 260K the VSF are within 4% rms of 1.0. Below 260K the errors grow. Overall the rms deviation from 1.0 is 6%. The fact that the mean VSF value is 1.0 means that the derived band intensities are consistent with the spectra. The absense of any slope with respect to temperature implies that the E" values are consistent with the assumed partition functions and cannot be improved.

Looking at the RAL and UT results individually, the RAL data points alone have mean VSF value of 1.02 with a negative slope of -1% over their 92K temperature range. The UT points alone have a mean VSF value of 0.98 with a slope of +5% over 60K. Thus the UT cross-sections are about 4% larger than those of RAL,

averaged over all temperatures. The T-sensitivity of HCFC-142b is such that an error in the E"of 35 cm^{-1} would cause a 5% change in the line strengths between 223 and 283K. So the E" values that would be derived from the UT data alone are abot 35 cm^{-1} larger than those derived from the RAL data alone.

In the UT spectra the 685 cm^{-1} band has a slightly steeper slope and larger error bars than the other bands, or the RAL data for the same band. It is possible that this behavior is related to the fact that the UT spectra start at 650 cm^{-1} and so clip the highest-J lines from the low-wavenumber edge of the P-branch, whereas the RAL spectra start at 600 cm^{-1}. or it could be related to the inconsistency in the frequency shifts.

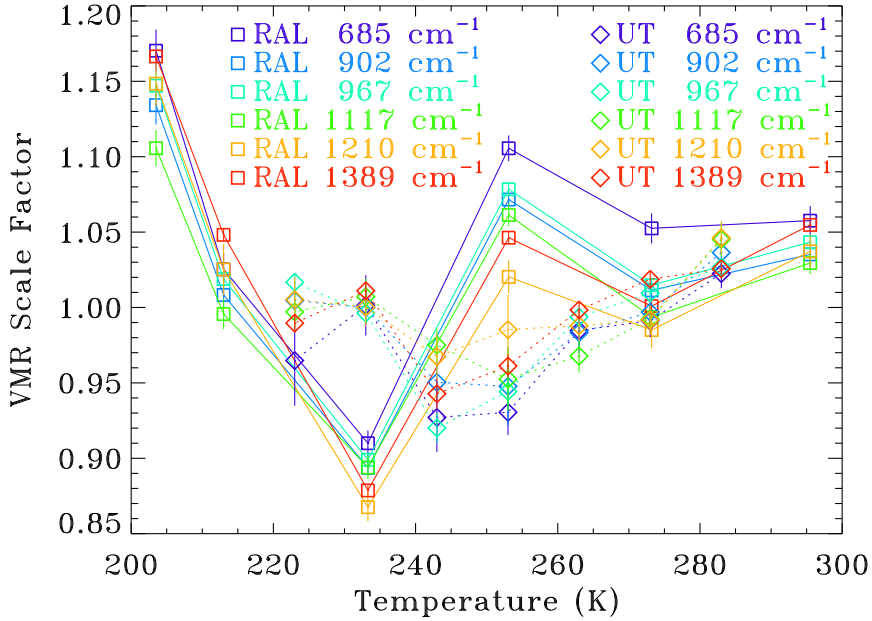

Figure 3. *VMR Scale Factors (VSF) retrieved from RAL and UT laboratory spectra. These represent the retrieved gas amounts relative to the true amounts calculated from the measurement conditions (T, P, cell length). Colors represent the six strongest absorption bands. Squares connected by solid lines denote RAL spectra. Diamond-shaped points connected by dotted lines denote UT measurements.*

Conclusions.

A PLL consisting of 51605 pseudo-lines has been developed to represent HCFC-142b absorption in the MIR. When used in conjunction with the partition function described earlier, this PLL should allow the retrieval of atmospheric HCFC-142b amounts to an accuracy of better than ±4% above 260 K and better than ±8% at lower temperatures. These uncertainty estimates are dominated by inconsistences between the two sets of cross-sections, which reach 10% at 233K and 253K, not their conversion into pseudo-lines. Fig 4 shows the derived intensities and E" values.

References.

Newnham D., and J. Ballard, Fourier transform infrared spectroscopy of HCFC-142b vapour, Journal of Quantitative Spectroscopy and Radiative Transfer, 53, 471–479, 1995

Le Bris K., and K. Strong, Temperature-dependent absorption cross-sections of HCFC-142b, Journal of Quantitative Spectroscopy and Radiative Transfer, 111, 364–371, 2010

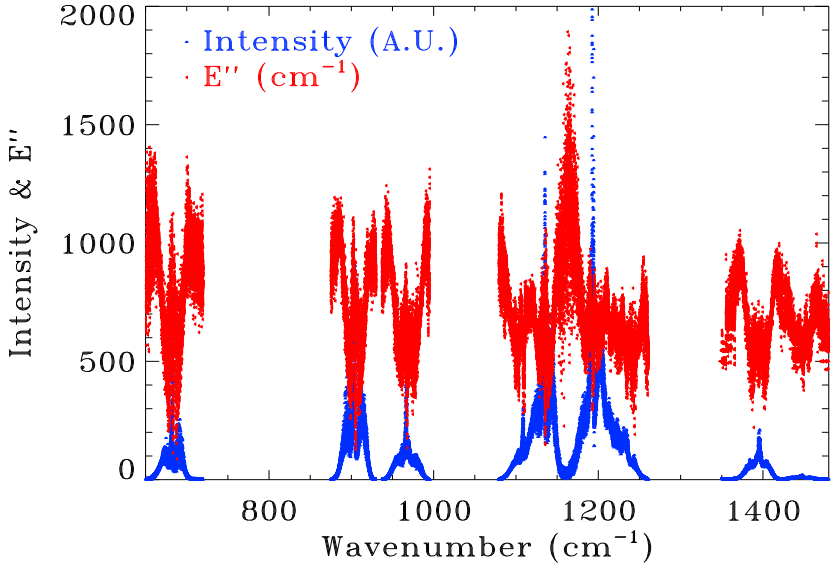

Figure 4a. *Empirically-derived pseudo-line intensities (blue) and ground-state energies (E"). The latter tend to be low near the band centers and high in the wings. The intensities have been arbitrarily scaled to fit in the figure, to facilitate their super-imposition onto the E" values.*

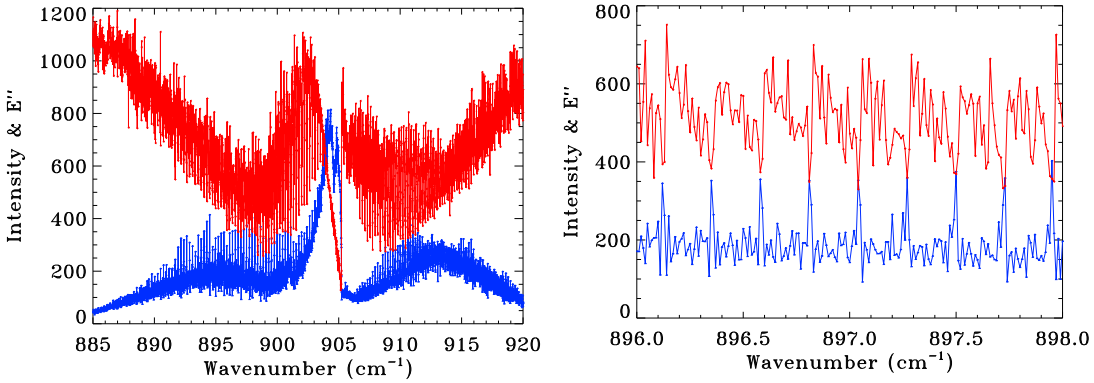

Figure 4b. *Left panel shows the variation of line intensity (blue) and E" (red) across the 905 cm^{-1} band. Lowest E" values occur at 905 cm^{-1} at the Q-branch band head. They then increase monotonically toward lower wavenumber into the tail of the Q-branch. Right panel shows variation of intensity and E" in a narrow section of the P-branch. A regular series of manifolds is seen with a spacing of 0.23 cm^{-1}. As in the Q-branch, Low E" values correspond to the high intensities. E" values then increase toward lower wavenumbers until the next manifold.*