Tech Note: Assessment of Molecular Cross-Section Data (v2)

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18 Jan 2018

Abstract

This is an update of the orignal Tech Note (29 June 2015) to include new data which have become available for CFC-11, CCl_4 and SF_6. Significant changes are indicated in blue.

This report assesses the molecular cross-section data that have been used for the look-up tables (LUTs) used in the ESA retrievals of MIPAS L2 products. While there have been several updates to the molecular line database, until now there has been no equivalent review of the cross-section data, which have been used since before launch (2002).

In the current MIPAS processing, there are 14 molecules represented by cross-section data, ranging from molecules which have strong enough signatures to be retrieved as L2 products (e.g., CFC-11) to those which are only modelled as minor contaminant species (e.g., CFC-13).

This report compares the originally used data with any new data that have subsequently become available, and assesses whether the cross-sections have been provided over an appropriate range of pressure and temperature values for atmospheric paths viewed from a limb sounder.

New data are available for 9 molecules (CFC-11, CFC-12, CFC-14, HCFC-22, CFC-113, CCl_4, $ClONO_2$, HNO_4, SF_6) and the recommendation is to use these although for 3 molecules (CFC-11, CFC-113, SF_6) the new data are not (currently, Jan 2018) on the HITRAN web-site.

For N_2O_5, no new data are available but the old data appear to be adequate.

The range of pressures and temperatures covered in existing data for CFC-13, HCFC-21, CFC-113, CFC-114, CFC-115, HNO_4 and just the 1680–1790 cm^{-1} band of $ClONO_2$ is inadequate and more comprehensive datasets are desirable.

Some of the issues regarding the conversion of the raw cross-section data to LUTs, in particular the problems caused by noise on the measured data, are outlined in an Appendix.

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1 Introduction

The absorption for most atmospheric molecules is evaluated line-by-line, using compilations (such as HITRAN) of the basic line parameters and adapting these for particular local path conditions of pressure and temperature (p, T), using well-established models such as the Voigt lineshape. However, for some more complex molecules (Table 1.1), individual transitions have not been identified and instead spectra of absorption cross-section (X/S) [cm^2 $molec^{-1}$] are directly measured in the laboratory at specific p, T values. Within a radiative transfer model, these tabulations then have to be interpolated to the local path p, T.

Table 1.1: List of molecules represented by cross-section data, together with ID number assigned for MIPAS Look-Up Tables and Code used for microwindows.

ID	Code	Formula	Full name
51	^{a}F11	$CFCl_3$	CFC-11
52	^{a}F12	CF_2Cl_2	CFC-12
53	*F13	$CClF_3$	CFC-13
54	^{b}F14	CF_4	CFC-14
55	*F21	$CHCl_2F$	HCFC-21
56	^{b}F22	$CHClF_2$	HCFC-22
57	†F113	$C_2Cl_3F_3$	CFC-113
58	†F114	$C_2Cl_2F_4$	CFC-114
59	*F115	C_2ClF_5	CFC-115
60	^{b}CCL4	CCl_4	Carbon Tetrachoride
61	^{a}CLNO	$ClONO_2$	Chlorine Nitrate
62	^{a}N2O5	N_2O_5	Dinitrogen Pentoxide
63	*HNO4	HNO_4	Peroxynitric Acid
64	†SF6	SF_6	Sulphur Hexaflouride

^{a} ML2PP V6 retrieved species
^{b} ML2PP V7 retrieved species
†Potential future retrieved species
*Probably too weak for profile retrievals

While much effort has gone into improving the line data by selective modification of the the HITRAN compilation, there has been no comparable update, or even assessment of the X/S datasets.

The main purpose of this report, then, is to survey the current state of available cross-section data, identify the molecules for which improved data are available, and the molecules for which the data remain unsatisfactory for accurate modelling of limb emission radiances.

Appendix A highlights some of the practical considerations when using cross-section data within the MIPAS retrievals.

2 Assessment Summary

Table 2.1 summarises the assessments and recommendations for each molecule, which are discussed in detail in subsequent sections.

Table 2.1: Summary and Recommendations for each molecule.

ID	Molecule	Assessment/Recommendation
51	CFC-11	Use new Harrison data
52	CFC-12	Use new Harrison data
53	CFC-13	Inadequate pT coverage
54	CFC-14	Use new HITRAN data
55	HCFC-21	Inadequate pT coverage
56	HCFC-22	Use new Harrison data
57	CFC-113	Use new Bris data[1]
58	CFC-114	Inadequate pT coverage
59	CFC-115	Inadequate pT coverage
60	CCl_4	Use new Harrison data
61	$ClONO_2$	Use new HITRAN data[2]
62	N_2O_5	Use existing HITRAN data
63	HNO_4	Use new HITRAN data[1]
64	SF_6	Use new Manceron *et al.* data

[1] Although pT coverage still inadequate
[2] pT coverage inadequate for 1680–1790 cm^{-1}

3 CFC-11 (updated)

Alternative CFC-11 data from Harrison now included.

CFC-11 is one of the current ESA L2 products.

See Appendix B.1 (p. 33) for profiles and radiance calculations.

3.1 Datasets

The Old and New CFC-11 data from the HITRAN web-site are both from reference #15: P. Varanasi, private communication (2000). The only difference is that the New data contains extra tabulations at 7.5 Torr. Alternative data has subsequently been supplied by Harrison (private communication, 2017).

The data are summarised in Table 3.1.

Table 3.1: Spectral resolution [cm^{-1}] and number of pT datasets within the CFC-11 cross-section data

	Max/Min Resl		n_{pT}
810–880 cm^{-1} **Band**			
Old	0.0030	0.0134	46
New	0.0030	0.0134	55
1050–1120 cm^{-1} **Band**			
Old	0.0030	0.0134	46
New	0.0030	0.0134	55
710–1290 cm^{-1} **Range**			
Alt	0.0013	0.0025	30

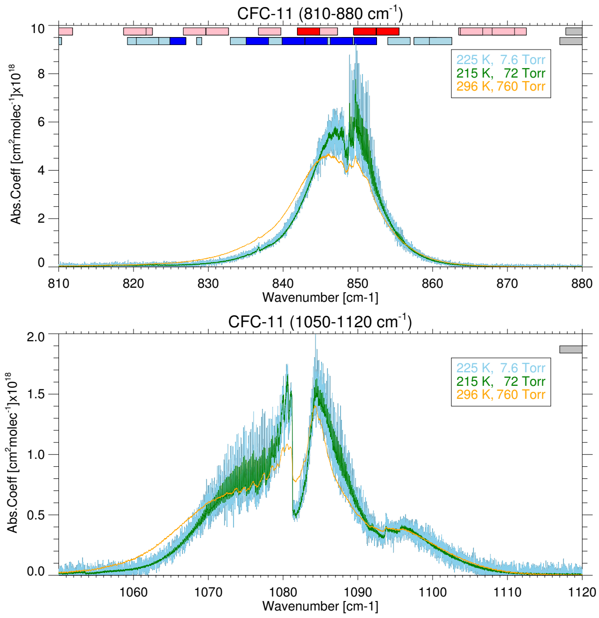

Figure 3.1: The New CFC-11 absorption coefficient at typical atmospheric profile conditions for the surface, tropopause and mid-stratosphere. The boxes along the top of each plot mark the locations of microwindows used for MIPAS retrievals: top row for Full Resolution and bottom row for Optimised Resolution. Red/blue are microwindows used for the retrieval of CFC-11, pink/pale blue are microwindows for which CFC-11 is included as a contaminant gas, and grey boxes are locations of other local microwindows where CFC-11 absorption is neglected.

3.2 Spectral coverage

The data are tabulated for two spectral ranges, plotted in Fig. 3.1. The Harrison data is tabulated as a single spectral range, fully overlapping both bands in the Old and New data.

Only the 810–880 cm^{-1} range is relevant for MIPAS, the 1050–1120 cm^{-1} band is mostly obscured by strong ozone absorption and does not overlap any of the current microwindows used for the retrieval of CFC-11 or any other species.

3.3 pT Coverage

The pT coordinates of the data (which are the same for both spectral bands in the Old and New data) are shown in Fig. 3.2. The New data contain the same points as the Old data, plus 9 extra datasets at 7.5 Torr. The Old and New HITRAN contain almost duplicated points at 37.5 and 40 Torr, and also at 70 and 75 Torr, originating from measurement sets with different underlying spectral resolutions.

The Harrison data has fewer p, T points, but covers a wider range of temperatures. All three datasets seem to have adequate coverage of the required p, T domain.

3.4 Low Pressure data

The additional pT datasets at 7.5 Torr in the new CFC-11 data extend the vertical range over which the data can be applied, as well as demonstrating the ability to resolve spectral fine structure and the random noise of the measurements. Fig. 3.3 shows a comparison of the low pressure datasets for the New and Alt data.

These plots show that the rotational structure near 850 cm^{-1} is clearly represented in both datasets but that the Harrison data is much less noisy (more clearly evident at the edge of the band).

3.5 CFC-11 Data Quality Summary

- The New HITRAN CFC-11 data have additional tabulations at low pressure compared to the Old

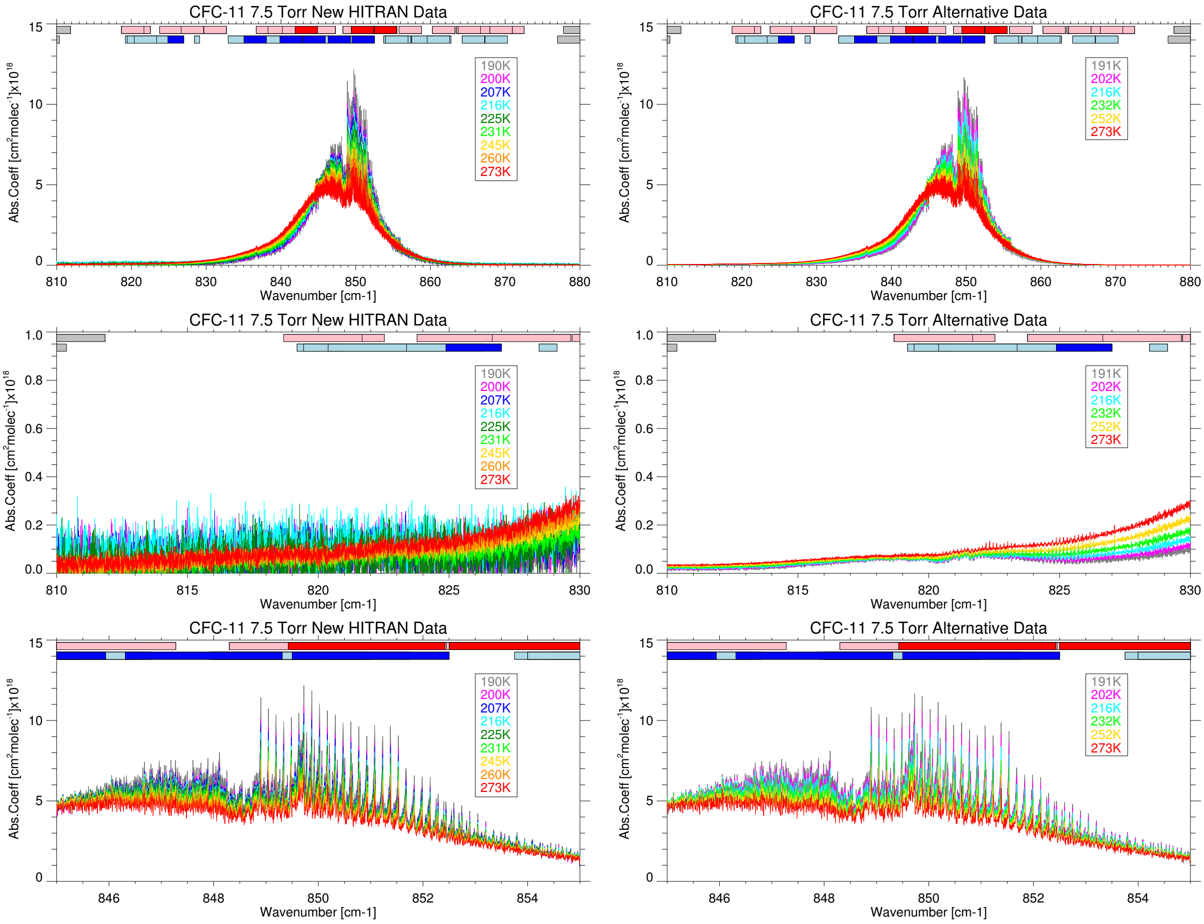

Figure 3.3: CFC-11 cross-section data 7.5 Torr from the New (left) and Alt (right) data, at different tabulation temperatures, full 810–880 cm^{-1} band in the top plots, and details in the lower plots.

data, extending the vertical range to 7.5 Torr.

- The Alternative CFC-11 data (from Harrison) covers the same spectral range as the HITRAN data but with improved spectral resolution and S/N.
- Only the 810–880 cm^{-1} band is of interest for MIPAS.
- The range of pT values represents good coverage for atmospheric path conditions.
- The (new) recommendation is to use the Harrison data.

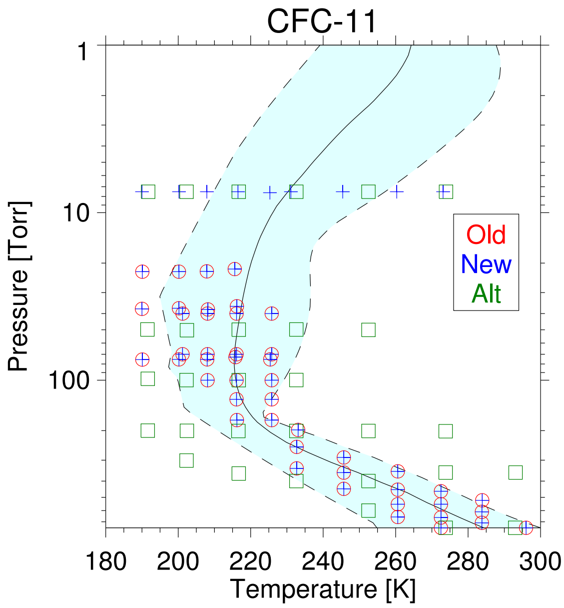

Figure 3.2: pT coordinates of the Old, New and Alt tabulated CFC-11 cross-section data (same for both bands). The light blue area represents the typical range of atmospheric temperature profiles, with the solid black line representing a standard mid-latitude profile.

4 CFC-12

CFC-12 is one of the current ESA products.

See Appendix B.2 (p. 34) for profiles and radiance calculations.

4.1 Datasets

The Old and New CFC-12 data from the HITRAN web-site are both given as reference #15: P. Varanasi, private communication (2000). The New data includes the Old data plus additional datasets at lower pressure.

Alternative CFC-12 data, covering the same two spectral bands, has also been provided by J. Harrison (private communication, 2014).

The data are summarised in Table 4.1.

Table 4.1: Spectral resolution [cm^{-1}] and number of pT datasets within the CFC-12 cross-section data

	Max/Min Resl		n_{pT}
850–950 cm^{-1} **Band**			
Old	0.0033	0.0134	39
New	0.0033	0.0134	52
Alt	0.0013	0.0025	32
1050–1200 cm^{-1} **Band**			
Old	0.0033	0.0134	33
New	0.0033	0.0134	52
Alt	0.0013	0.0025	32

4.2 Spectral coverage

The data are tabulated for two spectral ranges, plotted in Fig. 4.1.

The CFC-12 850–950 cm^{-1} band is of primary interest for MIPAS, but there is one (FR) retrieval microwindow in the 1050–1200 cm^{-1}band, and several other microwindows in this region include it as a contaminant.

Although the Alt data covers the same spectral ranges as the Old/New HITRAN data, they are tabulated at higher spectral resolution.

4.3 pT Coverage

The pT coordinates of the data are shown in Fig. 4.2.

The Old data have more points in the 850–950 cm^{-1} band than in the 1050–1200 cm^{-1} band, but the New and Alt data each have common sets of pT points for the 2 bands.

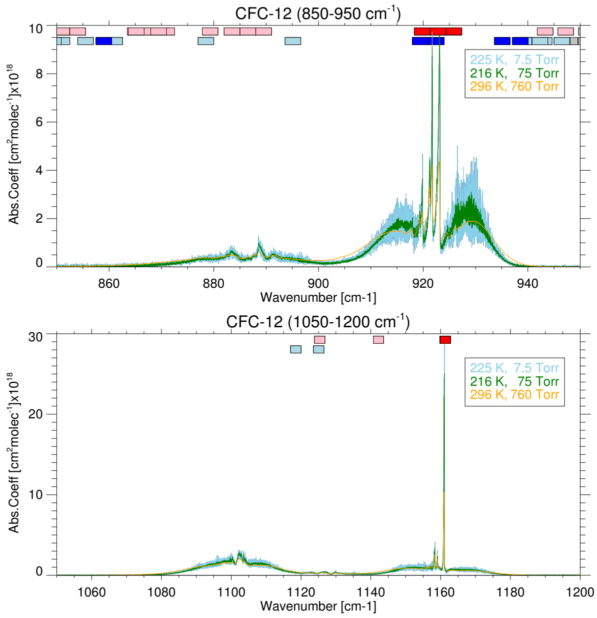

Figure 4.1: The New CFC-12 absorption coefficient for typical atmospheric profile conditions, with locations of MIPAS microwindows across the top (See Fig. 3.1 caption for details).

The New and Alt data have good coverage of the range of pT values required to represent atmospheric paths.

Between 40–80 Torr there appear to be almost duplicate points in the Old/New data, representing data merged from two different sources.

4.4 Low Pressure data

The additional pT tabulations at 7.5 Torr in the New and Alt data extend the vertical range over which the data can be applied, but inevitably have lower signal/noise. The low pressure data are compared in Fig. 4.3.

Both New and Alt data resolve the rotational structure between 925–930 cm^{-1} with similar amplitude, suggesting that the lower spectral resolution of the New data is not an issue. However, comparing the edge of the bands, it seems that the Alt data has lower noise, despite the higher spectral resolution.

4.5 CFC-12 Data Quality Summary

- The New HITRAN CFC-12 data have additional tabulations at low pressure compared to the Old data, extending the vertical range to 7.5 Torr.
- The Alternative CFC-12 data (from Harrison) cover a similar range of pT values to the New

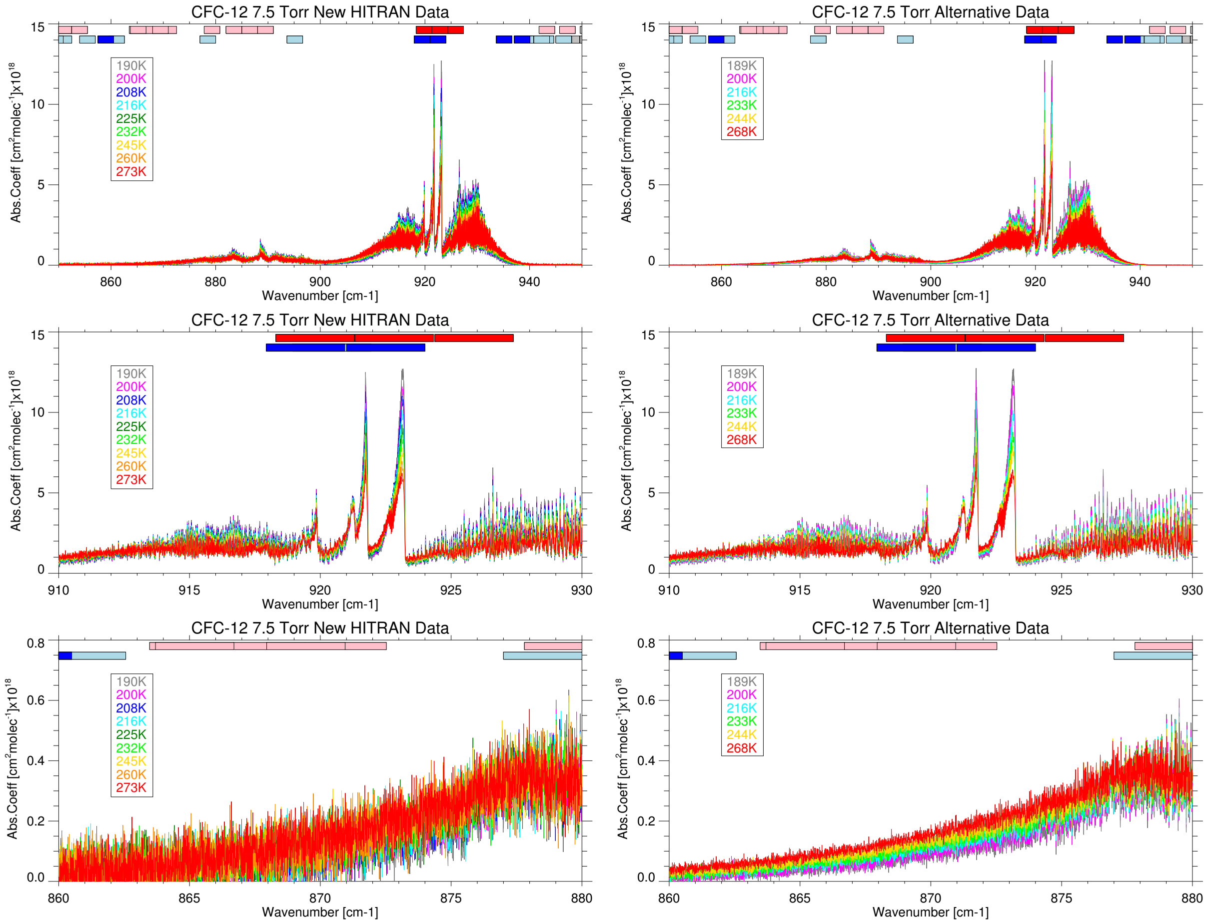

Figure 4.3: CFC-12 cross-sections for 7.5 Torr from the New (left) and Alt (right) data, at different tabulation temperatures, full 850–950 cm^{-1} band in the top plots, and details in the lower plots.

data but with higher spectral resolution and better S/N at low pressure.

- The 850–950 cm^{-1} band is of primary interest for MIPAS, but the 1050–1200 cm^{-1} band is also used.
- The range of pT values in both the New and Alt data represents good coverage for atmospheric path conditions.
- The recommendation is to use the Alternative data from Harrison.

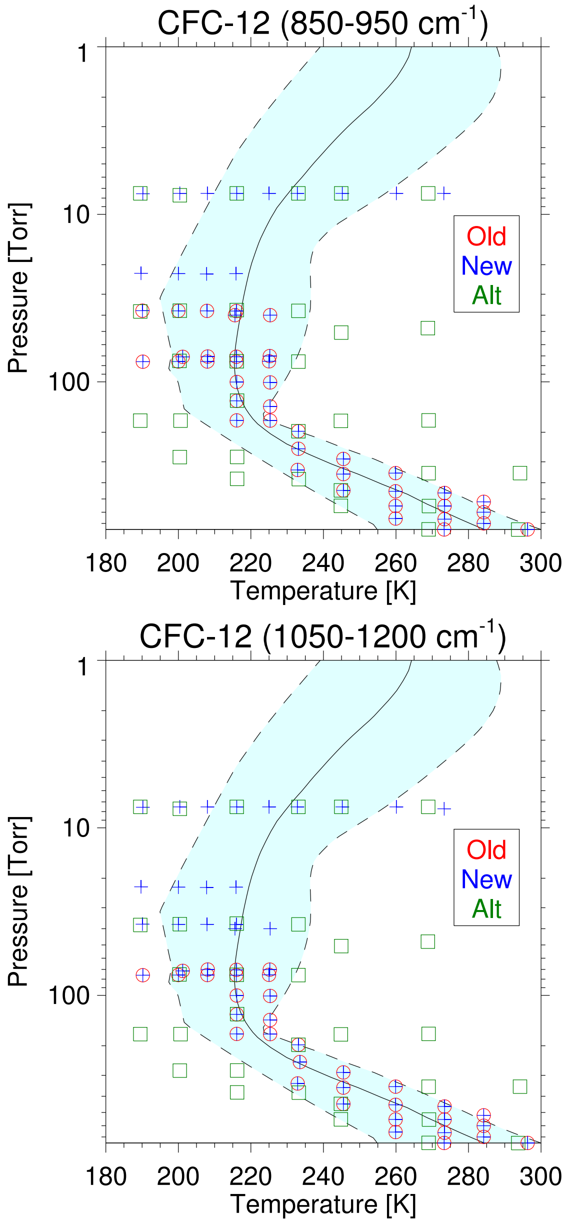

Figure 4.2: pT coordinates of the Old, New and Alt tabulated CFC-12 cross-section data for the two bands. The light blue area represents the typical range of atmospheric temperature profiles.

5 CFC-13

CFC-13 seems too weak to be retrieved as single profiles, although it does register as a contaminant in microwindows for the retrieval of other species.

See Appendix B.3 (p. 35) for profiles and radiance calculations.

5.1 Datasets

The Old data from the HITRAN web-site has not been updated. These measurements have reference #2: McDaniel *et al.* (1991)[1] The data are summarised in Table 5.1.

Table 5.1: Spectral resolution [cm^{-1}] and number of T datasets within the CFC-13 cross-section data

	Max/Min Resl		n_T
765–805 cm^{-1} **Band**			
HITRAN	0.0148	0.0148	6
1065–1140 cm^{-1} **Band**			
HITRAN	0.0148	0.0148	6
1170-1235 cm^{-1} **Band**			
HITRAN	0.0148	0.0148	6

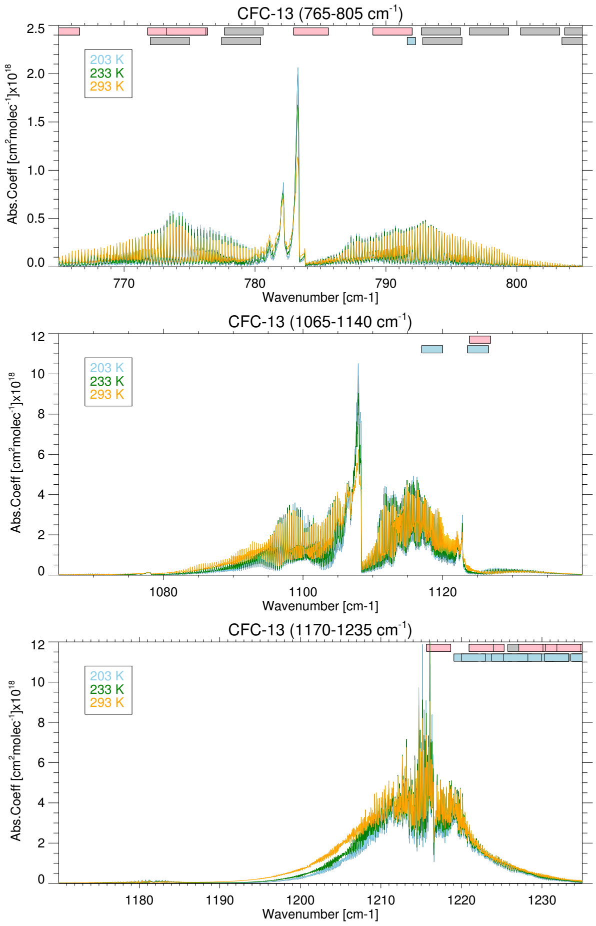

Figure 5.1: The tabulated CFC-13 absorption coefficient at different temperature values, with locations of MIPAS microwindows across the top (see caption for Fig. 3.1 for details).

5.2 Spectral Coverage

The data are provided for 3 spectral ranges, plotted in Fig. 5.1.

All three bands contain features which are modelled as contaminants in MIPAS retrievals.

5.3 pT Coverage

The CFC-13 data are tabulated, for each spectral range, at 6 temperatures: 293, 273, 253, 233, 213 and 203 K. Pressure values in the HITRAN files are set to 0.0, indicating undefined pressure, but in the original paper states that the measurements were made for pure samples at pressures of 0.25–2 Torr (which would explain the visibility of the rotational structure in Fig. 5.1).

5.4 CFC-13 Data Quality Summary

- CFC-13 is not a retrieved species but it is included as a contaminant in the retrieval of other species.
- The HITRAN data were originally published in 1991 and have not been updated.
- The data do not contain any explicit pressure dependence, although are apparently at low pressures which are inappropriate for modelling the (mostly tropospheric) radiance contribution from CFC-13.
- The recommendation, in the absence of any alternative, is to continue to use the existing data. But data with better p, T coverage is desirable.

6 CFC-14 (CF_4)

CFC-14 (CF_4) is one of the new ESA products.

See Appendix B.4 (p. 36) for profiles and radiance calculations.

6.1 Datasets

The Old and New CFC-14 data from the HITRAN web-site are both from reference #15: P. Varanasi, private communication (2000). The New data contain 9 extra pT tabulations at 8 Torr.

The data are summarised in Table 6.1.

Table 6.1: Spectral resolution [cm^{-1}] and number of pT datasets within the CFC-14 cross-section data

	Max/Min Resl		n_{pT}
1250–1290 cm^{-1} **Band**			
Old	0.0052	0.0105	46
New	0.0026	0.0105	55

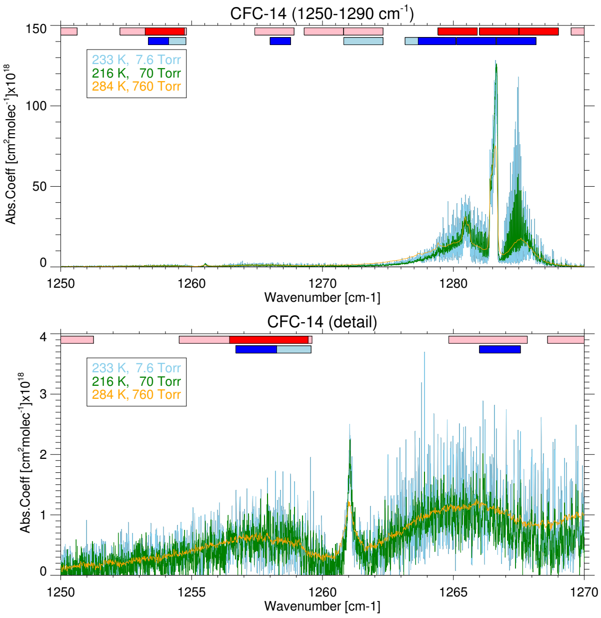

Figure 6.1: The New CFC-14 absorption coefficient at typical atmospheric profile conditions, with locations of MIPAS microwindows across the top (See Fig. 3.1 caption for details). The lower plot shows the 1250–1270 cm^{-1} region, covering the ^{13}C isotopologue, in more detail.

6.2 Spectral coverage

The data are tabulated for a single spectral band, 1250–1290 cm^{-1}, plotted in Fig. 6.1

The MIPAS CF_4 retrieval primarily uses microwindows in the main part of the band, 1275–1288 cm^{-1}, with a couple of low-information microwindows target the smaller feature from 1255–1270 cm^{-1}(presumably the ^{13}C isotopologue).

6.3 pT Coverage

The pT coordinates of the Old and New data are shown in Fig. 6.2.

The New data include all the Old data, plus an extra 9 tabulations at a lower pressure of 8 Torr. This gives good coverage of the range of atmospheric conditions required to simulate limb-path radiances. Note also the set of 4 almost duplicated pT points around 35–40 Torr, 190–216 K. Since the data are at the same spectral resolution these are presumably from the same source.

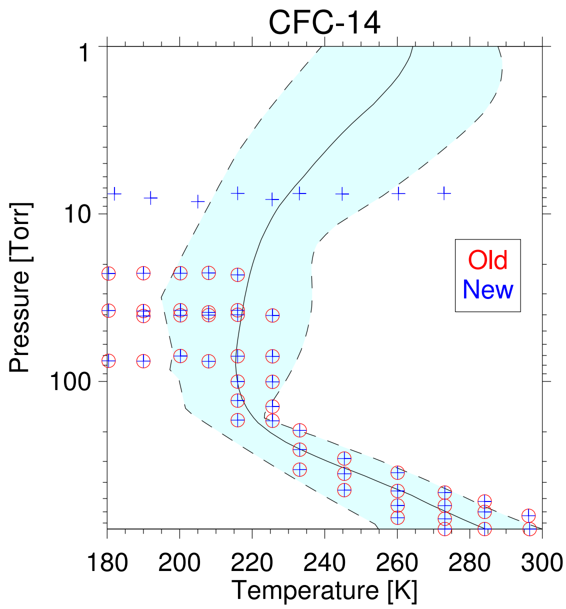

Figure 6.2: pT coordinates of the Old and New CFC-14 cross-section data. The light blue area represents the typical range of atmospheric temperature profiles.

6.4 Low Pressure data

Fig. 6.3 shows the CFC-14 absorption cross-section data measured at 8 Torr, which has been added in the New data.

It can be seen that the low pressure data is mostly noise for the 1250–1270 cm^{-1}region but for the R-branch of the main absorption feature (1284–1286 cm^{-1}) the rotational structure is resolved with good S/N.

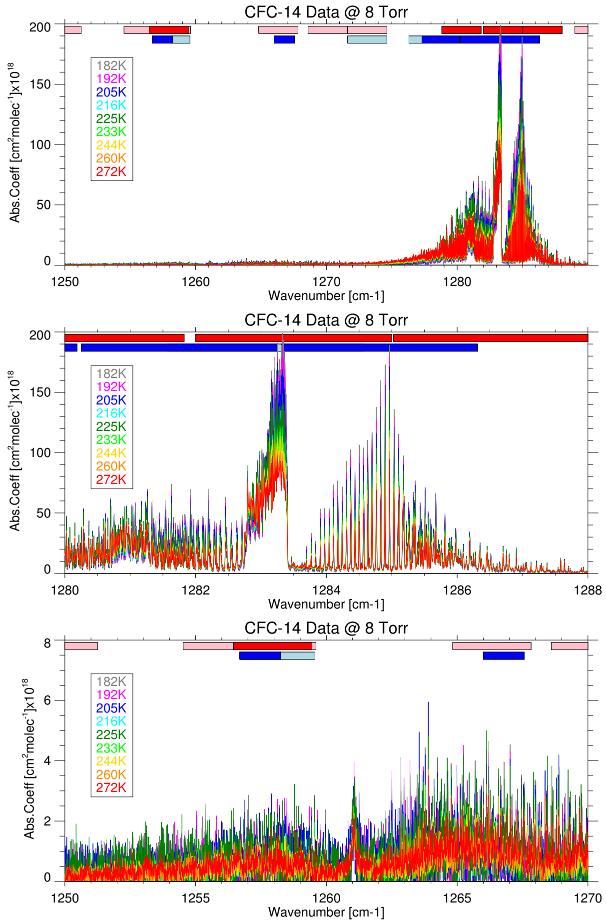

Figure 6.3: CFC-14 cross-section data for 8 Torr tabulated at 9 different temperatures. The top plot shows the full spectral range while the lower plots are subsets in the region of the CFC-14 retrieval microwindows.

6.5 CFC-14 Data Quality Summary

- The New HITRAN data has additional pT tabulations at low pressure, extending the range to 8 Torr.
- The data have good coverage of the range of pT conditions required required for atmospheric path calculations
- The recommendation is to use the New data after the following modifications
  1. Remove near-duplicate sets of pT coordinates near 40 Torr.

7 HCFC-21

HCFC-21 is too weak to be retrieved as single profiles, although it does register as a contaminant in microwindows for the retrieval of other species.

See Appendix B.5 (p. 37) for profiles and radiance calculations.

7.1 Datasets

The Old data from the HITRAN web-site have been updated, but only in the sense that one of the two original spectral bands (1050–1100 cm^{-1}) has now been removed, leaving only the 785–840 cm^{-1} band. These measurements have reference #1: Massie *et al.* (1985)[2], and the original paper refers to both spectral bands.

The data are summarised in Table 7.1.

Table 7.1: Spectral resolution [cm^{-1}] and number of pT datasets within the HCFC-21 cross-section data

	Max/Min Resl		n_{pT}
785–840 cm^{-1} **Band**			
Old	0.0110	0.0110	1
New	0.0110	0.0110	1
1050–1100 cm^{-1} **Band**			
Old	0.0110	0.0110	1

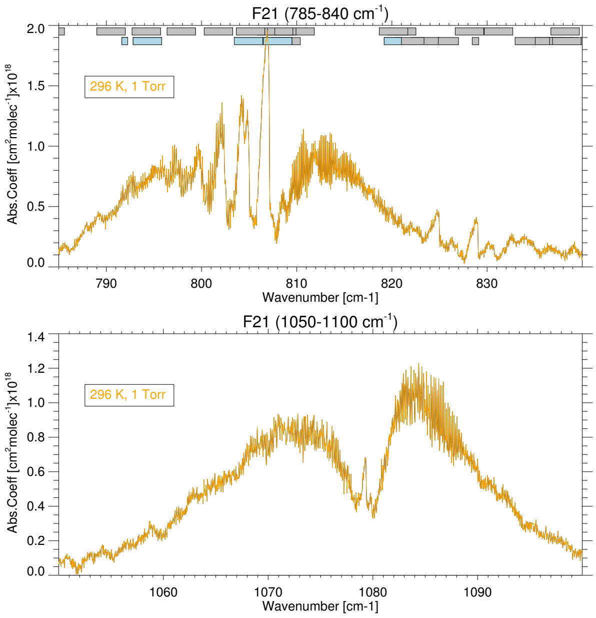

Figure 7.1: The tabulated HCFC-21 absorption coefficient, only measured at 296 K (Old data). Also plotted are the locations of microwindows used for the retrieval of other species (none in the 1050–1100 cm^{-1}range).

- The Old HITRAN data was published in 1985 and has only been modified in the sense that the 1050–1100 cm^{-1} band has been removed in the New data, but this band is in a region of strong ozone absorption and does not overlap any MIPAS microwindows in any case.
- The data were measured at a single temperature, 296 K, and pressure, 1 Torr, neither of which is representative of atmospheric limb path conditions required to model the absorption from this molecule.
- The recommendation, in the absence of any alternative, is to continue to use the existing data. But data with better p, T coverage is desirable.

7.2 Spectral Coverage

The Old data are tabulated for 2 bands, each containing a major absorption feature centred at 805 and 1080 cm^{-1}, plotted in Fig. 7.1.

Only the 785–840 cm^{-1}band overlaps with any MIPAS microwindows but is only strongly enough to register as a contaminant species in some of the OR microwindows (which has a lower threshold for inclusion than FR due to the lower NESR level).

7.3 pT Coverage

The HCFC-21 data are tabulated at a single temperature (296 K) and pressure (1 Torr). Since HCFC-21 is a mainly tropospheric molecule this is inadequate for modelling limb radiance calculations.

7.4 HCFC-21 Data Quality Summary

- HCFC-21 is not a retrieved species but is included as a (minor) contaminant in the retrieval of other species

8 HCFC-22

HCFC-22 is one of the new ESA products.

See Appendix B.6 (p. 38) for profiles and radiance calculations.

8.1 Datasets

The Old data from the HITRAN web-site contained 3 spectral ranges, the first two, 760–860 cm^{-1} and 1070–1195 cm^{-1}from reference #15: Varanasi private communication (2000), and the third, 1275–1380 cm^{-1}, from #14: Clerbaux *et al* (1993)[3]. The #15 data are tabulated for a variety of p, T values. The #14 data have no listed pressure but were apparently made for pure samples at pressures from 1–4 Torr.

The New data for range 760–860 cm^{-1}include the Old data but with 3 extra datasets from #14 (with indeterminate pressure). The data for range 1070–1196 cm^{-1} include all the Old data but with significantly more p, T values and, again, indeterminate pressure data from #14. The data for the third band, 1275–1380 cm^{-1}, appear to be identitical.

There is also Alternative data from Harrison (2014, private communication) covering all 3 spectral ranges at a different set of p, T values.

The available data are summarised in Table 8.1.

Table 8.1: Spectral resolution [cm^{-1}], number of p, T datasets and number of T-only datasets within the HCFC-22 cross-section data

	Max/Min Resl		n_{pT}	n_T
760–860 cm^{-1} **Band**				
Old	0.0050	0.0103	26	0
New	0.0050	0.0103	26	3
Alt	0.0013	0.0025	30	0
1070–1195 cm^{-1} **Band**				
Old	0.0121	0.0134	14	0
New	0.0030	0.0134	31	3
Alt	0.0013	0.0025	30	0
1275–1380 cm^{-1} **Band**				
Old	0.0086	0.0086	0	3
New	0.0086	0.0086	0	3
Alt	0.0013	0.0025	30	0

8.2 Spectral Coverage

The data are tabulated for 3 bands, as shown in Fig. 8.1.

The HCFC-22 retrieval microwindows are all in the 760–860 cm^{-1} band, but HCFC-22 contributions from the other two bands are included as a contaminant in the microwindows for the retrieval of other species.

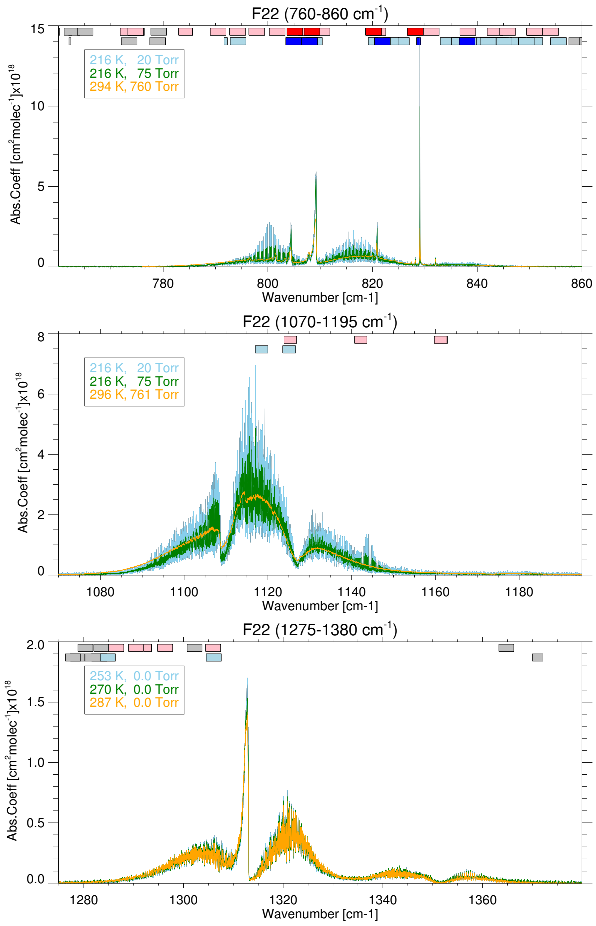

Figure 8.1: The 3 spectral bands for tabulated HCFC-22 absorption coefficient (from the Alt data).

8.3 pT Coverage

For the 760–860 cm^{-1} range the HCFC-22 data are tabulated for the same set of 26 p, T conditions in the Old and New data (see Fig. 8.2).with, as previously mentioned, the addition of 3 datasets from #14 in the New data, which have not been plotted since the pressure is not defined.

In the 1070–1195 cm^{-1} band the p, T conditions are different between the Old and New and, unlike with other cross-section molecules, are generally different from the 760–860 cm^{-1}band.

For the 1275–1380 cm^{-1} band the Old and New data are only tabulated at 3 temperatures.

The Alt data are tabulated at the same set of 30 p, T coordinates for all three bands, and extend to lower pressures (7.5 Torr compared to 20 Torr).

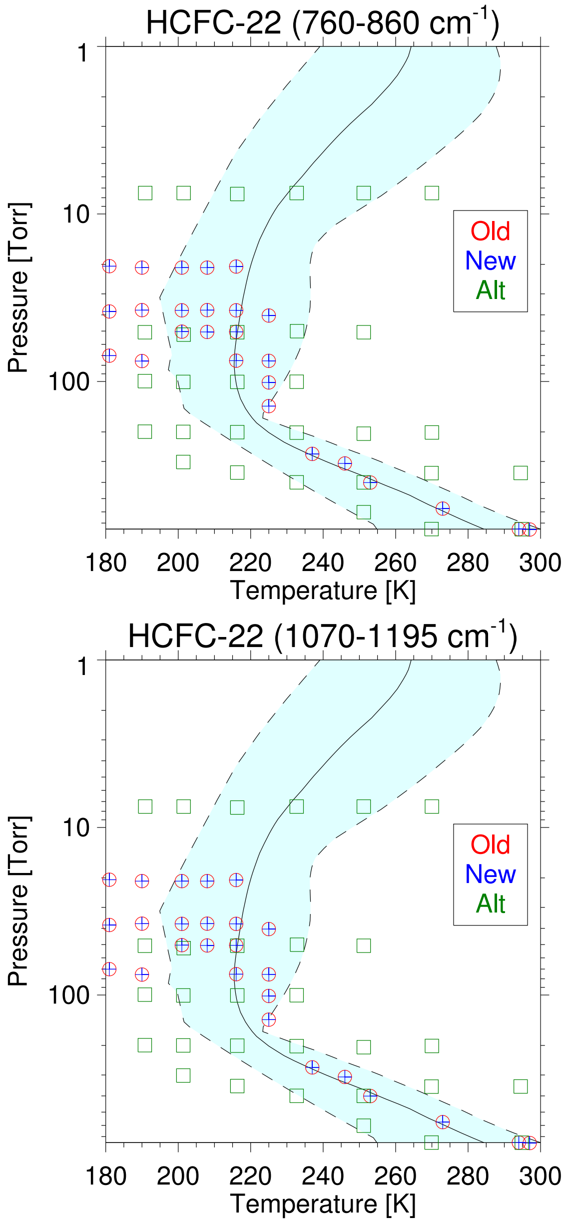

Figure 8.2: p, T coordinates of the different sources of HCFC-22 cross-section data for two spectral bands.

8.4 Low Pressure Data

The lowest pressure cross-section tabulations for the New and the Alt data are compared in Fig. 8.3. Note that there is a significant difference in the lowest pressure between the two sources.

The rotational features in the Alt data have larger amplitude in in the New data, as would be expected at the lower pressure. At the edge of the band the New data appears noisier, despite the coarser spectral sampling.

8.5 HCFC-22 Data Quality Summary

- The 760–860 cm^{-1} band is of primary interest for MIPAS, but HCFC-22 in other bands is modelled as a contaminant.
- The New data for this band is the same as the Old data with the addition of 3 tabulations at indeterminate pressure which are therefore not useful
- The Alternative HCFC-12 data covers a wider range of pT coordinates than the New data, although not as densely sampled, but with higher spectral resolution and better S/N at low pressure.
- The range of pT values in both the New and Alt data represent good coverage for atmospheric limb path conditions.
- The recommendation is the use the Alternative data, since it seems less noisy and extends to lower pressures.

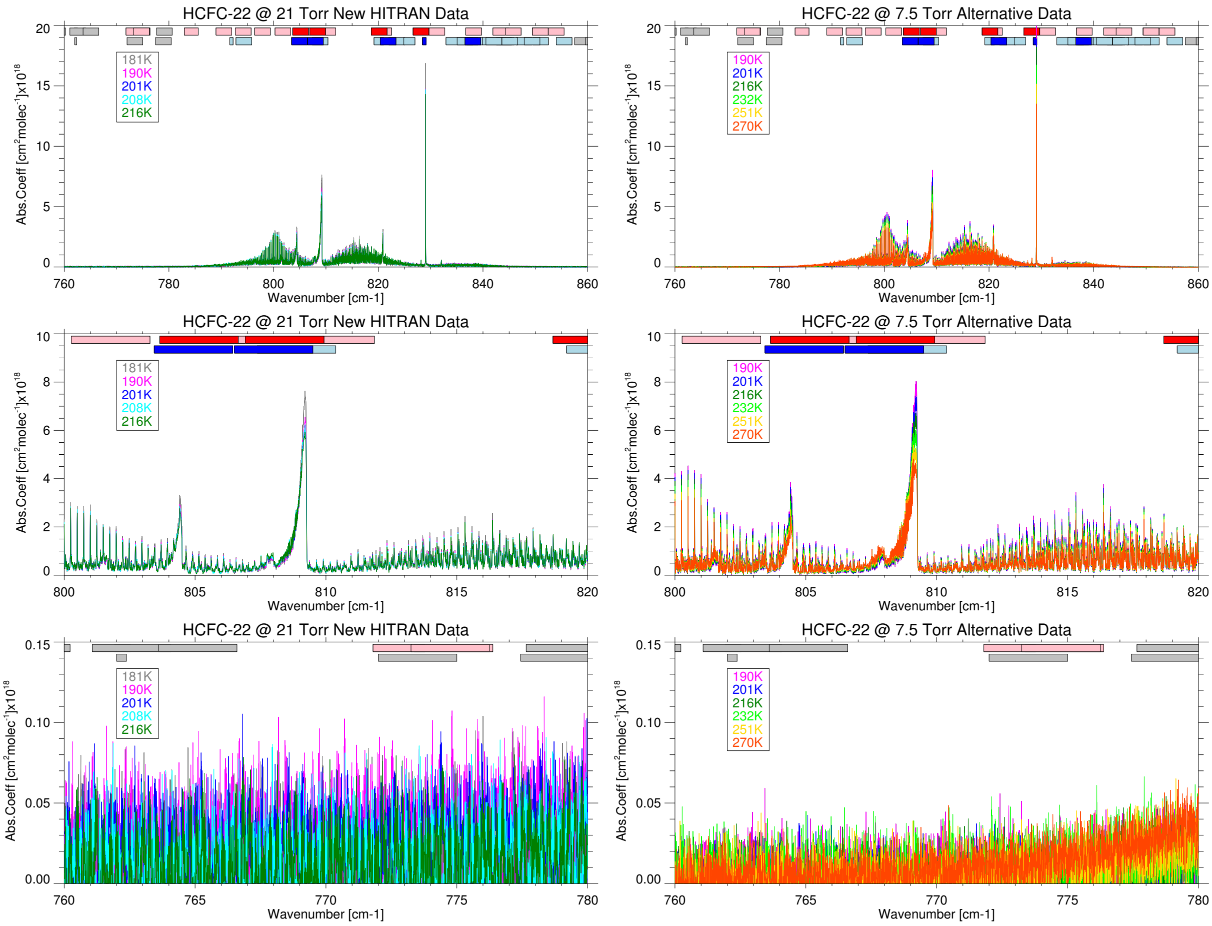

Figure 8.3: HCFC-22 cross-sections for 20 Torr from the New (left) and 7.5 Torr from the Alt (right) data, at different tabulation temperatures, full 760–860 cm^{-1} band in the top plots, and subsets in the lower plots.

9 CFC-113

CFC-113 is currently being tested as a potential new retrieval product.

See Appendix B.7 (p. 39) for profiles and radiance calculations.

9.1 Datasets

The HITRAN data have been reformatted but not updated, and originate from reference #2: McDaniel *et al.* (1991)[1]. The data contain 2 spectral ranges, 780–995 cm^{-1} and 1005–1232 cm^{-1}, each containing several distinct absorption features. The absorption cross-sections tabulated at 6 temperatures but have no pressure information.

There are Alternative data from le Bris *et al.* (2011)[4], which represent the absorption as a single spectral range, 600–1250 cm^{-1}, tabulated at 7 temperatures, but also with no pressure information.

The available data are summarised in Table 9.1.

Table 9.1: Spectral resolution [cm^{-1}] and number of T datasets within the CFC-113 cross-section data

	Max/Min Resl		n_T
780–995 cm^{-1} **Band**			
HITRAN	0.5000	0.5000	6
1005–1232 cm^{-1} **Band**			
HITRAN	0.5000	0.5000	6
600–1250 cm^{-1} **Band**			
Alt	0.0151	0.0151	7

9.2 Spectral Coverage

The spectral coverage of the HITRAN data is plotted in Fig. 9.1.

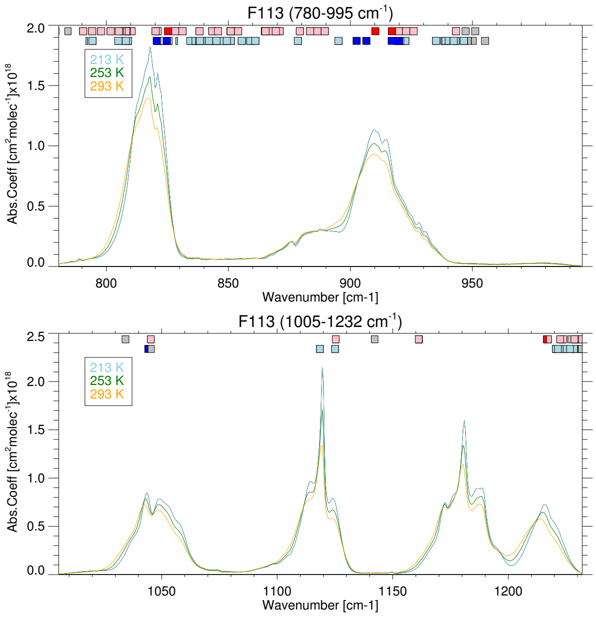

Figure 9.1: The two spectral ranges for tabulated CFC-113 data from HITRAN, plotted for 3 tabulation temperatures. Locations of MIPAS microwindows are shown across the top (see Fig. 3.1 for details).

The MIPAS microwindows for the retrieval of CFC-113 mostly target the two peaks in the 780–995 cm^{-1} band, although the 2nd priority FR microwindow is at 1216 cm^{-1} and there is a low priority OR microwindow at 1043 cm^{-1}. CFC-113 in 780–995 cm^{-1} band also contributes as a contaminant to many more microwindows than the 1005–1232 cm^{-1} band.

The Alt data includes an extra minor feature between 600–700 cm^{-1}. This is probably obscured by CO_2 absorption so not significant for MIPAS.

The Alt data is also tabulated at significantly higher resolution: 0.0151 cm^{-1} compared with 0.5 cm^{-1}(Le Bris *et al.* only claim an actual data resolution of 0.05 cm^{-1}, which is still a factor 10 higher than the tabulation interval of the HITRAN data).

Both datasets include a tabulation at 253 K, which allows a direct comparison to be made. Fig. 9.2 shows the HITRAN and the Alt data near the 800 cm^{-1} peak.

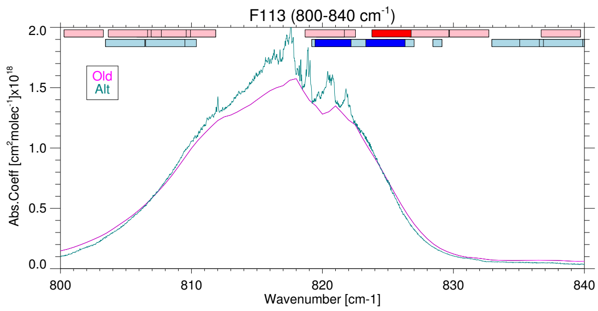

Figure 9.2: Comparison of the HITRAN data and the Alt data tabulated for 253 K near the major absorption peak.

Apart from the obvious improvement in spectral resolution the Alt data values are of the order of 20 % higher at the peak absorption.

9.3 pT Coverage

All the datasets are represented as cross-sections of temperature only, the HITRAN data at 6 temperatures from 203–293 K and the Alt data at 7 temperatures from 223–283 K. [2] state that pure samples were used with pressures 0.25–2 Torr while Le Bris *et al.* used pressures of 2–10 Torr.

Fig. 9.3 shows the Alt data for the different temperatures overplotted. Much of the fine structure near the peak is reproduced, suggesting that these are real features, while the lower panel shows that the lower temperature data are generally more noisy.

9.4 CFC-113 Data Quality Summary

- A number CFC-113 absorption features in the range 780–1230 are used for retrievals or as a contaminant.

- The Alternative data from Le Bris *et al.* is at higher spectral resolution than the existing HITRAN data, and peak absorption values are also up to 20 % higher.

- Neither the HITRAN data nor the Alternative data have any pressure dependence, and are tabulated for pressures much lower than the typical pressures required to model CFC-113 absorption in limb paths.

- The recommendation is to use the data from le Bris *et al.*, although data with better coverage of limb path p, T conditions are desirable.

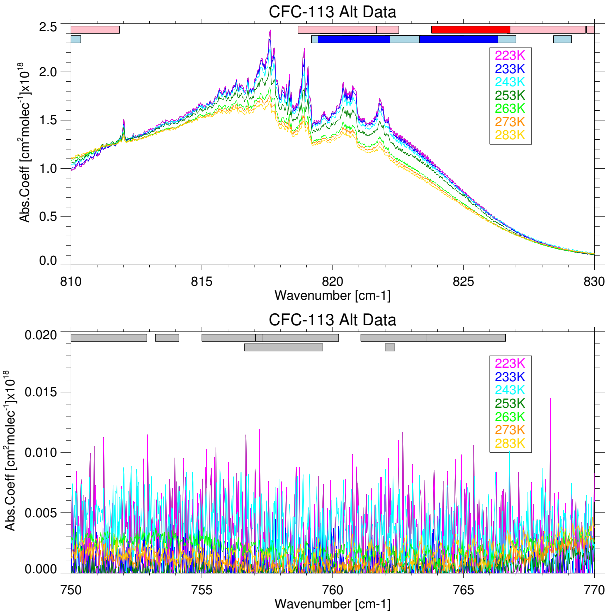

Figure 9.3: CFC-113 Alt data plotted for the different tabulated temperature values near the absorption peak (top) and in a low absorption region (bottom).

10 CFC-114

CFC-114 is currently being tested as a potential new retrieved product.

See Appendix B.8 (p. 40) for profiles and radiance calculations.

10.1 Datasets

The Old data from the HITRAN web-site contains 4 spectral ranges, with tabulations at 6 temperatures for each but with no pressure information. The New data are the same, and have reference #2: McDaniel *et al.* (1991)[1]

The data are summarised in Table 10.1.

Table 10.1: Spectral resolution [cm^{-1}] and number of T datasets within the CFC-114 cross-section data

	Max/Min Resl		n_T
815–860 cm^{-1} **Band**			
HITRAN	0.0148	0.0148	6
870–960 cm^{-1} **Band**			
HITRAN	0.0148	0.0148	6
1030–1067 cm^{-1} **Band**			
HITRAN	0.0148	0.0148	6
1095–1285 cm^{-1} **Band**			
HITRAN	0.0148	0.0148	6

10.2 Spectral Coverage

The spectral coverage of the HITRAN data is plotted in Fig. 10.1.

The microwindows selected for the retrieval of CFC-114 are all in the 815–860 cm^{-1} band, but other microwindows include CFC-114 contributions from all bands as a contaminant.

10.3 pT Coverage

The absorption datasets are represented as functions of temperature only, at 6 temperatures from 203–293 K. McDaniel *et al.* state that pure samples were used with pressures 0.25–2 Torr.

Fig. 10.2 shows the data for the different temperatures overplotted. The gross absorption features are reproduced for all the datasets but there doesn't seem to be much real structure at the data resolution.

10.4 CFC-114 Data Quality Summary

- All bands used for MIPAS, with CFC-114 retrieval microwindows concentrated in the 815–860 cm^{-1} band.
- The HITRAN were originally published in 1991 and have not been updated.
- The data do not contain any explicit pressure dependence, but were made at low pressures which are inappropriate for modelling the (mostly tropospheric) radiance contribution from CFC-114.
- The recommendation, in the absence of any alternative, is to continue to use the existing data,

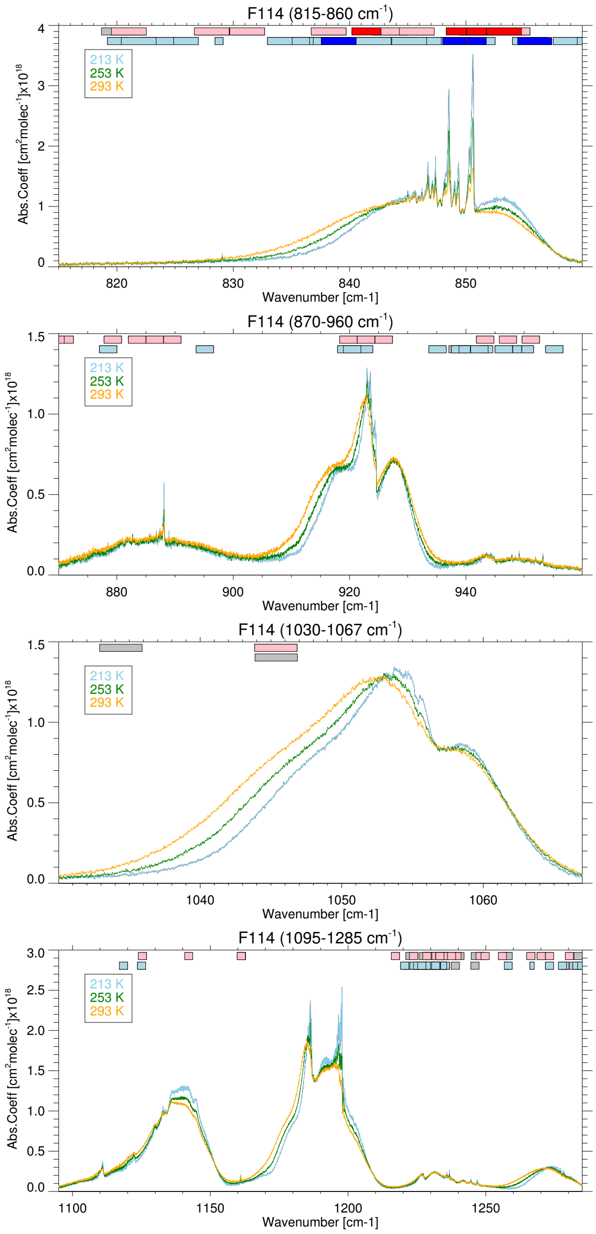

Figure 10.1: The spectral bands for tabulated CFC-114 cross-section data. Locations of MIPAS microwindows are shown across the top (see Fig. 3.1 for details.)

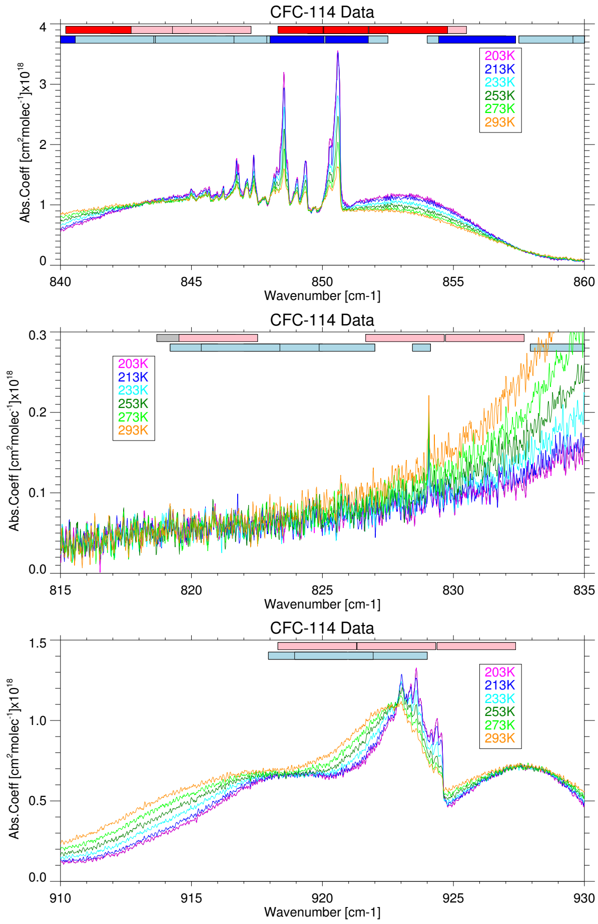

Figure 10.2: Details of the CFC-114 absorption cross-section data plotted for the different tabulated Temperature values.

although data with better p, T coverage is desirable.

11 CFC-115

CFC-115 is too weak for a profile retrieval but is included as a contaminant species.

See Appendix B.9 (p. 41) for profiles and radiance calculations.

11.1 Datasets

The HITRAN data has been reformatted but not updated, and originates from McDaniel *et al.* (1991) [1]. The data are provided in 3 spectral ranges and for 6 temperatures, but with no pressure information.

The data are summarised in Table 11.1.

Table 11.1: Spectral resolution [cm^{-1}] and number of T datasets within the CFC-115 cross-section data

	Max/Min Resl		n_T
955–1015 cm^{-1} **Band**			
HITRAN	0.0148	0.0148	6
1110–1145 cm^{-1} **Band**			
HITRAN	0.0148	0.0148	6
1167–1260 cm^{-1} **Band**			
HITRAN	0.0148	0.0148	6

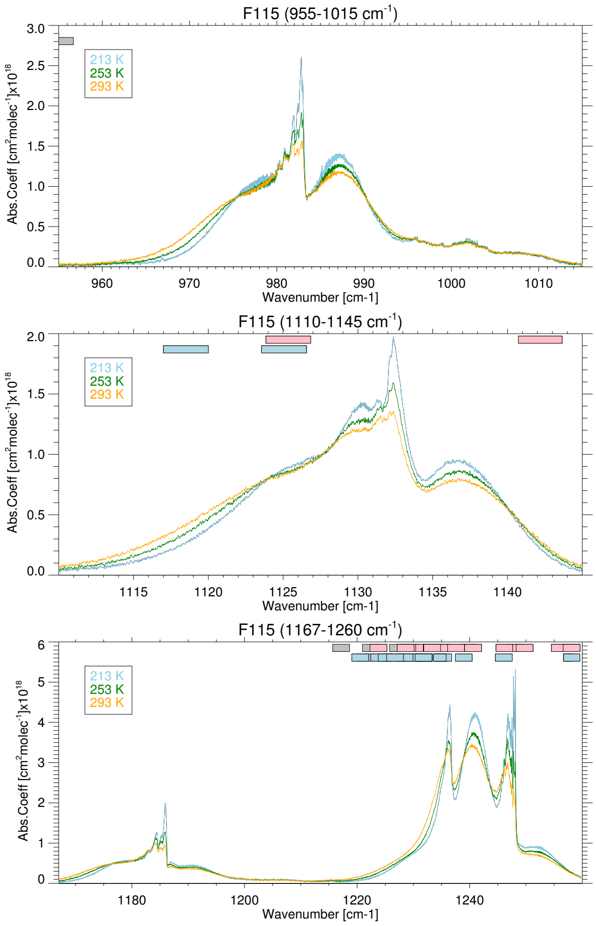

Figure 11.1: The spectral bands for tabulated CFC-115 cross-section data. Locations of MIPAS microwindows are shown across the top.

11.2 Spectral Coverage

The spectral coverage of the HITRAN data is plotted in Fig. 11.1.

The strongest absorption feature is around 1220–1260 cm^{-1}, which coincides with numerous microwindows in the MIPAS B-band (1215–1500 cm^{-1}), while the 955–1050 cm^{-1} does not coincide with any microwindows and mostly lies in the gap between the A (685–970 cm^{-1}) and AB (1020–1170 cm^{-1}) bands (see Radiance plots, Fig. B.18, p. 41).

11.3 pT Coverage

The data are tabulated for 5 temperatures: 203, 213, 233, 253, 273 and 293 K. No pressure is specified but according to McDaniel *et al.* the measurements were made with pure samples at pressures from 0.25–2 Torr.

11.4 CFC-115 Data Quality Summary

- CFC-115 is too weak to be retrieved, but is included as a (minor) contaminant in the retrieval of other species. The 1220–1260 cm^{-1} band is the most signifincant for MIPAS.
- The HITRAN data were originally published in 1991 and have not been updated
- The data are representative of low pressure conditions, inconsistent with the pressures required for accurate modelling the radiance contribution in limb paths.
- The recommendation, in the absence of any alternative, is to continue to use the existing data, although any new datasets with improved pT coverage are desirable.

12 CCl4 (updated)

Alternative CCl_4 data from Harrison now included.

CCl_4 is one of the new ESA products.

See Appendix B.10 (p. 42) for profiles and radiance calculations.

12.1 Datasets

The HITRAN data have been reformatted but not updated, and originate from: Varanasi, private communication (2000). There is also recently published Alternative data from Harrison (2017)[5] covering a wider spectral range at higher spectral resolution (now, 2017, also available on the HITRAN web-site but for consistency will be referred to as 'Alt' data).

The data are summarised in Table 12.1.

Table 12.1: Spectral resolution [cm^{-1}] and number of p, T datasets within the CCl_4 cross-section data

	Max/Min	Resl	n_{pT}
750–812* cm^{-1} **Band**			
Old	0.010	0.010	32
Alt	0.001	0.003	26

*700–860 cm^{-1} for Alt data

12.2 Spectral Coverage

The spectral range of the Old HITRAN data is plotted in Fig. 12.1. Although the Alt data covers a much wider range it does not include any significant extra spectral features.

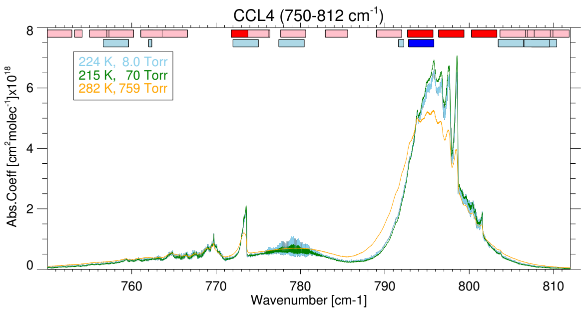

Figure 12.1: The tabulated Old HITRAN CCl_4 cross-section data at typical atmospheric profile conditions.

The retrieval microwindows are mostly concentrated around the ν_3 peak between 790–805 cm^{-1} although there is one FR microwindow at the smaller $\nu_1+\nu_4$ feature around 772 cm^{-1}(see [5] for discussion of spectral features).

It can be seen that the shape of the band changes significantly as a function of pressure.

12.3 pT Coverage

The pT coordinates of the two datasets are plotted in Fig. 12.2.

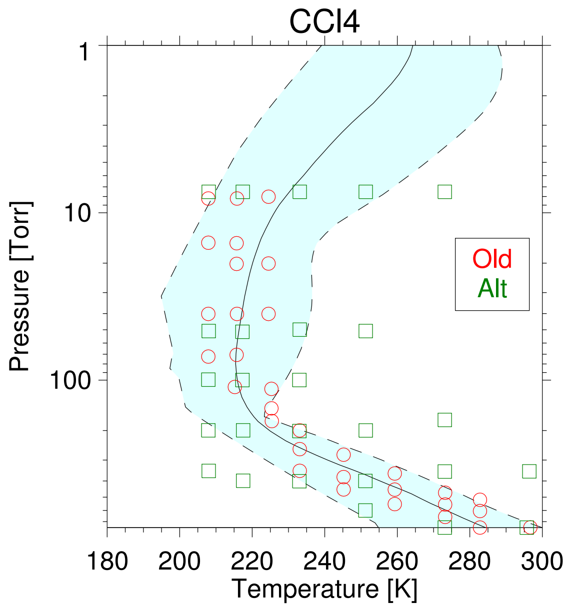

Figure 12.2: The pT coordinates of the tabulated CCl_4 cross-section datasets.

In the Old HITRAN data the pressure axis is well-sampled from surface pressure down to 8 Torr, although the temperature coverage is slightly limited. The Alt data has a similar pressure range and wider temperature range, although a sparser density (particularly between 7.5 and 50 Torr).

12.4 Low Pressure Data

Fig. 12.3 shows parts of the CCl_4 absorption cross-section measured at 8 Torr at various temperatures, for the two datasets.

The Old data is smoother but this appears to be because the Alt data better resolves the fine structure, as can be seen from the reproducible spectral features at the different temperatures, particular near the 750 cm^{-1} edge of the band where the HITRAN data seems to be largely noise.

12.5 CCl4 Data Quality Summary

- The Old HITRAN CCl_4 data has adequate pressure coverage although the temperature coverage is restricted.

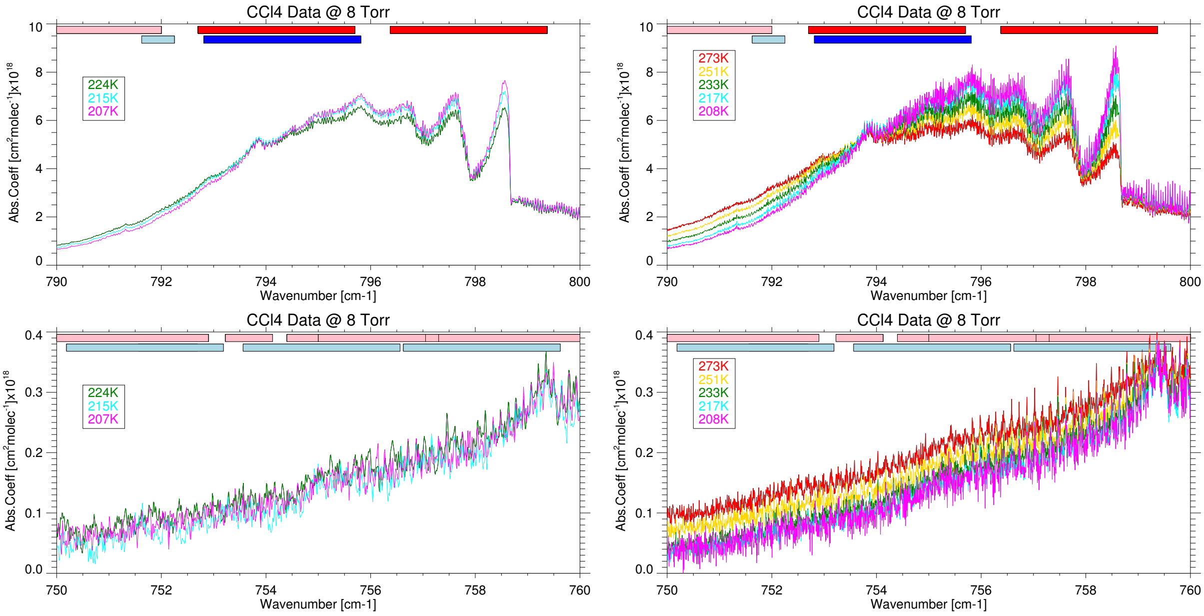

Figure 12.3: CCl_4 cross-section data measured at 8 Torr from the Old HITRAN (left) and Alt (right) data, at different tabulation temperatures, near the main absorption feature (top) and at the edge of the band (bottom).

- Alternative data from Harrison (now also on the HITRAN web-site) has a wider temperature coverage but sparser pressure coverage. However it has higher spectral resolution which better resolves features at low pressure and is less noisy.
- The (new) recommendation is to use the Alt Harrison data.

13 $ClONO_2$

$ClONO_2$ is one of the ESA products.

See Appendix B.11 (p. 43) for profiles and radiance calculations.

13.1 Datasets

The $ClONO_2$ dataset on the HITRAN web-site has been updated for two of the three bands (750–830 cm^{-1}, 1260–1320 cm^{-1}), with data from reference #18 Wagner & Birk (2003)[6], while the old data from #5 Ballard *et al.* (1988)[7], are retained for 1680–1790 cm^{-1}.

HITRAN line parameter data is also available for $ClONO_2$, but this unsuitable since it only covers a limited spectral range 763–798 cm^{-1}(see also Fig. B.23, p. 43).

The cross-section data are summarised in Table 13.1.

Table 13.1: Spectral resolution [cm^{-1}] and number of pT and T-only datasets within the $ClONO_2$ cross-section data

	Max/Min Resl		n_{pT}	n_T
750–830 cm^{-1} **Band**				
Old	0.0015	0.0015	55	7
New	0.0015	0.0015	25	0
1260–1320* cm^{-1} **Band**				
Old	0.0015	0.0015	55	7
New	0.0015	0.0015	25	0
1680–1790 cm^{-1} **Band**				
Old	0.0714	0.0714	0	2
New	0.0714	0.0714	0	2

*1330 cm^{-1} for Old data

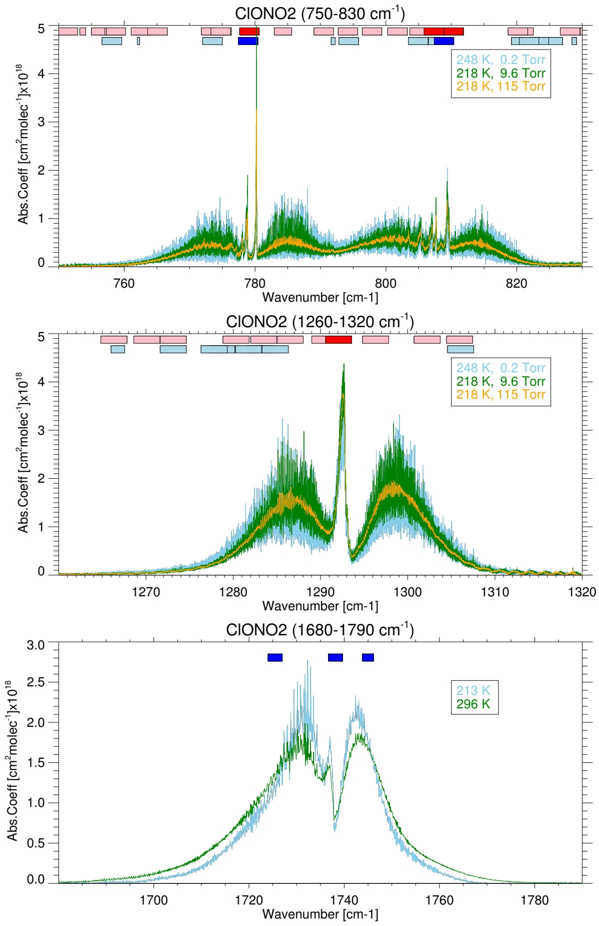

Figure 13.1: The $ClONO_2$ absorption coefficient for different bands at typical atmospheric profile conditions (although note that the 1680–1790 cm^{-1} data is only tabulated for two temperatures and has no pressure coordinate). The locations of MIPAS $ClONO_2$ microwindows superimposed for Full (FR) and Optimised (OR) resolution modes.

13.2 Spectral coverage

The spectral ranges of the New HITRAN data are plotted in Fig. 13.1.

The MIPAS $ClONO_2$ retrieval uses, primarily, microwindows in the 750–830 cm^{-1} band, although there is one FR microwindow in the 1260–1320 cm^{-1}band and 3 OR microwindows in the 1680–1790 cm^{-1} band. The first (highest priority) microwindows for both FR and OR cover the two sharp features between 777–781 cm^{-1}.

13.3 pT Coverage

In the Old data the first two bands are tabulated at 55 pT coordinates (plus 7 coordinates with undefined pressure) while the New data have 25 pT coordinates (see Fig. 13.2). The maximum pressure, for both the Old and New data, is about 115 Torr (150 hPa), reflecting that fact that $ClONO_2$ is primarily found in the stratosphere. The low pressure measurements (<1 Torr) in the New data are made with pure samples of $ClONO_2$ while the higher pressure measurements are made in air.

The third band is only tabulated at two temperature values, 213 K and 296 K, with undefined pressure, although Ballard *et al.* state that the measurements were made using pure samples of $ClONO_2$ at pressures from 0.1–6 Torr.

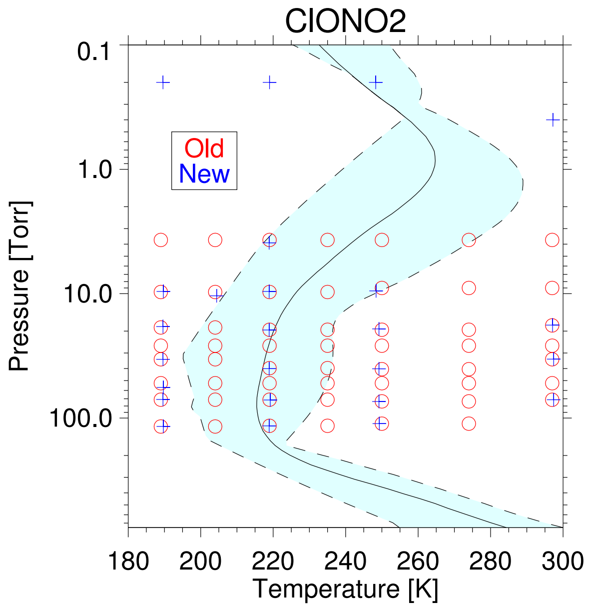

Figure 13.2: The p, T coordinates of the tabulated $ClONO_2$ cross-section data for both the 750–830 cm^{-1} and 1260–1320 cm^{-1} bands. The light blue area represents the typical range of atmospheric temperature profiles, with the solid black line representing a standard mid-latitude profile.

13.4 Low Pressure data

Fig. 13.3 shows the low-pressure data for the New $ClONO_2$ absorption cross-section.

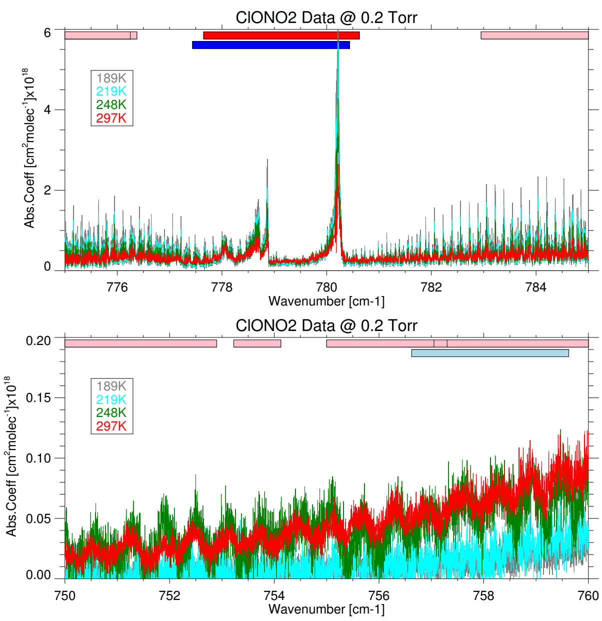

Figure 13.3: $ClONO_2$ cross-section data measured at 0.2 Torr (0.4 Torr for 297 K) near the main absorption feature (top) and at the edge of the band (bottom).

The rotational structure is clearly reproduced at the different temperatures but at the edge of the band exhibits noise but also some periodic oscillations which are, presumably, measurement artefacts.

13.5 $ClONO_2$ Data Quality Summary

- The HITRAN $ClONO_2$ data has been updated for two of the 3 spectral bands. The pT coverage for these two bands is good, but the 1680–1790 cm^{-1} band is only tabulated for 2 temperatures.
- The recommendation is to use the New data, although better data for the 1680–1790 cm^{-1} band is desirable.

14 N_2O_5

N_2O_5 is one of the ESA products.

See Appendix B.12 (p. 44) for profiles and radiance calculations.

14.1 Datasets

The original cross-section dataset for N_2O_5 on the HITRAN web-site has not been updated. The data source is identified with HITRAN reference#18, Wagner & Birk (2003)[6], although the paper only mentions N_2O_5 briefly, and mostly concerns $ClONO_2$ measurements.

The data are summarised in Table 14.1

Table 14.1: Spectral resolution [cm^{-1}] and number of T datasets within the N_2O_5 cross-section data

	Max/Min Resl		n_T
540–1380 cm^{-1} **Band**			
HITRAN	0.0482	0.0482	5

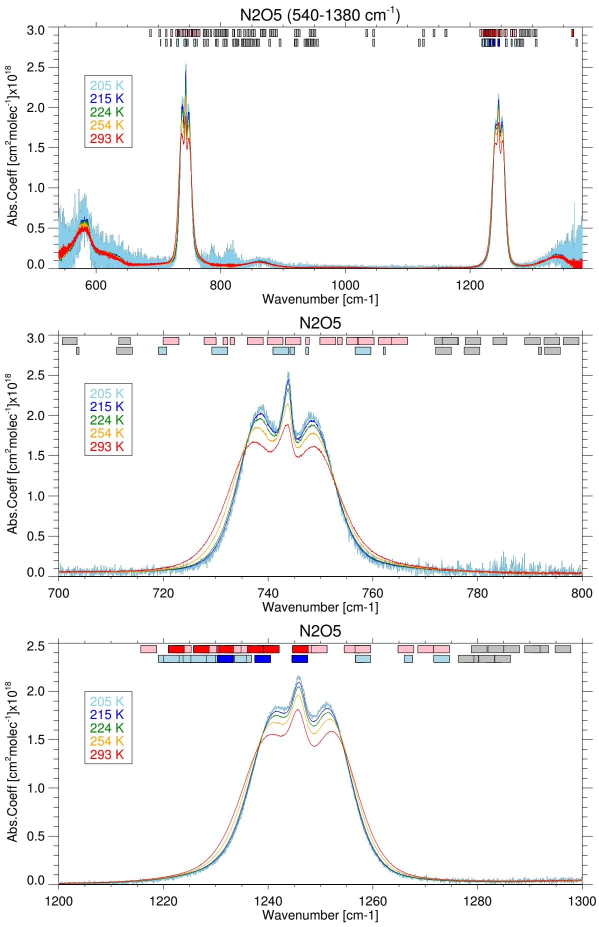

Figure 14.1: The N_2O_5 absorption coefficient tabulated at different temperatures. The top plot shows the full spectral range of the data, the lower plots expand the regions around the two peaks. Boxes along the top show the locations of MIPAS microwindows (see Fig. 3.1 for details).

14.2 Spectral coverage

The data are presented as a single spectral range covering several bands, Fig. 14.1. Most of the MIPAS microwindows lie between 1200–1300 cm^{-1}, although one FR microwindow (#4 in the priority list) lies at 1365 cm^{-1}.

14.3 pT Coverage

There N_2O_5 data are tabulated for 5 temperatures covering the range of interest for atmospheric conditions, but have '0' for the pressure values. Wagner & Birk state that the N_2O_5 pressure was 0.88 mb. Since there are no rotational features present even at this low pressure, it could be argued that the N_2O_5 absorption cross-section only has a weak pressure-dependence anyway.

It can be seen in Fig. 14.1 that the data for 205 K are particularly noisy.

14.4 N_2O_5 Data Quality Summary

- The N_2O_5 dataset on the HITRAN web-site has not been updated. It contains tabulations over a broad spectral range (540–1380 cm^{-1}) at 5 temperatures but with no pressure-dependence
- Assuming that there is no significant pressure-dependence, the recommendation is to continue to use the existing data.

15 HNO_4

HNO_4 is too weak for a profile retrieval but is included as a contaminant species.

See Appendix B.13 (p. 45) for profiles and radiance calculations.

15.1 Datasets

The data on the HITRAN web-site has been updated, but still only contains a single tabulation: one spectral range and one pair of p, T coordinates. The New data have reference #27: May & Friedl (1993)[8]

The data are summarised in Table 15.1.

Table 15.1: Spectral resolution [cm^{-1}] and number of p, T datasets within the HNO_4 cross-section data

	Max/Min Resl		n_{pT}
770–830 cm^{-1} **Band**			
Old	0.0110	0.0110	1
780–830 cm^{-1} **Band**			
New	0.0025	0.0025	1

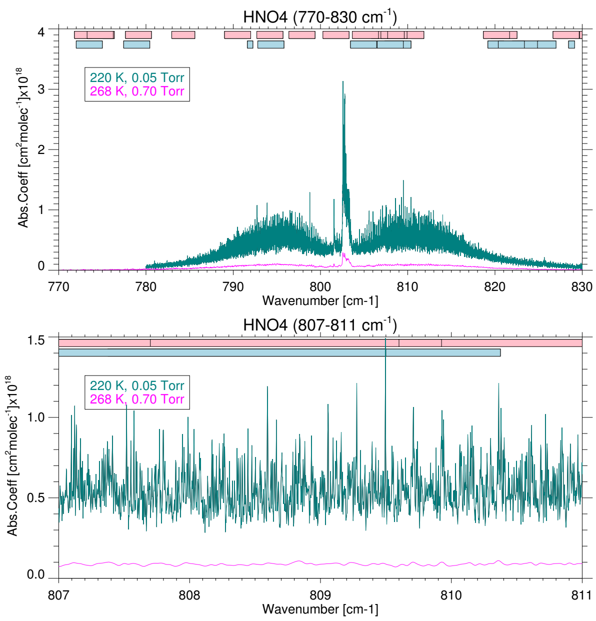

Figure 15.1: The HNO_4 absorption cross-section data for the Old (268 K) and New (220 K) data, full range (top) and close-up of the 807–811 cm^{-1} region (bottom).

15.2 Spectral Coverage

The Old and New HNO_4 spectral cross-section data are plotted in Fig. 15.1.

The obvious difference is the order of magnitude increase in the New absorption cross-section compared to the Old data, which may represent a strong temperature-dependence of the HNO_4 cross-section.

Although there appears to be some periodicity in the New data at about 0.3 cm^{-1}, it it difficult to determine how much of this is real and how much simply noise.

15.3 pT Coverage

Both the Old and the New data are provided for a single pair of pT conditions: 268 K, 0.7 Torr for the Old data, 220 K, 0.05 Torr for the New data.

15.4 Data Quality Summary

- The HITRAN HNO_4 data have been updated
- The Old and New HNO_4 data each contain a single tabulation at different Temperature conditions, and the New (220 K) cross-section values are up to an order of magnitude larger than the Old (268 K) values. The New data are probably more representative of atmospheric conditions for limb radiance calculations.
- Although HNO_4 is not a MIPAS retrieved species, it is modelled as a contaminant in microwindows for other species. The New data would register as significant in more microwindows and may even be retrievable as individual profiles.
- The recommendation is to use the New data, although any new datasets with improved pT coverage are desirable.

16 SF_6 (updated)

Alternative SF_6 data from Manceron *et al.* now included.

SF_6 is currently retrieved with the Oxford processor but has not yet been implemented in the ESA processor.

See Appendix B.14 (p. 46) for profiles and radiance calculations.

16.1 Datasets

The Old data from the HITRAN web-site has not been updated. These measurements are mostly reference #15: P. Varanasi, private communication (2000), but with some data from reference #10, Varanasi *et al.* (1994)[9]. An alternative dataset has subsequently been provided by Manceron *et al.* (private communication).

The data are summarised in Table 16.1.

Table 16.1: Spectral resolution [cm^{-1}] and number of pT datasets within the SF_6 cross-section data

	Max/Min Resl		n_{pT}
925–955 cm^{-1} **Band**			
Old	0.0055	0.0110	32
Alt*	0.0001	0.0086	23

*Range 910–922 to 960–965 cm^{-1}

A large (> 10^7 records!) HITRAN line parameter compilation is also available for SF_6, covering a broader spectral range: 580–996 cm^{-1}. This is discussed further in the Appendix B.14 (p. 46).

16.2 Spectral Coverage

The spectral coverage of the HITRAN data is shown in Fig. 16.1. The data are for a single band, 925–955 cm^{-1}, with the main absorption feature between 940–952 cm^{-1}, and a minor feature (^{34}S isotopologue?) near 930 cm^{-1}. The Alt data covers the same features with a wider (although variable) spectral range and higher resolution.

16.3 pT Coverage

The HITRAN data contains absorption coefficient tabulated at 32 pairs of p, T coordinates, at two underlying spectral resolutions (see Fig. 16.2). 5 of the datasets (Res2) are at 0.0100 cm^{-1} sampling, while the remaining 27 (Res1) are either at 0.0055 or 0.0110 cm^{-1}. The Alt data has a spectral resolution which varies with pressre from 0.086 cm^{-1} at 600 Torr down to 0.0001 cm^{-1} at 7.6 Torr.

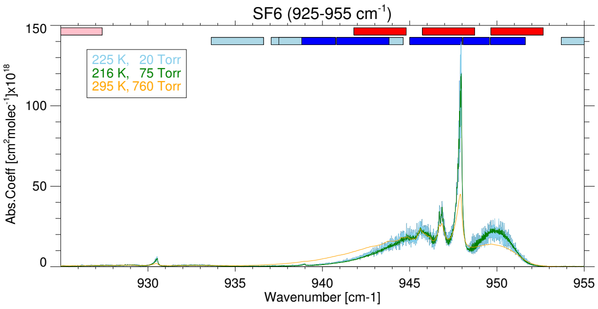

Figure 16.1: The SF_6 absorption coefficient at typical atmospheric profile conditions, with locations of MIPAS microwindows (see Fig. 3.1 for details).

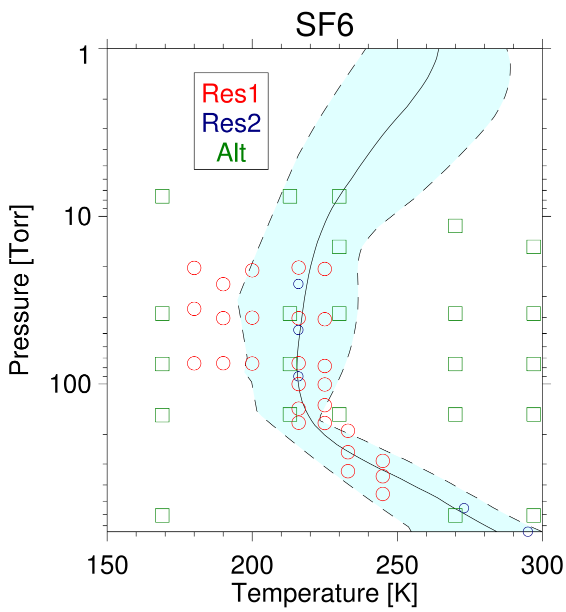

Figure 16.2: p, T coordinates of the tabulated SF_6 cross-section data plotted according to underlying HITRAN resolution: 0.0055 cm^{-1} (Res1) or 0.0100 pts (Res2), and the Alt data from Manceron *et al.* The light blue area represents the typical range of atmospheric temperature profiles, with the solid black line representing a standard mid-latitude profile.

All three HITRAN p, T measurements labelled reference #10 are tabulated at 0.0100 cm^{-1}, but also two measurements labelled as reference #15 (at the higher pressure values). The Alt data covers a wider range of p, T values, although with reduced density in the region required for modelling atmospheric transmittance.

16.4 Low Pressure data

The lowest pressure in the HITRAN data is 20 Torr, while in the Alternative data it is 7.6 Torr, so the data cannot be directly compared at the same pressure. However the low pressure data in both datasets is plotted in Fig. 16.3.

The HITRAN low pressure data seems to represent real structure in the P and R branches but the coarser spectral data (from reference #10, in red) has smaller amplitude, suggesting that the rotational structure is not being resolved at this resolution.

The fine structure in the alternative data has a higher amplitude as expected for the lower pressure, which seems well resolved, but the main Q-branch peak itself also seems to be larger.

16.5 SF_6 Data Quality Summary

- The SF_6 data from the HITRAN web-site has not been updated.
- The HITRAN data have adequate pT coverage but include some older, lowere resolution data which should be removed
- Alternative data from Manceron covers a wider range of pT values, although with a lower sampling density in the required range, generally at a higher spectral resolution. The SF_6 peak also seems larger (hence retrieved values could be 10s of percent lower)
- The (new) recommendation is to use the Alternative data from Manceron *et al.*

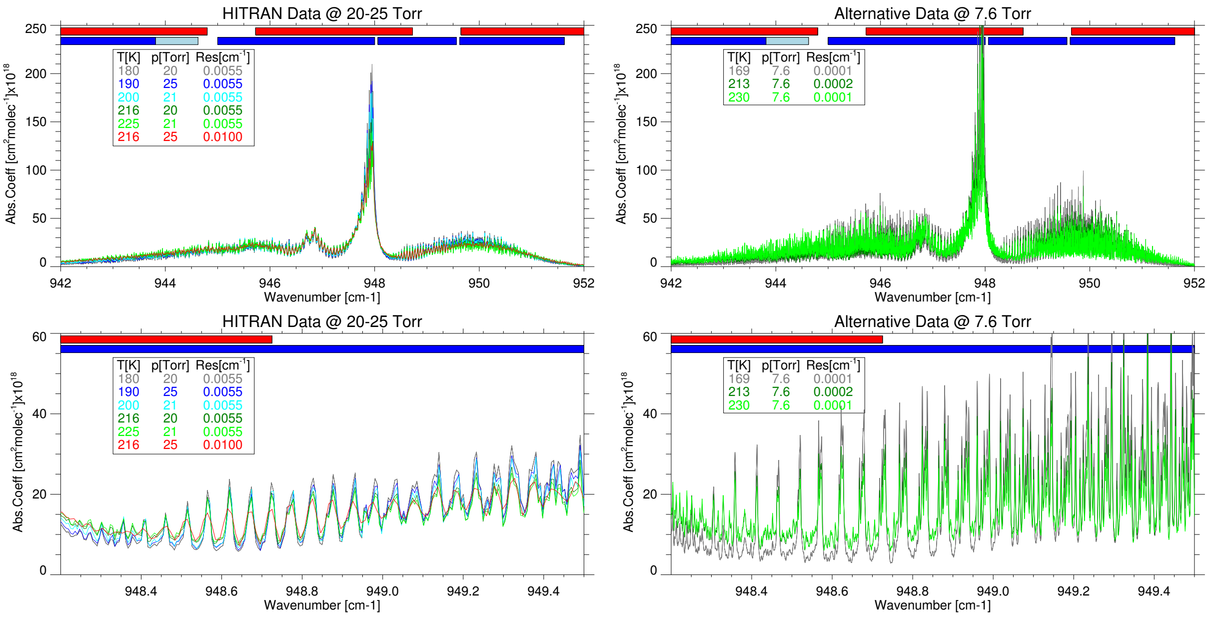

Figure 16.3: SF_6 cross-section from the HITRAN (left, at 20–25 Torr) and Alternative (right, 7.6 Torr) data, at different tabulation temperatures, for the major absorption feature (top) and expanded detail (bottom).

A MIPAS Look-Up Tables

The 'optimised forward model' in the MIPAS retrievals uses pretabulated absorption coefficients $k(\nu, p, T)$ for both line and cross-section molecules, in the form of Look Up Tables (LUT), one file per molecule per microwindow. In the case of the line molecules this provides a significant gain in speed compared to a line-by-line calculation using the Voigt lineshape. Such gains are not so evident for X/S data but it is convenient to have *all* molecular absorption data in the same format.

In principle the MIPAS LUTs contain the same information as the X/S data. However there are some significant differences

1. The MIPAS LUTs are tabulated on a grid of fixed increments in $\ln p$ and T while the X/S data are at arbitrary pT coordinates

2. The MIPAS LUTs are further compressed using Singular-Vector Decomposition (SVD)

A.1 Creating LUTs

The LUTs are created with the aim of matching 'reference' limb radiance calculations to within 10 % of the nominal instrument NESR. In the case of 'line' molecules the reference is a line-by-line calculation, while for X/S data it is a direct interpolation the original data pT domain using triangulation.

There are 3 stages in generating LUTs:

1. Establishing array dimensions in p, T domain for an accurate representation of $k(\nu, p, T)$

2. Compression using Singular Vector Decomposition and determining the number of singular vectors required to represent k

3. Subsampling spectral grid to determine mininum set of points required ν axis in $k(\nu, p, T)$ (the 'irregular grid')

A third of the total 10 % NESR error budget is assigned to each stage.

The first stage of LUT generation is to create a table of $k(\nu, p, T)$ at fine spacing in the $\ln p$ and T axes (typically 60 pressures from 1000–1 mb $\times$ 40 temperatures from 180–300 K). Assuming this initially matches the reference calculation to high accuracy, the axes are progressively subsampled until the difference with respect to the reference calculation reaches NESR/30.

The second stage is to combine the p, T axes so the subsampled 3D LUT, $k(\nu, p, T)$, is represented as a 2D matrix typically of dimension 6700$\times$100 (6700 representing 3 cm^{-1} microwindow plus extra 0.175 cm^{-1}at each edge to allow for AILS convolution, sampled at 0.0005 cm^{-1}.) This is then compressed using SVD to l=30 singular vectors (i.e., represented as a pair of matrices of typical dimensions 6700$\times$30 and 30$\times$100). The number of singular vectors l is then progressively reduced until the difference with respect to the reference calculation reaches NESR/15.

The third stage is to compare the radiance generated with the SVD-compressed LUTs with the reference calculation and progressively remove spectral points (replacing them with interpolated radiances) until the difference with respect to the reference calculation reaches NESR/10.

A.2 Problems with X/S LUTs

In theory, LUTs created from absorption X/S data should be smaller than from line molecules. Firstly, the data are initially represented at a relatively small set of (albeit irregular) p, T coordinates, so should not require a dense grid of regular $\ln p, T$ coordinates to capture the variation. Secondly, the spectral structure in the ν domain is relatively smooth and therefore should be represented by only a small number of singular vectors.

In practice, however, LUTs generated from X/S data are often larger, both in the p, T domain and number of singular vectors required and often cause the error budgets for each stage of the LUT generation to be exceeded. The reason for this is 'noisy' data. The X/S data represent 'real' lab spectra and, for low pressure conditions in particular, a large noise component is evident. Within the LUT generation, this noise structure is indistinguishable from real spectral structure and consequently a large number of p, T coordinates and singular vectors are used effectively just to reproduce the measurement noise.

Three solutions are suggested

1. Spectrally filter the X/S data to reduce the noise while retaining real structure
2. Truncate 'noisy' wings of bands to zero where the underlying absorption is sufficiently close to zero to be negligible
3. Eliminate completely p, T datasets which are too noisy, or redundant in terms of closely matching p, T coordinates of other datasets

B Profiles & Radiance Calculations

B.1 CFC-11

See section 3 (p. 4) for main discussion on absorption cross-section data.

The profiles of CFC-11 in the 5 MIPAS reference atmospheres are shown in Fig. B.1.

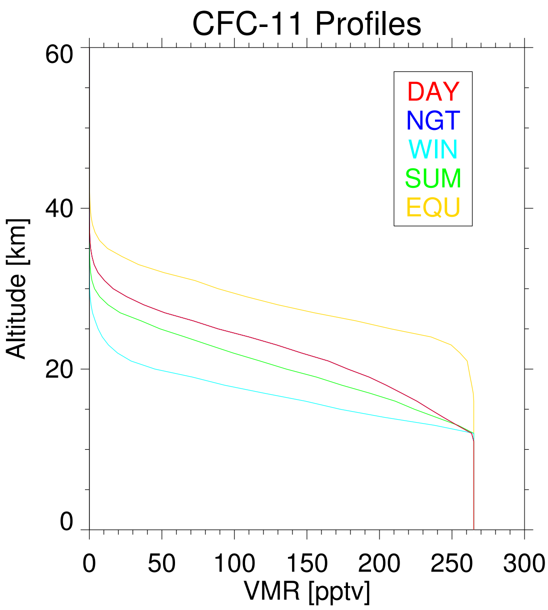

Figure B.1: The CFC-11 volume mixing ratio profiles in the 5 MIPAS reference atmospheres (the DAY and NGT profiles coincide).

Limb radiance calculations for the mid-latitude night-time profile (NGT) are shown in Fig. B.2.

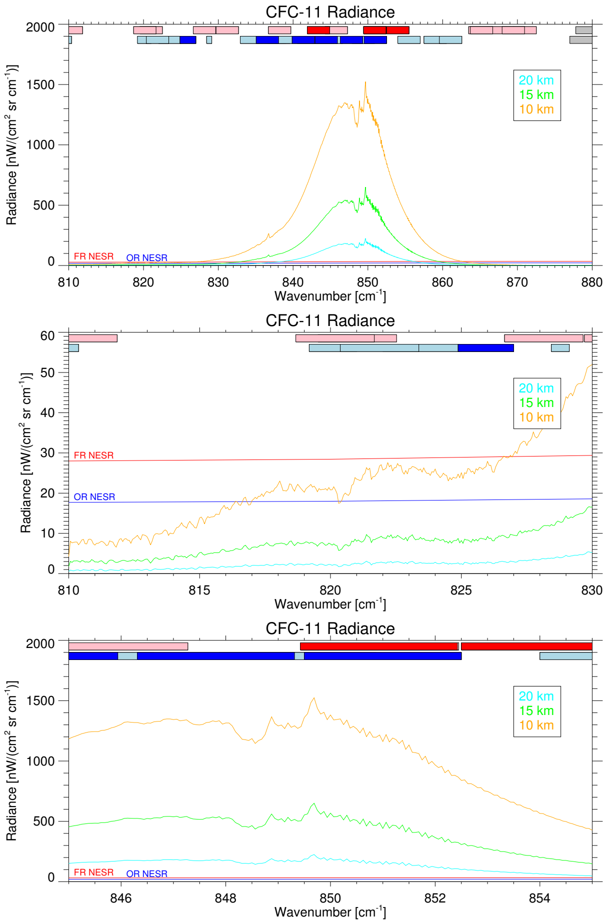

Figure B.2: The limb radiance contribution of CFC-11 at various tangent heights for the spectral ranges plotted in Fig. 3.1. Red and Blue lines correspond to nominal MIPAS NESR values for FR and OR respectively.

B.2 CFC-12

See section 4 (p. 7) for main discussion on absorption cross-section data.

The profiles of CFC-12 in the 5 MIPAS reference atmospheres are shown in Fig. B.3.

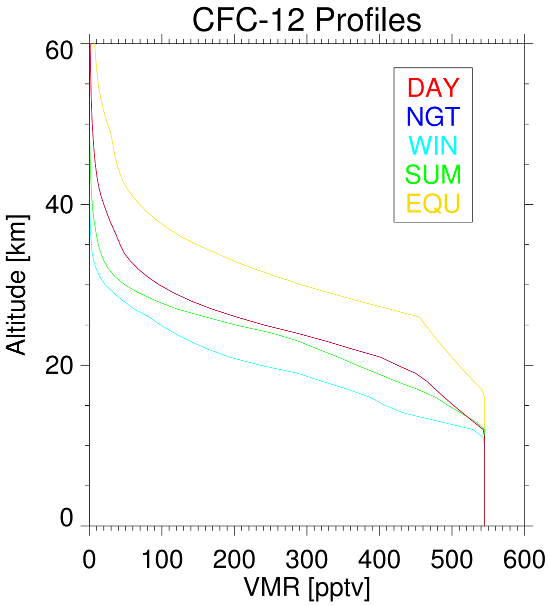

Figure B.3: The CFC-12 volume mixing ratio profiles in the 5 MIPAS reference atmospheres (the DAY and NGT profiles coincide).

Limb radiance calculations for the mid-latitude night-time profile (NGT) are shown in Fig. B.4.

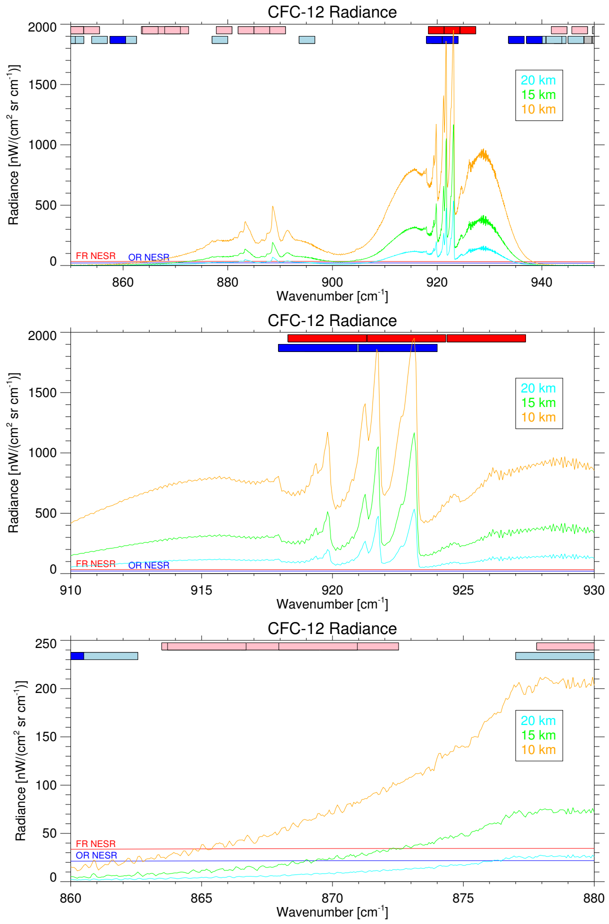

Figure B.4: The limb radiance contribution of CFC-12 at various tangent heights for the spectral ranges plotted in Fig. 4.3. Red and Blue lines correspond to nominal MIPAS NESR values for FR and OR respectively.

B.3 CFC-13

See section 5 (p. 10) for main discussion on absorption cross-section data.

CFC-13 is not included in the set of MIPAS reference atmospheres, so the assumed profile, shown in Fig. B.5, is taken from the FASCODE set of single profiles for minor species.

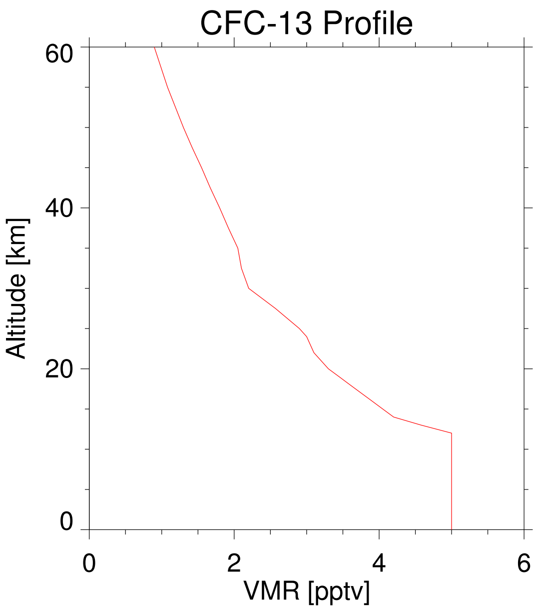

Figure B.5: The CFC-13 volume mixing ratio profile from the FASCODE atmosphere.

Limb radiance calculations for the mid-latitude night-time profile (NGT) are shown in Fig. B.6.

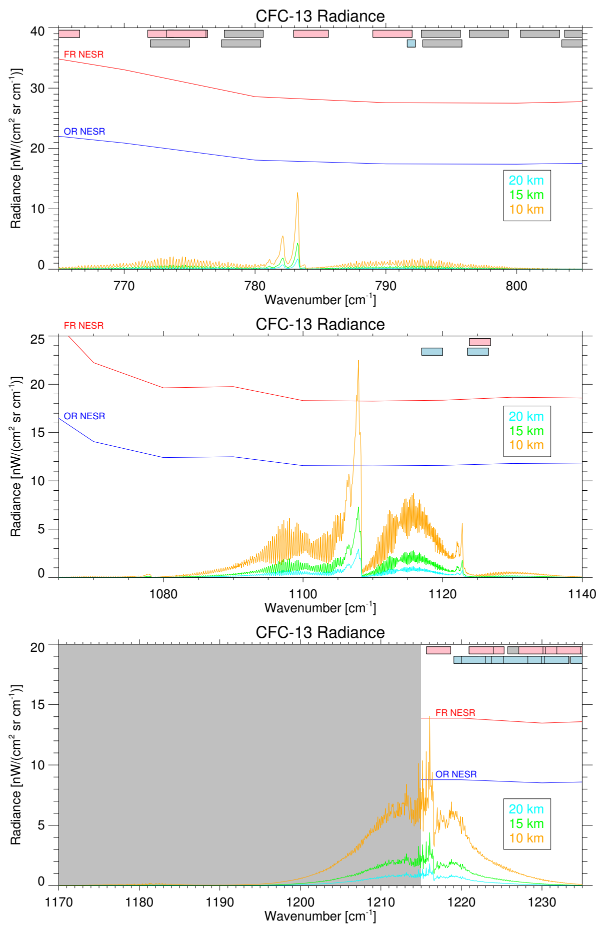

Figure B.6: The limb radiance contribution of CFC-13 at various tangent heights for the spectral ranges plotted in Fig. 5.1. Red and Blue lines correspond to nominal MIPAS NESR values for FR and OR respectively. The grey area in the lower plot corresponds to the gap between the MIPAS AB and B bands.

B.4 CFC-14

See section 6 (p. 11) for main discussion on absorption cross-section data.

The profile of CFC-14 is the same in all 5 MIPAS reference atmospheres, shown in Fig. B.7.

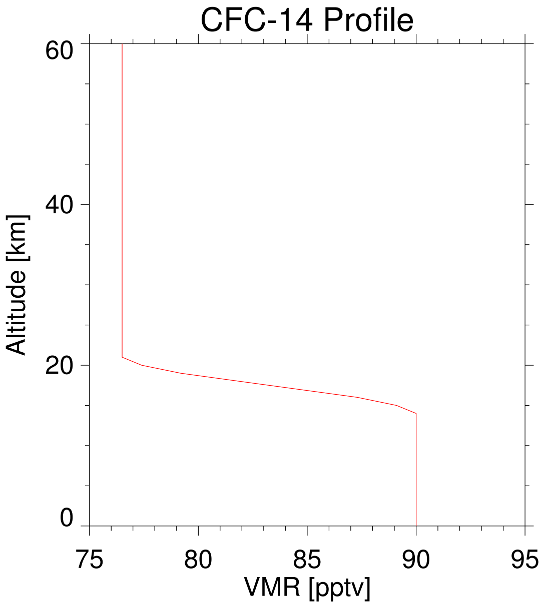

Figure B.7: The CFC-14 volume mixing ratio profile in the 5 MIPAS reference atmospheres.

Limb radiance calculations for the mid-latitude night-time profile (NGT) are shown in Fig. B.8.

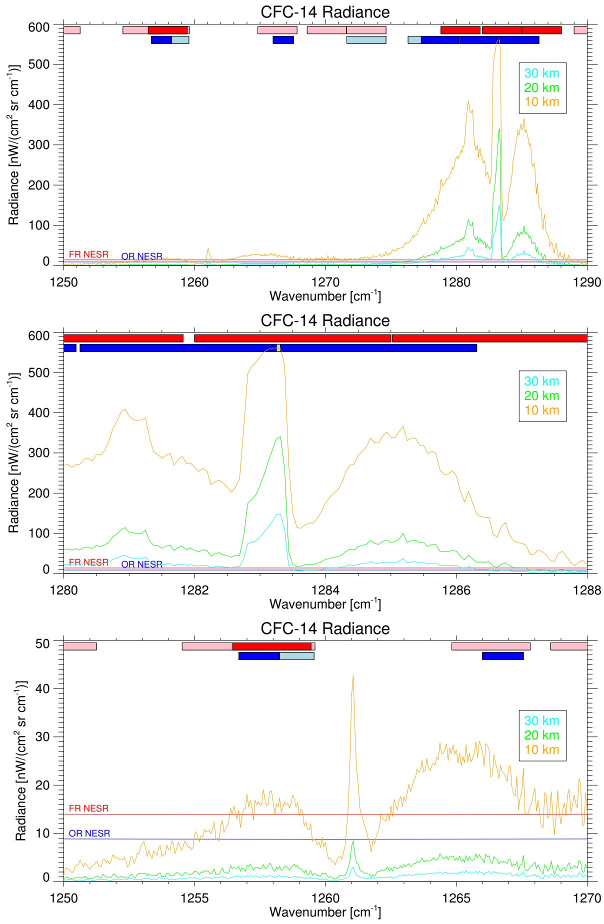

Figure B.8: The limb radiance contribution of CFC-14 at various tangent heights for the spectral ranges plotted in Fig. 6.1. Red and Blue lines correspond to nominal MIPAS NESR values for FR and OR respectively.

B.5 HCFC-21

See section 7 (p. 13) for main discussion on absorption cross-section data.

HCFC-21 is not included in the set of MIPAS reference atmospheres, so the assumed profile, shown in Fig. B.9, is taken from the FASCODE set of single profiles for minor species.

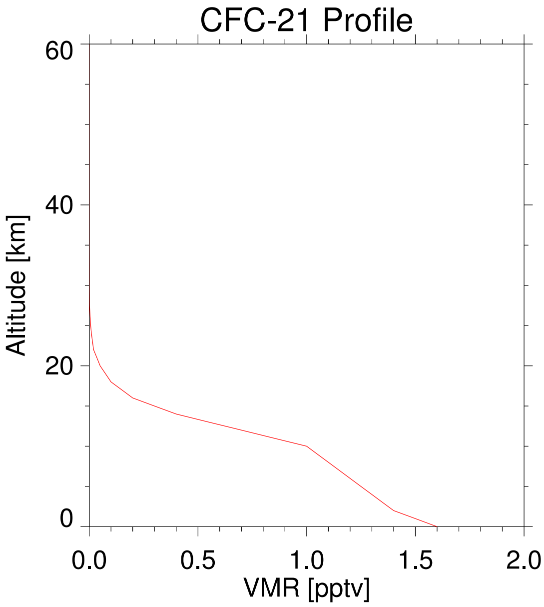

Figure B.9: The HCFC-21 volume mixing ratio profile from the FASCODE atmosphere.

Limb radiance calculations for the mid-latitude night-time profile (NGT) are shown in Fig. B.10.

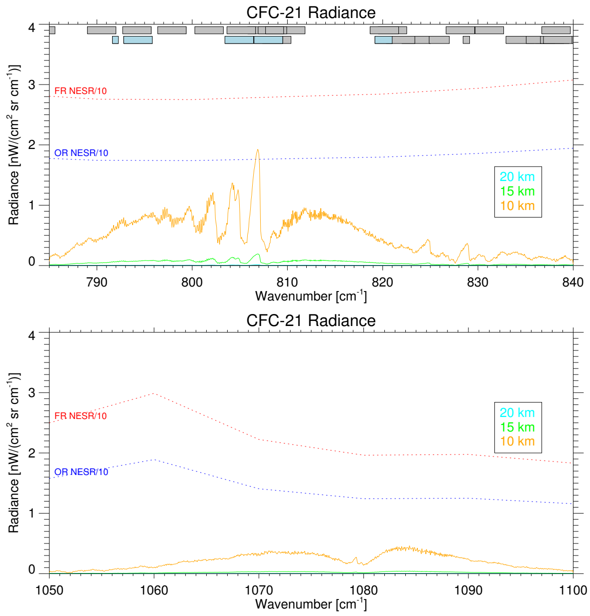

Figure B.10: The limb radiance contribution of HCFC-21 at various tangent heights for the spectral ranges plotted in Fig. 7.1. Red and Blue dotted lines correspond to nominal MIPAS NESR values divided by 10 for FR and OR respectively.

B.6 HCFC-22

See section 8 (p. 14) for main discussion on absorption cross-section data.

The profile of HCFC-22 is the same in all 5 MIPAS reference atmospheres, and plotted in Fig. B.11.

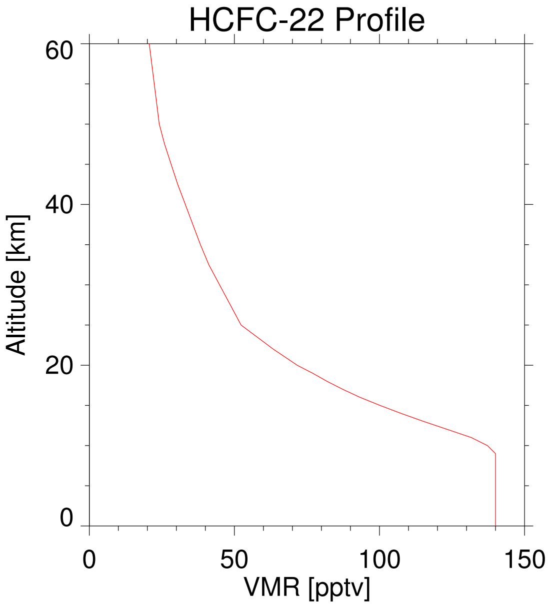

Figure B.11: The HCFC-22 volume mixing ratio profile in the MIPAS reference atmospheres.

Limb radiance calculations for the mid-latitude night-time profile are shown in Fig. B.12.

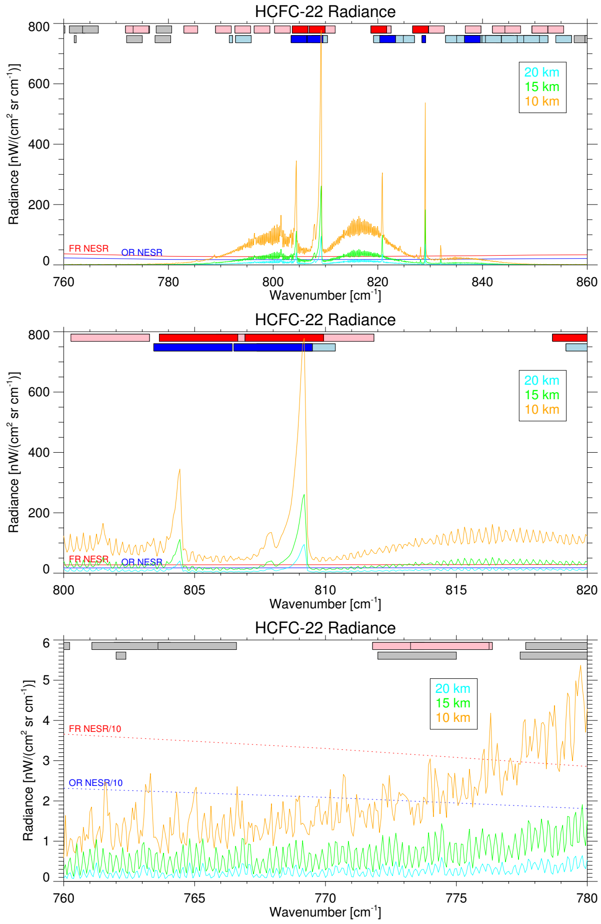

Figure B.12: The limb radiance contribution of HCFC-22 at various tangent heights for the spectral ranges plotted in Fig. 8.3. Red and Blue solid lines correspond to nominal MIPAS NESR values FR and OR respectively, dotted lines to NESR/10.

B.7 CFC-113

See section 9 (p. 17) for main discussion on absorption cross-section data.

CFC-113 is not included in the set of MIPAS reference atmospheres, so the assumed profile, shown in Fig. B.13, is taken from the FASCODE set of single profiles for minor species.

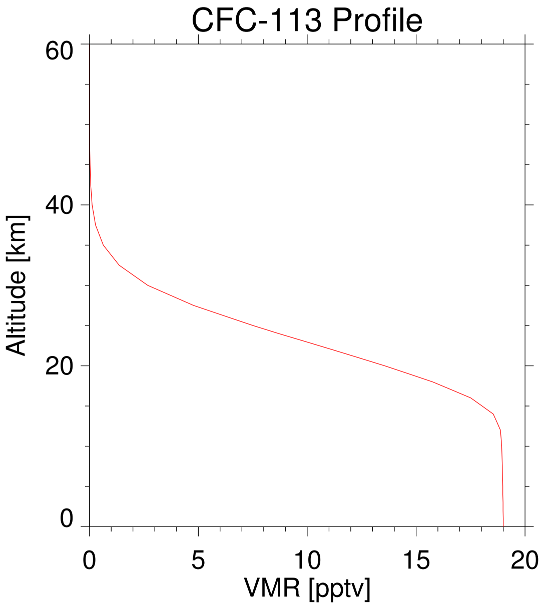

Figure B.13: The CFC-113 volume mixing ratio profile from the FASCODE atmosphere.

Limb radiance calculations for the mid-latitude night-time profile (NGT) are shown in Fig. B.14.

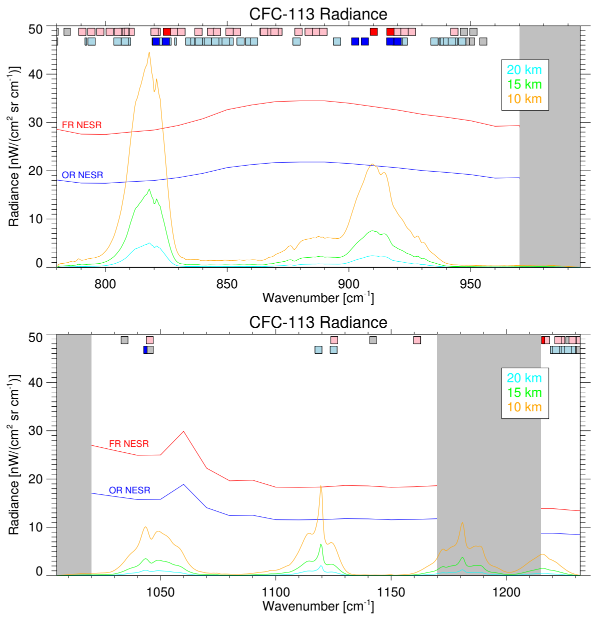

Figure B.14: The limb radiance contribution of CFC-113 at various tangent heights for the spectral ranges plotted in Fig. 9.1. Red and Blue lines correspond to nominal MIPAS NESR values for FR and OR respectively. The grey area in the lower plot corresponds to the gaps between the MIPAS bands.

B.8 CFC-114

See section 10 (p. 19) for main discussion on absorption cross-section data.

CFC-114 is not included in the set of MIPAS reference atmospheres, so the assumed profile, shown in Fig. B.15, is taken from the FASCODE set of single profiles for minor species probably dating from c. 1980. A more recent tropospheric value taken from Martinerie *et al.* (2009)[10] is approximately 30 % higher.

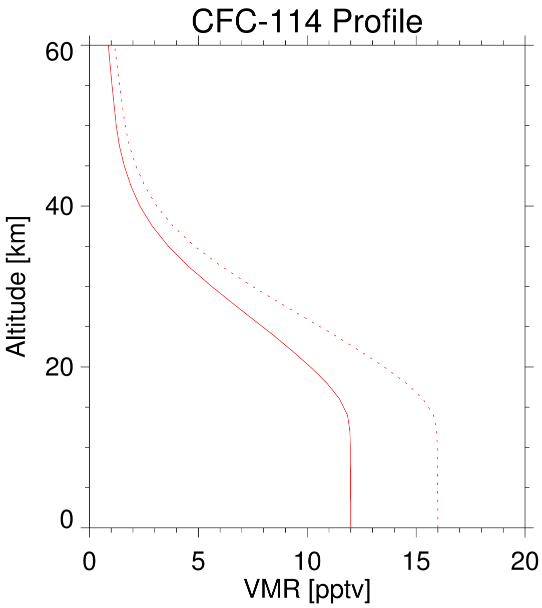

Figure B.15: The CFC-114 volume mixing ratio profile from the FASCODE atmosphere (solid line) and scaled to match 2000–2010 tropospheric values (dotted line).

Limb radiance calculations for the mid-latitude night-time profile (NGT) are shown in Fig. B.16.

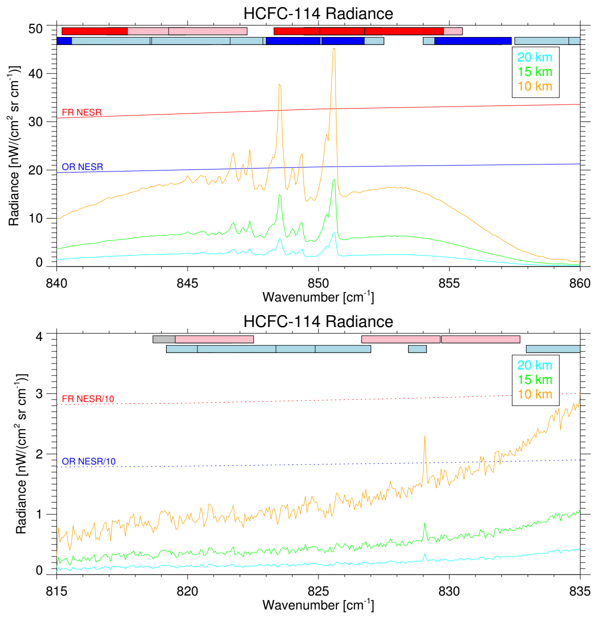

Figure B.16: The limb radiance contribution of CFC-114 at various tangent heights for the spectral ranges plotted in Fig. 10.2. Red and Blue lines correspond to nominal MIPAS NESR values for FR and OR respectively.

B.9 CFC-115

See section 11 (p. 21) for main discussion on absorption cross-section data.

CFC-115 is not included in the set of MIPAS reference atmospheres, so the assumed profile, shown in Fig. B.17, is taken from the FASCODE set of single profiles for minor species dating from c. 1980. A more recent tropospheric value taken from Martinerie *et al.* (2009)[10] is approximately twice as large.

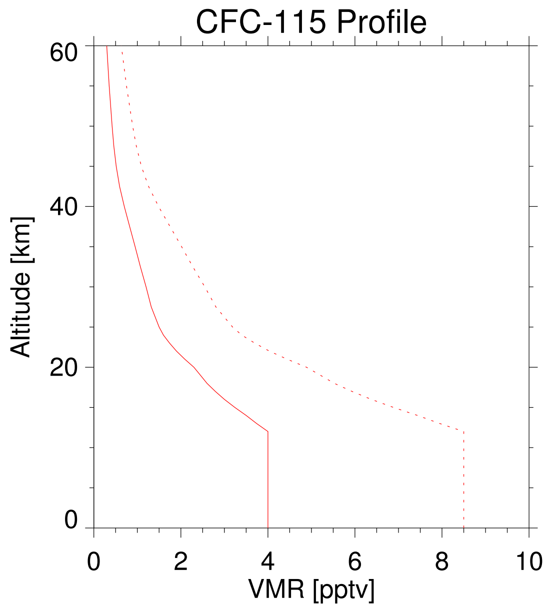

Figure B.17: The CFC-115 volume mixing ratio profile from the FASCODE atmosphere (solid line) and scaled to match 2000–2010 tropospheric values (dotted line).

Limb radiance calculations for the mid-latitude night-time profile (NGT) are shown in Fig. B.18.

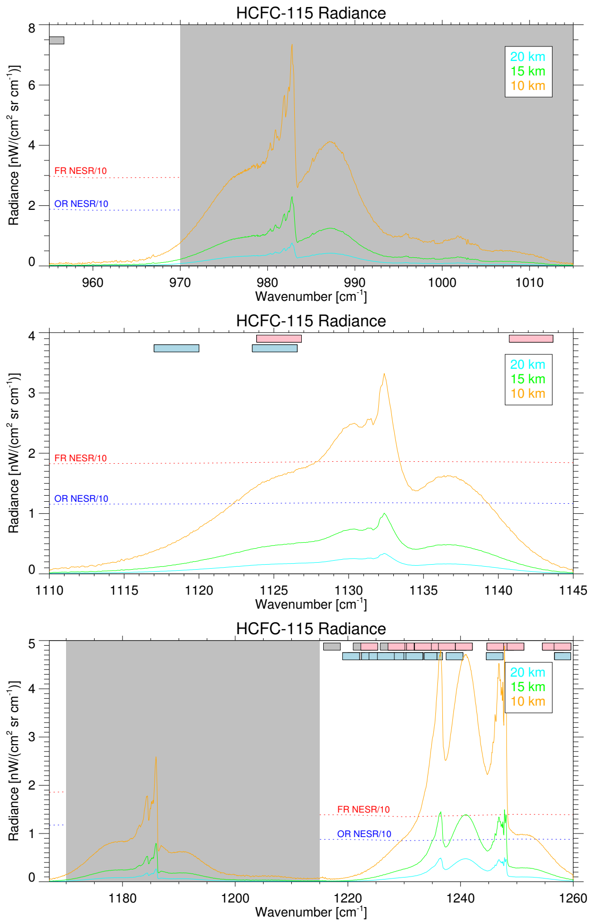

Figure B.18: The limb radiance contribution of CFC-115 at various tangent heights for the spectral ranges plotted in Fig. 11.1. Red and Blue dotted lines correspond to nominal MIPAS NESR values divided by 10, for FR and OR respectively. Shaded areas are the gaps between MIPAS bands.

B.10 CCl_4

See section 12 (p. 22) for main discussion on absorption cross-section data.

CCl_4 is represented by the same profile in all 5 MIPAS reference atmospheres, shown in Fig. B.19.

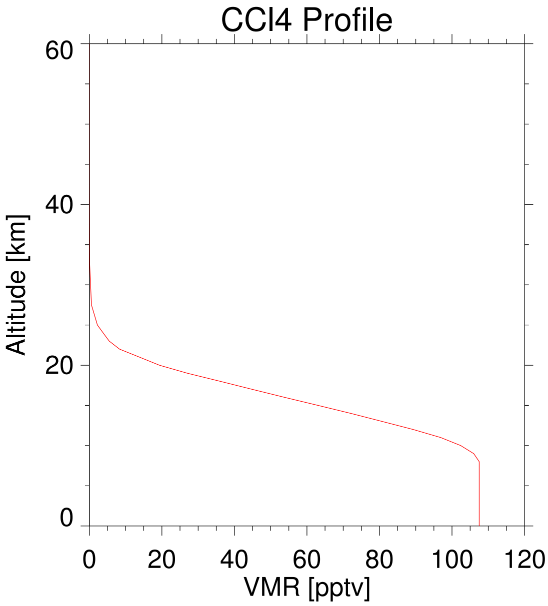

Figure B.19: The CCl_4 volume mixing ratio profile in the MIPAS reference atmospheres.

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Limb radiance calculations for the mid-latitude night-time profile are shown in Fig. B.20.

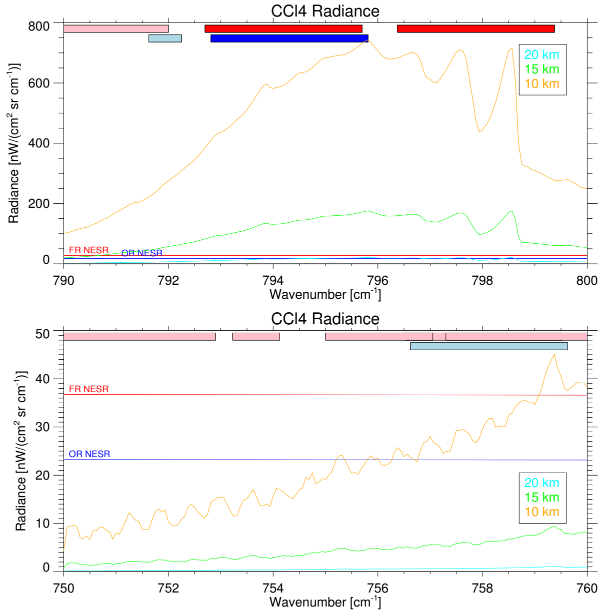

Figure B.20: The limb radiance contribution of CCl_4 at various tangent heights for the spectral ranges plotted in Fig. 12.3. Red and Blue lines correspond to nominal MIPAS NESR values for FR and OR respectively.

B.11 ClONO2

See section 13 (p. 24) for main discussion on absorption cross-section data.

The profiles of ClONO2 in the 5 MIPAS reference atmospheres are shown in Fig. B.21.

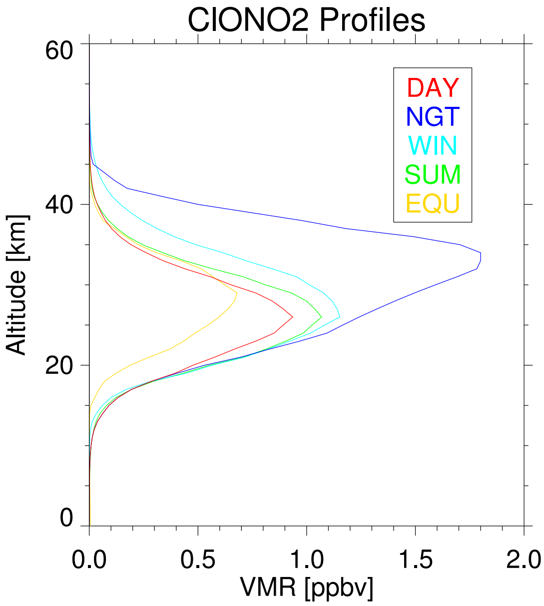

Figure B.21: The $ClONO_2$ volume mixing ratio profiles in the 5 MIPAS reference atmospheres.

Limb radiance calculations for the mid-latitude night-time profile (NGT) are shown in Fig. B.22.

A comparison of limb radiance calculations using line data and cross-section data is shown in Fig. B.23. The cross-section data calculation is the same as shown in Fig. B.22 for the 20 km tangent height, but limited to the spectral range covered by the line data.

It can be seen that radiances (or absorption) calculated using the line parameters is of the order of 50 % lower.

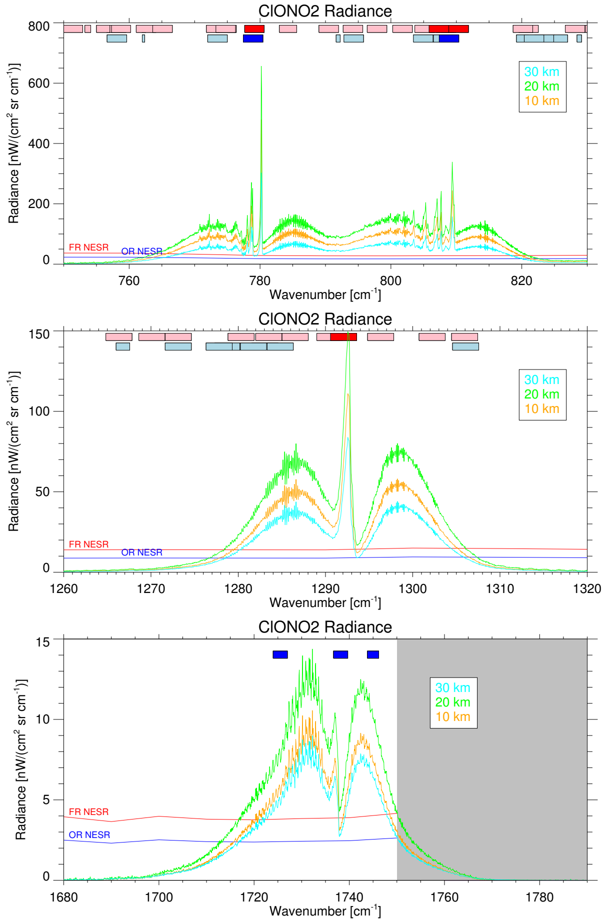

Figure B.22: The limb radiance contribution of $ClONO_2$ at various tangent heights for the spectral ranges plotted in Fig. 13.1 (p. 24). Red and Blue lines correspond to nominal MIPAS NESR values for FR and OR respectively. The grey shaded area is the gap between the MIPAS C and D bands.

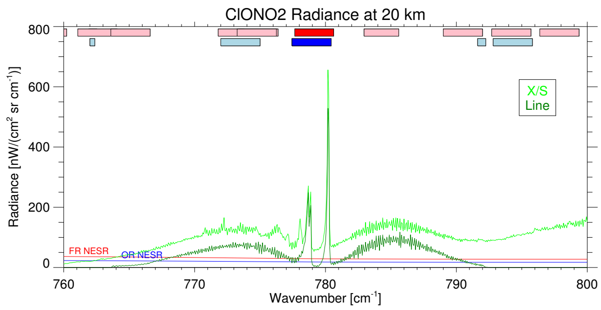

Figure B.23: Comparison of the limb radiance contribution of $ClONO_2$ at 20 km calculated using cross-section data (as in Fig. B.22) and using the HITRAN line parameters.

B.12 N_2O_5

See section 14 (p. 26) for main discussion on absorption cross-section data.

The profiles for N_2O_5 in the 5 MIPAS reference atmospheres are shown in Fig. B.24.

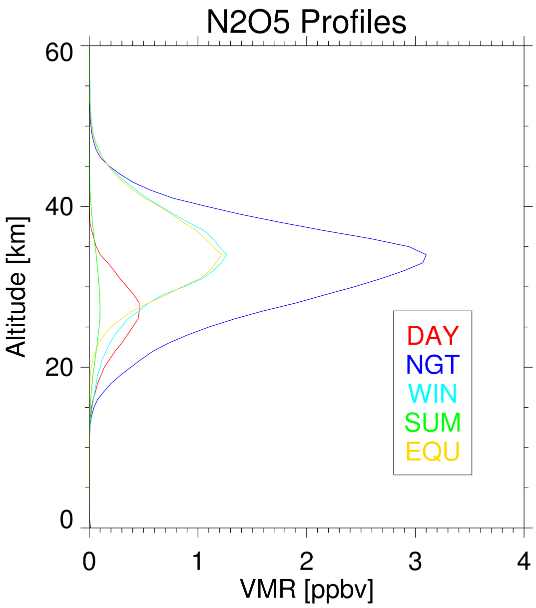

Figure B.24: The N_2O_5 volume mixing ratio profiles in the 5 MIPAS reference atmospheres.

Limb radiance calculations for the mid-latitude night-time profile (NGT) are shown in Fig. B.25.

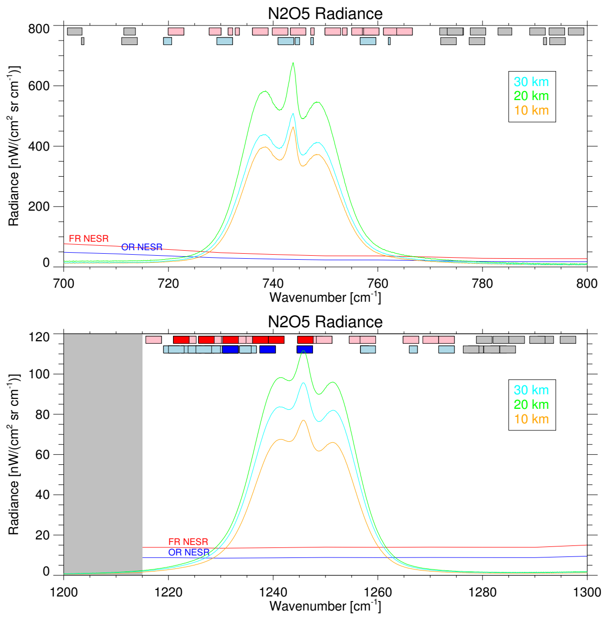

Figure B.25: The limb radiance contribution of mid-latitude nighttime N_2O_5 at various tangent heights for the two spectral ranges shown in Fig. 14.1. Red and Blue lines correspond to nominal MIPAS NESR values for FR and OR respectively. The grey area in the lower plot corresponds to the gap between the MIPAS AB and B bands.

B.13 HNO_4

See section 15 (p. 27) for main discussion on absorption cross-section data.

The profiles of HNO_4 in the 5 MIPAS reference atmospheres are shown in Fig. B.26.

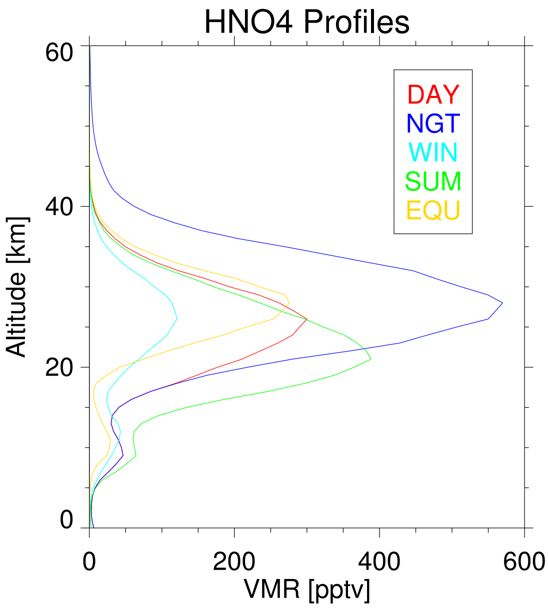

Figure B.26: The HNO_4 volume mixing ratio profiles in the 5 MIPAS reference atmospheres.

Limb radiance calculations for the mid-latitude night-time profile (NGT) are shown in Fig. B.27.

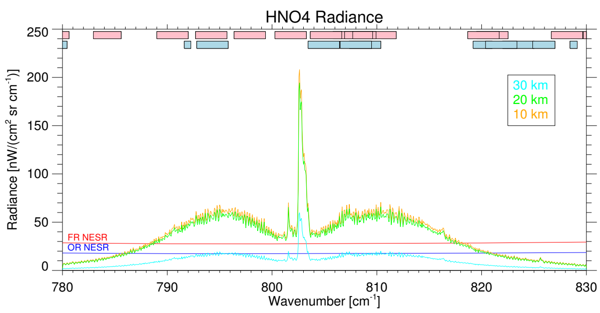

Figure B.27: The limb radiance contribution of HNO_4 at various tangent heights using the New data (220 K) shown in Fig. 14.1. Red and Blue lines correspond to nominal MIPAS NESR values for FR and OR respectively.

B.14 SF_6

See section 16 (p. 28) for main discussion on absorption cross-section data.

SF_6 is represented by the same profile in all 5 MIPAS reference atmospheres, shown in Fig. B.28.

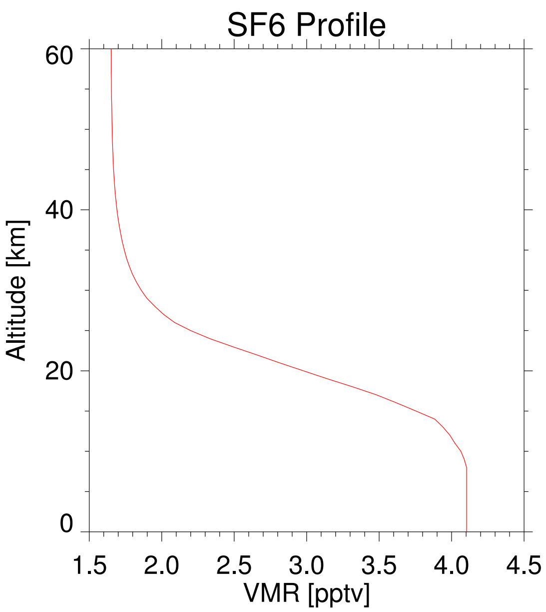

Figure B.28: The SF_6 volume mixing ratio profile in the MIPAS reference atmospheres.

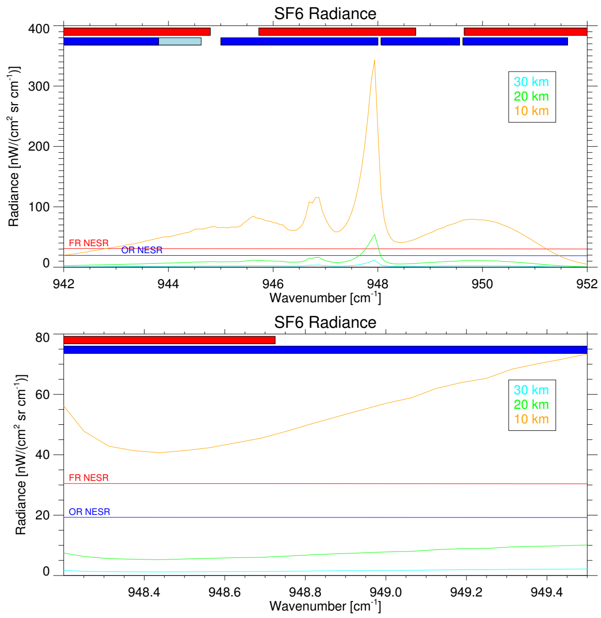

Figure B.29: The limb radiance contribution of SF_6 at various tangent heights for the spectral ranges plotted in Fig. 16.3. Red and Blue lines correspond to nominal MIPAS NESR values for FR and OR respectively.

Limb radiance calculations for the mid-latitude night-time profile are shown in Fig. B.29.

The SF_6 line compilation includes an addition spectral feature from 590–640 cm^{-1}, as shown in Fig. B.30. However this is outside the spectral range of MIPAS (and probably obscured by CO_2 anyway).

Radiances calculated using the SF_6 cross-section and line parameters in the 925–955 cm^{-1} region are directly compared in Fig. B.31. The cross-section data calculation is the same as shown in Fig. B.29 for the 10 km tangent height.

It can be seen that radiances (or absorption) calculated using the line parameters is of the order of 50 % lower than the cross-section calculation.

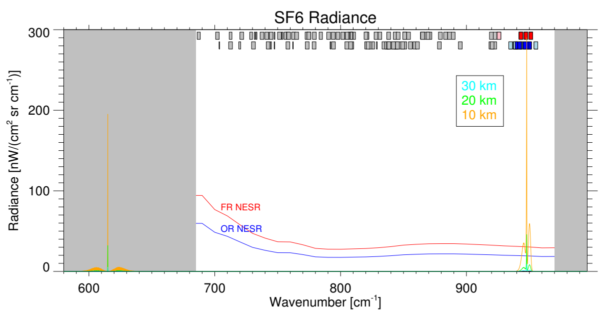

Figure B.30: The limb radiance contribution of SF_6 at various tangent heights calculated from the SF_6 line parameter compilation. Red and Blue lines correspond to nominal MIPAS NESR values for FR and OR respectively, grey shading represents regions outside the MIPAS bands.

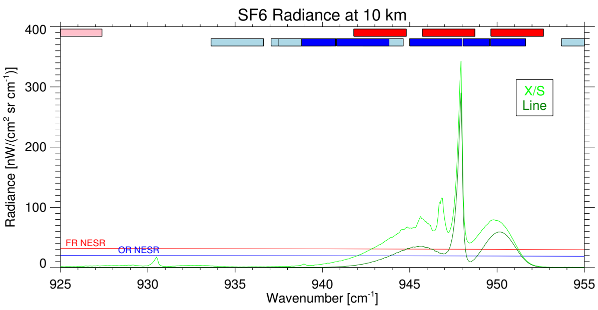

Figure B.31: Comparison of the limb radiance contribution of SF_6 at 10 km calculated using cross-section data (as in Fig. B.29) and using the HITRAN line parameters.

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