AO01: Measurement of Stratospheric CFCs

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Abstract

Since the Montreal Protocol in the mid 1980s there has been a concerted effort to cut down the production and usage of chlorofluorocarbons (CFCs). The input of these gases into the atmosphere has been shown to cause a depletion of the ozone layer, which could lead to an increase in the number of cases of skin cancer. This report considers how precisely measurements of a range of the main CFCs, and their replacements (hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs)), can be made. Using the Reference Forward Model (RFM) developed for the MIPAS instrument, simulations of atmospheric radiance spectra are produced, and the least squares fit method applied, to determine the precision that could be obtained in retrievals. The precisions obtainable from measurements made at both normal and reduced resolution are considered.

1 Introduction

For over two hundred years the byproducts and waste from industrial processes have been released into the atmosphere. The impact of the substances entering our atmosphere was largely unknown, and it is only in the last century that efforts have been made to understand the effect on our climate and atmosphere. A major effect of human input into the atmosphere is the depletion of the ozone layer, which could lead to an increase in skin disease.

The Montreal Protocol [1] and its revisions, aim to reduce the production of gases that cause ozone depletion, so it is important to be able to monitor precisely the level of these substances. The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is an instrument designed to measure concentrations of gases contributing to ozone depletion. The aim of this project is to determine how precisely MIPAS is able to measure these contributions.

1.1 Ozone depletion

In 1930 Sydney Chapman [2] tried to explain the existence of the ozone layer using a series of four basic reactions. However, this set of reactions did not account for the levels of ozone observed as there are reactions that destroy ozone which were unconsidered in the Chapman scheme. A chemical X may act as a catalyst in the destruction of ozone through the following pair of reactions:

$$X + O_3 \rightarrow XO + O_2 \tag{1}$$

$$XO + O \rightarrow X + O_2 \tag{2}$$
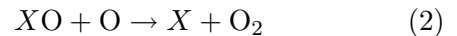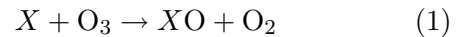
Having the net effect of:

$$O_3 + O \rightarrow 2O_2 \tag{3}$$
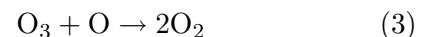
This process may be faster than the ozone destroying reaction considered by Chapman, so can play an important role in ozone chemistry, reducing the amount of ozone present in the lower stratosphere. Chemicals that act as catalysts in this way include the hydroxyl radical, nitric oxide and chlorine [3]. In reality there are many more reactions contributing to the creation and destruction of ozone, but these are sufficient for this study.

Natural sources of chlorine include volcanoes and ocean spray. These do not have an impact on stratospheric ozone, as chlorine (being soluble) is washed out of the atmosphere before reaching the stratosphere. The main source of chlorine in the stratosphere is anthropogenic, arising from CFCs released into the atmosphere. CFCs are very stable compounds so are not broken down in the troposphere. They are transported to the stratosphere where they are broken down by ultraviolet radiation, releasing chlorine that catalyses the destruction of ozone. As a catalyst is not used up, the chlorine is able to break down a large number of ozone molecules before, reacting to form hydrogen chloride or chlorine nitrate, it is removed from the cycle.

The ozone layer provides important protection from harmful ultraviolet radiation, and its depletion could lead to an increase in skin cancers. This was one of the reasons why the Montreal Protocol was agreed in 1987 to reduce the production of ozone depleting substances. Whilst

production of some CFCs was to cease by 1996, they will be present in the atmosphere for a long time because of their stability.

1.2 CFCs/HCFCs/HFCs

CFCs are chemicals that contain chlorine, fluorine and carbon atoms. HCFCs are similar, but contain hydrogen atoms instead of some chlorine or fluorine atoms, and HFCs consist of fluorine, hydrogen and carbon atoms. CFCs, HCFCs and HFCs are named according to the quantities of each atom in the molecule. For example in CFC-123a the first digit is the number of carbon atoms minus 1, the second is the number of hydrogen atoms plus 1 and the third is the number of fluorine atoms. The letter identifies the isomer of the chemical [4]. Table 1 contains a list of the names and chemical formulae for the CFCs, HCFCs and HFCs studied in this project.

CFCs have low boiling points, low toxicities, and are non-flammable and not reactive. These properties make them suitable for a range of applications including as refrigerants, propellants in aerosols, cleaning agents for electronic circuit boards, and blowing agents, used in the production of foams [5].

The main short-term replacements, HCFCs, despite being less effective, are better than CFCs as they have a significantly lower Ozone Depletion Potential (ODP)[1], hence they are less damaging to the ozone layer. HCFCs contain hydrogen atoms, making them more likely to react in the lower atmosphere (frequently with hydroxyl radicals), and therefore less likely to reach the stratosphere. As HCFCs still cause some depletion of the ozone layer, production of these is due to be stopped by 2030 under the terms of the Montreal Protocol.

HCFCs have a reduced ODP, whereas HFCs have an ODP of zero as they contain no destructive chlorine atoms (Appendix B). For this reason HFCs are seen as a long-term replacement for both CFCs and HCFCs.

Both HCFCs and HFCs have shorter lifetimes than CFCs (Appendix B) so are destroyed more quickly, causing less damage to the ozone layer.

CFCs, HCFCs and HFCs contribute to the anthropogenic greenhouse effect due to their absorption of radiation emitted from the surface. Generally HCFCs and HFCs have lower Global Warming Potentials (GWPs)[2] than CFCs (Appendix B), so are suitable replacements for the CFCs banned in the Kyoto Protocol [7].

1.3 Previous measurements

For most of the twentieth century, measurements of the concentrations of gases in the atmosphere have been made using ground-based, shuttle-based and satellite-based instruments.

1.3.1 AGAGE/ALE/GAGE

The Advanced Global Atmospheric Gases Experiment (AGAGE), the Atmospheric Life Experiment (ALE) and the Global Atmospheric Gases Experiment (GAGE) are a series of ground-based programs that have monitored the composition of the lower troposphere since 1978 [8]. The range of CFCs, HCFCs and HFCs measured by these programs are shown in Table 1, with the precisions of the measurements [8]. As these measurements are mainly made *in situ*, the precision is better than the remote sounding instruments discussed below.

1.3.2 Solar occultation

The Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) [9] and Atmospheric Trace Molecule Spectroscopy (ATMOS) [10] instrument are solar occultation devices. They measure the composition of the atmosphere by viewing the Sun's radiation through the atmosphere at both sunrise and sunset. ATMOS was flown on a number of shuttle missions during the 1980s and 1990s and viewed a variety of regions including polar, mid-latitude and tropical regions. ACE was launched on the SCISAT-1

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[1]'The ODP is the ratio of the impact on ozone of a chemical compared to the impact of a similar mass of CFC-11.'[6]

[2]'The GWP is the ratio of the warming caused by a substance to the warming caused by a similar mass of carbon dioxide.'[6]

Gas	Formula	AGAGE	CLAES	ATMOS	ACE	CRISTA	MIPAS
CFC-11	CCl_3F	0.15%	-	3-5%	31.14%	2.5%	10%
CFC-12	CCl_2F_2	0.05%	9.8%	3-5%	6.60%	-	-
CFC-14	CF_4	0.15%	-	20-40%	4.83%	-	-
HCFC-22	CHF_2Cl	0.3%	-	12-25%	3.13%	-	-
CFC-113	$Cl_2FCCClF_2$	0.2%	-	-	8.26%	-	-
HFC-134a	CH_2FCF_3	0.4%	-	-	12%	-	-
HCFC-141b	CH_3CCl_2F	0.4%	-	-	-	-	-
HCFC-142b	CH_3CClF_2	0.6%	-	-	23.16%	-	-
HFC-152a	CH_3CHF_2	1.2%	-	-	-	-	-

Table 1: Formulae of species, and the precision obtained in previous measurements.

mission in 2003 and views from 85°N to 85°S, at altitudes from 10–100km.

ATMOS has been able to measure concentrations of CFC-11, CFC-12, CFC-14 and HCFC-22 [11]. ACE has measured concentrations of CFC-11, CFC-12, HCFC-22 [12], CFC-14 [13], CFC-113, HCFC-142b [14] and HFC-134a [15]. Generally the precisions of measurements (Table 1) by ACE are better than those by ATMOS, due to the greater global coverage and number of occultations recorded by ACE.

1.3.3 Infrared limb emission sounders

Infrared limb emission sounders measure the infrared radiation emitted by the Earth's limb, from which they can infer the amount of each chemical present in the atmosphere.

In 1991, the Cryogenic Limb Array Etalon Spectrometer (CLAES) [16] was launched on board the Upper Atmosphere Research Satellite (UARS). It observed the atmosphere between altitudes of 10 and 60km in the latitude range 80°N to 80°S. CLAES was in orbit for 19 months by which point the cryogens that kept the instrument cooled had evaporated. During its mission, CLAES was able to measure concentrations of CFC-12 with a precision of 9.8% [17]. It was capable of measuring CFC-11, although no results were reported in the literature.

The Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere (CRISTA) [18] was launched on board the CRISTA-SPAS satellite from the space shuttle in 1994 and 1997, viewing between heights of 10 and 150km.

CRISTA was in orbit for about 8 days during each mission, and observed a range of latitudes from 74°N to 74°S. It was able to detect concentrations of CFC-11 with a precision of 2.5% [19].

Both the High Resolution Dynamics Limb Sounder (HIRDLS) [20] and the Tropospheric Emission Spectrometer (TES) [21] were launched on board the satellite Aura in 2004 on a five year mission. HIRDLS takes measurements from the mid-troposphere to the mesosphere, whilst TES views from the ground to the mid-stratosphere (~32km). TES can view from 82°N to 82°S, whilst HIRDLS can only view between 82°N and 65°S, due to a blockage that occurred during launch. HIRDLS should be able to measure concentrations of CFC-11 and CFC-12; however no records have been reported in the literature. There are also no measurements of CFCs, HCFCs or HFCs by TES reported in the literature.

MIPAS was launched on the European Space Agency's Environmental Satellite (Envisat) in 2002. It measures emission spectra from 6–68km, and has complete global coverage. Concentrations of CFC-11 have been retrieved with a precision of better than 10% [22], and retrievals of CFC-14 have been considered by Piccolo and Dudhia (2006) [23]. The precision obtained in retrievals of CFC-11 is comparable with those of ATMOS and CRISTA.
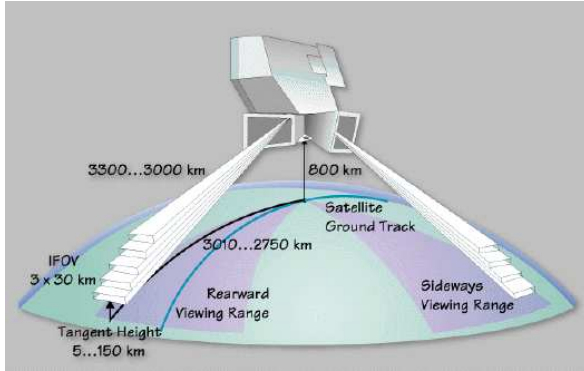
2 Experimental Details

2.1 MIPAS

Figure 1: MIPAS (courtesy of Envisat - MIPAS handbook).

MIPAS [24] was launched in 2002 with a number of aims, including monitoring concentrations of stratospheric ozone and CFCs.

Envisat is in a sun-synchronous, polar orbit at a height of 800km. MIPAS views the Earth's limb at approximately 3300km from the satellite in one of two directions (Figure 1). Mostly it measures in a $35°$ wide viewing range in the rearwards direction, but for observing special events, such as eruptions, it measures in a $30°$ viewing range on the anti-solar side of the satellite.

MIPAS operates in the region 685–2410 cm^{-1} (4.15–14.6 microns). It has eight detectors, and combinations of the output of these yield five spectral bands, with the nominal noise equivalent signal radiance (NESR) values shown in Table 2.

MIPAS is an infrared Fourier transform spec-

Band	Spectral range (cm^{-1})	NESR $(nW/(cm^2 srcm^{-1}))$
A	685-970	50
AB	1020-1170	40
B	1215-1500	20
C	1570-1750	6
D	1820-2410	4

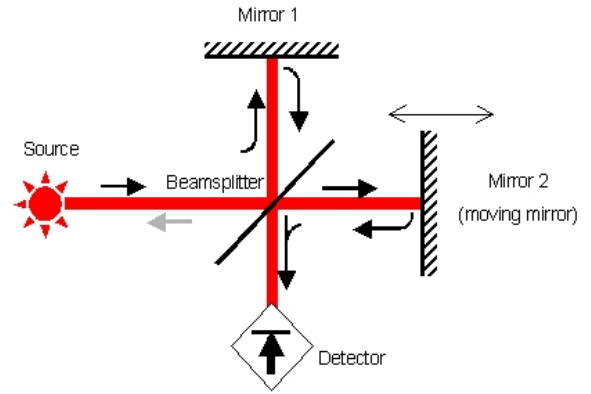Table 2: Nominal noise equivalent signal radiance values for MIPAS bands.

Figure 2: Michelson interferometer similar to that used in MIPAS (courtesy of Envisat - MIPAS handbook).

trometer that works by splitting incoming radiation into two beams, which are then reflected, so that they return and interfere with each other (see Figure 2). Due to variations in optical path length, caused by mirrors moving along an arm, an interference pattern, an interferogram, is produced. By taking the Fourier transform, the incoming spectrum can be obtained.

The instrument line shape (ILS) for a perfect Fourier transform spectrometer is a convolution of a sinc function with a term due to the angular aperture. For a real instrument the ILS is similar. The spectrum which MIPAS records is a convolution of the atmospheric spectrum with the ILS, and thus a sharp peak would be recorded as a sinc function. Hence, in order to observe a peak a broad spectral range must be observed; to avoid this readings are apodised. Apodisation causes the side lobes of the ILS to die off more quickly, reducing the spectral range that must be considered. This reduces the spectral resolution of the measurements.

In 2004 a fault with the mirror drive caused the maximum path difference to be reduced. Consequently this reduced the resolution at which MIPAS was operating, from $0.025cm^{-1}$ to $0.0625cm^{-1}$. The reduced path difference also meant that the measurement time was reduced, allowing more measurements to be made. The different scan patterns are shown in Appendix A.
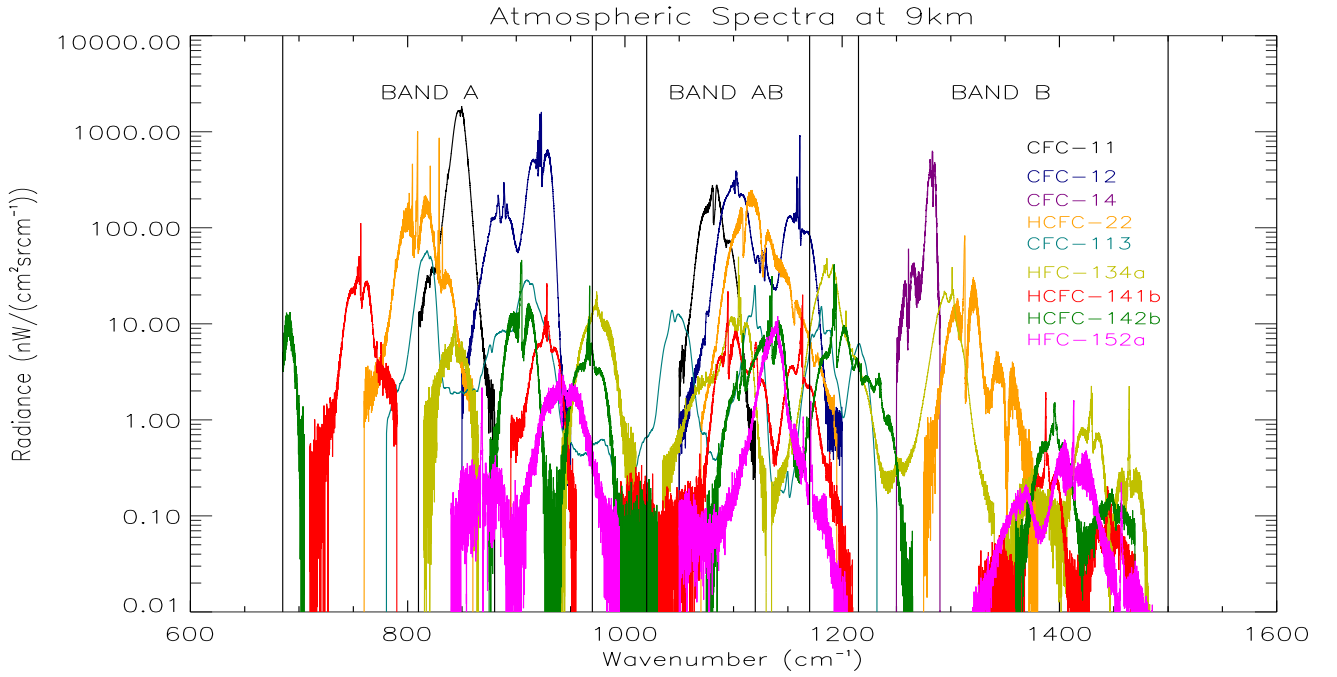
Figure 3: Spectrum produced by the Reference Forward Model for a 9km tangent height.

2.2 RFM

The Reference Forward Model (RFM) [25] is a radiative transfer model that generates a predicted MIPAS spectrum given a set of predefined parameters. The model is run by specifying atmospheric profiles, a list of absorbers in the atmosphere, the spectral range and resolution, and parameters pertaining to the instrument in the file controlling the model, the driver table (Appendix A). Figure 3 shows the atmospheric spectra of the species under consideration at a tangent height of 9km as produced by the RFM.

For this project it was necessary to have concentration profiles [26] and absorption cross-sections [27] for the species under consideration in order to run the RFM. Concentration profiles were unavailable for HCFC-141b, HCFC-142b, HFC-134a and HFC-152a, so new ones were created (Figure 4). It was assumed that the profiles had the same shape as HCFC-22 as these chemicals react in the same way in the troposphere, so a similar concentration distribution is expected.
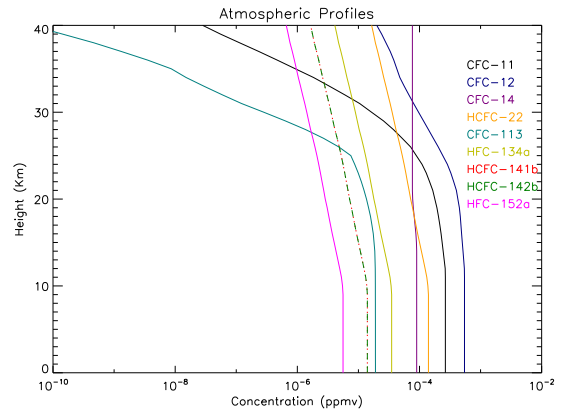

Figure 4: Atmospheric profiles used in the RFM.

2.3 Retrieval theory

In atmospheric physics certain parameters, such as composition, need to be obtained from measurements of radiance; this is known as the retrieval problem. Consider a set of measurements y_m, recorded with an error due to noise ϵ_m that is linearly related to the desired data x_n by:

$$\mathbf{y} = \mathbf{Kx} + \boldsymbol{\epsilon} \qquad (4)$$

Whilst the radiances, y are not linearly related

to the concentration profiles x, this assumption can be justified as the error analysis is assumed to be linear about the correct solution.

$\mathbf{K}$ is the Jacobian matrix that maps $\mathbf{x}$ onto $\mathbf{y}$, whose elements are:

$$K_{ij} = \left(\frac{\partial y_i}{\partial x_j} \right) \qquad (5)$$

To retrieve the required data an inverse function $\mathbf{G}$ is necessary.

$$\mathbf{x} = \mathbf{G}\mathbf{y} \qquad (6)$$

Due to noise in the original measurements, the data produced ($\mathbf{x}$) is only an estimate of the actual values. The least squares fit technique can be used to find the best estimate of the data. This seeks to minimise the difference between actual measurements and predicted measurements, $\mathbf{Kx}$. This produces the result:

$$\mathbf{x} = \left(\mathbf{K^T K} \right)^{-1} \mathbf{K^T y} \qquad (7)$$

Hence,

$$\mathbf{G} = \left(\mathbf{K^T K} \right)^{-1} \mathbf{K^T} \qquad (8)$$

This project is concerned with the error in the quantity $\mathbf{x}$ arising from noise in the measurements. Associated with each measurement value y_i, there is a noise variance σ_i^2, which is the expectation value of the error due to the noise.

$$S_{ii} = \sigma_i^2 = \langle \epsilon_i \epsilon_i \rangle \qquad (9)$$

Assuming that the noise remains constant in a spectral region, the noise covariance is:

$$\mathbf{S}_y = \sigma_y^2 I \qquad (10)$$

The covariances of $\mathbf{x}$ and $\mathbf{y}$ are related by:

$$\mathbf{S}_x = \mathbf{G} \mathbf{S}_y \mathbf{G^T} \qquad (11)$$

The method outlined so far assumes that the measurements all have equal errors, but when this is not the case a weighted least squares fit is required. This leads to different values:

$$\mathbf{x} = \left(\mathbf{K^T S_y^{-1} K} \right)^{-1} \mathbf{S_y^{-1} y} \qquad (12)$$

$$\mathbf{G} = \left(\mathbf{K^T S_y^{-1} K} \right)^{-1} \mathbf{S_y^{-1}} \qquad (13)$$

Hence,

$$\mathbf{S}_x = \left(\mathbf{K^T S_y^{-1} K} \right)^{-1} \qquad (14)$$

For further details see Rodgers (2000) [28].

For this project $\mathbf{y}$ was an $(m \times 1)$ measurement vector containing the radiance measured at m spectral points, $\mathbf{x}$ was an $(n \times 1)$ vector containing the concentration at n tangent heights and $\mathbf{K}$ was an $(m \times n)$ matrix. To allow for apodisation, which correlates the noise between adjacent spectral elements, $\mathbf{S}_y$ was a band-diagonal with dimensions $(m \times m)$.

Taking the square root of the diagonals of the covariance matrix $\mathbf{S}_x$, the standard deviation, and hence the precision, of $\mathbf{x}$ values can be found.

2.4 Atmospheric absorbers

The presence of other, absorbing, gases in the atmosphere interferes with measurements of CFCs, HCFCs and HFCs, reducing the precision with which concentrations can be retrieved. To represent this effect some of the major absorbing gases present in the real atmosphere were introduced into the model (Figure 5). These major absorbers were CO_2, CH_4, H_2O, HNO_3, N_2O, NO_2 and O_3. Whilst they are not the most abundant gases in the atmosphere, they are, due to their structure and properties, the most absorbing. The effect of these absorbers was most pronounced when their strong absorption bands coincided with those of the CFCs etc. To reduce the impact of this, measurements were made in atmospheric windows, where interference was least.

Windows were selected at spectral points where the predicted radiance of a species was greater than that of the major absorbers. As there is an uncertainty in the concentration of the major absorbers, to select windows, the signal produced by the uncertainty in their concentrations was compared with the signal from the species under consideration. A mask was created to represent the array of windows, which
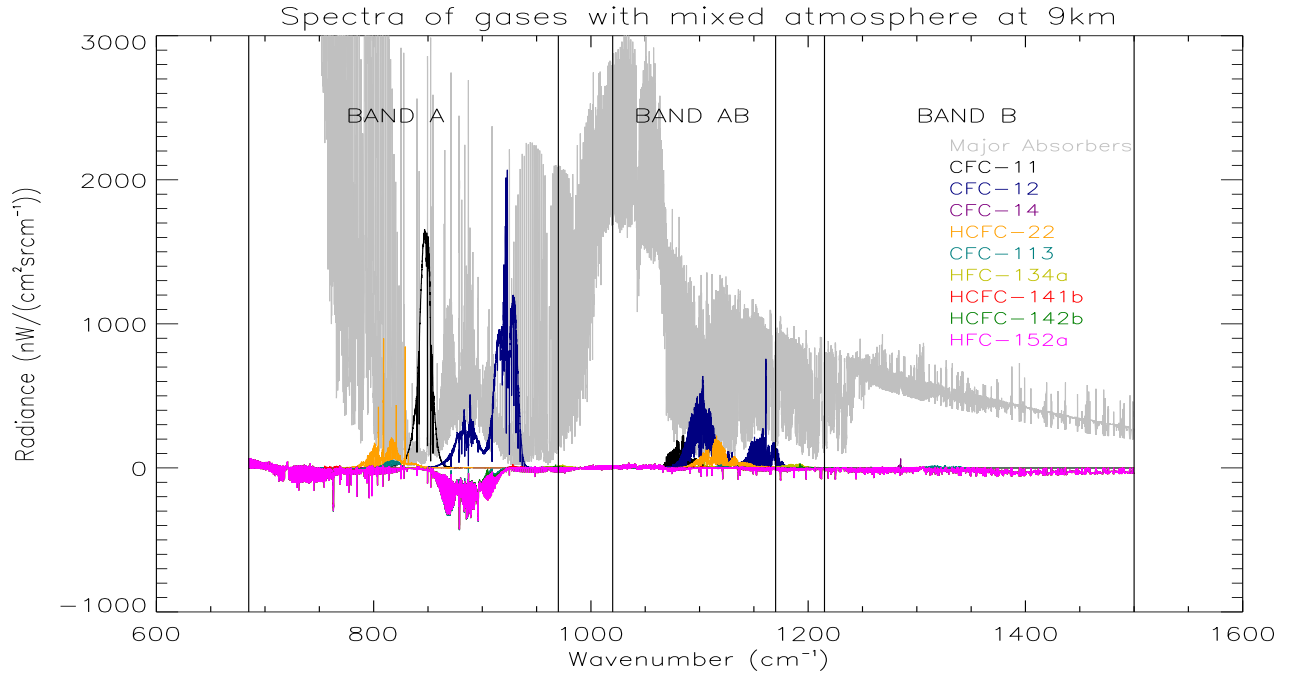
Figure 5: Spectrum produced by RFM for CFCs, HCFCs and HFCs in an atmosphere including the impact of CO_2, CH_4, H_2O, HNO_3, N_2O, NO_2 and O_3.

was multiplied by the Jacobian spectra to rule out points with excessive contamination.

3 Results

3.1 Single species

Initially an unrealistically optimistic case was considered in which the model atmosphere consisted solely of the species being considered. For each species, peaks were selected, and the retrieval precision values calculated. The retrieval precision distributions were compared, and the peak producing the most precise retrieval of each chemical identified (Table 3). Figure 6 shows a comparison of the retrieval precision distributions obtained from the selected peaks. Spectral features used were restricted to a bandwidth of 30cm^{-1}, centered on the main peak, as anything larger than this made calculations lengthy.

3.2 Mixed atmosphere

Using the spectral features selected (Table 3), retrieval precision values were calculated for

Gas	Range (cm^{-1})	MIPAS band
CFC-11	830-860	A
CFC-12	910-940	A
CFC-14	1275-1290	B
HCFC-22	800-830	A
CFC-113	800-830	A
HFC-134a	1285-1315	B
HCFC-141b	740-770	A
HCFC-142b	890-920	A
HFC-152a	1120-1150	AB

Table 3: Spectral features selected for use.

an atmosphere containing the major absorbers. The uncertainty in the concentrations of the absorbers was varied to see how precisely the species could be measured. Absorber uncertainty values of 0%, 2%, 10% and 100% were used. The mask discussed in section 2.4 was used to select regions with the least interference. Figure 7 shows the obtainable precision and the number of points used for each uncertainty value.
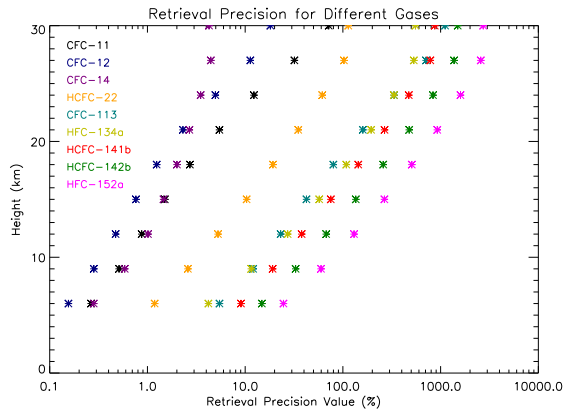
Figure 6: Retrieval precision values for CFCs, HCFCs and HFCs in a single species atmosphere.

3.3 Reduced resolution

The possible precision of retrievals was calculated assuming a reduced resolution of 0.0625cm^{-1}, in a mixed atmosphere. The noise value used for each band was reduced by a factor of $\sqrt{0.4}$ to account for the change in resolution. In the reduced resolution case the scan pattern records more spectra than the normal resolution. To make a comparison, retrievals were considered on the same 3km grid. The resulting precision distributions are shown in Figure 7 alongside those for normal resolution retrievals.

The effect of reduced resolution is discussed by Dudhia [29]. Fewer measurements are made which causes the precision to worsen, as does the use of a mask as this further reduces the number of measurements used. More spectra are recorded in the reduced resolution mode, and a reduced noise value used, which causes an improvement in the precision. The overall result is dependent upon the magnitude of the aforementioned effects.

4 Discussion

As discussed in section 1, the concentrations of some gases have previously been measured to a high level of precision, whereas the concentrations of others have been measured with a low precision, or not at all. Thus, precision values that may be unacceptable for the first class of species would be acceptable for the second. For the purposes of this discussion, a precision of order 10% is useful for the long-lived species, the CFCs, and a precision of order 100% is useful for the short-lived, poorly measured gases, the HCFCs and the HFCs.

The right-hand set of plots in Figure 7 show the number of spectral points used in the model once the mask has been applied to a spectral feature. The less uncertain the concentration of the major absorbers the more points are used. The plots show that, in general, where more points are included, the precision of retrievals is better.

4.1 CFCs

In a single species atmosphere, CFC-11, CFC-12 and CFC-14 could be retrieved with a precision of better than 10% for most of the altitudes considered. CFC-11 and CFC-12 could not be retrieved with a useful precision above heights of about 24km and 27km, whereas CFC-113 could only be retrieved up to 9km with such a precision.

Figure 7 shows that in a more realistic atmosphere concentrations of CFC-11 and CFC-12 could be retrieved in the normal resolution mode with a useful precision up to 21km and 24km. This assumes a 100% uncertainty in the concentrations of the major absorbers. A lower uncertainty would allow retrievals up to 24km for both CFC-11 and CFC-12. In the reduced resolution mode a useful precision could be obtained to an altitude of 26km and 27km.

For CFC-14 retrievals at low altitudes the obtainable precision is worse than 100%, regardless of the uncertainty in absorber concentration or resolution mode used. This is because the CFC-14 band considered coincides with strong absorption by the major absorbers at low altitudes. Figures 3 and 5 show that the CFC-14 peak is more affected in an absorbing atmosphere than the CFC-11 peak. With an uncertainty in the absorbers' concentrations of less than 10%, retrievals could be carried out with a precision of better than 10% for heights in the range 9-30km. A slightly better precision can be obtained using the reduced resolution mode.
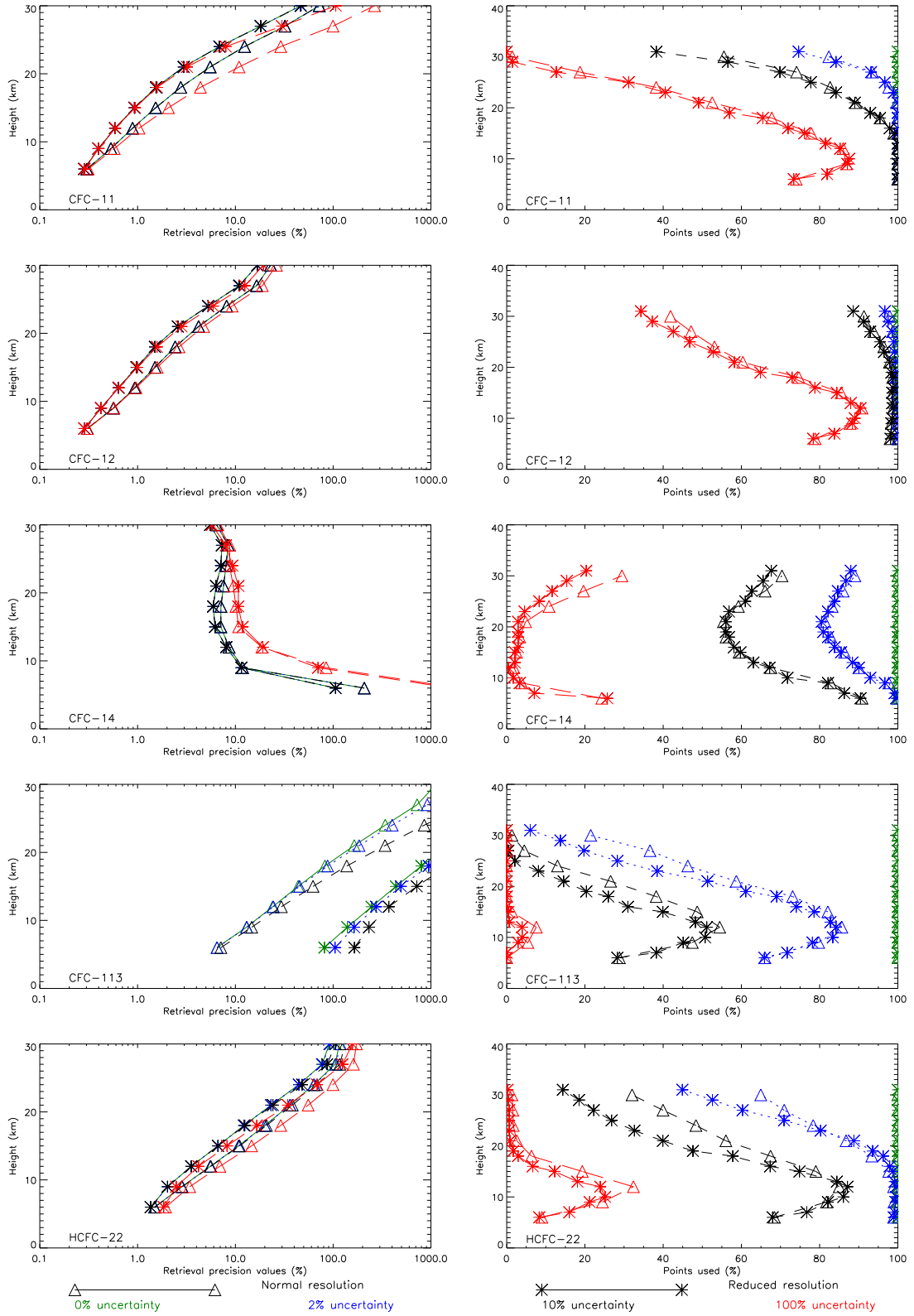
Figure 7: Comparison of normal and reduced resolution retrieval precision values for a number of uncertainties in the concentrations of atmospheric absorbers. Right hand set of plots shows the percentage of points used in calculations for each absorber concentration uncertainty.
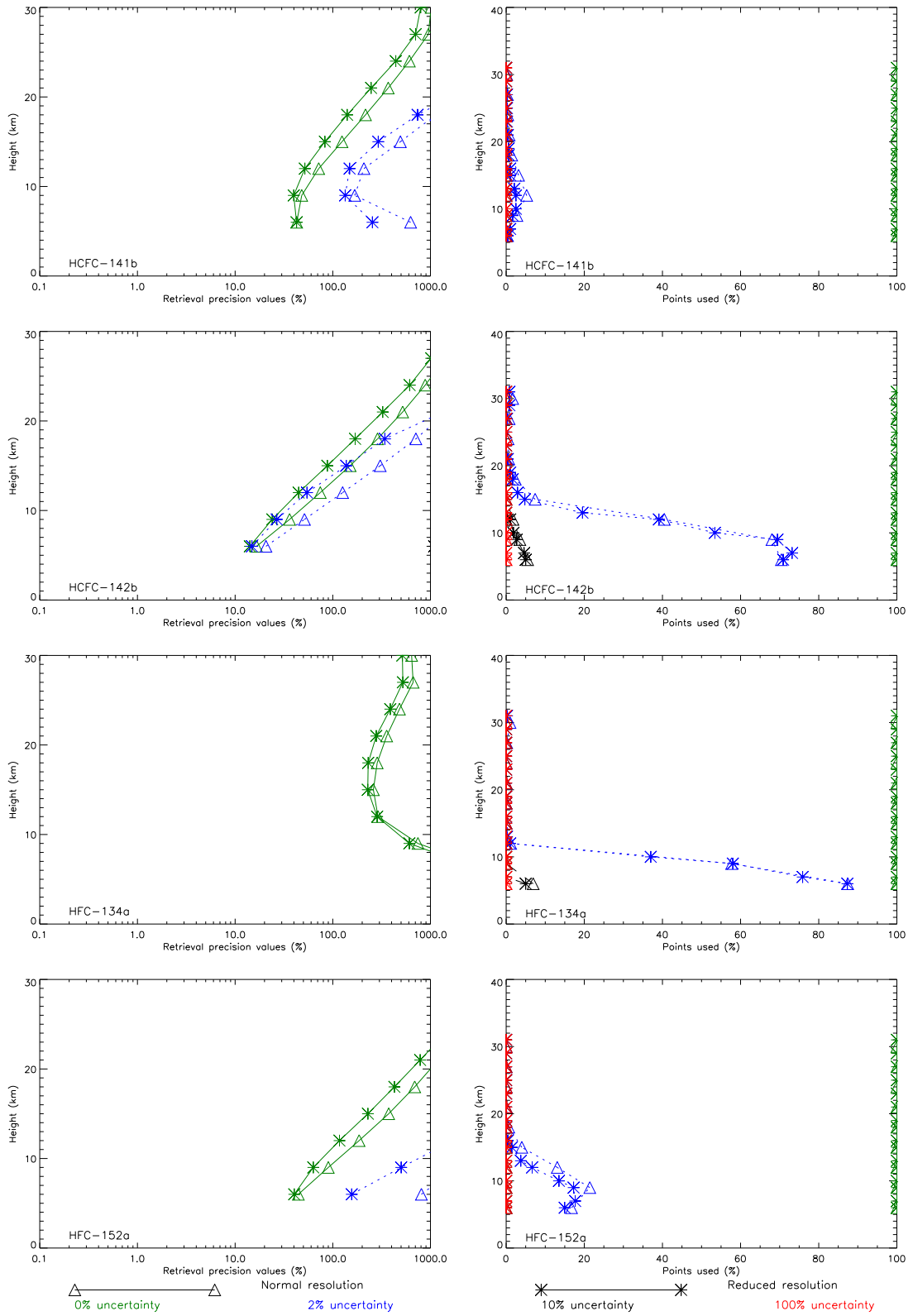
Figure 7: cont'd.

	Normal Resolution			Reduced Resolution		
Chemical	12km	21km	30km	12km	21km	30km
CFC-11	0.89%	5.52%	71.9%	0.59%	2.96%	46.5%
CFC-12	0.94%	4.21%	22.9%	0.64%	2.58%	16.8%
CFC-14	8.62%	7.58%	6.43%	8.07%	6.35%	5.53%
HCFC-22	5.54%	36.1%	116%	3.54%	23.2%	91.6%
CFC-113	24.0%	164%	1130%	247%	1600%	13200%
HFC-134a	290%	357%	641%	284%	279%	516%
HCFC-141b	71.7%	370%	1010%	51.8%	247%	795%
HCFC-142b	74.5%	519%	1523%	44.7%	325%	1170%
HFC-152a	186%	1200%	3100%	117%	785%	2430%

Table 4: Obtainable precisions at 12km, 21km and 30km for both normal and reduced resolution modes.

CFC-113 can only be retrieved with a useful precision below a height of 8km if the uncertainty in absorber concentration is less than 10%, and the retrieval is carried out in the reduced resolution mode. Normal resolution mode retrievals would not yield useful precisions.

4.2 HCFCs

In a single species atmosphere, HCFC-22 could be retrieved with a useful precision (<100%) at all of the altitudes considered, whereas HCFC-141b and HCFC-142b could only be retrieved up to 18km and 15km respectively.

Including the effect of the major absorbers, HCFC-22 concentrations can be retrieved, in the normal mode, to a height of between 25km and 27km depending on the uncertainty in the absorbers' concentration. In the reduced resolution mode precise retrievals could be carried out up to 30km. HCFC-141b could be retrieved with a useful precision up to heights of 14km and 16km in the normal and reduced resolution modes, given that there is no uncertainty in the absorber concentration. For HCFC-142b useful normal and reduced mode retrievals could be made to altitudes of 11km and 14km if the uncertainty in the absorbers' concentration was 2%. However, with no uncertainty, useful retrievals could be carried out to heights of 13km and 15km.

4.3 HFCs

In a single species atmosphere, retrievals of HFC-134a and HFC-152a could be obtained with useful precisions, up to heights of 18km and 12km. In a more realistic atmosphere containing the major absorbers, HFC-134a could not be retrieved with a useful precision value, the best precision obtainable being 200%. Figure 7 shows that useful precisions for retrievals of HFC-152a could only be obtained below 9km and 12km in normal and reduced resolution modes. Again, this would require the concentrations of the major absorbers to be known completely.

5 Conclusions

These results show that it is possible to retrieve concentrations of CFC-11, CFC-12, CFC-14 and HCFC-22 with a useful level of precision up to the lower-mid stratosphere, HCFC-141b and HCFC-142b up to the upper troposphere/lower stratosphere (UTLS) region, and CFC-113 and HFC-152a in the troposphere. The results indicate that it would be difficult to obtain precise retrievals of HFC-134a. Table 4 shows a brief summary of the precisions obtained, assuming the concentrations of major absorbers are known.

From considerations of both normal and reduced resolution modes, this report shows that, in general, reduced resolution improves the precision obtainable in retrievals. The main exception to this is CFC-113, retrievals of which benefit from use of higher resolution measurements.

The possible precisions for retrievals of CFC-11, CFC-12 and HCFC-22 are similar to those obtained by previous measurements at low alti-

tudes. However, in the lower-mid stratosphere calculated precision values are worse. Obtainable precision values for CFC-14 retrievals are comparable with the precision of previous measurements, whilst those calculated for CFC-113 and HCFC-142b retrievals are worse than the precision obtained by ACE. The precision values calculated for retrievals of HFC-134a are significantly worse than the precision obtained by ACE. These results represent a single scan of the atmosphere and could be improved by making multiple scans (spatial averaging).

6 Further work

Further work would involve carrying out a retrieval on actual data, to see whether predictions match observations. Before this is possible, more realistic concentration profiles need to be established and spectral features in MIPAS data positively identified. The effect of spectral averaging should also be investigated.

Appendices

A RFM

Below is a typical driver table used to operate the RFM in this project:

```
*HDR
Reduced resolution driver table for CFC-11
*FLG
RAD ILS FOV JAC
*SPC
830 860 0.0625
*GAS
F11, CO2, CH4, H2O, HNO3, N2O, NO2, O3
*ATM
../rfm/rfm_files/atm/hgt_nom.atm
../rfm/rfm_files/atm/day.atm
*TAN
6, 7.5, 9, 10.5, 12, 13.5, 15, 16.5, 18, 19.5, 21,
23, 25, 27, 29, 31
*HIT
../rfm/rfm_files/bin/hitran_mipas.bin
*XSC
../rfm/rfm_files/xsc/*.xsc
*ILS
../rfm/rfm_files/ils/ofm_16.ils
*FOV
../rfm/rfm_files/fov/rfm_1km5.fov
*JAC
F11 3, 6, 9, 12, 15, 18, 21, 24, 27, 30, 33
*END
```

The *HDR flag defines the header text that is used in the output file. The *FLG section specifies a list of flags enabled for use in the RFM. In this section, the RAD flag allows the output filename of radiance spectra to be changed. The *ILS and *FOV flags activated here specify the instrument line shape and field-of-view files used in the model. The *JAC flag specifies the heights at which Jacobian calculations are to be made. The *SPC section defines the spectral range and resolution to be used, the *GAS section lists the absorbers to be incorporated in the atmospheric model and the *ATM section provides the location of the atmospheric concentration profiles.

Scan heights (km)	
Normal Resolution	Reduced Resolution
6	6
9	7.5
12	9
15	10.5
18	12
21	13.5
24	15
27	16.5
30	18
-	19.5
-	21
-	23
-	25
-	27
-	29
-	31

Table 5: Altitudes used in normal resolution and reduced resolution scan patterns.

The tangent heights to be used are shown in the *TAN section, and the locations of HITRAN and molecular cross-section data are specified in the *HIT and *XSC sections.

During this project two sets of tangent heights were used (Table 5): in the normal operating case 6–30 km in 3 km intervals, and in the reduced resolution case, 6–21 km in 1.5 km intervals and 21–31 in 3 km steps.

The perturbation to the atmospheric profile defined in the *JAC flag causes extra spectra to be produced that represent the change in the spectrum that would arise. Simply having the

Gas	Concentration	
	(pptv)	Relative
HCFC-22	191.028	1
HCFC-141b	19.973	0.1
HCFC-142b	18.713	0.1
HFC-134a	47.283	0.25
HFC-152a	7.966	0.04

Table 6: Scaling factors used for creating concentration profiles.

gas under consideration in this flag causes the whole profile to be shifted by 1%, whereas if perturbation heights are specified as well, the profile is altered by 1% at these heights, and then smoothed back to the original profile.

To obtain profiles for the gases HCFC-141b, HCFC-142b, HFC-134a and HFC-152a the fortran program scaatm.f was used. The profile of HCFC-22 was scaled according to the concentration of the gas compared with that of HCFC-22. Concentrations for these alterations were taken from AGAGE measurements made at Mace Head on 1st March 2007. The concentrations and scaling factors used can be seen in Table 6.

B CFCs/HCFCs/HFCs

The lifetimes of the chemicals used in the project can be seen in Table 7, alongside values of ODP and GWP.

Gas	Lifetime (yrs)	ODP	GWP
CFC-11	45	1	4750
CFC-12	100	1	10890
CFC-14	50000	-	5820
HCFC-22	12	0.05	1810
CFC-113	85	1	6130
HFC-134a	13.8	-	1320
HCFC-141b	9.3	0.12	725
HCFC-142b	17.9	0.07	2310
HFC-152a	1.4	-	122

Table 7: Atmospheric lifetimes, and ODP and GWP values [6] for CFCs, HCFCs and HFCs.

Carbon tetrafluoride or tetrafluoromethane is described as a CFC in this project; however it is more commonly known as a perfluorocarbon or a PFC.

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