The Impact of Chlorofluorocarbons (CFCs) on Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) measurements

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Abstract

Radiances of 21 CFCs, HCFCs and HFCs at near infrared in the atmosphere were computed, using the Reference Forward Model (RFM) developed at the University of Oxford for the forthcoming European Space Agency (ESA) Michaelson Interferometer for Passive Atmospheric Sounding (MIPAS) mission, to determine whether it was necessary to consider the species in developing models for the instrument. It was found that most of the CFCs, HCFCs and HFCs were present in significant concentrations and so do need to be considered, but that a number of 'minor' HFCs and HCFCs produced negliable results and so will not need to be considered.

1 Introduction

Envisat-1 is a satellite of the European Space Agency (ESA), launching in October 2001. It will have on board ten instruments designed to observe the earth and its atmosphere, including MIPAS [Table 1].

MIPAS is a Fourier transform spectrometer, designed for measurement of high-resolution gaseous emission spectra at the Earth's limb. It operates in the near to mid infrared region where many of the atmospheric trace gases playing a major role in atmospheric chemistry [1]. It has a high spectral resolution and range, allowing global measurement of more than 20 trace gases during all seasons, as well as atmospheric pressure and temperature. MIPAS can operate equally well during daylight and dark, and will be able to retrieve and process altitude profiles of high priority CFCs/HFCs/HCFCs in near real time [2, 3].

Man-made chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs) and hydrochloroflurocarbons (HCFCs) are relatively new chemicals - they have only been produced by man and released to the atmosphere in the last few decades. The main property of CFCs that makes them so useful is their chemical inertness and ease of transition from liquid to vapour form and vice versa, hence their use in aerosol cans and coolants.

CFCs are generally present in the atmosphere in very small concentrations - normally measured in ppbv (parts per billion by volume) or pptv (parts per trillion by volume). However, CFCs generally remain in the atmosphere for a considerable length of time, and their radiative forcing impact (RFI) per molecule is far greater than for other gases present in the atmosphere. For example, CFC-12 has a typical lifetime of 120 years and has about 15,800 times the radiative forcing impact of CO_2, molecule for molecule [4], but is far less abundant in the atmosphere. As well as contributing to global warming, CFCs are the most significant chemicals destroying the ozone layer which is vital for life on earth.

HFCs and HCFCs are replacement chemicals that have been brought into production more recently as alternatives to CFCs (which are being phased out by signatories to the Montreal Protocol.), as they do not deplete ozone in the atmosphere. They still have a high RFI and so contribute to global warming, but their lifetimes are considerably shorter and [4] currently their concentrations in the atmosphere are much lower [6].

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Acronym	Full Name
ASAR	Advanced Synthetic Aperture Radar
MWR	Microwave Radiometer
MERIS	Medium Resolution Imaging Spectrometer
LRR	Laser Retro-Reflector
AATSR	Advanced Along-Track Scanning Radiometer
GOMOS	Global Monitoring by Occulation of Stars
RA-2	Radar Altimeter
MIPAS	**Michelson Interferometer for Passive Atmospheric Sounding**
DORIS	Doppler Orbitography and Radio Positioning Integrated by Satellite
SCIAMACHY	Scanning Imaging Absorption Spectrometer for Atmospheric Cartography

Table 1: The instruments on board Envisat-1 [2]

It is important to be able to identify what, if any, effect that CFCs, HFCs and HCFCs will have on the results from MIPAS so that they may be modelled within the retrieval of other CFCs/HFCs/HCFCs.

CFCs, HFCs and HCFCs are difficult to detect because of their low concentrations (typically orders of ppbv for CFCs and pptv for HFCs/HCFCs) and because their emission spectra can be difficult to distinguish from other emitters. CFCs have been observed before from ground stations, aircraft, stratospheric balloons and satellites [1]. However, it is not yet clear to what level the MIPAS instrument will be able to detect CFCs/HFCs/HCFCs.

The purpose of this study is to determine the levels to which the CFCs/HFCs/HCFCs considered will affect the data from MIPAS results.

2 The MIPAS Instrument

MIPAS is a high-resolution Fourier transform spectrometer, designed to make measurements of gaseous emission spectra at the Earth's limb. Versions of MIPAS have already been operated from the ground, aircraft and stratospheric balloons. However, MIPAS on Envisat-1 will be the first spaceborne high spectral resolution limb emission spectrometer which covers the whole mid infrared.

One of the objectives of MIPAS is to make simultaneous and global measurements of geophysical parameters in the middle atmosphere, including temperature. In particular, the instrument is designed to observe emission lines due to the six major species O_3, H_2O, HNO_3, CH_4, N_2O and NO_2 with the aim of generating climatology data and improving our understanding of stratospheric chemistry. The retrieval of these parameters is to be performed in Near Real Time (NRT). Further products will be able to be retrieved non-operationally, particularly by scientific institutions such as the Department of Atmospheric, Oceanic and Planetary Physics (AOPP) at the University of Oxford.

MIPAS's spectral coverage is in the range 14.6 μm to 4.15 μm or 685 cm^{-1} to 2410 cm^{-1} in five wavelength bands. Its design sensitivity is better than $50nW/cm^2$ sr cm^{-1}, decreasing to $4.2nW/cm^2$ sr cm^{-1} at the short wavelength side. Ground tests have indicated a noise performance a factor of two better than this.

3 The Reference Forward Model

3.1 General Information

In order to determine the radiance of the CFCs, HCFCs and HFCs that would be detected by MIPAS, a modelling program, the Reference Forward Model (RFM) was used. The RFM is a GENLN2-based line-by-line radiative transfer model, designed to perform reference calculations to be used in the development of MIPAS. It was developed under an ESA contract at AOPP at the University of Oxford, UK [5].

3.2 Use of the RFM in modelling the CFC/HFC/HCFC spectra

In the simulation used here, the RFM models atmospheres containing only the CFCs/HFCs/HCFCs considered in this study.

3.3 Atmosphere Profiles (RFM .atm files)

Atmosphere files were created containing known vertical profiles of the various CFCs/HFCs/HCFCs considered in this study. The files also contained vertical profiles detailing typical temperature and pressure variations with height.

Where there were no vertical profiles were available, namely for HCFC-123, HCFC-124, HCFC-225ca, HCFC-225cb and HFC-134, a 'worst case' uniform concentration of 10pptv or 1pptv was assumed (see below.) Many of the other HCFCs/HFCs had concentrations well below this [Table 2].

According to *Sihra et al* [8], HFC-23 (not considered in this study) and HCFC-134a are the only two HFCs detectable in 'significant quantities'. This justifies the use of 10pptv for the other, unknown HFCs/HCFCs, as this concentration is of the order of magnitude of that for HCFC-134a. A concentration of 1pptv is used for HCFC-123 and HCFC-124 as they were 'at or below the detection limit of 0.1ppt' [11] in 1998 and this is unlikely to have increased more than a 'worst case' tenfold in the last three years.

It should be noted that production of HCFCs and HFCs is likely to continue to increase significantly as they are not currently regulated [11]. According to [9], the tropospheric concentration of HFC-134a in particular is 'exponentially' growing at roughly 100%/yr. The concentrations of HCFC-141b and HCFC-142b are also 'increasing rapidly' [10]. Rates of increase for the other HCFCs and HFCs are not available but are also expected to be significant, although on a smaller scale.

CFC/HFC/HCFC concentrations generally decrease with an increase in altitude - above 20km, the concentrations decrease dramatically [12]. This study is therefore limited to analysing the effects of the CFCs/HFCs/HCFCs on MIPAS satellite measurements at the lowest altitude. This is typically 9km above the earth's surface.

3.4 CFC/HFC/HCFC cross-sections (RFM .xsc files)

CFC/HFC/HCFC cross-section data was used from the HITRAN 2000 database (HITRAN 1996 for CFC-11, HITRAN 1992 for CFC-13/113/114/115.) Data was used from various different temperature and pressure pairs.

3.5 The RFM driver table

A sample RFM 'driver table' is shown in Table 3. The driver table acts like a list of options and used to specify what the RFM is to process.

3.6 Mathematics of the Retrieval [13]

The monochromatic radiance I from a line-of-sight through a non-scattering atmosphere in local thermodynamic equilibrium can be represented by

$$I = -\int_0^\infty B\frac{d\tau}{dx}dx \tag{1}$$

where B is the Planck function, and τ is the transmittance from space to a point at distance x along the path. The atmospheric contribution to this radiance is therefore a spatially-weighted average of the Planck function along the path, $d\tau/dx$ being the 'weighting function'. Since B is a known function of temperature and wavelenght, determining $B(x)$ from the above relationship is equivalent to retrieving the temperature profile. However, to use Eq. 1 it is also necessary to know the transmittance $\tau(x)$ along the path. The optical depth χ, hence transmittance can be defined in terms of the molar air density ρ and some general absorption coefficient κ

$$\chi = \int_0^x \kappa\rho dx \tag{2}$$

$$\tau = e^{-\chi} \tag{3}$$

At thermal wavelengths, κ is a function of pressure, temperature and the concentrations of the various CFCs, HFCs and HCFCs.

The RFM .atm files contain the pressure, temperature and CFC/HFC/HCFC concentration data, as a function of altitude. The RFM .xsc files

Name	Formula	RFM Code	Concentration [pptv] at 9km	RFM profile source	RFM cross-section source
CFC-11	$CFCl_3$	51	139.4	usa.atm [6]	HITRAN 1996
CFC-12	CF_2Cl_2	52	239.4	usa.atm [6]	HITRAN 2000
CFC-13	$CClF_3$	53	5.00	usa.atm [6]	HITRAN 1992
CFC-14	CF_4	54	57.8	usa.atm [6]	HITRAN 2000
HCFC-21	$CHCl_2F$	55	1.05	usa.atm [6]	HITRAN 2000
HCFC-22	$CHClF_2$	56	59.63	usa.atm [6]	HITRAN 2000
CFC-113	$C_2Cl_3F_3$	57	18.94	usa.atm [6]	HITRAN 1992
CFC-114	$C_2Cl_2F_4$	58	11.98	usa.atm [6]	HITRAN 1992
CFC-115	C_2ClF_5	59	4.00	usa.atm [6]	HITRAN 1992
HCFC-123	$CHCl_2CF_3$	70	(1)	(unknown)	HITRAN 2000
HCFC-124	$CHClFCF_3$	71	(1)	(unknown)	HITRAN 2000
HCFC-141b	CH_3CCl_2F	72	9.82	minorcfc.atm [7]	HITRAN 2000
HCFC-142b	CH_3CClF_2	73	10.2	minorcfc.atm [7]	HITRAN 2000
HCFC-225ca	$CHCl_2CF_2CF_3$	74	(10)	(unknown)	HITRAN 2000
HCFC-225cb	$CClF_2CF_2CHClF$	75	(10)	(unknown)	HITRAN 2000
HFC-32	CH_2F_2	76	(10)	(unknown)	HITRAN 2000
HFC-125	CHF_2CF_3	77	0.400	minorcfc.atm [7]	HITRAN 2000
HFC-134	CHF_2CHF_2	78	(10)	(unknown)	HITRAN 2000
HFC-134a	CHF_2CF_3	79	8.36	minorcfc.atm [7]	HITRAN 2000
HFC-143a	CF_3CH_3	80	2.38	minorcfc.atm [7]	HITRAN 2000
HFC-152a	CH_3CHF_2	81	0.600	minorcfc.atm [7]	HITRAN 2000

Table 2: Concentrations (pptv), with sources, of the CFCs/HFCs/HCFCs considered in this study, at a tangent height of 9km. Where the concentrations are unknown, a value of 10pptv or 1pptv has been assumed. This is indicated by the bracketed numbers.

contain the general absorption coefficient κ as a function of wavenumber. The RFM output files are set, by the driver table (3.5) to output radiances as a function of wavenumber, using the above formulae.

3.7 Results

The RFM was used to calculate the radiance spectrum from each CFC/HFC/HCFC individually, using driver tables similar to that shown in Table 3.

The results are shown in Graph 1.

4 Conclusion

4.1 Criteria

Based on the results, the CFCs, HFCs and HCFCs can be sorted into three groups:

Group A: The contribution is insignificant and not likely to become significant during the lifetime of MIPAS. This are defined as the maximum radiance being less than a tenth of the detector noise (indicated by the continuous line on the graphs.)

Group B: The contribution is currently insignificant but may become significant in the near future as concentrations in the atmosphere continue to increase. This is defined as the maximum radiance being no greater than the detector background noise.

Group C: The contribution is significant and should be considered within the overall model of results from MIPAS. This is defined as the maximum radiance being greater than the detector background noise.

4.2 Summary Table

Table 4 summarises the results with these criteria in mind.

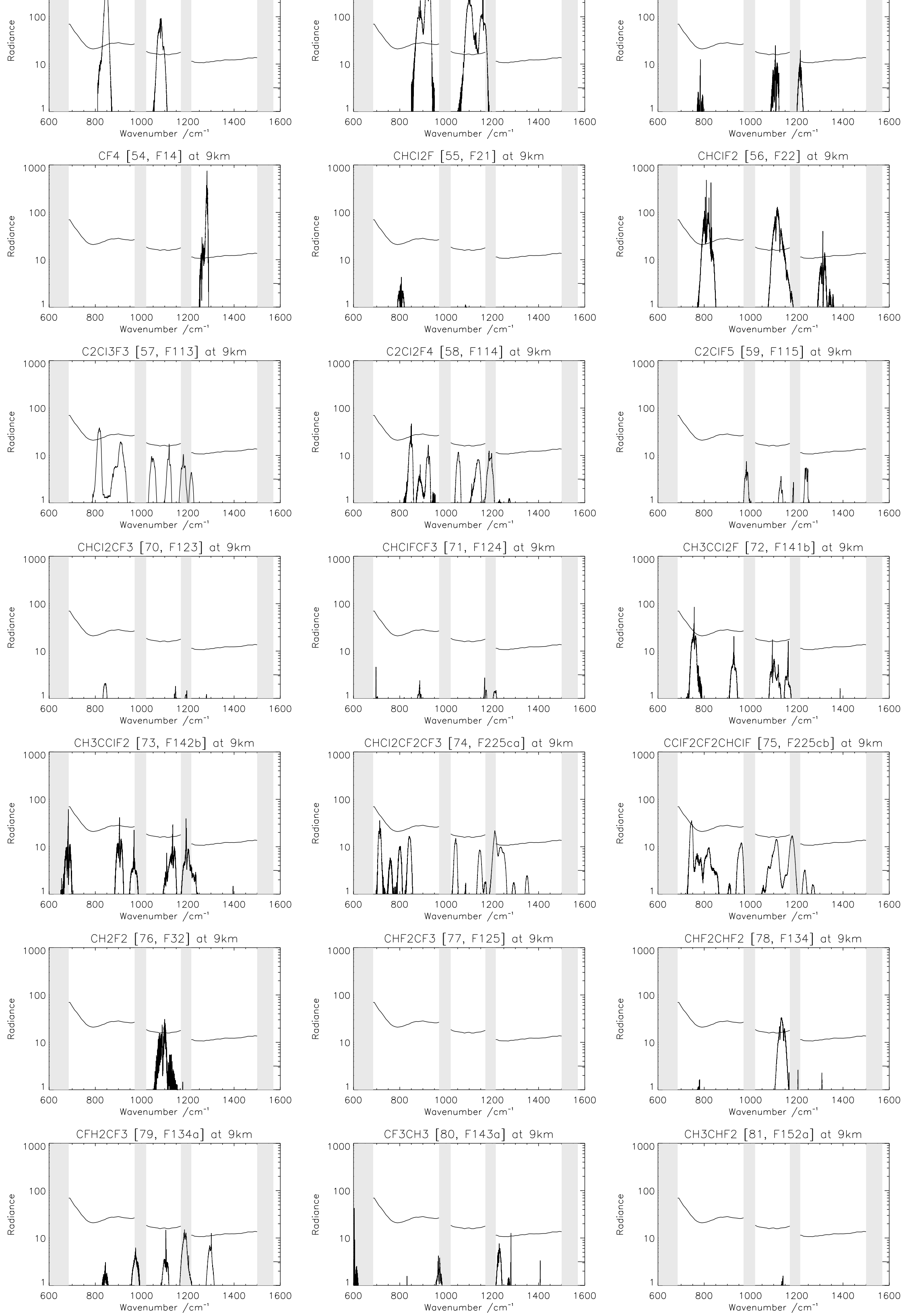

Figure 1: Individual radiances [nW/cm^2 sr cm^{-1}] of the CFCs, HFCs and HCFCs considered in this study, as output from the RFM [5], using the .atm and .xsc files in Table 2, at tangential altitude of 9km. The 1600-1800 wavenumber region is omitted as there were no significant results there. The grey bands indicate wavenumber regions that MIPAS cannot detect. The continuous line indicates the MIPAS detector noise level.

```
*HDR       !Text written into output header
      Individual CFCs with known profiles

*FLG       !List of RFM Option flags
      RAD ILS CTM

*SPC       !Spectral range / resolution
      F32 950 1500 0.025
          !950-1500 Wavenumbers, at
          !0.025 Wavenumber resolution

*GAS       !List of absorbing species
      F32 !HFC-32 on its own is considered

*ATM       !List of atmospheric profiles
      ~obrien/atm/unknowncfc.atm
      ~obrien/atm/minorcfc.atm
      ~obrien/atm/usa.atm

*TAN       !List of tangent heights
      9   !Tangent height of 9km only

*ILS       !Location of a file that defines
          !the MIPAS instrument line shape
      ~dudhia/rfm_files/ofm.ils

*XSC       !The F32 cross-section data file
      ~obrien/xsc/f32.xsc_h2k

*END
```

Table 3: A sample RFM driver table [5], for HFC-32 in an otherwise non-radiating atmosphere. Comments are preceded by exclamation marks.

Name	Group
CFC-11	C
CFC-12	C
CFC-13	C
CFC-14	C
HCFC-21	C
HCFC-22	C
CFC-113	C
CFC-114	C
CFC-115	B
HCFC-123	A
HCFC-124	A
HCFC-141b	C
HCFC-142b	C
HCFC-225ca	B
HCFC-225cb	B
HFC-32	C
HFC-125	A
HFC-134	C
HFC-134a	B
HCFC-225cb	B
HFC-143a	B
HFC-152a	A

Table 4: Summary of results of the CFCs, HFCs and HCFCs in this study.

References

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[3] *Carlotti et al* Development of an Optimised Algorithm for Routine p, T and VMR Retrieval from MIPAS Limb Emission Spectra (PDF Document) p 4 `http://envisat.esa.int/instruments/mipas/pdf/l2_atbd.pdf`

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