



SPSD II

EXPERIMENTAL STUDIES OF ATMOSPHERIC CHANGES II (ESAC II)

M. DE MAZIERE, M. CARLEER, R. COLIN, H. DE BACKER, E. MAHIEU



PART 2

GLOBAL CHANGE, ECOSYSTEMS AND BIODIVERSITY



ATMOSPHERE AND CLIMATE



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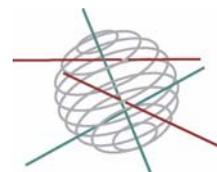
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Part 2:
Global change, Ecosystems and Biodiversity

FINAL REPORT



**EXPERIMENTAL STUDIES OF ATMOSPHERIC CHANGES II
(ESAC II)**

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ABSTRACT

Rationale

The Earth's atmosphere has been changing rapidly over the last decades. Many national and international research programmes have been set up to identify, quantify and understand the atmospheric variability and changes. An important example is the NDSC, Network for the Detection of Stratospheric Change. Also international policies have been established to address long-term changes, their anthropogenic origin and their socio-economic consequences. The effectiveness of these policies relies heavily on accurate scientific knowledge.

At present, various phenomena are understood. For example, the link between the long-term build-up of chlorine, mainly from anthropogenic sources, and the resulting decline of the stratospheric O₃ layer has been firmly established. The Montreal Protocol and its Amendments and Adjustments have responded hereto and large reductions in the atmospheric release of ozone depleting substances have been achieved. Another example is the evidence for global climate warming as a result of rising concentrations of tropospheric gases and particles that alter the thermal structure of the atmosphere, like carbon dioxide, methane, tropospheric O₃ and aerosols, to which the Kyoto Protocol tries to respond.

However, many questions still remain unanswered. Does the apparent decline of the inorganic chlorine loading continue, and at what speed? How will the O₃ layer respond to the halogen loading of the atmosphere, under conditions of increasing abundances of tropospheric radiatively active gases and aerosols? Which role are the bromine species playing and how well do we understand the total bromine budget? There is an as yet unassessed coupling between the stratospheric O₃ loss, the resulting cooling of the lower stratosphere, and the radiative forcing in the troposphere. How will this coupling affect the recovery of stratospheric O₃?

To answer such questions, long-term observations must be continued on a global scale, and more advanced measurements and studies must be performed.

Objectives / partnership

The general objectives of the project Experimental Studies of Atmospheric Changes II (ESACII) have been to provide a continuation of the Belgian contributions to the monitoring of the Earth atmosphere, to enhance the Belgian expertise in the field and to acquire a better understanding of the Earth atmosphere's behaviour from

observations and related modelling and experimental laboratory studies. The partners in the project are the Belgian Institute for Space Aeronomy (BIRA-IASB), the Service de Chimie Quantique et Photophysique (SCQP-ULB, formerly Laboratoire de Chimie Physique Moléculaire, LCPM-ULB) of the Université Libre de Bruxelles, the Royal Meteorological Institute of Belgium (KMI-IRM), and the Institut d'Astrophysique et de Géophysique of the Université de Liège (ULg). These partners have already worked together in previous multiannual research projects, in particular the preceding ESACI project (1996-2001).

A particular focus of the research in ESACII has been on the evolution of the ozone layer and chemical constituents and other parameters that are strongly related to the evolution of stratospheric ozone or climate, like the spectral UV irradiance, the aerosol load, and parameters of dynamical or meteorological nature. Enhancing the capabilities to make distinctive observations in the troposphere and stratosphere has been another important objective of the project. ESACII also aimed at a better integration between model and observational information.

The research approach has consisted of a combination of high-quality field observations, including continued long-term monitoring and campaign observations, new advanced data analyses and geophysical studies, and supporting laboratory measurements of fundamental spectroscopic parameters of atmospheric molecules.

The monitoring stations involved are Ukkel/Uccle (50.5°N, 4°E), Harestua (Norway, 60°N, 11°E) and the primary alpine station of the NDSC comprising Jungfraujoch (46.5°N, 8°E) and the Observatoire de Haute Provence (OHP, 44°N, 6°E). Harestua is a complementary station of the NDSC; Ukkel/Uccle acquired this status in the course of the project. New measurements have been initiated at Ile de La Réunion. The experimental techniques deployed in the project are spectral UV radiometry, UV-Visible zenith sky and off-axis DOAS spectrometry, high-resolution Fourier-transform spectrometry, Brewer and Dobson photometry as well as ozone soundings.

Major achievements

Long-term monitoring data

The existing time series of total abundances and/or vertical profiles of atmospheric constituents at the NDSC stations involved in the project have been extended with nearly 5 years of data.

From the series, many important conclusions related to the evolution of the ozone layer have been drawn:

- The chlorine (Cl_y) loading in the atmosphere above Jungfraujoch increased steadily in the 1986-1993 period at a rate of order of 4% per year, and then started to stabilize. The maximum loading was observed in the second half of 1996. Since then, a slight but statistically significant decrease of $(-1 \pm 0.3)\%/yr$ is apparent.
- The Montreal-controlled chlorine source gases like CFC-11 and CFC-12 are decreasing/ stabilizing as expected from their respective lifetimes. On the contrary, the abundance of HCFC-22, a substitute gas of which the phase out started in 2004 only, is still rising, at a rate of order of 3%/yr.
- The observed accumulation of inorganic fluorine loading is slowing down, with measured column changes amounting to 3% in 1997, 1.3% in 2002 and 0.6% in 2004, as a result of the phasing out of some important F-bearing source gases.
- Two important radicals involved in ozone depletion processes are BrO and OCIO: they have been monitored since 1998 at Harestua. The largest chlorine activation observed thus far occurred in winter 2004-2005, characterized by very cold conditions in the stratosphere. The time series of OCIO, O_3 and NO_2 at Harestua are exploited as part of the SAOZ polar network in order to estimate the annual degree of ozone loss in the Arctic during polar spring.
- Stratospheric bromine is much less abundant than chlorine, but has a much larger O_3 depletion potential: it accounts for about 25% in the contributions to the O_3 loss. Its long-term evolution has been monitored at Harestua, since 1994, and at OHP, between 1998 and 2002. The Harestua data indicate a positive trend until 2002, followed by stabilization, and first signs of a decline in the last years, which is consistent with published measurements of the evolution of the main bromine source gases.
- Among NO_y budget relevant species, only NO_2 increases significantly: in the 1986-2004 period, the mean annual trend amounts to $(0.5 \pm 0.1)\%/yr$. This trend is observed in the FTIR as well as in the DOAS measurements, and is consistent with other observations at other mid-latitude sites reported in the literature.
- Homogenization of the ozone data at Ukkel/Uccle has enabled reliable trend evaluations. Considered piecewise, the total column trends are $(-0.28 \pm 0.05)\%/yr$ and $(+0.60 \pm 0.17)\%/yr$ in the periods 1981-1996 and 1997-2004, before and after reaching the maximum chlorine loading, respectively.

However, it is too early to state that the recovery of ozone has been detected!

- From the ozone soundings at Ukkel/Uccle, trend profiles have been evaluated as a function of season and height above and below the tropopause. The most important negative trends occur in the stratosphere, especially during winter and spring. In the troposphere the trends are mainly positive.
- The UV spectral irradiance time series at Ukkel/Uccle confirm a perfect anti-correlation between the UV irradiance and the total Ozone content.
- A study concerning the occurrence of secondary maxima in the ozone profiles at Ukkel/Uccle from local soundings and from satellite measurements (SAGE) has led to the definition of an index characterizing the atmospheric circulation in the lower stratosphere. This index explains to a large extent the ozone variability in the lower stratosphere. The secondary maxima are related to planetary waves over mid-latitudes, advecting layers with different origins.
- Another study using the long-term O₃ sonde series at Ukkel/Uccle was devoted to the relationship between tropospheric ozone, meteorological parameters, and NO_x. A simple statistical model was built that can explain more than 60% of the variance of the ozone concentrations in the boundary layer.

These results derived from the long-term monitoring observations reported here confirm the stabilization of the halogen loading at northern mid-latitudes. They are consistent with measurements from satellite (e.g., HALOE) and from in-situ surface networks. They demonstrate the effectiveness of the Montreal Protocol and its Amendments and Adjustments.

Additional results concerning the evolution of greenhouse gases, relevant to climate change and the implementation of the Kyoto Protocol, are the following:

- The total columns of CO₂, CH₄ and N₂O above the Jungfrauoch have been multiplied by 1.25, 1.35 and 1.17, respectively, since early observations in 1950. The concentrations of these gases are still growing steadily, apart from CH₄ that exhibits stabilization over recent years. The results are commensurate with in-situ data.
- The column of SF₆ is growing rapidly, exceeding a rate of 4%/yr in 2004. The concentration values predicted for the future (between 2050 and 2100) are significantly lower than those reported in recent scenarios (WMO, 2003), indicating a pressing need for continuing the observations.

New observations

FTIR and UV-Visible MAXDOAS observations have been initiated at the Ile de La Réunion (21°S, 55°), with the purpose of adding new measurement capabilities at this complementary NDSC site that is among the few ones in the tropical belt. At present, there is a need for more continuous observations in the tropical regions.

The FTIR measurements were carried out during 2 campaigns, in 2002 and 2004. They required the development and implementation of a system called BARCOS, for allowing remotely-controlled and automatic operations of the instrument. BARCOS has now become a fully operational system. The campaigns have demonstrated that FTIR observations at Ile de La Réunion are perfectly feasible; somewhat better capabilities are achieved at the high-altitude Maïdo site (2200 m asl), where the future NDSC infrastructure will be built (2008) and where permanent operations are planned using BARCOS. First results for ozone, N₂O and HNO₃ profiles and columns have been compared with MIPAS and ACE overpass data and confirm the good quality of the data.

The newly designed MAXDOAS instrument has been operated between August 2004 and July 2005. The analysis of the data has revealed the capability to observe enhancements of the NO₂ concentrations near the surface, to distinguish stratospheric and tropospheric BrO contents, and to determine the tropospheric H₂CO and SO₂ columns. The results confirm the existence of a small but systematic content of BrO in the free troposphere (around 6 km altitude).

Advanced exploitation of spectral data

Advanced inversion algorithms based on the Optimal Estimation Method have been further developed and exploited for the retrieval and characterisation of atmospheric constituent profiles of low vertical resolution (5 to 10 km) from the UV-visible zenith sky DOAS and FTIR ground-based observations.

This has led to the retrieval and analysis of NO₂ profiles from UV-Visible zenith-sky DOAS observations at Harestua, between about 13 and 37 km altitude. In this case, the forward model consists of a stacked box photochemical model PSCBOX, initialised with 3D SLIMCAT model fields, coupled to a radiative transfer package UVspec/DISORT. The photochemical model allows accounting for the strong diurnal variation of NO₂. Important tasks have been to validate the forward model, as well as the retrieved NO₂ profiles, in comparison with correlative balloon and satellite data.

Vertical profiles have also been retrieved from the solar absorption FTIR data at Jungfraujoch and Ile de La Réunion, in particular for O₃, CO, N₂O, HNO₃, and HCl and HF. For the latter two species, it has been shown that the usually adopted Voigt lineshape is not appropriate, but that the effect of collisional narrowing must be

accounted for in the inversion. The theoretically estimated error budgets have been verified by extensive comparisons with independent satellite and in-situ surface data (when appropriate).

It has thus been demonstrated that reliable vertical information can be retrieved from the NDSC UV-Vis zenith-sky DOAS and FTIR solar absorption measurements. This adds a large potential to these observations, for example for the validation of satellite measurements and models. In particular, the FTIR and UV-visible DOAS ground networks provide unique information in the free troposphere that is very valuable for the validation of new tropospheric satellite data, like the data from MOPITT and SCIAMACHY. Moreover, the available time series go back to the eighties, being very useful for the verification of tropospheric models, and the past and present emission inventories that these have as inputs.

A new algorithm has been developed and implemented to extract aerosol information from the standard Brewer observations at Ukkel/Uccle. The retrieved values for the aerosol optical depth (AOD) show a clear seasonal cycle, with a maximum in summer. The trend over the period 1984-2002 has been evaluated to $(-1.6 \pm 0.28)\%/yr$. It has also been shown that the same algorithm can be applied to different instruments, provided they are well calibrated. The AOD information can also be used to improve the UV index predictions.

New instruments have been deployed at Ukkel/Uccle to characterise the cloud layer, namely a total sky imager and a cloud infrared radiometer providing the cloud cover and mean altitude of up to three cloud layers.

A second UV station has been installed at the Euro Space Center in Transinnes, and is operational since June 2004.

New spectroscopic data

High-quality spectroscopic data of atmospheric species, including line parameters (line positions and intensities, pressure broadening parameters, and assignments) and absorption cross-sections, have been obtained. The molecules studied were water vapour (H_2O and its isotopologue HDO), formaldehyde (H_2CO), nitrogen dioxide (NO_2), and oxygen and its collision complex O_2-X ($X=O_2, N_2, Ar$). The gaseous molecules were studied under different conditions of pressure of the pure (target) gas, of air mixtures and of nitrogen mixtures in the UV, visible and infrared. All data have been made available to the scientific community via a local archive accessible through the Internet, or via their integration in the latest revisions of HITRAN and GEISA.

- A new homogeneous linelist has been provided for H_2O in the visible-NIR (26000 – 9250 cm^{-1}). FTS measurements of H_2O vapour profiles

performed in Ukkel/Uccle have proven, after comparison with locally measured humidity profiles (PTU soundings), that using the new linelist gives more consistent retrieval results than using the HITRAN 2000 data. Especially at large solar zenith angles, where the impact of the weak lines and of the air-broadening parameters becomes more important, the advantages of the new linelist are significant. Also the water vapour continuum has been studied and preliminary continuum absorption cross-sections have been generated.

- Nitrogen dioxide measurements have been performed simultaneously in the UV-visible and infrared using two FTS instruments, to allow an accurate intercalibration of the cross-sections in both spectral ranges. Also the pressure- and temperature-dependences of the cross-sections have been determined. From the acquired data an empirical model has been built that allows calculating the NO₂ absorption cross-sections in the 15000-42000 cm⁻¹ range at any pressure and temperature between 220 and 294K, with an accuracy better than 4%. The impact of the uncertainties on the NO₂ cross-sections on retrievals of NO₂, BrO, and OCIO from ground-based measurements at Harestua has been evaluated; the results show the complexity of the choice of one or another dataset.

Valorisation of the results

The ESACII project has provided scientific knowledge to support Belgian policies and decisions regarding the Amendments to the Montreal and Kyoto Protocols, and to contribute to international research programmes like NDSC, WMO/UNEP, SPARC/WCRP, IGBP, and IPCC. This has been realized through participation to regional, national, European and international assessments. Observational data like the time series of atmospheric constituents and the UV spectral irradiance data at the NDSC stations involved in the project have been included in the relevant European, UV, NDSC and WOUDC databases. The data have been used extensively for validation of satellite data and model results. New and improved spectroscopic data of atmospheric gases obtained in the laboratory have been included in the HITRAN and GEISA databases. They have been and are used to improve the retrievals from the atmospheric spectra, from ground and satellite.

The ESACII partners benefit from their expertise in their participations in many EU scientific projects, often in leading roles. Many are members of scientific or strategic councils, like the NDSC Working Groups, or the Brewer Science Advisory Group.

The ESACII achievements have been disseminated to the world-wide community and to the public, via publications, presentations, and the WWW (<http://www.oma.be/ESACII/Home.html>).

Keywords: global change, long-term atmospheric monitoring, evolution of the ozone layer, greenhouse gases, ground-based networks, spectroscopy

1. INTRODUCTION

The general objectives of the project Experimental Studies of Atmospheric Changes II (ESACII) have been to provide a continuation of the Belgian contributions to the monitoring of the Earth atmosphere, to enhance our expertise in the field and to acquire a better understanding of the Earth atmosphere's behaviour from observations and related modelling and experimental laboratory studies.

A particular focus is on the evolution of the ozone layer and chemical constituents and other parameters that are strongly related to the evolution of stratospheric ozone or climate, like the spectral UV irradiance, the aerosol load, and parameters of dynamical or meteorological nature. Enhancing the capabilities to make distinctive studies in the troposphere and stratosphere has been among the particular objectives of the project. ESACII also aimed at a better integration between model and observational information.

The research approach has consisted of a combination of high-quality field observations, including continued long-term monitoring and campaign observation, new advanced data analyses and geophysical studies, and supporting laboratory measurements of fundamental spectroscopic parameters of atmospheric molecules. The monitoring stations involved are Ukkel (50.5°N, 4°E), Harestua (Norway, 60°N, 11°E) and the primary alpine station of the NDSC (Network for the Detection of Stratospheric Change) comprising Jungfraujoch (46.5°N, 8°E) and the Observatoire de Haute Provence (OHP, 44°N, 6°E). Harestua is a complementary station of the NDSC; Ukkel acquired this status in the course of the project. New measurements have been initiated at Ile de La Réunion. The experimental techniques deployed in the project are spectral UV radiometry, UV-Visible zenith sky and off-axis DOAS spectrometry, high-resolution Fourier-transform spectrometry, Brewer and Dobson photometry as well as ozone soundings.

It has also been an important objective of the project to provide scientific knowledge to support Belgian policies and decisions regarding the Amendments to the Montreal and Kyoto Protocols, and to contribute to international research programmes like NDSC, WMO/UNEP, SPARC/WCRP, IGBP, and IPCC.

2. METHODOLOGY: DEVELOPMENTS

2.1. Inversion methods for FTIR observations

During ESACII, significant know-how has been acquired as to profile retrieval from ground-based FTIR solar absorption measurements. Two different algorithms have been explored, namely the SFIT2 algorithm that has been developed in collaboration between several NDSC Infrared Working Group (IRWG) investigators and that is a standard in this community, and SFSP2, that has been developed at BIRA-IASB (and that has led to the development of AtmosPhit at ULB – see Section 4.1). In both algorithms the inversion uses an empirical implementation of Rodgers' Optimal Estimation Method (OEM) [Rodgers, 2000]. The characterization and error analysis of the retrieval products is not an integrated part of the above algorithms. Therefore specific tools have been developed at BIRA-IASB that – after thorough verification - have been distributed to the NDSC IRWG community and that are now used widely.

Ozone

At first, we focused on the retrieval of Ozone profiles from spectra taken at Jungfraujoch. The retrieval strategy (i.e., choice of microwindows, and other retrieval parameters) has been improved, essentially by widening the retrieval microwindow, resulting in the capability to retrieve at least 4 elements of information. In other words, quasi-independent information can be obtained for partial column abundances in 4 layers, that are the troposphere, the lower stratosphere (up to 18 km and 25 km, respectively, with a vertical resolution of order 6 km), and the middle stratosphere up to 40 km. The retrieved time series have been verified extensively in comparison with correlative LIDAR observations at OHP, microwave measurements at Bern and ozone soundings at Payerne: mean differences are always smaller than 5%, and their standard deviations are never larger than half the natural variability. The total column abundances agree with correlative Dobson data (Arosa) to better than 1% [Barret et al., 2002]. The FTIR data reproduce correctly the seasonal variations (magnitude and phase) in the individual layers (Figure 2.1-1 and Figure 2.1-2).

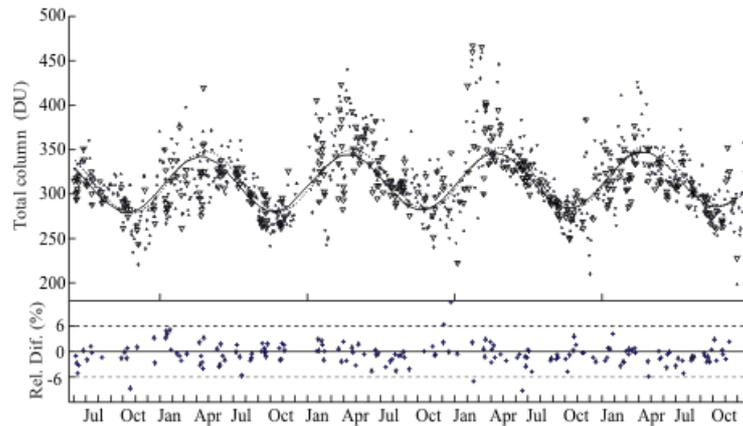


Figure 2.1-1: Upper plot: Ozone total columns above 3.58 km measured by the ISSJ FTIR spectrometer (empty triangles) and by the Arosa Dobson spectrophotometer (full diamonds). Corresponding annual cycles are indicated by sine fits, with solid and dashed lines for FTIR and Dobson, resp. Lower plot: total columns relative differences for coincident days.

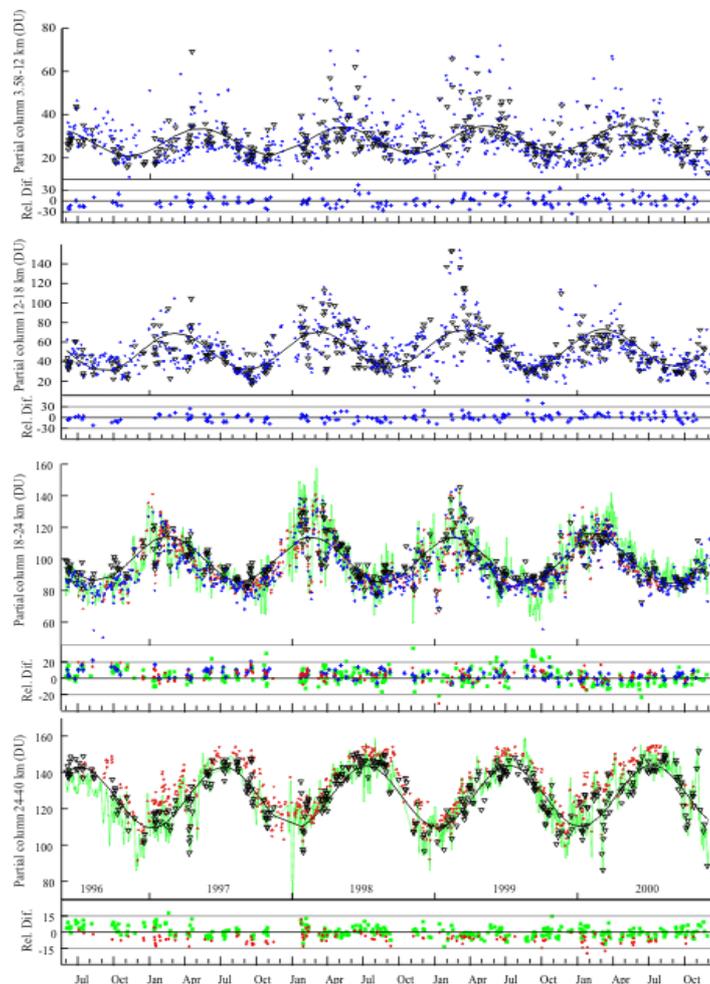


Figure 2.1-2: Time series of ozone partial column data for four layers 3.58-12 km, 12-18 km, 18-24 km and 24-40 km (from top to bottom) as measured by different instruments: black empty triangles: FTIR; blue diamonds: sondes; green dotted lines: microwave radiometer; orange circles: lidar. The FTIR annual cycles are indicated by sine fits in black solid lines. For each layer, the relative discrepancies between the ozone data from the FTIR and the other instruments, $(FTIR-X)/X$, in %, are shown in the lower plots.

CO

Second, time series of CO profiles at Jungfraujoch have been retrieved and characterized. The Jungfraujoch FTIR data have been compared with correlative MOPITT data and in-situ surface observations from EMPA. It has been shown that the FTIR data capture very well the variations of CO in the surface layer above the station (3.58 km – 6 km): the mean difference with the in-situ measurements is about zero, and the standard deviation of the differences is less than half the natural variability. The comparisons between FTIR and MOPITT day and night total column measurements, taking into account the different vertical resolutions of both data sets, have indicated that MOPITT night (day) columns are $4 \pm 6\%$ ($5 \pm 5\%$) larger than the ones from the FTIR (Figure 2.1-3). It is demonstrated herewith that vertical profiles of CO obtained from ground-based FTIR measurements provide important data for new satellite measurements in the troposphere. More details can be found in [Barret et al., 2003].

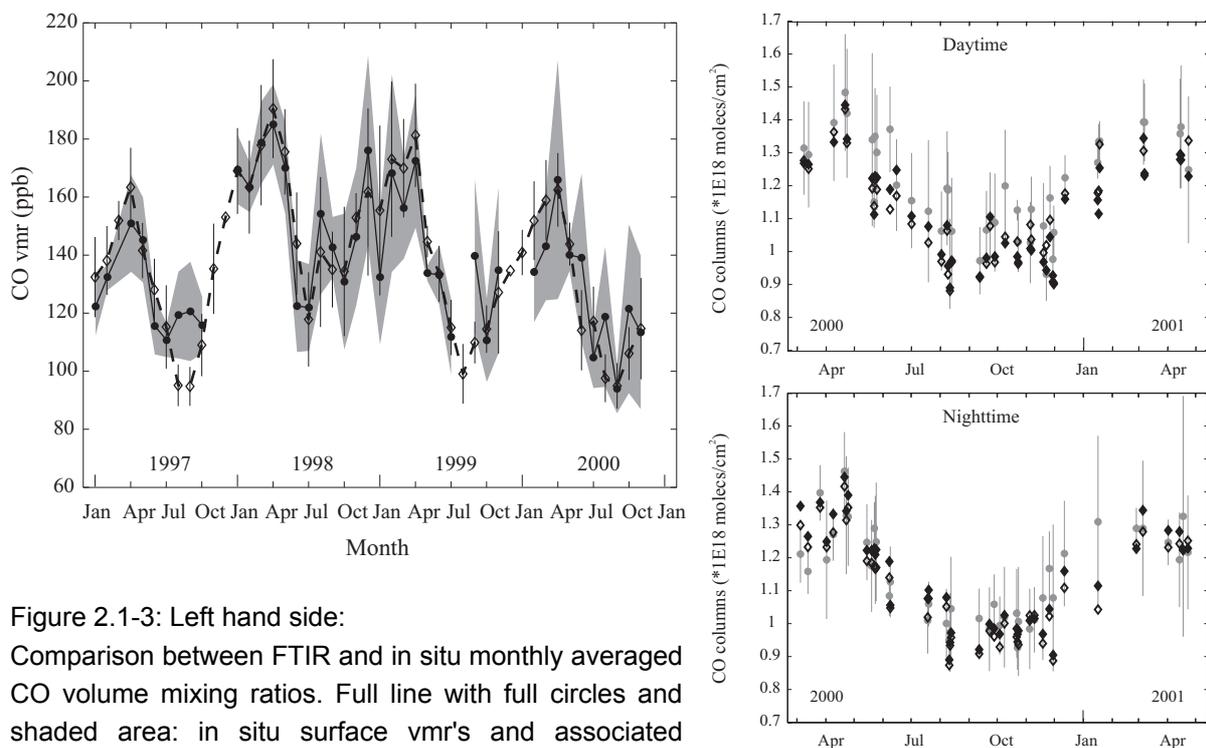


Figure 2.1-3: Left hand side:

Comparison between FTIR and in situ monthly averaged CO volume mixing ratios. Full line with full circles and shaded area: in situ surface vmr's and associated monthly variability (1σ). Dashed line with empty diamonds and associated error bars: FTIR 3.58-6.5 km averaged vmr and associated monthly variabilities.

Right hand side: FTIR and MOPITT daily averaged columns. Upper plot for daytime, lower plot for night time MOPITT measurements. Full diamonds: FTIR total columns; empty diamonds: FTIR total columns smoothed with MOPITT kernels; full grey circles: MOPITT partial columns above the ISSJ altitude; grey error bars represent the MOPITT variability (1σ) for all the pixels entering the daily average.

HF and HCl

The SFIT2 algorithm adopts a Voigt line shape. From spectroscopic laboratory studies it is known that the line shapes for HF and HCl are different because of collisional narrowing. A study concerning the impact of these line shape differences on the retrieval of vertical profiles from ground-based atmospheric absorption spectra has been conducted at BIRA, in collaboration with ULB, using high-quality spectra taken at the Jungfraujoch. To this end, it was necessary to use the alternative codes SFSP2, and later on, AtmosPhit. The study also served the validation of the latter code against SFIT2. It has been demonstrated, by comparing the retrieval results with HALOE data, that it is important to account for the collisional line narrowing effect in the retrieval of HF, while it the effect is weak, but non-negligible, in the case of HCl (Figure 2.1-4 and Figure 2.1-5). The results have been published in [Barret et al., 2005].

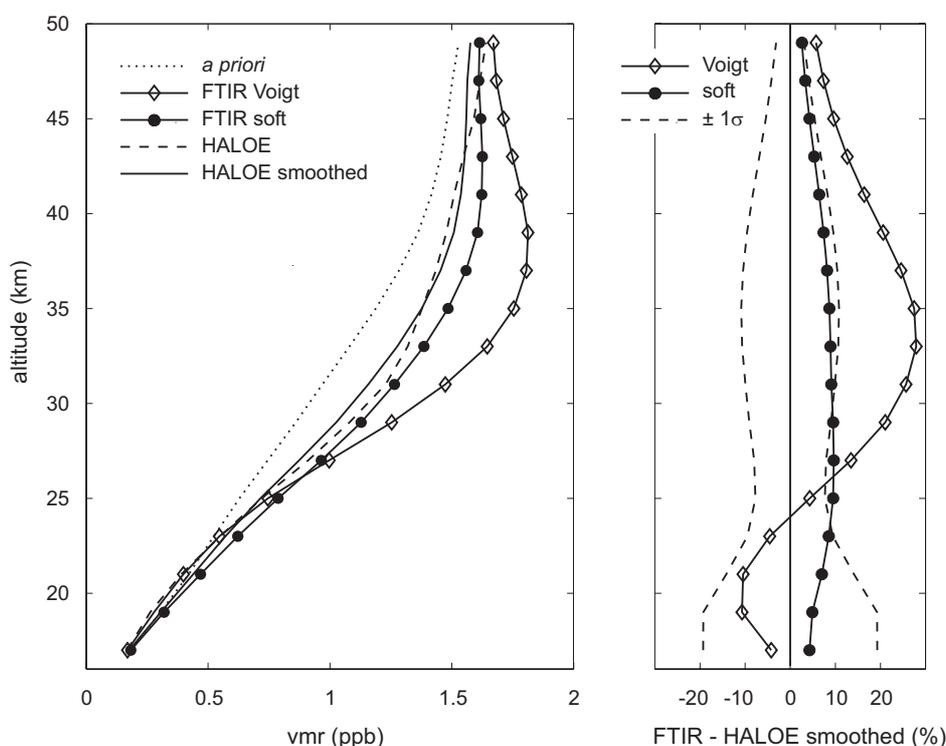


Figure 2.1-4: HALOE and ground-based FTIR HCl profiles. Left: mean of all correlative profiles. The FTIR data have been analyzed with the AtmosPhit algorithm running with the Voigt and with the soft-collision models. The HALOE profiles have been smoothed by the coincident FTIR averaging kernels for the comparison. Right: mean relative differences between the correlative HALOE and FTIR profiles \pm standard deviation of the differences (1σ).

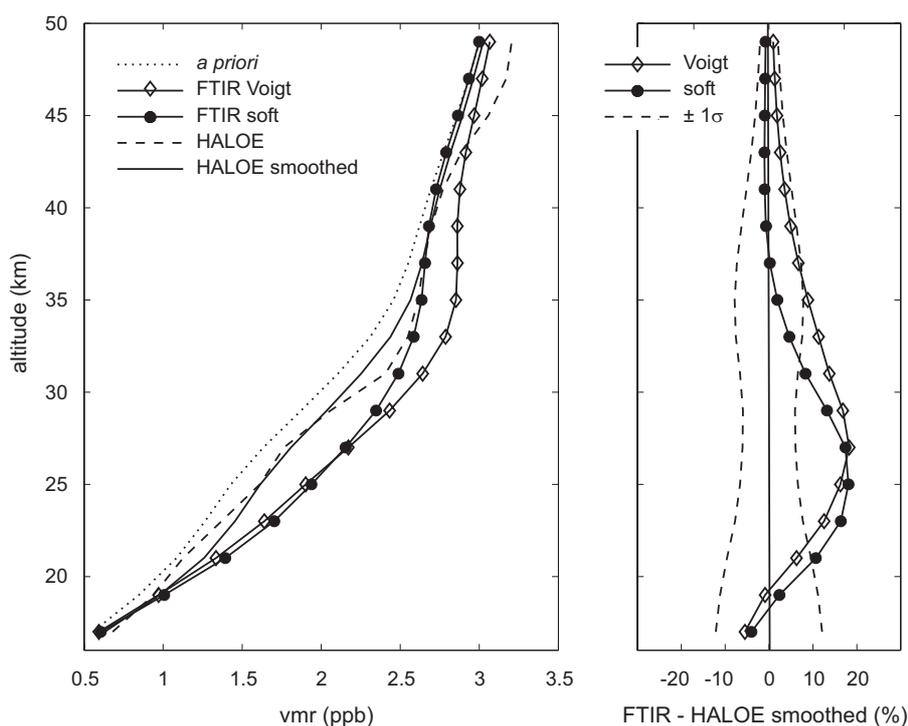


Figure 2.1-5: HALOE and ground-based FTIR HF profiles. Left: mean of all correlative profiles. The FTIR data have been analyzed with AtmosPhit running using the Voigt and the soft-collision line shape models. The HALOE profiles have been smoothed by the coincident FTIR averaging kernels (equation (14)) for the comparison. Right: mean relative differences between the correlative HALOE and FTIR profiles \pm standard deviation of the differences (1σ).

Link with UFTIR

In the frame of the EC project UFTIR (<http://www.nilu.no/uftir>; coordinator BIRA-IASB), a homogenised optimal retrieval strategy has been developed for the inversion of O_3 , N_2O , C_2H_6 , HCFC-22, CO and CH_4 . The strategies for ozone and CO rely heavily on the progress achieved in ESACII. Based here upon, the corresponding spectral data from Jungfraujoch between 1995 and 2004 have been reprocessed and the resulting time series are being archived on the UFTIR database at NILU. The UFTIR experiences are shared with the NDSC IRWG; the archiving of FTIR vertical profile data in the NDSC database is still under discussion.

2.2. Inversion methods for DOAS observations

A reliable retrieval algorithm based on the Rodgers optimal estimation method (Rodgers, 2000) has been developed at IASB-BIRA in order to provide vertical distributions of NO_2 in the stratosphere from ground-based (GB) zenith-sky UV-visible observations. The algorithm relies on the study by Preston et al. [1997], and

on the experience acquired at IASB-BIRA in the development of profiling inversion techniques for GB observations in the infrared region [Barret *et al.*, 2002]. It is similar in concept to the algorithm developed by Denis *et al.* [2004]. The forward model consists in the IASB-BIRA stacked box photochemical model PSCBOX [Errera and Fonteyn, 2000] initialized with 3D-CTM SLIMCAT fields [Chipperfield, 1999] and coupled to the radiative transfer (RT) package UVspec/DISORT (Mayer and Kylling, 2005). A photochemical model is required to reproduce the effect of the diurnal variation of NO₂ concentration on slant column (SCD) measurements. It also provides a priori NO₂ profiles for the inversion. The radiative transfer model is used to calculate SCD values from the NO₂ concentrations predicted by the photochemical model.

An important preliminary task has been to validate both components of our forward model. PSCBOX has been successfully compared to two other models - BRAPHO (University of Bremen) and SLIMCAT1D (University of Leeds) - in the framework of the Stratospheric BrO EC project [Hendrick *et al.*, 2000]. Concerning UVspec/DISORT, it has been validated as part of the EU QUILT project through an intercomparison exercise with five other RT models, which are those from the University of Bremen (UBRE), University of Heidelberg (UHEI), Norwegian Institute for Air Research (NILU), Istituto di Scienze dell'Atmosfera e del Clima (ISAC-CNR, Italy), and National Institute of Water and Atmospheric Research (NIWA, New-Zealand). The consistency between these models has been tested through several SCD simulation comparison tests performed using identical settings for all models. Both ground zenith-sky (trace gases: BrO, NO₂, and OCIO) and multi-axis (MAX) geometries (trace gases: NO₂ and HCHO) have been considered for these tests, the photochemical enhancement being taken into account only in zenith-sky geometry. All the intercomparison results are presented and discussed in detail in Hendrick *et al.* [2005]. Only the most relevant for stratospheric NO₂ profiling is highlighted here. Figure 2.2-1 shows BrO, NO₂, and OCIO SCDs simulated in zenith-sky geometry. Good agreement is observed between the IASB RT model and the other ones, which gives us confidence in the reliability of our RT model in simulating SCDs in zenith-sky geometry. It should be noted that all the comparison results and initialization data have been gathered in a "RT model validation package" enabling the testing of other RT codes and made publicly available through the QUILT project website (<http://nadir.nilu.no/quilt/>).

The forward model being validated, the retrieval algorithm has been applied to the set of NO₂ SCD measurements performed by IASB-BIRA at the complementary NDSC (Network for Detecting Stratospheric Change) station of Harestua (Norway, 60°N). A few retrieval results have been also obtained from measurements performed in March 2003 at Andøya (Norway, 69°N) during the NDSC intercomparison campaign of GB

zenith-sky instruments [Vandaele et al., 2005]. In a first step, an important effort has been made for characterizing the information content and the retrieval errors.

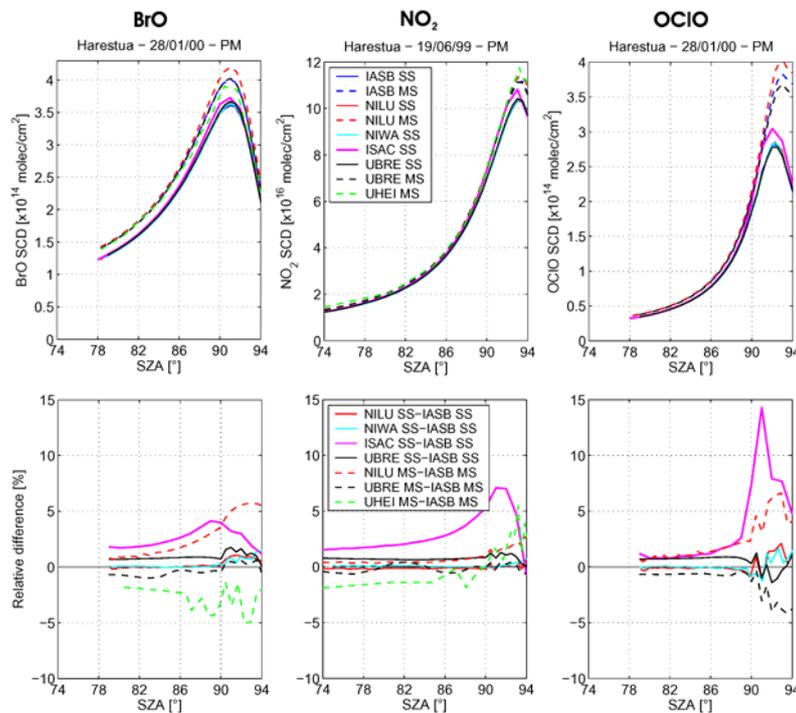


Figure 2.2-1: Sunset BrO, NO₂, and OCIO SCDs calculated in the comparison test in zenith-sky geometry. The upper plots correspond to the SCDs and the lower plots to the relative differences between the different models and the IASB one arbitrarily chosen as reference.

Figure 2.2-2 shows a typical example of NO₂ GB UV-visible averaging kernels we obtained. The vertical resolution of the retrieval at a given altitude can be estimated from the full-width at half-maximum (FWHM) of the corresponding averaging kernel. For example, the FWHM of the 13 km curve is approximately 10 km. The averaging kernels between 13 km and 37 km are reasonably sharply peaked at their nominal altitude. The 13-37 km is therefore the altitude range where the measurements give information about the vertical distribution of NO₂. The information content can be quantitatively derived by calculating the trace of the averaging kernels matrix \mathbf{A} which is called the number of degrees of freedom for signal, providing an estimate of the number of independent pieces of information contained in the measurements. In our case, a typical value for the trace of \mathbf{A} is 2, which is consistent with the derived vertical resolution of the technique.

Concerning the error budget, the total error on the retrieved profiles can be characterized by the sum of three main sources of errors [Rodgers, 2000]: the smoothing error, measurement noise, and forward model parameter error. The profiles of all these errors as well as the NO₂ natural variability derived from HALOE (HALOgen Occultation Experiment) observations are plotted in Figure 2.2-3.

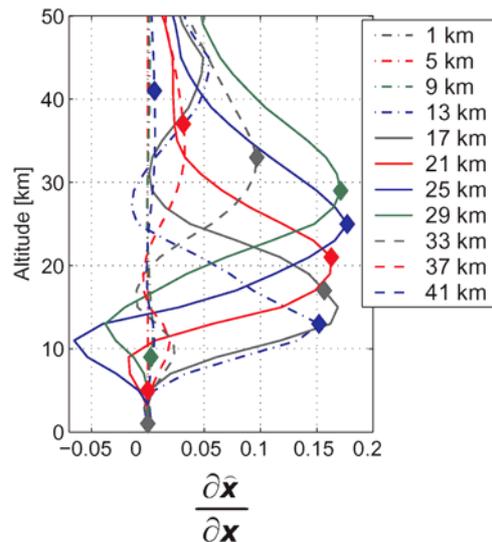


Figure 2.2-2: Typical example of GB NO₂ averaging kernels (calculated for Harestua May 25, 2001 at sunset). Plain diamonds indicate the nominal altitude of each averaging kernel.

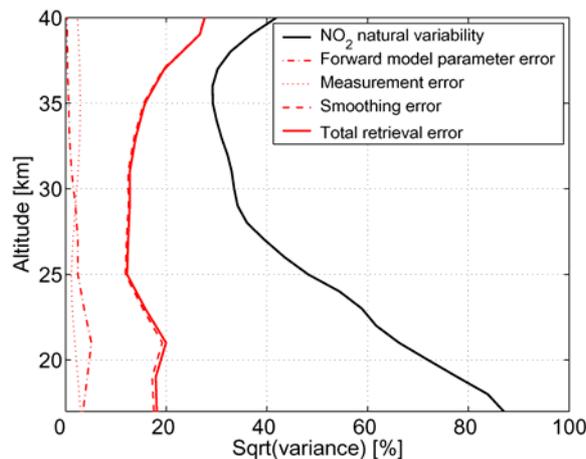


Figure 2.2-3: profiles of the smoothing, measurement, forward model parameter, and total retrieval errors and NO₂ natural variability (retrieval errors calculated for Harestua May 25th, 2001 at sunset).

The main contribution to the total retrieval error is clearly due to the smoothing error, both measurement and forward model parameter errors being only minor error sources. Note that the total error is also significantly smaller than the NO₂ natural variability in the 17-37 km altitude range, which means that variations of the NO₂ profile smaller than the variations due to the natural variability can be easily detected from our GB UV-visible observations.

In order to validate the algorithm, retrieved NO₂ vertical profiles have been compared to correlative data. These are measurements from the balloon-borne CNRS-SAOZ and Heidelberg-DOAS instruments and the POAM III and HALOE satellite instruments. These balloon and satellite techniques have been chosen because they cover complementary altitude ranges (~15-30 km for the balloons and ~20-45 km for the satellites) and they all offer a good vertical resolution of about 1-2 km. In order to

allow direct comparison, the high-resolution balloon and satellite profiles must be degraded to the low-resolution of the GB UV-visible profiles. This is done by convolving the correlative data with the GB UV-visible averaging kernels [Connor et al., 1994]. Here below, we summarize the results of this validation exercise. The whole study can be found in Hendrick et al. [2004].

All the flights used for the CNRS-SAOZ balloon-borne comparisons originated in Kiruna (Sweden, 68°N) and occurred at sunset. As the balloon data have not been corrected for photochemical variations along the line of sight, only the ascent data are taken into account for the comparisons. Five coincident events were found, three in summer (Harestua data) and two in early spring (Andøya data).

Figure 2.2-4 shows good agreement for the cases of Harestua 13 and 28 August and Andøya 16 March, the profiles differing by less than 7%, 25%, and 21%, respectively. For both other coincident events, the relative difference is smaller than 25% above 20 km but larger discrepancies are observed below (up to 70%). For Andøya 27 March, dynamical effects cannot explain the observed discrepancies since an examination of the potential vorticity at 475 K shows that both measurements were outside the vortex. The vertical columns integrated over the balloon-borne height range show agreement of better than 17% for each case. Concerning the Heidelberg-DOAS balloon data, the level of agreement with the GB profiles and columns is similar as the one obtained with CNRS-SAOZ balloon data.

POAM (Polar Ozone and Aerosol Measurement) III is a solar occultation instrument launched on SPOT 4 satellite in 1998, measuring stratospheric profiles of NO₂ from 20 to 45 km at sunset. Retrievals do not include a correction for the variation of NO₂ along the line of sight. 76 coincident events (within 5° latitude and longitude of Harestua) were found between June 1998 and September 2000. Above 25 km of altitude, agreement between averaged profiles is reasonably good with differences less than about 20% (see Figure 2.2-5). Below 25 km, the GB profiles systematically underestimate the POAM III ones with relative difference values reaching 40%.

Except two days in 2000, the POAM III columns in Figure 2.2-6 are larger than GB columns by up to 26%, but the difference varies with year and season.

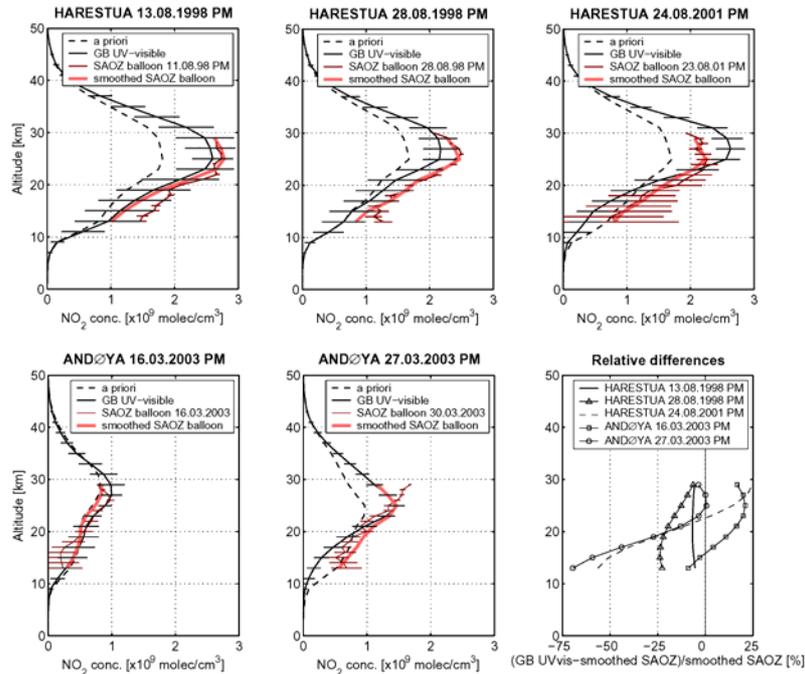


Figure 2.2-4: Comparison between GB UV-visible profiles at Harestua (sunset, summer conditions) and Andøya (sunset, late winter-early spring conditions) and SAOZ balloon profiles.

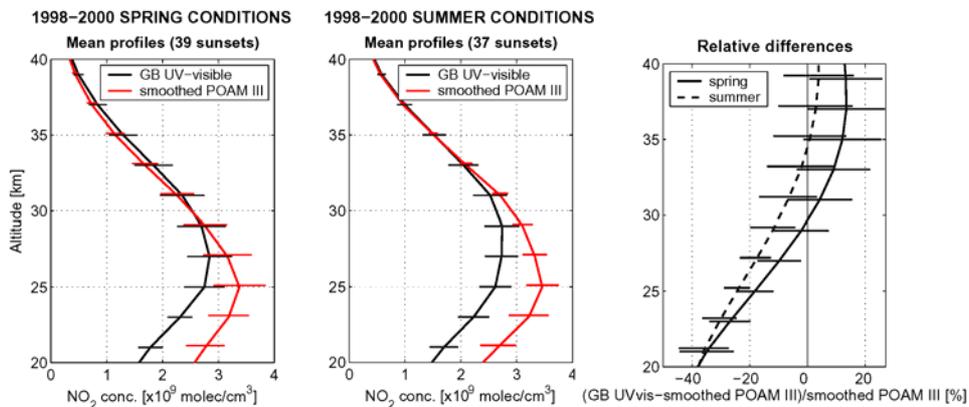


Figure 2.2-5: Comparison of averaged GB UV-visible and smoothed POAM III profiles for sunset spring (left plot) and sunset summer (middle plot) conditions at Harestua for the period from mid-June 1998 to mid-September 2000. The error bars represent the standard deviations of the GB, POAM III, and relative difference profiles.

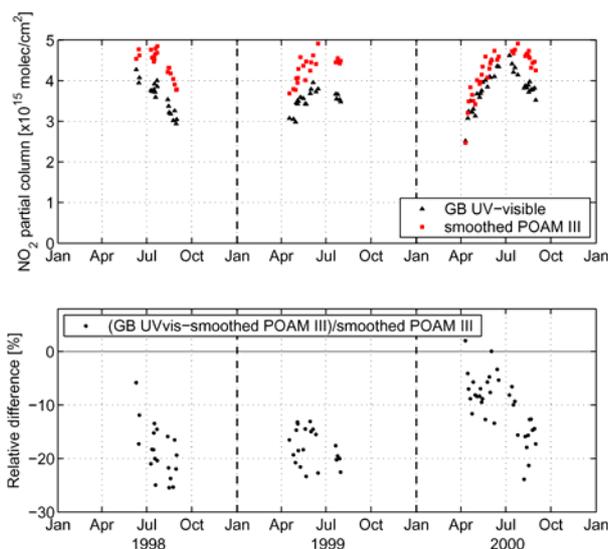


Figure 2.2-6: Comparison of the sunset 20-37 km NO₂ partial columns calculated from the coincident GB UV-visible and smoothed POAM III profiles at Harestua for the period 1998-2000.

The HALOE instrument, launched on UARS satellite in 1991, also observes solar occultation and NO₂ vertical profile measurements extend from about 10 to 50 km. Comparisons between GB UV-visible and HALOE profiles (not shown here) display qualitatively similar features as for POAM III, i.e. the GB profiles are systematically less than HALOE below 25 km. However, the differences observed with HALOE below this altitude are significantly smaller than with POAM III (smaller than 20% instead of being comprised between 20% and 40%), due to the fact that HALOE retrieval includes a correction for the line of sight changes of NO₂.

The good agreement with both balloon-borne instruments suggests that the disagreement with both satellite instruments at low altitudes is due to a problem with the satellite instruments at these altitudes, where HALOE error bars increase while POAM III neglects the correction for the line of sight variations. This results in an overestimation of the NO₂ concentration below 25 km, of the order of 20% at 20 km, which partially explains the reported differences. However other estimates are smaller suggesting that the correction may have a large uncertainty.

The results of this validation study strengthen our confidence in the reliability and the robustness of the IASB-BIRA retrieval algorithm and, more generally, of the retrieval of the vertical distribution of stratospheric trace gas species from GB zenith-sky UV-visible observations. This technique offers new perspectives in the use of GB UV-visible networks such as the NDSC for the purpose of validation of satellite and balloon experiments as well as modelling data. In the near future, the IASB-BIRA retrieval algorithm will be used for the validation of the level 2 products from the MIPAS (trace species: NO₂), SCIAMACHY (trace species: NO₂ and BrO), and GOMOS (trace species: NO₂) instruments onboard the ENVISAT satellite. It will be also extended to the interpretation of observations in MAX geometry (including

zenith) performed by IASB-BIRA at the Observatoire de Haute Provence (44°N, France) and Reunion Island (22°S, France) in order to retrieve information on the vertical distribution of BrO, NO₂, and HCHO in both the stratosphere and troposphere.

2.3. Spectral UV measurements: new equipment and associated methodologies and retrieval of aerosol information from Brewer measurements

New equipment and associated methodologies

A new double Brewer spectrophotometer (Brewer 178) was installed at KMI in Ukkel in September 2001. This instrument has an extended wavelength range (286-363 nm) as compared to the single monochromator Brewer 016, operational since 1983 at the same location. The instrument was acquired with the funding of the National Lottery. The exploitation of the observations was done under this project.

After the collection of about one year of simultaneous observations, the ozone data of the two Brewer instruments were compared and it turned out that the values of the new Brewer were about 6% higher than those of the old instrument. A new calibration of both instruments was therefore necessary. Initially there was also a problem with the zenith sky observations of the new instrument. After some investigations it was found that a filter that was mounted in a wrong position caused this. After replacement, the problem with the zenith sky measurements was solved.

The calibration in May 2003 revealed that an adjustment of the calibration constants was necessary. With these new constants the observations of previous years were recalculated. A new comparison (Figure 2.3-1) shows that the differences (generally < 2%) between the two instruments are now within the expected error bars.

Also the calibration level of the spectral UV measurements is carefully checked. A comparison of the UV spectra obtained with both instruments is shown in Figure 2.3-2. The correlation coefficient at wavelengths above 290 nm is larger than .90, at wavelengths above 298 nm even higher than .99. The weak correlation at short wavelengths is caused by problems of straylight in the single monochromator instrument. Due to the fact that the absolute intensities at these wavelengths are very low, there is almost no impact on the calculation of the UV index from the data of both instruments. The correlation coefficient for the UV indices derived from data of both instruments is 0.996. Details of this intercomparison were presented at a "Brewer User Group Meeting" and can be consulted at <ftp://ftp.kmi-irm.be/dist/meteo/hugo/posters/Brewer2002.pdf>.

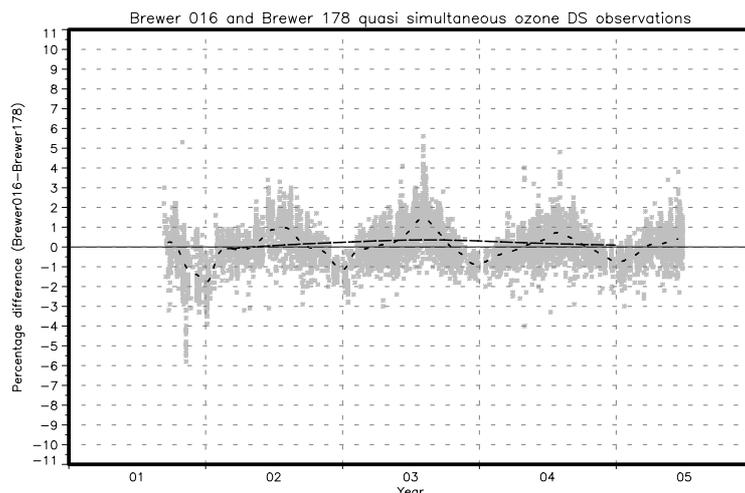


Figure 2.3-1: Percentage differences between total ozone measurements from direct sun observations with Brewer instruments 016 and 178 with the calibration constants established during an intercomparison in 2003. The dashed and the dotted lines represent running yearly and monthly means, respectively.

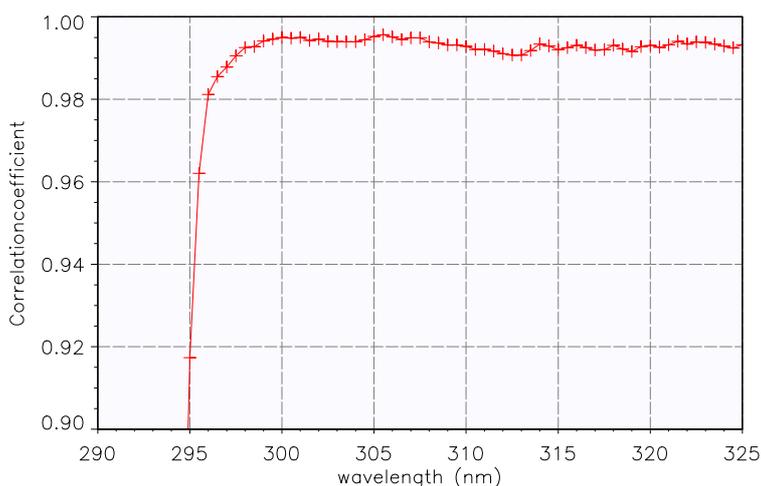


Figure 2.3-2: Correlation coefficient between quasi-simultaneous UV observations with Brewers 016 and 178 as function of wavelength.

The UV calibration level of the instruments was checked two times during the project. In May 2003, during the ozone calibration activities, the spectral response for the global UV measurements was checked with 1000W NIST traceable lamps. The calibration which was determined from the monthly routine stability checks with the 50 W lamps deviated less than 2%, which is within the expected calibration errors. In September 2004, simultaneous observations were made with a travelling reference instrument from the QASUME project of the Joint Research Centre. The results (Gröbner et al., 2004) showed that our Brewer instruments measured slightly lower UV intensities (~5%) compared to the reference. A probable explanation can be

found in the differences in free horizon of our location (roof of KMI) and the location of the reference instrument (roof of BIRA).

Retrieval of aerosol information from Brewer measurements

A new algorithm for the extraction of aerosol information from the Brewer standard observations was developed. At first the results were examined to verify the method. Figure 2.3-3 shows the time series of the aerosol optical depth (AOD) at 306.3 nm at Ukkel. A clear seasonal cycle is observed with a maximum in summer. The trend over the period 1984-2002 is $-1.60 \pm 0.028\%$ per year.

The AODs obtained with this method were compared with what is found in literature. Afterward a sensitivity study was performed to investigate the influence of the total ozone content and effective temperature of the ozone layer on the AOD retrievals. The effective temperature is important for the calculation of the effective cross-section of ozone molecules for the absorption of UV radiation. The absorption of UV radiation strongly depends on the total ozone content of the atmosphere and therefore the contribution of the error in total ozone to the error in the AOD has to be determined. The results indicate that at 306.3 nm the retrieval of AODs is strongly affected by the effective ozone temperature. Therefore this temperature is taken into account for all AOD retrievals. To assess the influence of the total ozone content on the AOD retrieval, Figure 2.3-4 shows the relative differences between the AODs retrieved on the basis of an ozone column of 330 DU and those derived with the actual measured ozone column. From the calculations it follows that at a typical error of 1% on total ozone (for a well calibrated spectrophotometer) introduces an error in AOD of 3% at 306.3 nm and of only 0.4% at 320.1 nm.

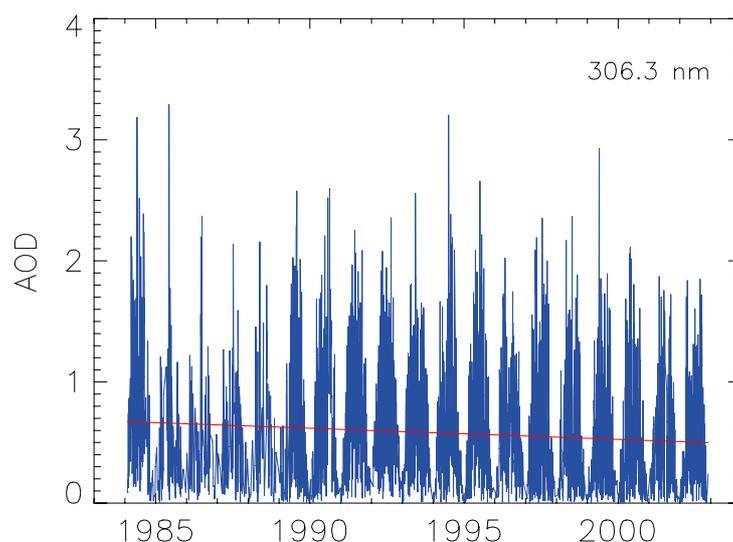


Figure 2.3-3: Aerosol optical depth at Ukkel, as it was derived from the standard direct sun ozone observations with Brewer 016. The straight line is the result of a linear regression.

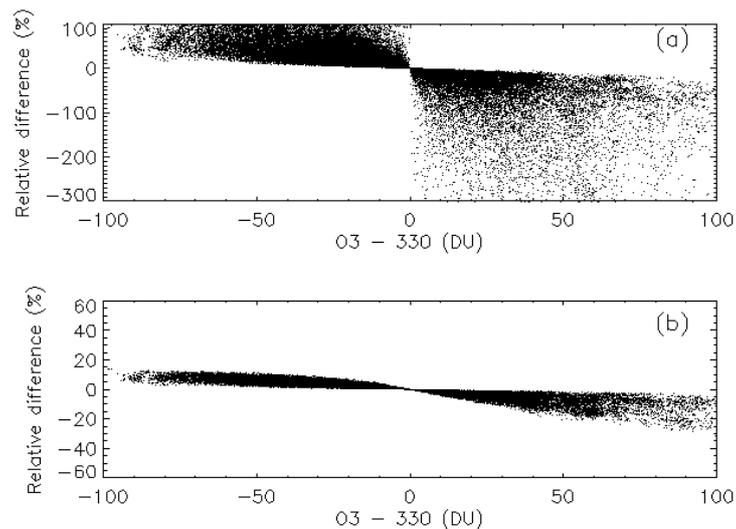


Figure 2.3-4: Relative differences between the AODs retrieved with and without the use of the measured ozone fluctuations in the atmosphere at (a) 306.3nm and (b) 320.1 nm.

A method was also developed to determine the calibration constants in a more objective way as compared to the technique described in Cheymol and De Backer [2003].

Detailed results were presented at a Workshop in 2003 and can be downloaded from <ftp://ftp.kmi.be/dist/meteo/hugo/posters/Brewer2003.pdf>.

As mentioned above a new spectrophotometer (Brewer 178) was installed in 2001, performing since then observations at the same location as instrument 016. This gave us the opportunity to compare the results of the AODs retrieved from the data of both instruments. Figure 2.3-5 shows a scatterplot of the AODs derived from data of both instruments. There is a high correlation: the correlation coefficient amounts to 0.9877. Also the bias between both data sets is low (less than 1%). This proves that the method used to determine AODs gives the same results when applied to different instruments, provided they are well calibrated. This will make it possible to retrieve AOD data from other Brewer instruments that have long time series of AODs with this validated algorithm.

Daily UV index predictions are made for Belgium (see section 3.4). The information on the AODs retrieved from the data at Ukkel can be used to determine the influence of the AODs on the actual UVI and eventually improve the predictions. Figure 2.3-6 show that the use of a daily mean AOD improved the forecasted UV index with respect to what is obtained with a monthly mean value.

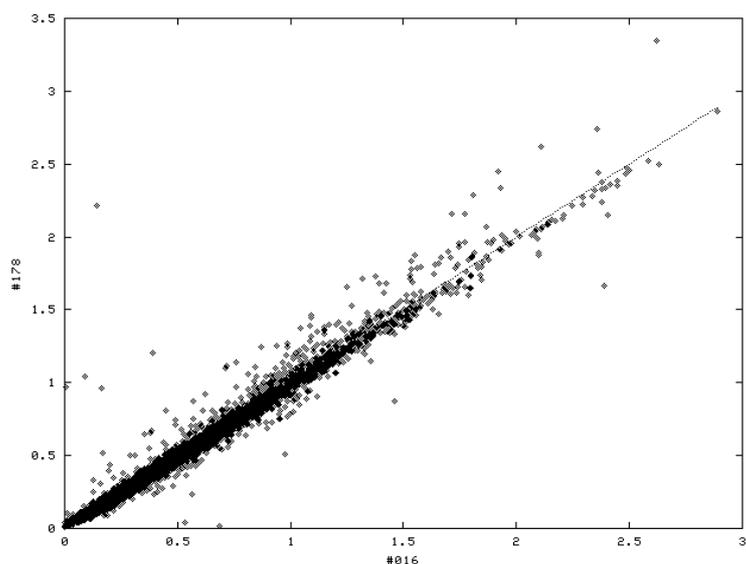


Figure 2.3-5: Scatterplot of AODs derived from observations with Brewer 178 as a function of those of Brewer 016 (crosses). The dashed line represents the ideal curve ($f(x) = x$).

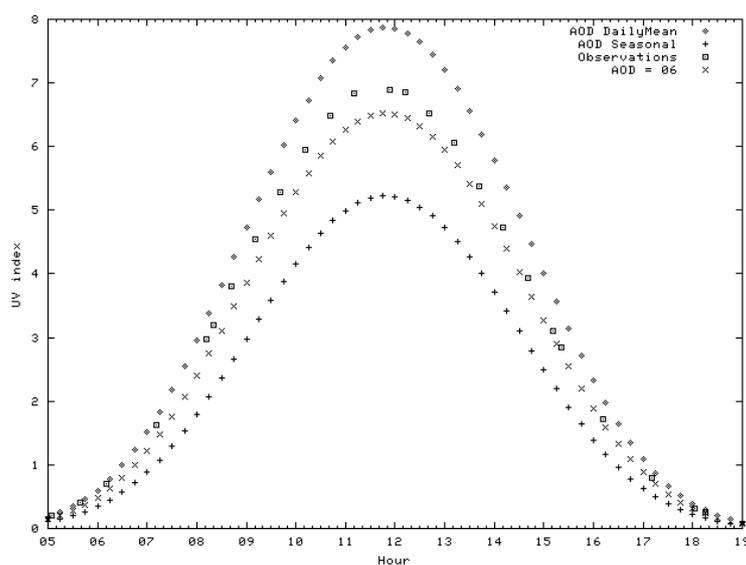


Figure 2.3-6: Observed UV indices (squares), UV indices forecasts with daily mean AODs (diamonds), UV indices forecasts with monthly mean AOD (plusses) and UV indices forecasts with a constant AOD (crosses) at Ukkel for 14 July 2003.

During the ESACII project, IASB-BIRA has also deployed new equipments and techniques for the monitoring of UV-Visible Solar Irradiances.

In 2004, a Bentham DTM 300 double monochromator has been installed at the Ukkel station. Together with the modified Jobin-Yvon HD-10 they constitute the core instruments of the station. Measurements are performed every 15 minutes between 280 nm and 500 nm with a step of 0.5 nm and a FWHM of 0.26 nm.

The Bentham spectro-radiometer was validate during the European CAMSUM campaign.

In 2003-2004, a set of two shadowed filter-radiometers (UVMFR-7 and MFR-7 from Yankee Environmental System) with respectively 7 channels in the UV (300-368 nm) and the visible (415-940 nm) were deployed at IASB-BIRA in Ukkel. In addition to the monitoring of global, diffuse and direct components of the UV-Visible solar irradiances, these instruments allow, by a Langley plot method, to access the ozone and aerosol column optical depths. These data are presently under validation.

Moreover during the ESACII period, a special care has been put on the determination and the characterisation of the cloud layers. Two instruments are deployed for this purpose a TSI (Total Sky Imager) providing the cloud cover (%) by the analyses of visible CCD pictures of the sky dome, and a CIR (Cloud Infrared Radiometer) that measures the temperatures of 1170 points of the sky dome and provides day and night the cloud cover (in octa's or %) and the mean altitude of up to three cloud layers.

A second station has been installed in 2004 at the Euro Space Center in Transinnes, (Belgian Ardennes) it includes broadband radiometers (UV-B, UV-A and TSP), a 5-channels filter radiometer (GUV-511c) and a meteo station providing the basic parameters (Temperature, pressure, relative humidity, pluviometry). It is operational since June 2004.

3. LONG-TERM OBSERVATIONS

3.1. FTIR observations at Jungfraujoch

Atmospheric-dedicated high-resolution solar observations have been regularly performed with Fourier Transform InfraRed (FTIR) spectrometers at the International Scientific Station of the Jungfraujoch (ISSJ) since the mid-1980's. This high-altitude facility, located in the Swiss Alps (46.5°N, 8.0°E, 3580m asl), has been selected in the late 80's as the FTIR component of the Primary Alpine Station of the Network for Detection of Stratospheric Change (NDSC, visit <http://www/ndsc.ws>).

Two NDSC-qualified FTIRs are currently operated at ISSJ, one homemade instrument build at ULg and a modified Bruker IFS 120HR. They record wide band spectra in the 2 to 15 μm domain with a maximum resolution of 0.0025 cm^{-1} . These observations encompass characteristic absorption features of more than two dozen atmospheric species. The spectrometric analysis of selected spectral regions (microwindows) with NDSC-recommended algorithms allows to determine total and, in many cases, partial column abundances of these gases. Those routinely monitored at ISSJ are listed in Table 3.1-1, together with an estimate of the precision of the retrieved total columns.

Table 3.1-1: List of constituents routinely retrieved from FTIR solar observations performed at the Jungfraujoch.

Reference gas:	N_2 (~1%)
Minor constituents:	CO_2 (<2%), O_3 , CH_4 ($\leq 2\%$), N_2O ($\leq 2\%$), CO ($\leq 3\%$)
Trace constituents:	
Halogenated source gas:	CCl_2F_2 ($\leq 4\%$), CCl_3F ($\leq 12\%$), CHClF_2 ($\leq 5\%$), CCl_4 ($\leq 15\%$), SF_6 ($\leq 25\%$)
Halogenated reservoirs:	HCl ($\leq 3\%$), ClONO_2 ($\leq 12\%$), HF ($\leq 3\%$), COF_2 ($\leq 10\%$)
Nitrogenated reservoirs:	NO ($\leq 5\%$), NO_2 ($\leq 6\%$), HNO_3 ($\leq 4\%$)
Other source gases:	C_2H_6 ($\leq 5\%$), C_2H_2 ($\leq 20\%$), HCN ($\leq 7\%$), OCS ($\leq 6\%$), H_2CO (monthly avg., $\leq 25\%$), H_2CO_2 ($\leq 12\%$)

Over the ESAC-II time period, 1134 days of attendance at the site have allowed to record FTIR observations under clear sky conditions during 541 days (at the end of May 2005). Despite a low yield in 2004 due to very bad weather conditions, we have obtained an average of 122 days of observations per year over the last four years, i.e. an excellent ratio of one day over three.

Hereafter, we give an overview of the results relevant to the Montreal and Kyoto Protocols.

Montreal Protocol relevant results (O_3 , NO_y , Cl_y , F_y)

The study of the evolution of the stratospheric chlorine loading over mid-latitudes has been pursued, in relation with the development of the organic chlorine burden (noted CCl_y) in the troposphere monitored by *in situ* international networks (AGAGE; <http://agage.eas.gatech.edu/> and NOAA/CMDL; <http://www.cmdl.noaa.gov/>) and to chlorine concentrations at the stratopause levels (50 to 55km altitude) derived from global observations made since October 1991 by the HALOE/UARS instrument. Further comparisons with results collected at other NDSC sites have also been performed and reported in the literature [Rinsland *et al.*, 2003].

Anthropogenic organic chlorine-bearing source gases (such as CFCs and HCFCs) with a sufficiently long lifetime are transported into the stratosphere where they undergo photolysis and reactions with OH and $O(^1D)$. Chlorine is then redistributed among several inorganic chlorine reservoirs (noted Cl_y , see equation), with conservation of chlorine atoms implying that Cl_y is equal to CCl_y when accounting for a time delay necessary to carry the source gases in the stratosphere, globally.

$$Cl_y = [HCl] + [ClONO_2] + [HOCl] + [ClO] + [OCIO] + [COCIF] \\ + 2 [Cl_2O_2] + [ClONO] + [Cl] + 2 [Cl_2] + [BrCl]$$

As shown by Zander *et al.* [1992, 1996], HCl and $ClONO_2$ are by far the most important reservoirs at mid-latitudes under normal background conditions (i.e. in absence of chlorine activation). Together, they account for more than 92% of the total inorganic chlorine abundance and their summation corresponds to a good Cl_y surrogate.

The upper frame of Figure 3.1-1 reproduces the monthly mean total column time series of HCl (red circles) and $ClONO_2$ (green triangles), as derived from the Jungfraujoch observational database; Cl_y (blue triangles) results from the summation of the corresponding HCl and $ClONO_2$ data points (update from Mahieu *et al.*, [2004]).

To avoid the influence of the significant variability affecting measurements in winter- and spring-time, these time series have been limited to the June to November months. Nonparametric least-square fits to these data sets are reproduced as thick black curves; they help to appraise the two-decade mean evolution of HCl, $ClONO_2$ and Cl_y . After a steady increase at a mean rate close to 4% during the 1986-1993 period, the Cl_y loading above the Jungfraujoch started to stabilize, with a maximum found in the second half of 1996. Since then, we have observed a slight decrease at a mean rate of -1 ± 0.3 %/yr, significant at the 1σ level despite the noticeable inter-annual variability present in the measurements.

The sum of the HCl and $ClONO_2$ contributions as deduced from 2-D model runs performed for 47°N by M. Chipperfield from the University of Leeds are also reproduced on Figure 3.1-1 (orange trace). They are based on the evolution of the relevant source

gas concentrations characterised by past measurements and by the predicted so-called "Ab baseline scenario" [WMO, 2003]. Overall, model results are in good agreement with the observations, particularly with respect to the time of occurrence of the maximum and subsequent yearly rate of change (close to $-1\%/yr$).

The long-term evolution of Cl_y is also consistent with the temporal development of the surface organic chlorine loading (see lower frame of Figure 3.1-1) as deduced from the AGAGE *in situ* measurements, when accounting for a time delay of about 3.5 years for tropospheric air to propagate and mix into the mid-latitude stratosphere. In addition, the CCl_y post-peak rate of change of about $-0.7\%/yr$ derived from the AGAGE data compares well with our findings and model calculations when taking into account the statistical uncertainties affecting these trend determinations.

These results confirm the stabilization of inorganic chlorine at northern mid-latitudes, followed by a slow decrease that is now statistically significant at the 1σ level. This demonstrates the appropriateness and proper implementation of the phase out scenarios imposed by the Montreal Protocol, its Amendments and Adjustments. Further measurements will be necessary to corroborate this tendency and to improve the precision of the decreasing trend determination.

Within the same context, monitoring of chlorinated source gases has also been part of our ESAC-II activities. Time series of CFC-12 (CCl_2F_2) and HCFC-22 ($CHClF_2$) have been updated while recent specific modifications implemented by ULg to the SFIT-2 algorithm have allowed performing retrievals of two additional species, i.e. CFC-11 (CCl_3F) and CCl_4 . Current monthly mean time series of three of these source gases are shown in Figure 3.1-2. Although year round data points are reproduced here, only averaged total columns of the quietest June to November months (filled symbols) have been used to characterise the long-term evolutions of these compounds. Corresponding trends and annual column changes are available in Zander *et al.* [2002, 2005]. It is interesting to point out here the contrasted evolutions of these source gases: (i) the Montreal-controlled CFC-11 and CFC-12 are decreasing/stabilising as expected from their respective lifetimes (45 and 100 yr); (ii) progressive phase out of HCFC-22 (an important CFC substitute) has begun in 2004 and its production is supposed to reach zero in developed countries in 2030; its concentration is expected to continue rising until about 2010 before stabilisation and rapid decrease thereafter [WMO, 2003]. Our measurements indicate a steady increase of the HCFC-22 total columns with recent rate of change still significant, on the order of $3\%/yr$.

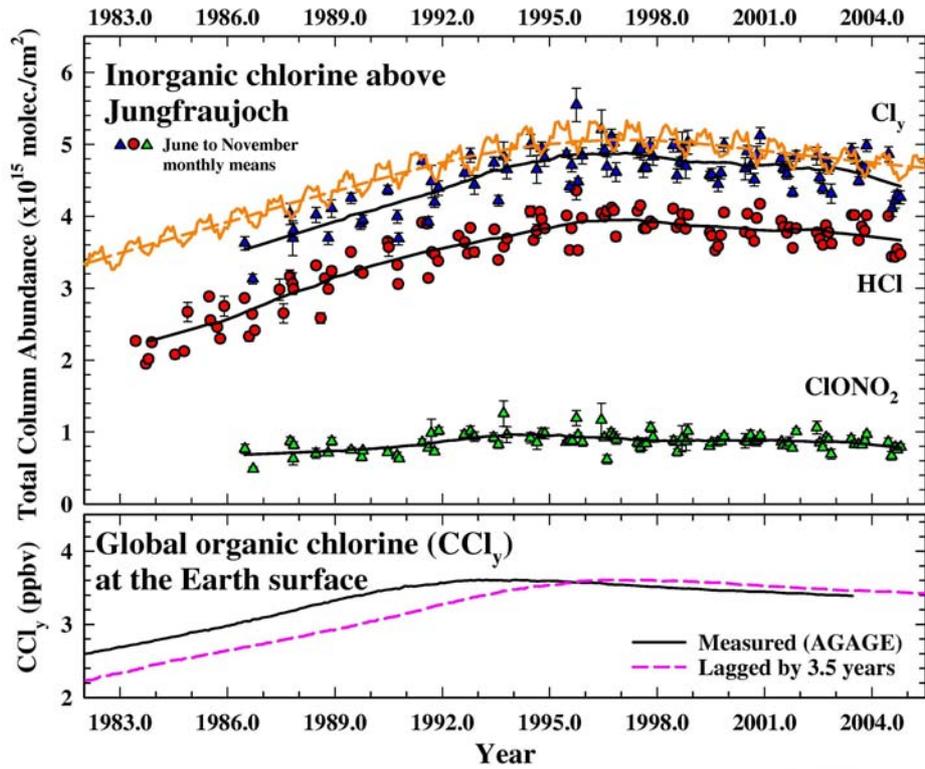


Figure 3.1-1: Top frame: timely evolutions of the monthly mean total columns of HCl, ClONO₂ and their summation, Cl_y above the Jungfraujoch station. The upper trace corresponds to the sum of the HCl and ClONO₂ columns calculated by the U. of Leeds 2-D model. Bottom frame: evolution of total surface organic chlorine derived from measurements performed by the AGAGE network.

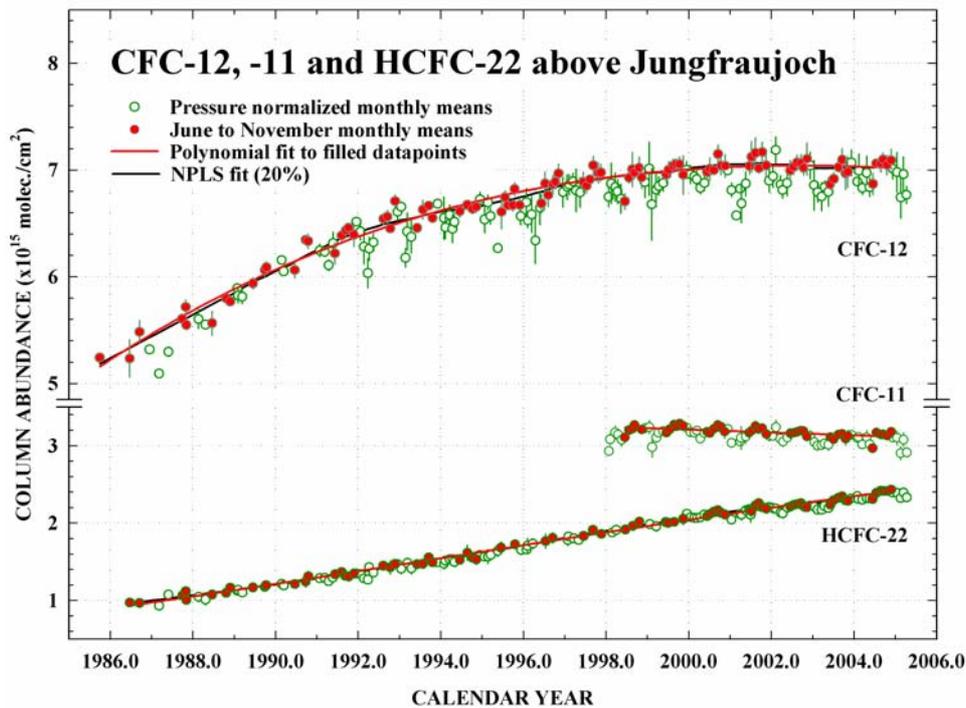


Figure 3.1-2: Contrasted evolutions of the monthly mean total vertical column abundances of CFC-12, CFC-11 and HCFC-22 above the Jungfraujoch.

Comparisons of the above results with findings deduced from *in situ* measurements performed by the AGAGE and NOAA/CMDL networks indicate very good agreement in terms of trends and atmospheric concentrations for these various species.

As recommended in various WMO-Assessments, the inorganic fluorine (F_y) budget evolution has also been given further attention, as Cl_y and F_y can help distinguishing between man-made and natural contributions to the stratospheric halogen loading. Among the three species to be considered here (HF, COF_2 and $COClF$), only $COClF$ cannot be monitored by FTIR. As it only accounts for at most 2% of the total F_y [Zander *et al.*, 1994a, Mahieu, 2001], the summation of the HF and two times the COF_2 loadings is an excellent surrogate to the total F_y burden in the stratosphere. Over recent years, we have noticed a slowing down of the F_y accumulation, with column changes amounting to 3% in 1997, 1.3% in 2002 and 0.6% in 2004. This has essentially resulted from the phasing out of important F-bearing source gases (CCl_2F_2 , CCl_3F , CFC-113,...), which at present have only been partially compensated by substitution products ($CHClF_2$, HFC-134a) [Anderson *et al.*, 2000; Anderson and Russell, 2004]. It is important to mention that, so far, U. Leeds 2-D model runs were unable to reproduce the long-term evolutions of these reservoirs as well as their partitioning, with overestimation of the COF_2 contribution to F_y . Likely causes for the latter discrepancy could be, e.g., a wrong assumption of how much COF_2 is produced from initial CFC decomposition and/or a too slow modelled photolysis rate for the conversion of COF_2 into HF.

Among NO_y budget relevant species (i.e. NO, NO_2 , NO_3 , N_2O_5 , HNO_3 , HNO_4 , $ClONO_2$, $BrONO_2$), the major daytime contributors HNO_3 , NO, NO_2 and $ClONO_2$ can be monitored by FTIR. Their summation thus gives a reliable evaluation of the NO_y loading above the site. Over the 1986-2004 period, only NO_2 presents a statistically significant annual trend of $[0.5 \pm 0.1]\%$, all other monitored nitrogenated species showing no significant long-term evolution over this two-decade time frame.

Measurements in support to the Kyoto Protocol (CO_2 , CH_4 , SF_6 , N_2O , HCFC, CFC)

In addition to the important greenhouse gases regulated by the Montreal Protocol, the 1997 "Kyoto Protocol on climate change" specifically targets CO_2 , CH_4 , N_2O and SF_6 which present characteristic IR absorption features allowing to quantify their atmospheric abundances. Regular analyses of all Jungfraujoch observations acquired during ESAC-II have resulted in updates of their temporal evolutions [Zander *et al.*, 2005]. Related time series, which cover now two decades, are reproduced in Figure 3.1-3.

The first obvious feature is the regular growth for three of these gases over the 1985-2004 time period, only methane exhibiting a stabilisation over recent years.

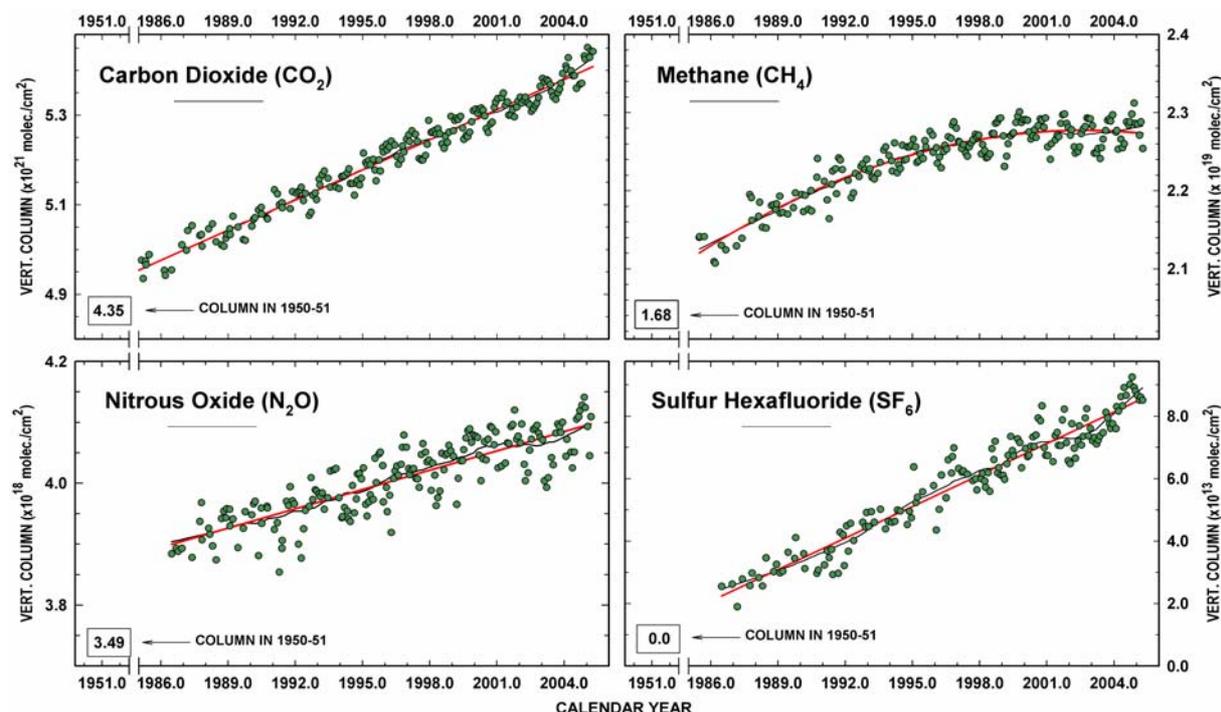


Figure 3.1-3: Long-term evolution of four species targeted by the Kyoto Protocol as derived from ground-based remote observations conducted at the Jungfraujoch station. Notice the different ordinate units for each frame.

Comparisons with abundances derived from pioneering observations performed in the early 1950s at the same site [e.g. Zander *et al.*, 1994b] indicate that the total columns of CO₂, CH₄ and N₂O have been respectively multiplied by 1.25, 1.35 and 1.17.

More specifically, trend determinations have indicated a yearly increase of 0.42% for CO₂, in excellent agreement with *in situ* surface measurements. The very long-lived nitrous oxide (120 yr) shows a similar behaviour, with an annual linear build up of 1.06×10^{16} molec./cm²; this corresponds to an increase of 0.26%/yr commensurate with *in situ* trend data.

Rapid increase of the total column abundance of SF₆ has been verified over recent years, with an annual load increase still exceeding 4%/yr in 2004. It is important to limit emissions of this compound to the atmosphere because it combines a very strong absorption of infrared radiation on a per-molecule basis with a very long lifetime of several thousand years [Ravishankara *et al.*, 1993; Mahieu *et al.*, 1996]. After conversion of total column to mean tropospheric SF₆ volume mixing ratios (vmr), time series from the NDSC sites Ny-Ålesund, Jungfraujoch and Kitt Peak have been compared with NOAA/CMDL northern hemispheric surface measurements [Krieg *et al.*, 2005]. Both techniques reveal comparable mean vmr increases when taking into account the uncertainties affecting the various datasets; extrapolations of linear and second-order fits to the Jungfraujoch data predict tropospheric SF₆ mixing ratios respectively equal to $[16.4 \pm 0.5]$ and $[14.7 \pm 0.6]$ in 2050, to $[28.2 \pm 0.9]$ and

[22.2±0.8] pptv in 2100 (actual concentration is close to 6 pptv). These values are significantly lower than those reported in recent scenarios [WMO, 2003], justifying future monitoring of this species to determine its effective future evolution and related climatic impact.

The levelling off observed for CH₄ will deserve future comparisons with models, to identify the relative contributions of changes in sources and sinks leading to this stabilisation.

Study of the variations of CO, observed at Jungfraujoch

CO anomalies observed in the northern hemisphere in 1998, 2002 and 2003 have been investigated in two recent studies coordinated by L. Yurganov [Yurganov *et al.*, 2004; 2005]. In the second study, time series derived from measurements performed at ground-based stations (by FTIR and *in situ*) and by the MOPITT instrument onboard TERRA have been collected and jointly used. They have revealed significant CO increases in summer and fall of 2002 and 2003 with respect to the unperturbed years of 2000 and 2001. Using a simple box model, extra CO emissions have been evaluated at 95 and 130 Tg, respectively in 2002 and 2003. Strong boreal fires that occurred in Russia during these two years are the most likely causes for the observed CO burden increases.

To enable a better understanding of the observed variability of CO above the Jungfraujoch, and of the discrepancies that have been observed in some seasons between the lowest layer volume mixing ratios derived from FTIR and *in situ* observations (see also Figure 2.1-3 of section 2.1) trajectory modelling studies using the programmes Flexpart and Flexstra (<http://zardoz.nilu.no/~andreas/flextra+flexpart.html>), as well as comparisons with Geos-Chem model results, in collaboration with I. Bey from EPFL (Lausanne). We have looked for signatures of vertical uplifting of boundary layer CO to the altitude of the Jungfraujoch station. It has turned out that the actually used tools do not have the appropriate resolution that is required to deal with the specific transport phenomena that occur in the high-alpine region. More appropriate modelling tools are available at EMPA (D. Fiolini *et al.*), and this activity will be pursued in collaboration with them.

3.2. (MAX)DOAS observations (O₃, NO₂, OCIO, BrO) at Jungfraujoch, OHP and Harestua

Observations of atmospheric trace gases have been regularly performed with UV-visible spectrometers at the International Scientific Station of the Jungfraujoch (ISSJ) (46.5°N, 8.0°E, 3580m asl) since 1990, at the Harestua Observatory (60.2°N, 10.8°E) in Southern Norway since 1994, and at the Observatoire de Haute Provence (OHP) (43.9°N, 5.7°E) in Southern France from 1998 until July 2002, and from January

2005. The ISSJ and OHP stations are major components of the Primary Alpine Station of the Network for Detection of Stratospheric Change (NDSC, visit <http://www.ndsc.ncep.noaa.gov/>), while Harestua is also affiliated to the NDSC with the status of Complementary Site.

The instruments operated by IASB-BIRA at these stations are UV-visible grating spectrometers measuring the zenith-scattered sunlight during morning and evening twilight periods. The retrieval technique is the Differential Optical Absorption Spectroscopy (DOAS), which provides vertical and/or slant column amounts of a number of trace gases (NO_2 , O_3 , BrO, OCIO, H_2CO , $\text{O}_2\text{-O}_2$, SO_2 , H_2O) having absorption bands in the 300-600 nm wavelength interval. At the Jungfraujoch, a SAOZ spectrometer designed by the French CNRS group is used, while instruments operated at other stations have been designed and assembled at IASB-BIRA. All spectrometers have been qualified for use in the NDSC, which means that they have successfully participated to one or several of the intercomparison campaigns regularly organised by the NDSC, the latest in date being the Andoya campaign organised in spring 2003 in Northern Norway [Van Daele *et al.*, 2005].

Monitoring of ozone and NO_2 total columns at the Jungfraujoch

NDSC-related UV-visible observations of stratospheric vertical columns of NO_2 and ozone have been conducted at the Jungfraujoch since 1990, using a SAOZ-type spectrometer [Pommereau and Goutail, 1988]. The original detector was a Hamamatsu PCD (photoconductive device) 512 diode-array detector. This was replaced in November 1991 with a Hamamatsu NMOS (negative metal oxide semiconductor) 512 diode-array detector having a better quantum efficiency and lower dark current, hence giving better signal to noise ratio. In December 1998 the SAOZ was upgraded to a 1024-pixel detector with a change in the grating from 200 mm^{-1} to 360 mm^{-1} . The slit width was increased from 25 to 50 μm , corresponding to 0.9 and 1.2 nm FWHM, resulting in an improvement of the sampling ratio from 2.4 to 3.5 pixels over the slit width and reducing the interpolation error.

The reduction of SAOZ data is performed using Windoas, a DOAS algorithm developed at BIRA-IASB for the retrieval of atmospheric trace gases from ground-based, balloon and satellite platforms [Van Roozendael *et al.*, 1999; Fayt and Van Roozendael, 2001]. In brief, the method uses non-linear least-squares fitting of the log-ratio of two atmospheric spectra (measurement and reference) to a set of molecular absorption cross-sections measured in the laboratory. The actual algorithm includes many advanced refinements, among which are capabilities for precise characterisation of both wavelength calibration and spectral resolution of the instrument, and calculation of the Ring effect based on Raman scattering modelling. In a special treatment designed for the SAOZ instrument, the slit function is determined for each spectrum and convoluted with the absorption cross-sections as

part of the DOAS fitting procedure. Total slant columns of NO₂ and ozone are derived in the 415-532 nm spectral window, taking into account additional absorption by O₄ and H₂O and converted in stratospheric vertical columns using climatological air mass factors (AMFs) appropriate for the Jungfraujoch location [Van Roozendaal et al., 1994, 1997, 1998]. Figure 3.2-1 displays the complete time-series of measurements currently available for both molecules. Interruptions in the time-series are associated to major instrumental failures. In particular, the transition to the new 1024-pixel detector system in late 1998 corresponds to a period of instability with several successive failures in between 1999 and 2001.

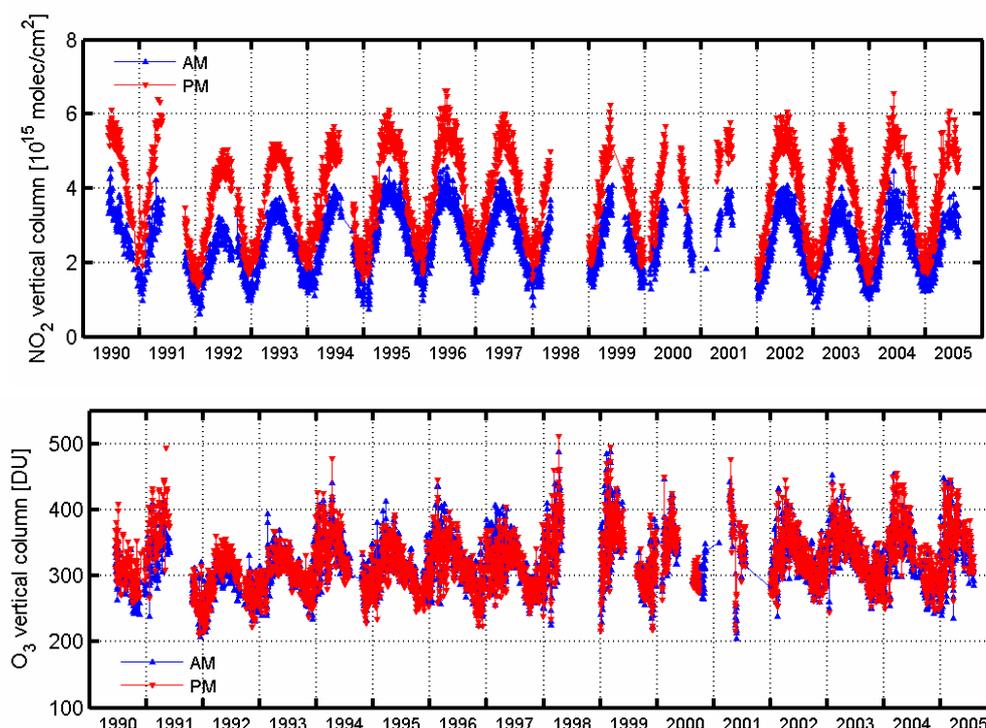


Figure 3.2-1: Evolution of the morning and evening twilight vertical columns of NO₂ and ozone recorded at the Jungfraujoch since 1990 using the SAOZ UV-visible spectrometer.

The monitoring of stratospheric NO₂ is an important adjunct to international efforts to monitor the health of the ozone layer, since NO₂ plays a significant role in the photochemistry of ozone. Spanning a period of 15 years duration, the Jungfraujoch NO₂ and ozone measurements allows characterizing the diurnal, seasonal, interannual and long-term variabilities of these trace gases for the Northern mid-latitudes. One of the longest duration time series of stratospheric NO₂ measurements is that from Lauder, New Zealand, which extends from 1980 to the present. Analysis of this record shows that the atmospheric column of NO₂ is increasing at approximately 5% per decade at 45° S [Liley et al., 2000]. Our measurements at Jungfraujoch as well as those from the mid-latitude site of Aberystwyth [Vaughan et al., 2005] show a similar trend, which is twice the rate of increase of nitrous oxide

(N₂O), its main source gas, and could be an indication of changes to the overall atmospheric circulation. Using a combination of photochemical and 3-D chemistry-transport models, McLinden et al. [2001] were able to show that the Lauder trend can be understood if the increase in N₂O is combined with the decrease in ozone, the change in odd nitrogen partitioning due to increased chlorine concentrations, and variations in volcanic aerosols. Continued measurements of NO₂ are necessary both to improve understanding of the photochemistry of ozone, and to help monitor and understand other critical atmospheric processes.

NO₂, O₃, and OCIO monitoring at Harestua

Total columns of NO₂ and ozone have been monitored at the Harestua observatory in Southern Norway since 1994. Measurements were first conducted on a campaign basis until January 1998 when a spectrometer was permanently installed.

The instrument operated at Harestua consists of two grating spectrometers mounted inside a thermally regulated box, covering respectively the visible region (400-550 nm) where NO₂ and O₃ are retrieved, and the UV range (330-390 nm) where BrO and OCIO columns can be measured. Both spectrometers are equipped with cooled low-noise diode-array detectors. The whole system has been designed and assembled at BIRA-IASB and is driven in a fully automatic way. Figure 3.2-2 displays the current time-series of NO₂ and ozone total column observations. These data are regularly submitted to the NDSC data base and used in various studies. In particular total ozone measurements are being exploited as part of the SAOZ polar sub-network in order to estimate the annual degree of ozone loss in the Northern hemisphere during polar spring. This is evaluated from comparisons between total ozone measurements and simulated data from the 3D models REPROBUS and SLIMCAT [Goutail *et al.*, 2005]. The climatology currently established over one full decade is displayed in Figure 3.2-3.

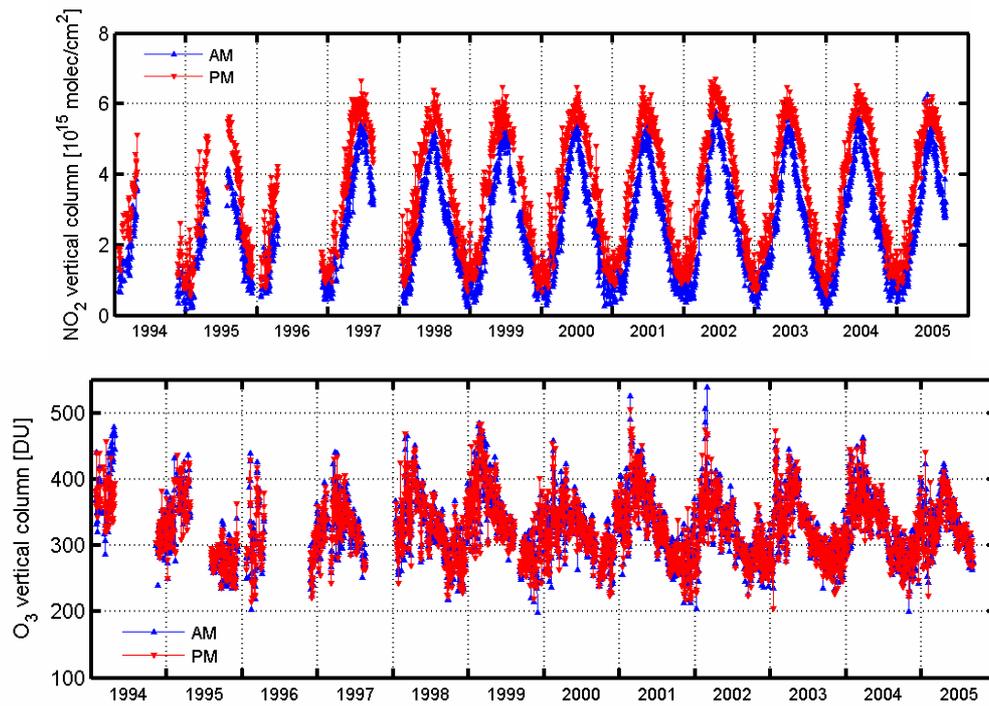


Figure 3.2-2: Evolution of the morning and evening twilight vertical columns of NO₂ and ozone recorded at Harestua (60°N, 10°E) since 1994 using a UV-visible grating spectrometer designed at IASB-BIRA.

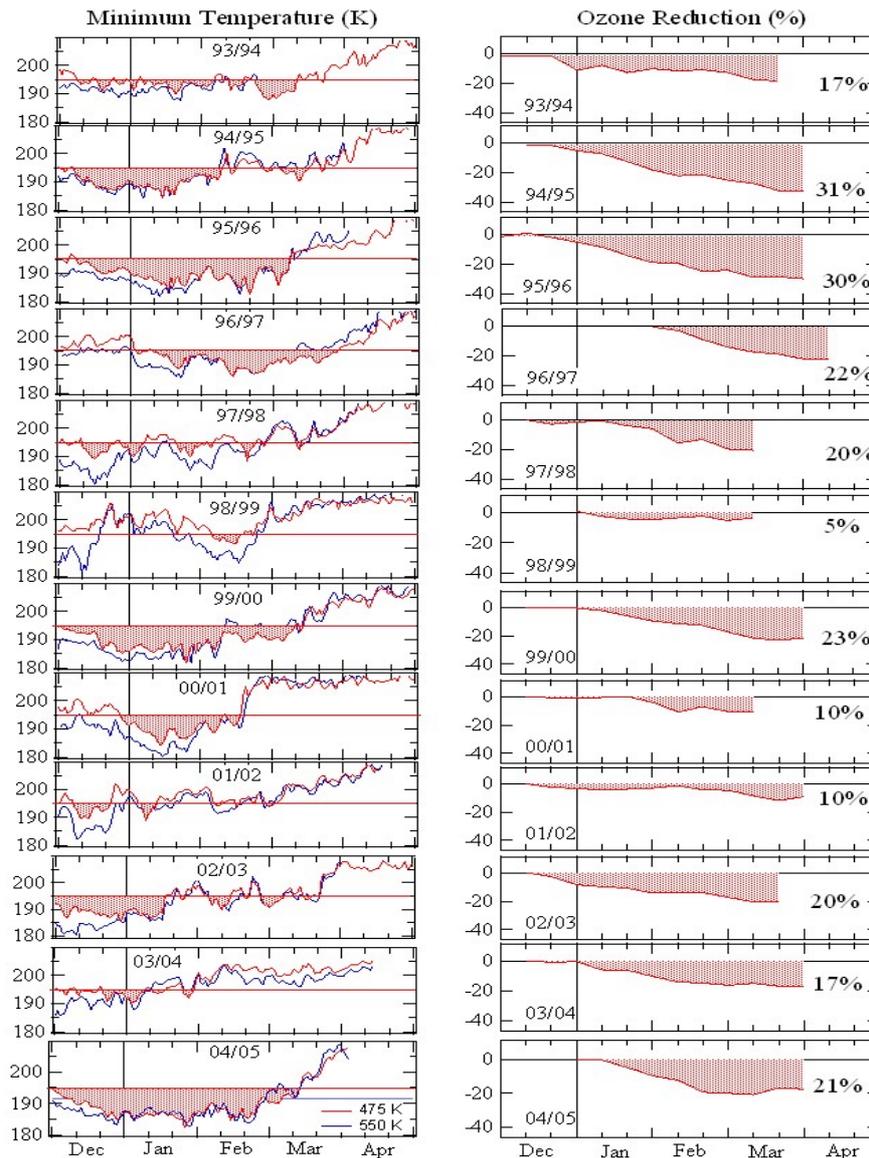


Figure 3.2-3: Left: minimum ECMWF temperature at 475K (red) and 550K (blue) north of 30°N and limits for NAT PSC formation. Right: Total ozone reduction in the vortex since 1993/1994 from the measurements of the SAOZ stations by comparison to the REPROBUS model.

The monitoring of ozone-related trace gases is complemented by measurements of two important active radicals: OCIO and BrO. OCIO is a direct indicator of the degree of activation of the chlorine gases which are responsible of the ozone loss. Its evolution since 1998 is displayed in Figure 3.2-4. Note that the largest chlorine activation observed so far was found in winter 2004-2005. This has been made in relation with the record cold conditions in the stratosphere during this winter (see Figure 3.2-3).

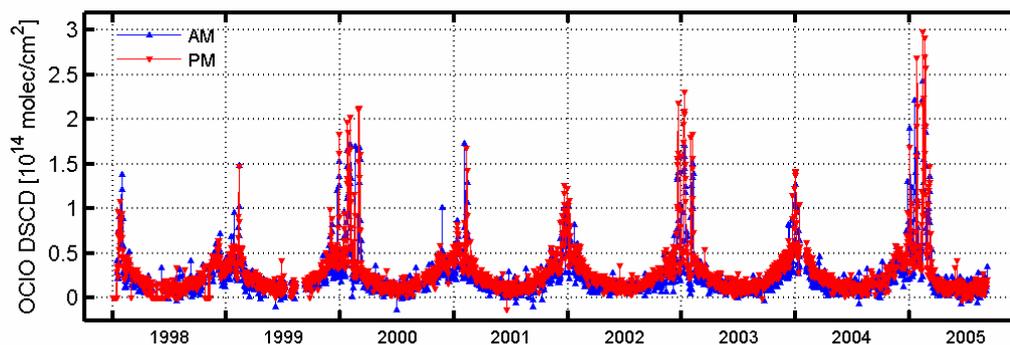


Figure 3.2-4: Time-evolution of the differential slant column of OCIO measured daily at twilight in Harestua (60°N, 10°E) since 1998. The variability of the chlorine activation from one year to another can be clearly identified and related to temperatures displayed in Figure 3.2-3.

BrO monitoring at Harestua and OHP

Although much less abundant than chlorine, stratospheric bromine presently contributes to the global ozone loss by about 25%, owing to its much larger ozone depletion potential relative to chlorine. This is why bromine emissions are controlled in the framework of the Montreal Protocol and its more recent Amendments. Hence it is important to monitor the bromine content at stratospheric altitudes and its long-term evolution. This can be achieved through measurement of BrO, the most abundant bromine bearing trace gas during the day. BrO differential slant column abundances, which have a large sensitivity towards the stratosphere [Aliwell et al., 2002; Sinnhuber et al., 2002], have been measured from Harestua since 1994, as well as from the mid-latitude station of OHP in the time period from 1998 until 2002. The measurements represented in Figure 3.2-5 display significant diurnal, seasonal and latitudinal variations, which are dominated by the chemical coupling between bromine and nitrogen families as well as by dynamical effects. The consistency between stratospheric BrO observations and current state-of-the-art 3D models of the atmosphere has been tested by Sinnhuber *et al.* [2002] leading to the conclusion that the chemical behaviour of bromine species is currently well understood. However the budget of stratospheric inorganic bromine appears to have been underestimated in past model studies likely due to incorrect estimation of the sources [Pfeilsticker *et al.*, 2000; Dorf *et al.*, 2005].

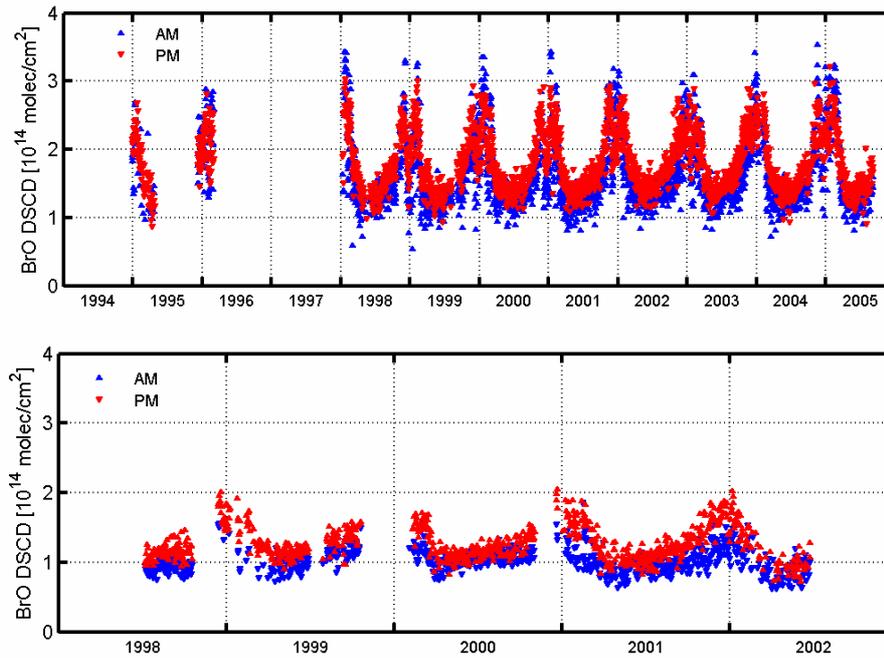


Figure 3.2-5: Time-evolution of the differential slant column of BrO measured daily at twilight in Harestua (60°N, 10°E) since 1994 (top panel), and in the period from 1998 until 2002 in OHP (44°N, 6°E) (bottom panel).

Using air mass factor and vertical profiling tools developed at IASB-BIRA (see section 2.2) the BrO slant column measurements from Harestua have been converted to stratospheric vertical columns. After additional removal of the strong signature from seasonal variations, the long-term evolution of the BrO column can be clearly identified as can be seen from Figure 3.2-6.

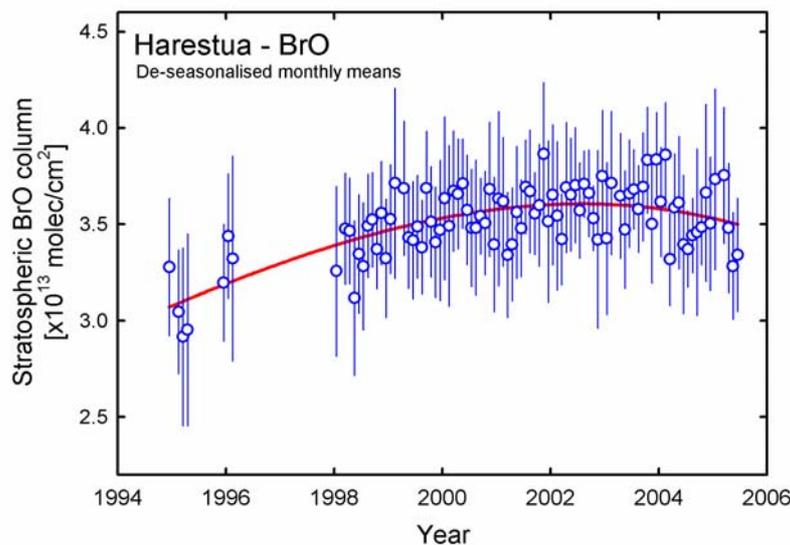


Figure 3.2-6: Time-evolution of the de-seasonalised stratospheric BrO vertical column derived over the 1994-2005 period from analysis of IASB-BIRA measurements at Harestua. The red curve represents a low order polynomial fit to the measurements.

Our observations indicate a positive tendency in the evolution of stratospheric bromine until 2002, followed by a stabilization and even first indications for a decline starting in most recent years. Taking into account the time lag associated to transport from troposphere to stratosphere (approximately 5 years), these observations are roughly in agreement with published measurements of the timely evolution of main bromine source gases at the earth surface which show a pronounced decline after 2000 [Montzka et al., 2003]. Continued BrO monitoring at Harestua will allow verifying in the next few years whether the decline of the bromine loading in the stratosphere can be confirmed.

3.3. O₃ measurements at Ukkel (sondes, Dobson, Brewer)

More than 600 balloon ozone soundings have been performed in the period January 2001 to June 2005. The total thickness of the ozone layer was measured almost daily with the Brewer spectrophotometers. On working days complementary measurements with the Dobson spectrophotometer were also made.

Due to the careful track of the calibration and other metadata the ozone observations at Ukkel could be homogenised and are useful for long-term trend analyses. For example the Brewer instruments were calibrated against a travelling standard instrument in 2003. Figure 3.3-1 shows the total ozone observations for the year 2004 in comparison with the long-term seasonal variation.

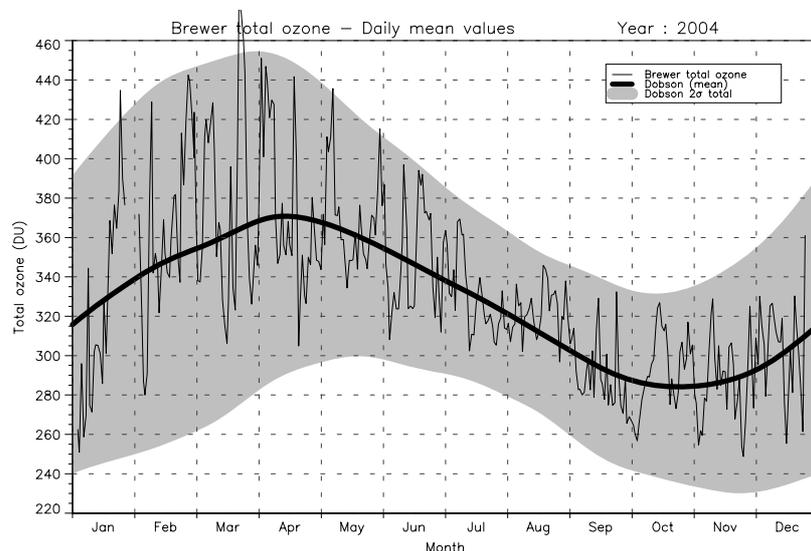


Figure 3.3-1: Evolution of the daily means of total ozone measured at Ukkel in 2004 with Brewer instrument 016, in comparison with the long term mean (1971-2003) and the standard deviation.

Over the more than 30 years of observations the changes in the ozone layer were not constant. It is generally accepted that the chemical depletion mainly started in 1980, when the anthropogenically produced chlorine compounds reached the

stratosphere. Recent analyses of the measurements of Cl and Br compounds in the stratosphere show that the maximum was reached in the second half of the 1990s. Therefore a piecewise trend is drawn through the data in Figure 3.3-2. This gives a trend of $-0.28 \pm 0.05\%$ and $+0.60 \pm 0.17\%$ per year for the periods 1981-1996 and 1997-2004, respectively. Although this shows that the first signs of a recovery of the ozone layer might be observed, one should be very cautious with the interpretation of trends calculated over relatively short periods like 1997-2004.

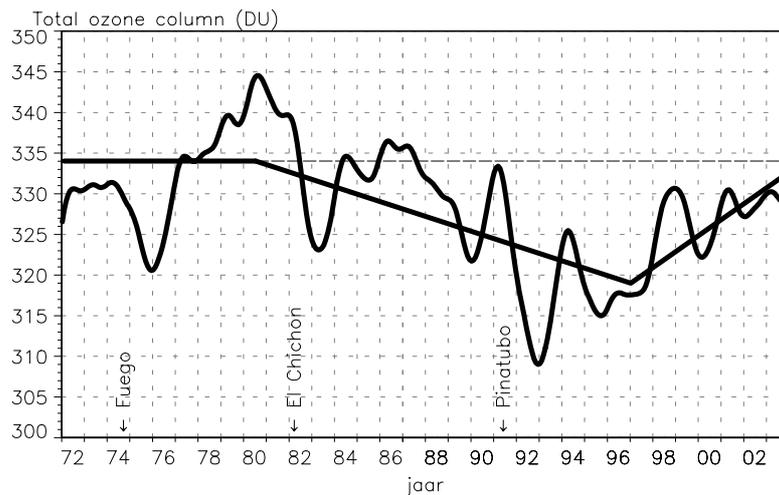


Figure 3.3-2: Running yearly means of the total ozone content observed with spectrophotometers at Ukkel, together with a piecewise trend line (see text for details). The times of the important eruptions of volcanoes is indicated with arrows.

The ozone profiles obtained with the balloon soundings allow us to get a picture of the heights at which the ozone trends occur. Figure 3.3-3 shows these trends. To make a better separation between the troposphere and the stratosphere a height scale relative to the tropopause is chosen as follows: positive values are km above the tropopause level, 0 is the tropopause and -10 is the ground level. Note that the mean tropopause level at Ukkel is about 9-10 km above mean sea level. The most important negative trends are seen in the stratosphere, especially during winter and spring. In the troposphere the trends are mainly positive. These differences are due to the different underlying processes. Ozone depletion in the stratosphere is mainly caused by the chemical reaction of chlorine and bromine compounds, while high ozone concentrations in the troposphere are related to photochemical reactions with pollutants (volatile organic compounds and NO_2).

The relation between the variability of the total ozone column and the general atmospheric circulation, especially in the lower stratosphere is an important research domain. Research at the KMI aids to estimate the influence of long-term changes of the air circulation on the ozone layer at mid-latitudes. Attempts are made to make a distinction between the changes caused by chemical and dynamical influences. The

observations of secondary ozone maxima in the stratosphere, obtained from balloon ozone soundings at Ukkel and with the SAGE instruments from space, were used to construct an index characterising the atmospheric circulation in the lower stratosphere. This index explains to a large extent the variability of the ozone concentrations in the lower stratosphere, and even for the total ozone column.

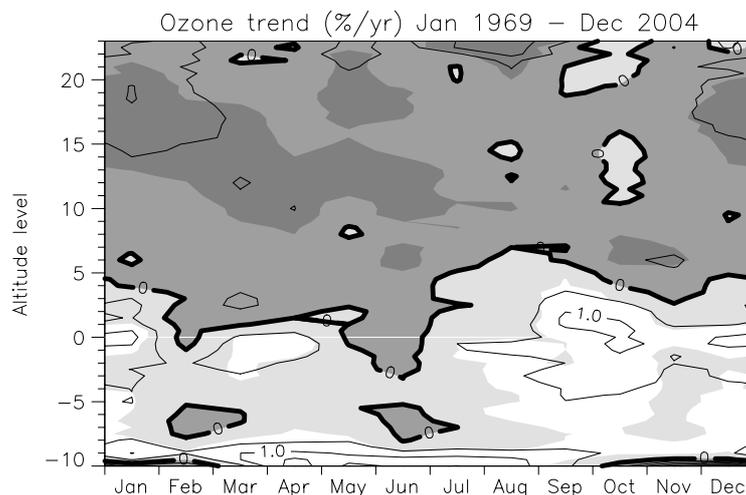


Figure 3.3-3: Height-season cross section of ozone trends as determined from the time series of ozone soundings at Ukkel. Light (dark) grey represent positive (negative) trends. The lightest (darkest) shades indicate the areas where the trend is statistically significant positive (negative). The height scale is relative to the tropopause level (details in text).

In the publication of Lemoine [2004] it is shown that up to 30% of the soundings performed during the months March, April and May experienced a secondary ozone maximum, but, although less frequent, they also occur in other periods of the year.

These maxima are related to planetary waves over mid latitudes, advecting layers with high and low ozone concentrations from different origins over a particular location. These conclusions could be drawn with the aid of trajectory calculations and were confirmed by analyses of potential vorticity fields.

Figure 3.3-4 shows that the distribution of the occurrence of the secondary maxima is not homogeneously distributed over a latitudinal band. The longitudinal differences are caused by the genesis and propagation of planetary waves, for example at the borders of the Atlantic Ocean.

The ozone profile observations were used for a study of the relation between tropospheric and meteorological parameters. These investigations were done through the research agreement MO/34/006 with the Belgian office for science policy, entitled "Studie van troposferisch ozon te Ukkel in relatie met meteorologische parameters". A statistical model was developed based on meteorological input and NO_x data. This relatively simple model could explain more than 60% of the variance

of ozone concentrations in the boundary layer at Ukkel (Delcloo and De Backer, 2005).

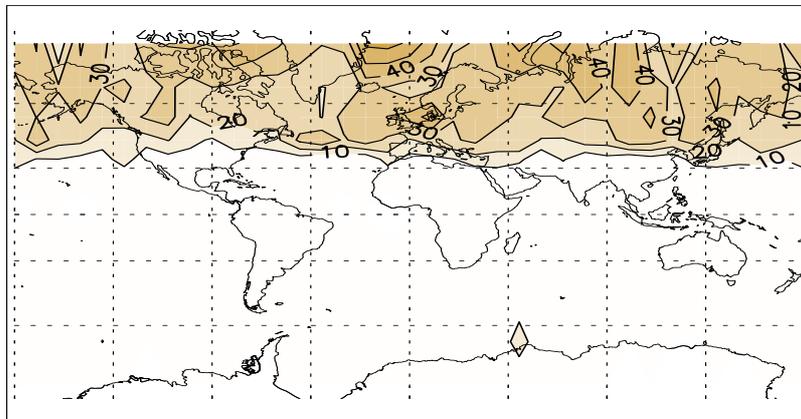


Figure 3.3-4: Geographical distribution of the secondary ozone maxima observed by the SAGE II instrument. The values represent the percentage of the profiles showing secondary ozone maximum, averaged for the months March, April and May over the period 1985-2000.

3.4. Spectral UV (climatologies, trends, UV index predictions)

Spectral UV measurements in the range 290-325 nm were continued with Brewer instrument 016. In September 2001 a double monochromator Brewer was installed and started also spectral UV measurements (286-363nm) from then.

The UV index for the next day is forecasted with a radiative transfer model. It is distributed to the media, where special attention is drawn to it during summer months (April-September).

Figure 3.4-1 shows the time series of the daily maxima of the UV index as measured with the Brewer instruments at Ukkel. Results of a spectral comparison of the data were already shown in Figure 2.3-3.

Spectral monitoring in the range 280-550 nm (with the modified Jobin-Yvon HD-10) and 280-500nm (with the Bentham DTM 300) were performed by IASB-BIRA during the all period. Figure 3.4-2 and Figure 3.4-3 illustrate the composite data base available in Ukkel and the time serie obtained at the EuroSpace Center.

With an available time series of about 17 years, it should be possible to investigate the long-term variation of UV-B effective doses (weighted for biological effects).

As confirmed by Figure 3.4-4, UV-B radiations are perfectly anticorrelated with ozone total column. Cloud corrections included in Figure 3.4-4 are performed taking into account the cloud measurements described above and the specific transmission UV spectra of each type of clouds.

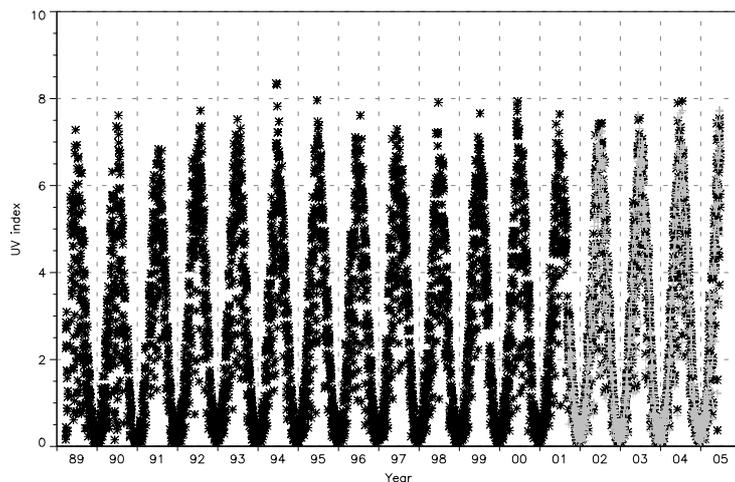


Figure 3.4-1: Time series of daily maximum of the UV index at Ukkel, as measured with Brewer 016 (black asterisks) and Brewer 178 (grey plusses).

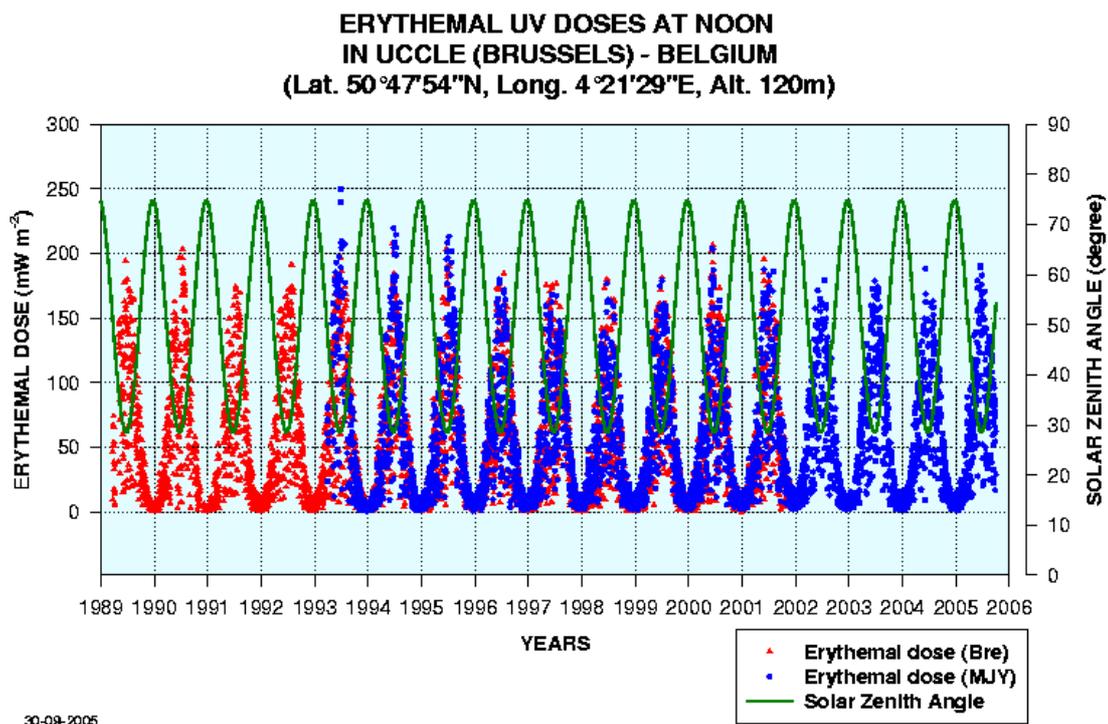


Figure 3.4-2: Erythemal UV doses at noon in Ukkel during the 1989-2005 period.

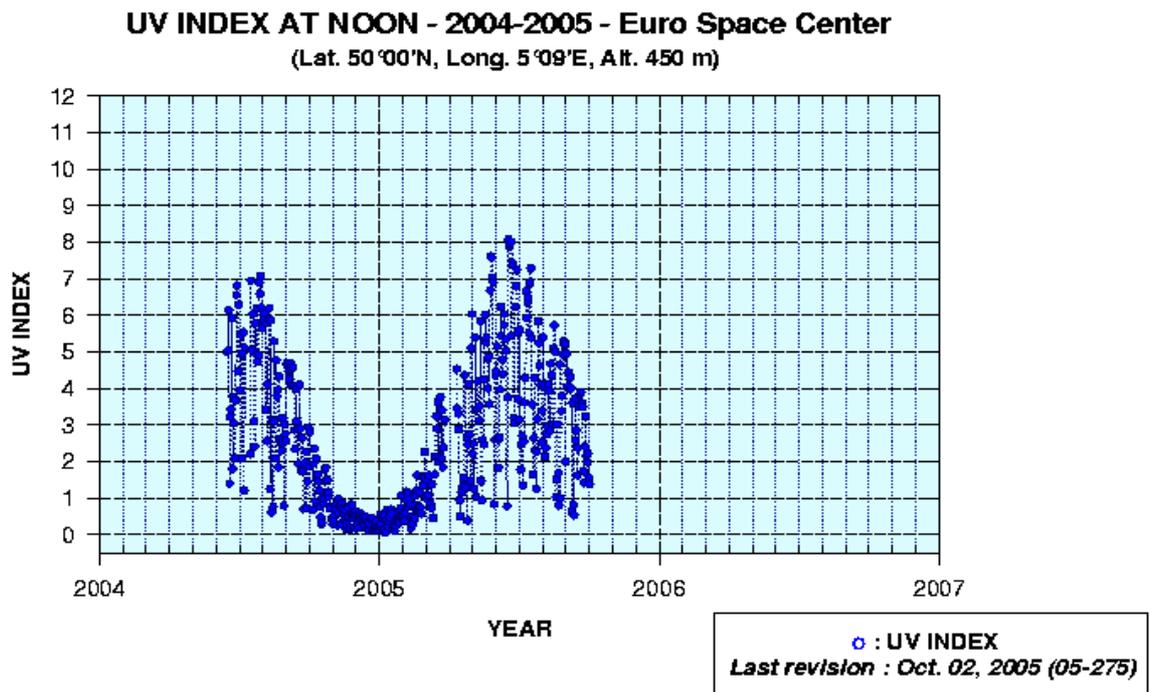


Figure 3.4-3: UV index at noon in Transinnes (Euro Space Center) during the 2004-2005 period.

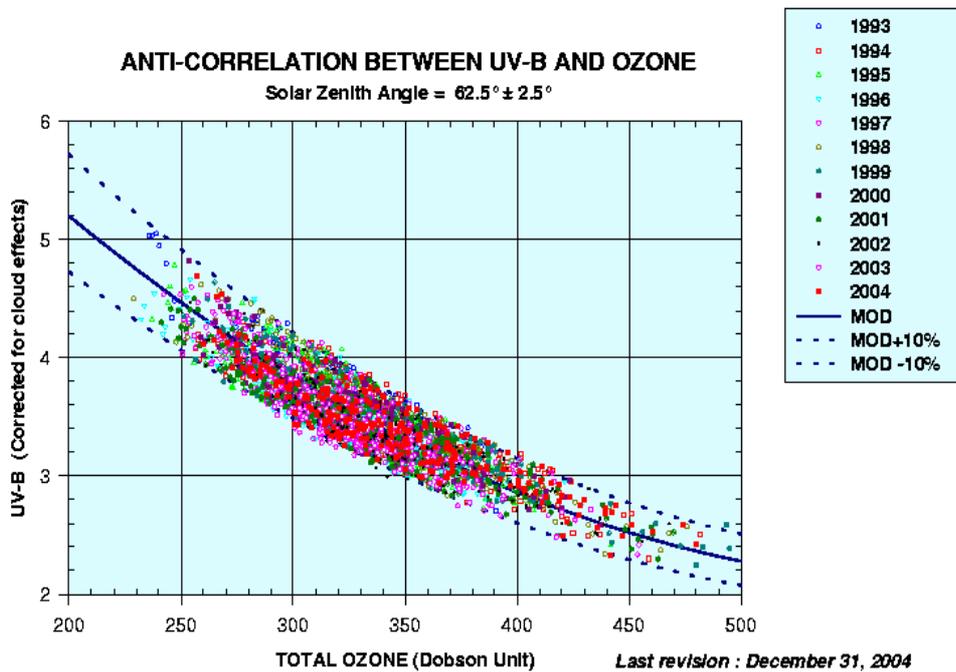


Figure 3.4-4: Anti-correlation between UV-B and Ozone in Ukkel during the 1993-2004 period.

Figure 3.4-5 and Figure 3.4-6 present the long-term variations of UV effective doses at noon in Ukkel over the all period (1989-2005), and during summer (April-September) and winter (October-March) periods. A linear fit gives a first estimation of these variations.

Due to the important variability of the UV-B measurements linked to the meteorological conditions, it seems fundamental to continue the efforts in this field of measurements in order to be able to predict more realistic trends value than we are able to produce today.

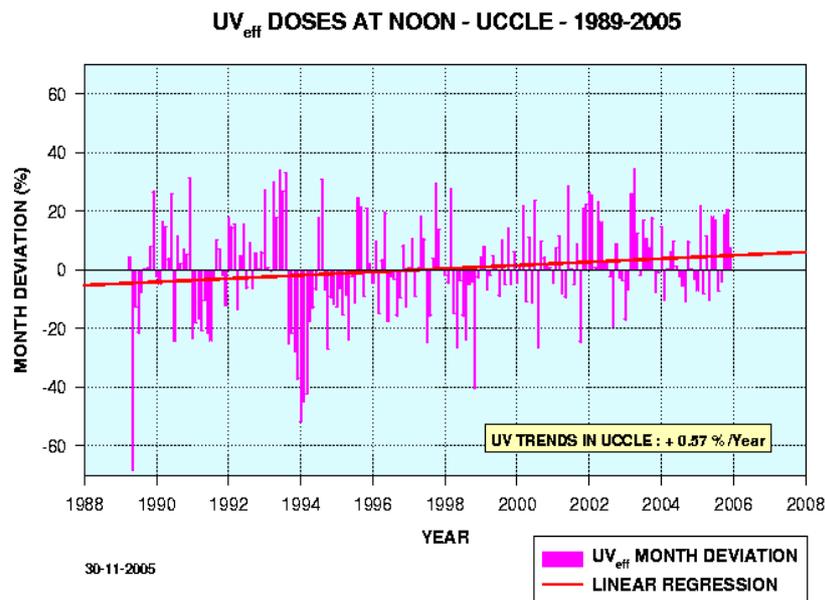


Figure 3.4-5: Variations of UV-B effective doses at noon in Ukkel during the 1989-2005 period.

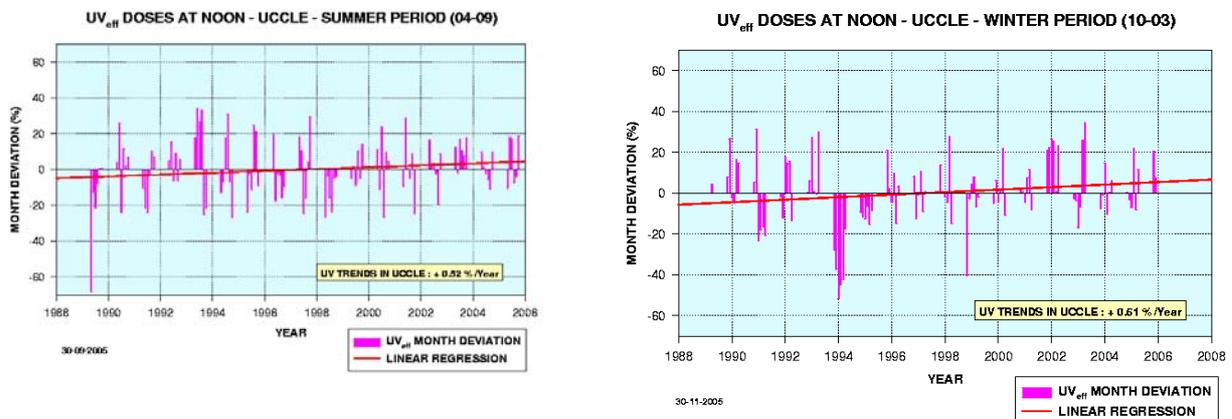


Figure 3.4-6: Variations of UV-B effective doses at noon in Ukkel during 1989-2005 for winter and summer periods.

4. CAMPAIGN OBSERVATIONS

4.1. At Ukkel (Brussels, 2001)

During the campaign (2002) at Ukkel data KMI-IRM collected of ozone profiles and columns. At the same time observations with other instruments were made by other institutes. The data were exchanged with the other partners. The humidity profiles were used by ULB to test the new algorithms to derive humidity profiles from spectral observations [Coheur et al., 2003].

A ground-based solar occultation measurement campaign took place at the Ukkel Plateau in Brussels, during 3 months in spring 2001. Spectra were recorded in cloudless conditions (clear sky days) and as far as possible from sunset to sunrise (SZA from 27 through 82). The sunlight captured by the solar tracker was split in two parts that were directed to two commercial portable high-resolution FTS Bruker IFS120M: one operated by the IASB-BIRA and the second one by the ULB, and dedicated to the IR and UV spectral regions respectively.

The campaign primarily aimed at instruments and software testing for future campaigns. The carried-out activities and the main outcomes are briefly summarized below:

- DOAS UV-VIS O₃ and NO₂ measurements were performed in the frame of the NDSC Arctic campaign (Andoya) preparation, and the analysis of the results includes assessment and validation of inversion algorithms developed at IASB-BIRA.
- The measurements and profiles retrievals of NDSC target stratospheric (HCl) and tropospheric (CH₄, N₂O) molecules allow testing the new IASB-BIRA FTS and acquiring expertise with the Sfit2 retrieval algorithm [Carleer *et al.*, 2002a].
- The good agreement between O₃ total columns retrieved from FTIR measurements in the 3µm micro-window and independent data (sondes and Dobson) obtained from the KMI-IRM validates the analysis method. Some discrepancies between O₃ and NO₂ column amounts retrieved from FTIR and low-resolution DOAS UV-Vis measurements remained however unexplained [Carleer *et al.*, 2002a].
- Water vapour retrievals in the visible spectral region were compared to humidity profiles obtained from balloon-borne PTU sondes launched by the KMI-IRM twice a week. The various retrievals performed in different conditions act as validation tests concerning (i) the choice of the database, of the resolution, of the best spectral interval, and (ii) the comparison of retrieval methods. Concerning the choice of the database, the better reliability of the BR Brussels-Reims database (see also V.2.1) compared to two other spectroscopic databases (HITRAN and ESA) was demonstrated, mainly because weak lines and air-broadening parameters are accounted for in our line list. Concerning the retrieval method comparison, the *SFSP*

inversion algorithm developed at BIRA-IASB was assessed and validated [Coheur *et al.*, 2003].

4.2. At Reunion Island

MAXDOAS measurements

Ground-based differential optical absorption spectroscopy (DOAS) measurements of the skylight scattered at zenith have a high sensitivity towards stratospheric absorbers, which makes them particularly well suited for stratospheric trace gases monitoring (see section 3.2). However, zenith-sky DOAS observation can be affected by trace gases in the troposphere, which potentially leads to an improper assessment of the stratospheric column:

1. Local pollution can cause strong increases in NO_2 column densities, which can lead to an overestimation of the stratospheric column if the tropospheric fraction of the NO_2 profile cannot be determined with sufficient accuracy.
2. A systematic bias between BrO vertical columns measured from ground and from satellite [Van Roozendaal *et al.*, 2002] indicates the possible presence of a global BrO background in the free troposphere and this tropospheric BrO background is expected to have a significant impact on measurements of the total column.

In order to overcome these difficulties and to extend the capabilities of the UV-visible technique, the multi-Axis- (MAX-) DOAS technique has been recently proposed. By observing scattered light not only from the zenith but also from sky close to the horizon, a long light path through the lowermost atmospheric layers and a strongly increased sensitivity to trace gases located close to the surface can be achieved (see Figure 4.2-1).

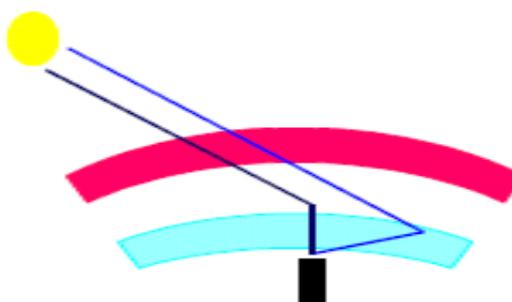


Figure 4.2-1: Sketch of the measurement geometry used by the MAX-DOAS instruments. With a scattering height in the middle troposphere, the zenith viewing measurement (black) is weighted towards the stratosphere, whereas the horizon viewing measurement (blue) has a large sensitivity to the layers close to the ground. In first approximation, the stratospheric light paths are the same for both measurement geometries, enabling the boundary layer concentrations to be derived.

As a result, MAXDOAS observations have the potential to derive independent information on the tropospheric and stratospheric parts of the measured columns.

During this project, a MAXDOAS instrument has been designed and operated at Ile de la Réunion (22°S, 56°E) from August 2004 until July 2005. Similarly, the spectrometer operated at OHP from 1998 until 2002 has been modified to allow multi-axis observations and re-installed on site in February 2005. In this report we concentrate on results obtained at Reunion Island. The Reunion instrument consists of a grating spectrometer equipped with a cooled (-40°C) CCD array detector from Princeton Inc. The wavelength range covered in the focal plane of the spectrometer extends from 296 until 450 nm, so that absorption bands from a number of trace gases can possibly be detected (NO₂, O₃, BrO, HCHO, SO₂, O₂-O₂, H₂O, IO). The spectrometer is connected to a telescope mounted inside an optical head that allows scanning of elevation viewing angles in a continuous way. Figure 4.2-2 displays an example of NO₂ slant column (SCD) measurements performed on 11 August 2004. Large enhancements observed for low elevation angles in the morning indicate the presence of significant amounts of surface NO₂ on this particular day. In its actual configuration the instrument allows measurement of NO₂ profiles (from the surface up to 40 km altitude), BrO columns separated into their tropospheric and the stratospheric contents, HCHO and SO₂ tropospheric columns. Additional information on the aerosol content might also be derived from analysis of the O₄ absorption.

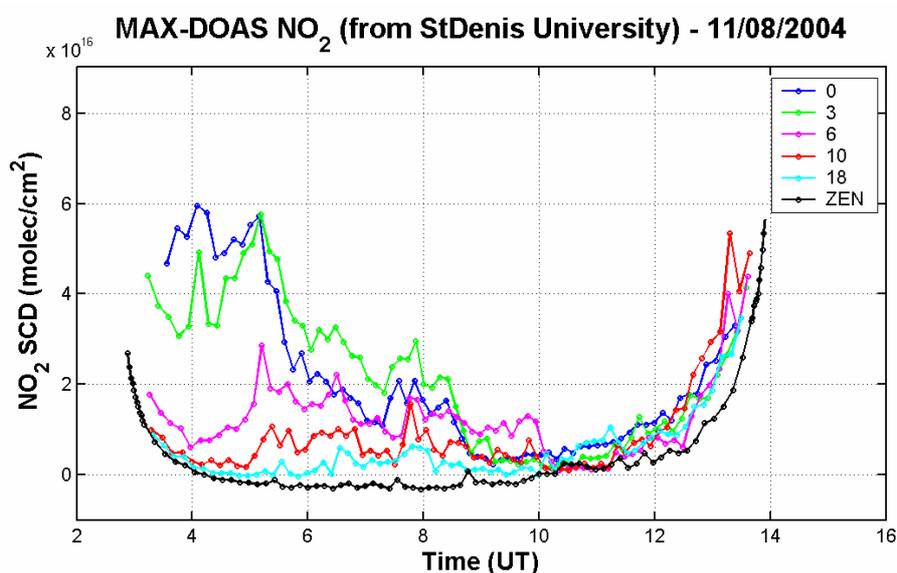


Figure 4.2-2: Example of NO₂ slant column (SCD) measurement performed on 11 August 2004 using the MAXDOAS instrument operated at Reunion Island (22°S, 56°E).

Inversion of stratospheric and tropospheric BrO vertical columns

As already mentioned in section 3.2, stratospheric BrO is an efficient catalyst of the ozone destruction, and is responsible for 50% of the Arctic seasonal ozone loss. However BrO has been shown to play a role in the troposphere as well, where it is responsible of ozone depletion events in the polar boundary layer [Wagner and Platt, 1998]. Moreover the suspected ubiquitous presence of BrO in the free troposphere with vertical columns of about $1\text{-}3 \times 10^{13}$ molec/cm² [Van Roozendael *et al.*, 2002] might have important consequences on our understanding of the free tropospheric ozone budget. Indeed recent modelling results have shown that this may represent a very strong sink for O₃ that has been so far ignored in most tropospheric chemistry studies [von Glasow *et al.*, 2004].

Based on an analysis of the full diurnal variation of the BrO slant columns, MAXDOAS measurements from Reunion Island have been analysed to infer the stratospheric and tropospheric BrO vertical columns. The analysis method relies on a validated forward model accounting for the transfer of the multiply scattered radiation in a pseudo spherical atmosphere and the diurnal variation of the stratospheric BrO modelled using recent photochemical reaction coefficients (JPL 2000) [Hendrick *et al.*, 2005]. An example of the resulting fit is displayed in Figure 4.2-3.

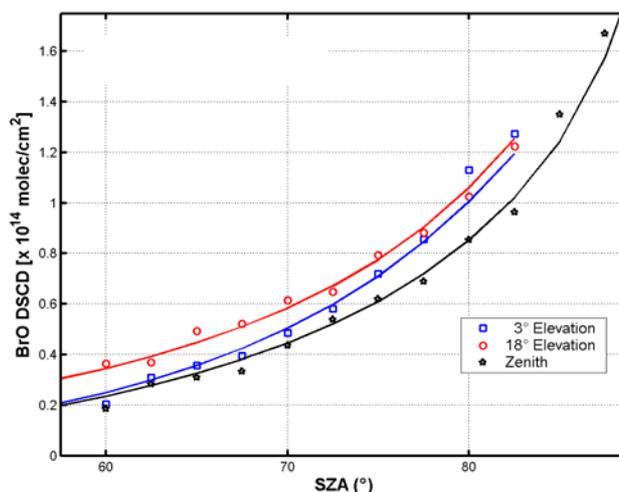


Figure 4.2-3: Fitting of the diurnal variation of BrO differential slant columns (DSCD) measured at Reunion Island in Spring 2004, using a dedicated forward model developed at IASB-BIRA (see text). The different behaviours of the measured DSCDs at zenith, 3 and 18 deg of elevation provide information on the bulk altitude of BrO in the troposphere.

The time-series of retrieved stratospheric and tropospheric BrO columns is displayed in Figure 4.2-4 for the complete period of measurements conducted at Reunion Island. Results confirm the existence of a small but systematic content of BrO in the free troposphere (bulk altitude around 6 km). These results will be used for validation of total BrO measurements from the GOME and SCIAMACHY satellite instruments.

They will also be confronted with model simulations of both stratospheric and tropospheric BrO.

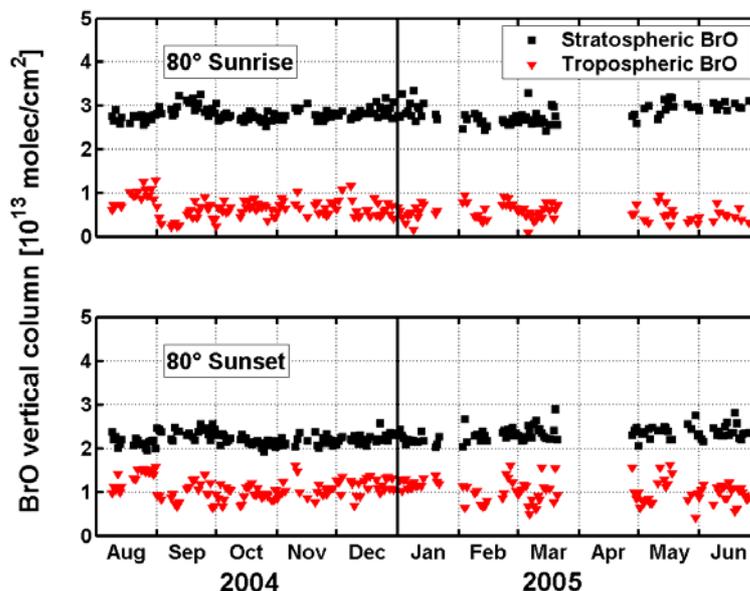


Figure 4.2-4: Stratospheric and tropospheric BrO columns retrieved from daily analysis of BrO slant column measurements performed in 2004-2005 at Reunion Island (22°S, 56°E).

FTIR campaigns

Development of BARCOS

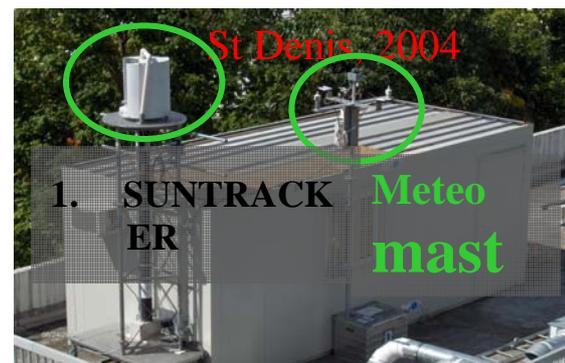
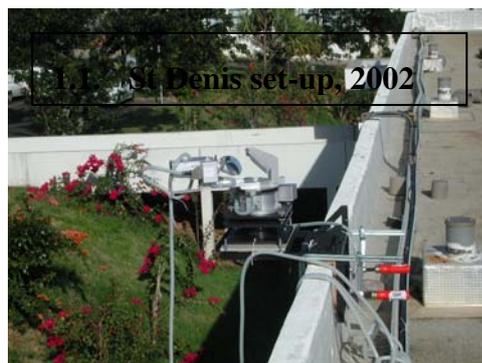
BIRA-IASB has acquired an IFS120M Bruker Fourier transform spectrometer (FTS) by the end of 2000, with a two-fold objective: (1) to be able to perform high-resolution spectroscopic laboratory measurements, complementary to and in collaboration with ULB, and (2) to perform atmospheric campaign measurements. For the latter purpose, we have developed a system for remote control and automatic operation of the instrument, called BARCOS (Bruker Automatic and Remote Control System). The system has been designed for performing atmospheric absorption measurements, using the sun or any other light source in the sky (moon, or possibly stars), without human assistance at the site. BARCOS includes the spectrometer with its operating software (OPUS), a sun tracker that has been developed in collaboration with Denver University, and a small meteorological station to control the meteorological conditions for operating the instrument. A data logger keeps track of the meteorological and other housekeeping data. An automatic liquid nitrogen filling system has been added, for cooling the infrared detectors. BARCOS also includes the possibility to perform calibration cell measurements – automatically or remotely controlled. The control S/W is written in Labview. BARCOS is a flexible system, allowing manual interventions at any time. To run BARCOS effectively, the only prerequisite is that Internet access is available at the site of operation. The complete H/W and S/W configuration of BARCOS has been described in [Neefs et al., 2005].

BARCOS was used successfully during two measurement campaigns at Ile de La Réunion, that are further discussed in the next section.

FTIR Campaign measurements

Two FTIR measurement campaigns have been held at the Ile de La Réunion (21°S, 55°E) in the ESACII time period, one in September-October 2002, and one from August to end of October 2004, in a collaboration between BIRA-IASB, ULB and the Laboratoire de Physique Atmosphérique from the Université de La Réunion.

The campaigns had several objectives: (1) implementation and verification of BARCOS, (2) verification of the feasibility of FTIR solar absorption measurements at this tropical site, (3) preparation of long-term monitoring at Réunion Island, in the frame of NDSC. Ile de La Réunion is already a complementary site of NDSC with O₃ soundings, and SAOZ and LIDAR measurements; additional FTIR observations are strongly encouraged by the NDSC, to contribute to filling the measurements gap in the tropics. An additional particular objective of the second campaign was to contribute to the validation of the ACE/Scisat experiment, launched in August 2003, in which three ESACII partners (BIRA-IASB, ULB and ULg) are strongly involved.



In the first campaign, two quasi-identical Bruker IFS120M instruments have been operated, namely the ULB one at the campus of St Denis (50 m asl) and the BIRA-IASB one at the Maïdo mountain site at 2200 m asl. At the latter site, we had to operate completely autonomously. BARCOS was implemented for the BIRA instrument, in its first phase of the development. The reason for having both instruments operating simultaneously was two-fold: (1) verify which of both sites is most appropriate for the measurements, and (2), perform some altitude-differentiated measurements.

The results from the first campaign have indicated that the small loss of information in the spectra recorded at St Denis because of the higher water vapour contamination, does not justify the significantly higher effort and cost of going to the Maïdo site, as long as there is no infrastructure available at that site. Therefore, the second campaign was performed at St Denis with only one FTIR instrument (the BIRA-IASB

one), with BARCOS in a near-complete phase of development. During the second campaign, the BIRA-IASB MAXDOAS instrument has also been installed at the St Denis campus and continued its measurements until mid-2005 – see Section 3.2.

The first campaign provided good-quality data during the month of October 2002. The second campaign provided data for about 63 days in the August to end of October 2004 period. Regular HBr cell measurements have been performed during both campaigns to verify the instrument alignment – as required by the NDSC IRWG data quality protocol. Preliminary profile retrievals have been performed for a number of species, for both campaigns, including HCl, HF, HNO₃, O₃, CO; they have been presented at various meetings (e.g., the NDSC Infrared Working Group meetings in 2003 and 2004), and on posters in some international workshops. An example of ozone profile retrievals in comparison with correlative data from a local ozonesonde and from the ACE-FTS satellite experiment is given in Figure 4.2-5 and Figure 4.2-6 shows the time series of the O₃ total column measurements during the 2004 campaign.

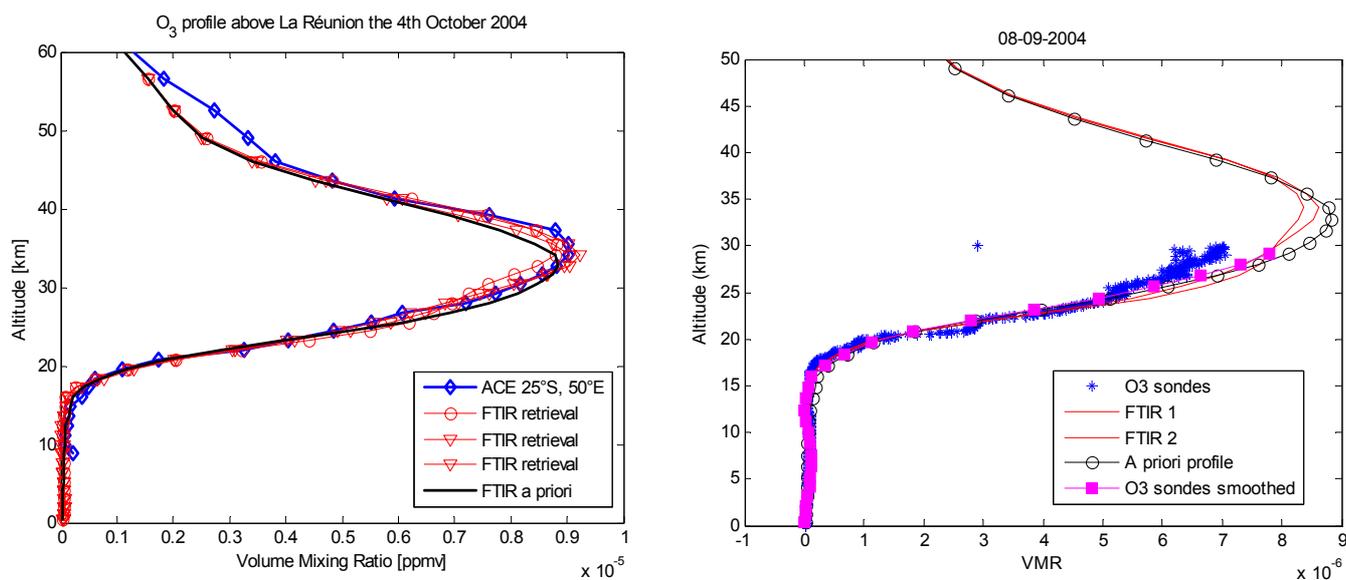


Figure 4.2-5: Comparisons between FTIR O₃ profiles above Réunion Island, and a correlative profile measured by ACE-FTS, on October 4, 2004 (left hand side) and a correlative O₃ sonde profile, on September 8, 2004 (right hand side). Both the ACE and sonde profiles have been degraded to the resolution of the FTIR retrieval.

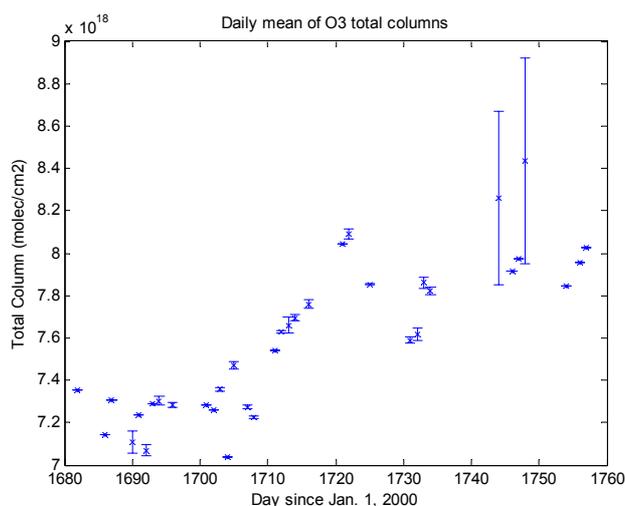


Figure 4.2-6: Time series of O₃ total column abundances from the FTIR observations between August 7 and October 26, 2004.

The campaign data analysis (profile retrievals and geophysical interpretation) is still ongoing. The data will be used in the frame of the EC SCOUT-O3 IP, and for satellite validation. Before submitting them to the NDSC database, a quality assessment must be performed according to the NDSC IRWG data quality protocol.

After the 2004 campaign, it was been decided to refurbish the solar tracker, among others to improve the alignment of the instrument and its stability. This work is nearly completed at present.

The perspective is to have at least one additional campaign with a fully operational BARCOS system in 2006 or 2007, before installing an instrument permanently at the Maido site in the NDSC infrastructure that is planned to become available in 2008.

5. LABORATORY DATA

The main objective of this work was to obtain high quality spectroscopic data of atmospheric species, i.e. line parameters (positions, intensities, pressure broadening coefficients, pressure-induced shifts, assignments) and absorption cross-sections. In order to deliver atmospherically usable data, it is important to conduct the measurements under temperature and pressure conditions similar to those existing in the Earth's atmosphere, and also to understand the pressure and temperature dependence of the line parameters. The ESAC II project was dedicated to improve the existing databases, to lower uncertainties and to resolve discrepancies between data sets. The molecules studied during this research period were: H₂O and one of its isotopologue HDO, H₂CO (formaldehyde), and NO₂ (nitrogen dioxide), with a special emphasis put on H₂O as can be seen from Table 5.1-1. The gaseous molecules were measured under different conditions of pressure of the pure gas, of air mixtures and of nitrogen mixtures in the IR, NIR, VIS and UV ranges using FTS's.

5.1. Experimental conditions

The laboratory measurements performed during the ESAC II project are listed in

Table 5.1-1. Absorption spectra were recorded at room temperature using two commercial portable high-resolution FTS Bruker IFS120M: one belonging to the ULB and the other one having been recently purchased by the IASB-BIRA. They both operate from the IR to the UV and display the same characteristics, except the maximum resolution, which is better in the case of the newly bought instrument (0.003 and 0.008 cm⁻¹ respectively). Both instruments are equipped with a variety of light sources, beam splitters, optical filters and detectors, to cover the desired spectral ranges. In experiments N°5 and N°6, the two FTS's were operating in parallel in order to acquire data simultaneously in two different spectral regions, whereas in experiment N°1, the aim was to inter-compare and inter-calibrate both spectrometers, in particular to characterize the new instrument.

The measurements were carried out at the Université de Reims Champagne-Ardennes (France), in collaboration with the Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA). They involved the coupling of the spectrometers with two long path absorption cells, manufactured by the GSMA. The first one is 50 m long and can cover optical path lengths up to 2 km. The second one, which is 5 m long and can reach paths up to 300 m, has the advantage to be temperature controlled.

Table 5.1-1: List of laboratory experiments performed in the frame of the ESAC II project.

Date	Molecule	Spectral range (cm ⁻¹)	Resolution (cm ⁻¹)	P _{tot} (hPa)	Path length (m)	Ref
1	H ₂ O, H ₂ O+air [§]	2400-26000	1, 2	0.7 → 400	600	(a)
2	H ₂ O, H ₂ O+air	2400-11000	0.015	4 → 356	200 → 1200	(b-e)
3	09/2001- H ₂ O, H ₂ O+air	8500-23000	0.03, 0.06	10 → 500	600	
4	01/2002 HDO [#] , HDO + N ₂	8500-23000	0.03, 0.06	2.5 → 804	600	(f, g)
5	H ₂ CO [§]	28000-39000	1	0.03 → 0.27	21	(h)
		2800-3200	0.005			
6	NO ₂ , NO ₂ +air [§]	9000-26000	1	0.03 → 618	20	(i, j)
		2000-4000	0.005			
7	06-07/2004 H ₂ CO	1300-3900	0.004-0.005	0.02 → 0.33	20	
8	08/2004 H ₂ O	6000-10000	0.028	5 → 16	200 → 1000	(k)

§ 2 FTS's coupled (see text)

mixture of H₂O/D₂O/HDO

(a) Carleer *et al.*, 2003 (b) Coheur *et al.*, 2002 (c) Fally *et al.*, 2003 (d) Mérienne *et al.*, 2003 (e) Tolchenov *et al.*, 2005 (f) Mérienne *et al.*, 2001 (g) Bach *et al.*, 2005a (h) Daumont *et al.*, 2003 (i) Vandaele *et al.*, 2002 (j) Vandaele *et al.*, 2003a (k) Jenouvrier *et al.*, 2004.

Table 5.1-1 provides the general experimental conditions for the various target species. Further details can be found in the references mentioned. The treatment of the spectra was performed using a number of programs, most of them home-made and running on personal computers, in particular bfit, Wspectra and Winprof.

5.2. Water vapour

As can be seen from Table 5.1-1, particular attention was paid to the study of the water vapour molecule and one of its isotopologue HDO during this work. Water vapour plays a unique role in atmospheric physical and chemical processes. It is not only the most abundant greenhouse gas, i.e. the most important absorber of outgoing thermal radiation, but it is also responsible for about 70% of the atmospheric absorption of the in-coming radiation (see for example [Bernath, 2002] and references therein). Discrepancies between models and observations of the average absorption are attributed to several reasons among them: errors in the water line intensities, myriad of weak water lines missing in the widely used databases whose integrated intensities could contribute significantly, water continuum, weakly bonded pairs of water molecules (H₂O)₂ or water dimers (WD) ([Vandaele *et al.*, 2003b] and references therein). The need for improved spectroscopic parameters for this molecule is therefore widely recognized and this work constitutes an important contribution to this crucial issue.

In continuation of our previous work initiated in the frame of the ESAC I project, in particular the analysis of data recorded during two substantial measurements campaigns held in '98 and '99, this study focuses on three aspects: (i) H₂O Vis.-NIR line parameters (26000-9250 cm⁻¹), (ii) HDO visible-NIR line parameters (23000-11500 cm⁻¹), and (iii) H₂O visible-IR continuum (2500-25000 cm⁻¹). The main results and conclusions are depicted below.

H₂O visible-NIR line parameters

By combining the measurements obtained during three campaigns, performed in many different experimental conditions of resolution, pressure, absorption path lengths,... the Brussels-Reims collaborative group provides a new homogeneous and extensive experimental database. The BR linelist, comprises 16400 lines covering the 26000-9250 cm⁻¹ spectral region and providing positions, intensities, self-broadened widths, N₂ and air-broadened widths, N₂ and air-broadened pressure shifts, and assignments. These data are available in electronic format from the Service de Chimie Quantique et Photophysique website (<http://www.ulb.ac.be/cpm>).

An overview of the water absorption spectrum is presented in Figure 5.2-1. This figure shows 5 overlapping regions corresponding to the different experimental set-up (combination of detectors, lamp, filters) used to cover the whole spectral range investigated. Very weak and very strong lines are observed, pointing out the unusual wide range of intensities covered by the lines (5 order of magnitude) and the resulting difficulty of analysis.

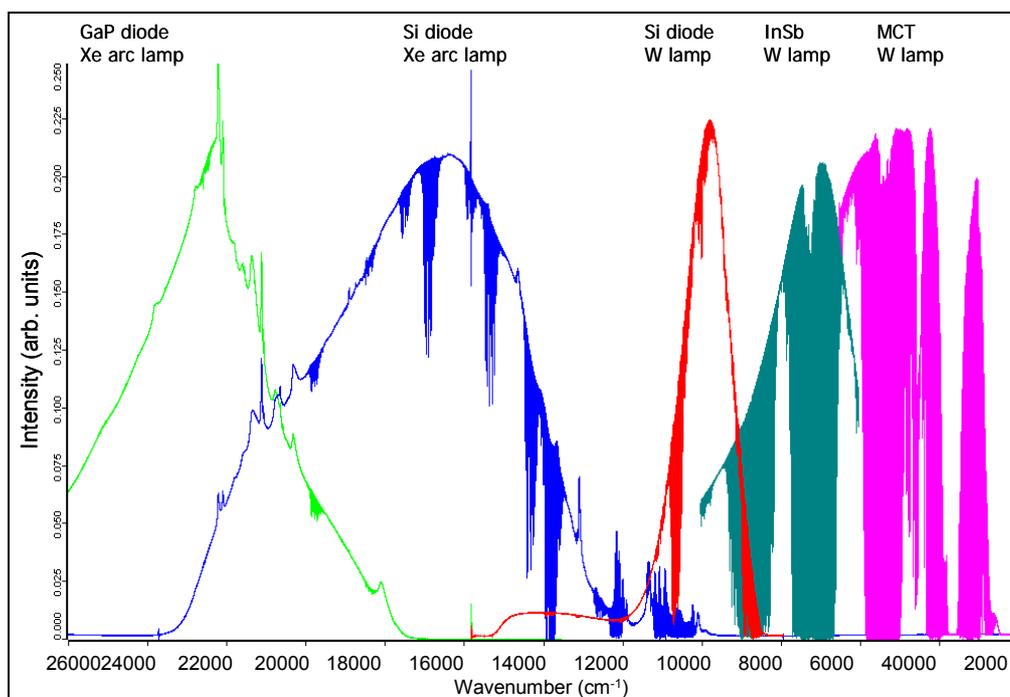


Figure 5.2-1: Raw spectrum of pure H₂O.

Three companion papers were published [Coheur *et al.*, JQSRT, 2002; Fally *et al.*, 2003; Mérienne *et al.*, JQSRT, 2003], in which the complete BR linelist has been compared in detail to existing literature data, in particular to the HITRAN spectroscopic database. The main conclusions of this work were the following:

(i) the main improvement in the line parameters concerns the weak lines in the blue region ($26000\text{-}20000\text{ cm}^{-1}$), (ii) some parameters, e.g. pressure-induced frequency shifts are reported for the first time, (iii) the integrated absorption cross section is larger by a few percent, and (iv) the great advantage of the BR linelist lies both in the broad spectral coverage and the consistency of the dataset.

The quality of the data was also assessed through retrievals of H₂O columns from ground-based Fourier Transform visible solar absorption spectra recorded in Brussels during spring 2001 [Coheur *et al.*, 2003]. Several microwindows between 14000 and 18000 cm^{-1} , containing water lines well isolated from solar lines and other atmospheric gases absorptions, were examined. It was shown that the use of the BR database in atmospheric models allows a better reproduction of the atmospheric spectra than the HITRAN 2000 database, especially at large zenith angles, where the weak lines contribute significantly and where accurate values of air-broadening parameters are needed (see Figure 5.2-2). An evaluation of four water vapour spectroscopic databases also concluded to the better quality of the BR line intensities data [Veihelmann *et al.*, 2002].

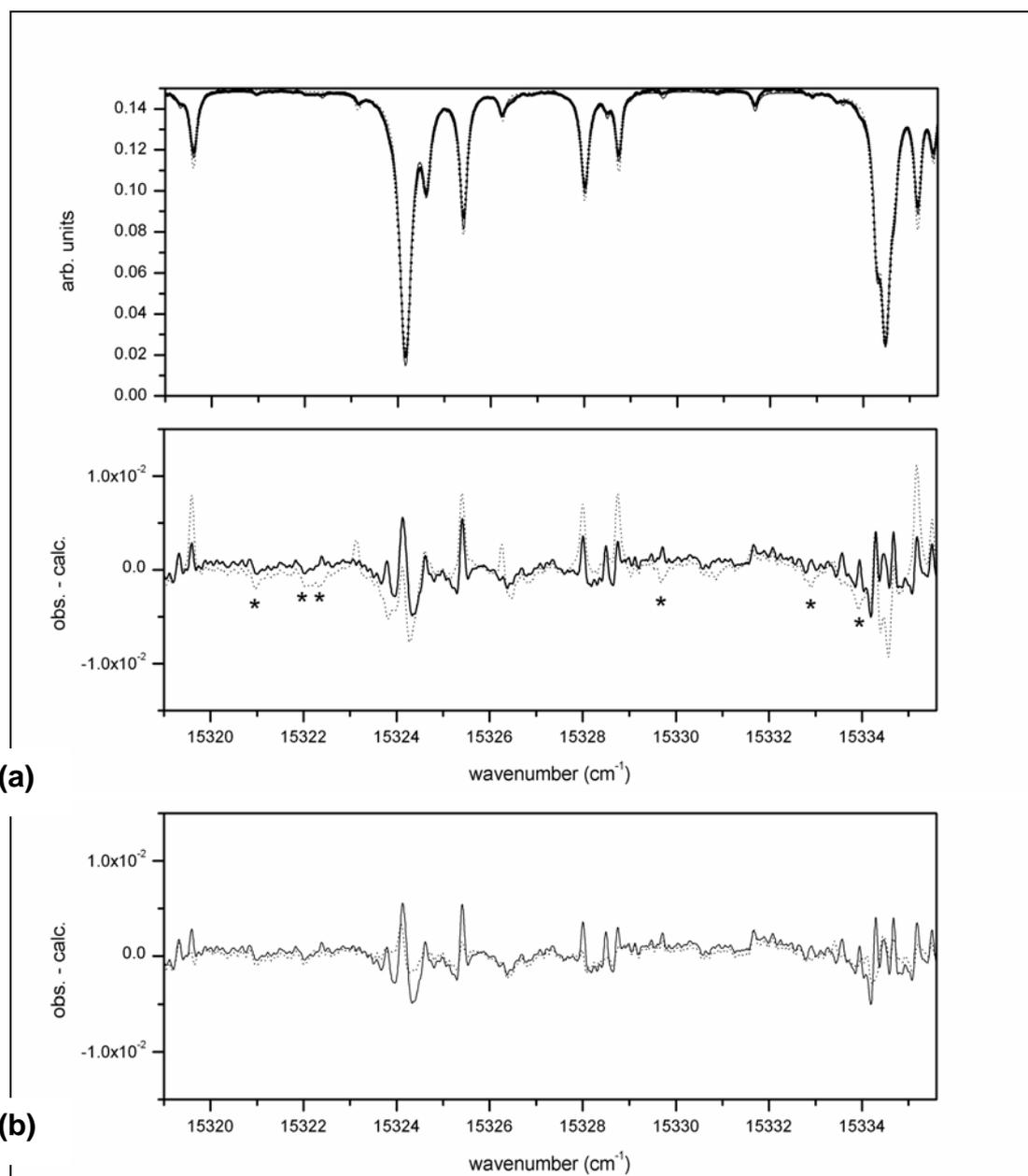


Figure 5.2-2: Retrieval of the water column from a spectrum measured at large zenith angle (81.76°) on the 25th of June (dots), using (a) HITRAN (dotted line) and BR (solid line) and (b) BR (solid line) and the updated list with measured air-broadening parameters (dotted line). In the residuals of Figure V.3a, asterisks are used to mark some of the weak lines not listed in HITRAN. The RMS values of the fits are the following: RMS[HITRAN 2000] = 0.10 10⁻¹, RMS[BR] = 0.33 10⁻², RMS[updated BR] = 0.12 10⁻².

According to the arguments given above, and to a general agreement by the scientific community, the BR data were partly included in the 2004 edition of HITRAN and the 2003 edition of GEISA worldwide databases (<http://cfa-www.harvard.edu/hitran> and <http://ara.lmd.polytechnique.fr/>) [Rothman *et al.*, in press; Jacquinet-Husson *et al.*, 2003].

On the basis of the BR experimental line parameters described above, a complete overhaul of the rotation-vibration spectrum was performed in collaboration with the theoretician group of J. Tennyson (University College, London, UK) [Tolchenov *et al.*, 2005]. First, several techniques, including variational nuclear motion calculations, were used to generate three synthetic linelists. Second, assignments were made using an expert system for automatic identification of rovibrational spectra. Finally, a systematic re-labelling exercise was undertaken. Over 15000 lines were assigned to transitions involving more than 150 excited vibrational states; twelve new vibrational bands origins were determined, and a further sixteen were estimated. Also, blended lines were identified and future improvements were pointed out. These data are available in the Journal of Molecular Spectroscopy supplementary material archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

The analysis of the infrared part ($< 9250 \text{ cm}^{-1}$) of the water vapour absorption spectrum is in progress and ongoing results have been and will be presented at several international congresses [Jenouvrier *et al.*, 2004; Tashkun *et al.*, 2005, Jenouvrier *et al.*, 2005].

HDO visible-NIR line parameters

The presence and detection of absorbing HDO lines was first investigated in the visible region ($22800\text{-}16300 \text{ cm}^{-1}$). More than 1300 lines could be identified over a 6000 cm^{-1} wide spectral region, and 410 lines were assigned to the OH stretching overtone bands $5\nu_3$, $6\nu_3$ and $7\nu_3$ plus combination bands [Jenouvrier *et al.*, 2001]. Due to the simultaneous presence of all three isotopologues in the measurements cell, through the chemical equilibrium $\text{H}_2\text{O} + \text{D}_2\text{O} \leftrightarrow \text{HDO}$ in the gaseous phase, it is very difficult to extract, identify, and analyse HDO lines, as well as to calculate correctly the partial pressures. An original procedure has been developed and the different steps to extract HDO lines are described in detail in [Bach *et al.*, 2005a]. The main phase consists in eliminating the H_2O lines by subtracting from an experimental absorbance spectrum a synthetic spectrum at the same pressure and resolution.

Figure 5.2-3 presents a raw HDO spectrum. A linelist of experimental parameters in the visible-NIR ($23000\text{-}11500 \text{ cm}^{-1}$) has been recently constructed by the BR group [Bach *et al.*, 2005a]. The list contains positions and absorption cross sections of more than 3000 lines, and, for many of them, N_2 -broadening coefficients as well as N_2 -induced frequency shifts are given. These data are available in the Journal of Molecular Spectroscopy supplementary material archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm). Assignments are in progress through collaboration with theoreticians from Russia and United Kingdom [Bach *et al.*, 2005]. The need for such data is largely recognized by the scientific community, and this region is entirely missing in the HITRAN 2004 database.

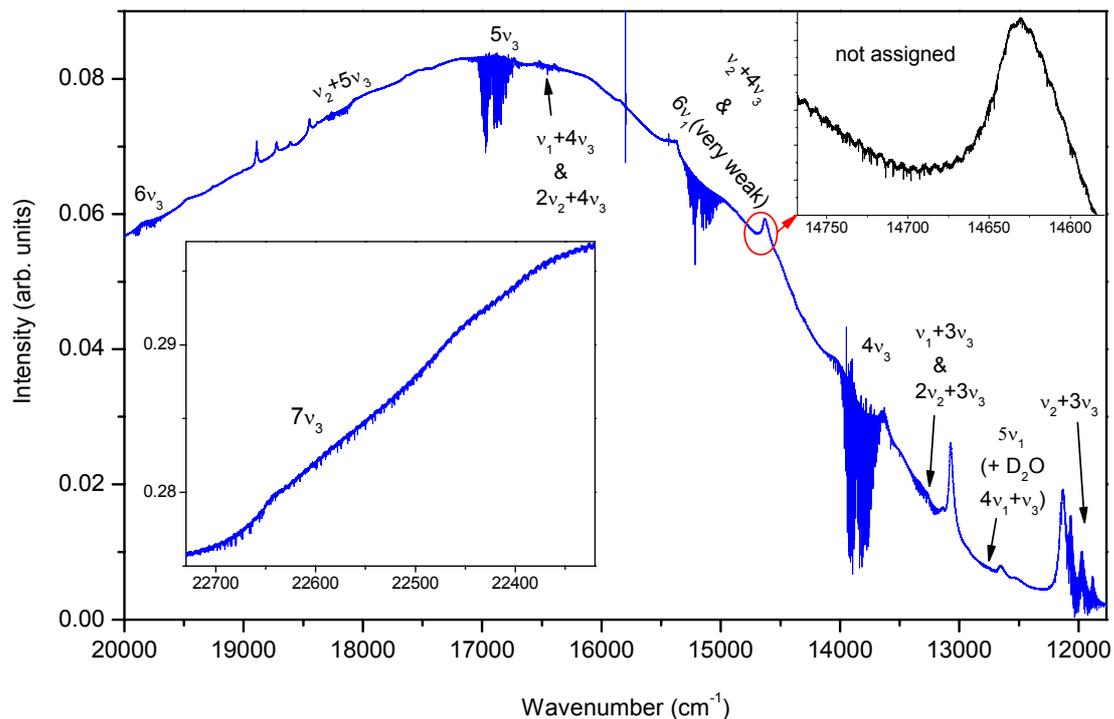


Figure 5.2-3: Overview of the HDO spectrum.

H₂O visible-IR continuum

As a missing absorber candidate in the modelled atmospheric energy budget, and due to the dearth of laboratory measurements in the visible-NIR range [Vaida *et al.*, 2001; Pfeilsticker *et al.*, 2003; Daniel *et al.*, 2004; Sierk *et al.*, 2004], the water continuum was investigated on a broad spectral range (22500-2500 cm⁻¹) by recording low resolution spectra (see experiment N°1 in Table 5.1-1).

A structureless broadband continuum was first emphasized (Figure 5.2-4). The shape of the broadband continuum was shown to match the extinction spectrum of small water droplets (0.8 μm radius) and was therefore attributed to the extinction of light by small water droplets that are forming in the cell during the experiments although the water vapour partial pressures were below the saturation pressure (about 20 hPa at 291 K) [Kiseleva *et al.*, 2002; Carleer *et al.*, 2003].

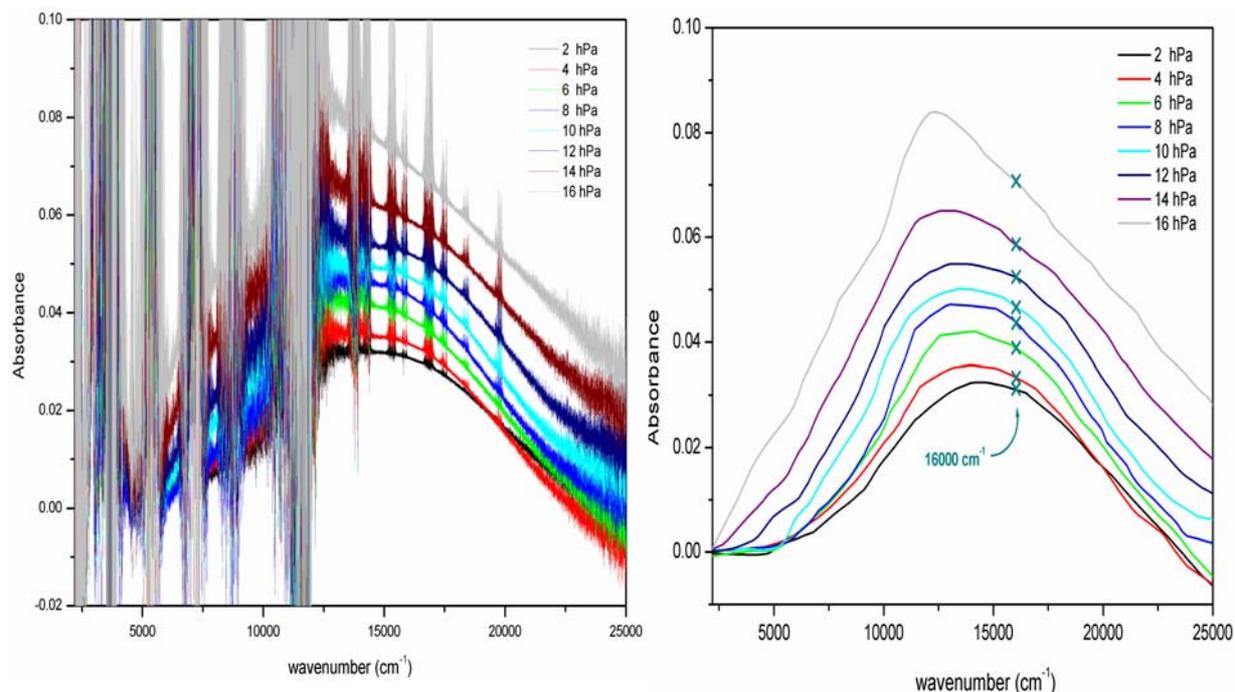


Figure 5.2-4: Absorbance spectra at different water vapour pressure (left) Isolation of the broadband continuum by subtraction of simulated water lines (right)

The existence of a narrow band continuum underlying the vibrational bands predicted by theory, due to the far-wings of spectral lines or to water dimers [Low & Kjaergaard, 1999; Schofield & Kjaergaard, 2003; Clough *et al.*, 2005] was then examined. Similarly to the HDO lines extraction procedure, the water lines were removed using a synthetic spectrum generated at every pressure from either the BR or the HITRAN spectroscopic parameters. A preliminary water continuum absorption cross-section was then generated from about 2400 to 9200 cm^{-1} and from 11900 to 14100 cm^{-1} [Fally *et al.*, 2005].

Figure 5.2-5 shows quite good similarities between the experimental and the different calculated dimer and continuum signatures for the region below 10000 cm^{-1} . Also shown on Figure 5.2-5 are large discrepancies at higher wave numbers between our experimental data and the recent dimer and continuum calculations. These results are not surprising, considering the weakness of the continuum and the difficulty of properly removing the water lines, especially in saturated regions.

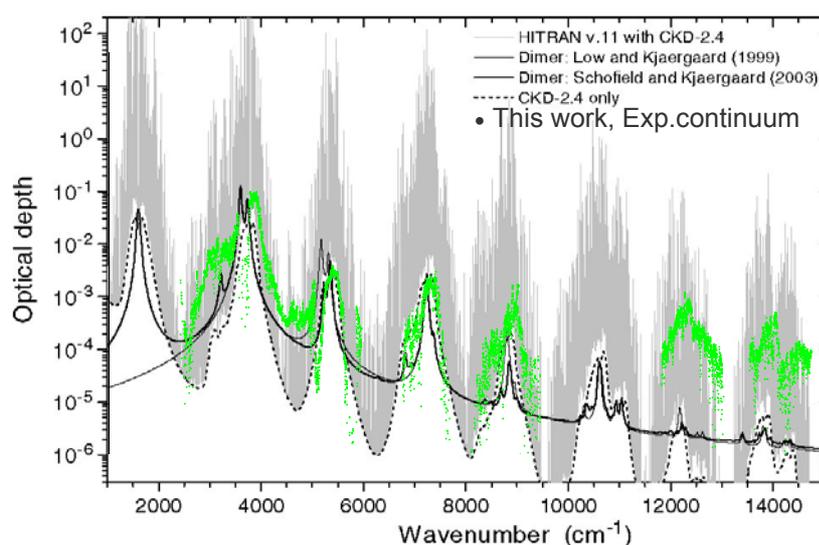


Figure 5.2-5: comparison of the water continuum optical depth obtained in this work with: (1) the optical depth of the water monomer including the CKD-2.4 continuum ("HITRAN v.11 with CKD-2.4"), (2) two theoretical estimates for the water dimer ("dimer") [Low & Kjaergaard, 1999; Schofield & Kjaergaard, 2003], (3) the self-broadening continuum ("CKD2.4 only"). The optical path length is 10 m, $P_{\text{H}_2\text{O}}=98$ hPa, $T=342$ K. (1), (2) and (3) are extracted from [Ptashnik *et al.*, 2005].

5.3. Nitrogen dioxide

The nitrogen dioxide (NO_2) measurements reported in Table 5.1-1, performed in parallel with 2 FTS's in order to acquire simultaneously spectra in the UV-visible ($14000\text{--}40000$ cm^{-1}) and in the IR ($2000\text{--}5000$ cm^{-1}) spectral ranges. Such measurements in both spectral regions allow an accurate relative intercalibration of the cross-sections over the complete spectral range and thus provide a homogeneous set of cross-sections throughout the IR to the UV. They could therefore be used to investigate the discrepancies reported in the measurements of atmospheric NO_2 concentrations when retrievals are performed separately from UV-visible and IR spectra [Carleer *et al.*, 2002b].

In continuation of our previous work initiated during the ESAC I project [Vandaele *et al.*, 1996; Vandaele *et al.*, 1998], the analysis of the temperature and pressure effects of NO_2 absorption cross-sections was carried on. The temperature and pressure dependences of the NO_2 absorption cross sections were determined in the $13200\text{--}42000$ cm^{-1} spectral range by considering 53 literature data sets taken from Coquart *et al.* (1995), Mérienne *et al.* (1995), Jenouvrier *et al.* (1996), Mérienne *et al.* (1997), Harder *et al.* (1997), Yoshino *et al.* (1997), Vandaele *et al.* (1998), Voigt *et al.* (2002), and Vandaele *et al.* (2002). They cover the 217.0–298.5 K temperature range. A linear temperature dependent relation was proposed in the temperature range investigated, whereas the influence of the total pressure was expressed as a temperature dependent broadening coefficient. Measurements performed with

mixtures of NO₂ / air and NO₂ / N₂ showing a strong pressure effect were used to deduce values of pressure broadening parameters (γ_{air}^0 , $\gamma_{\text{N}_2}^0$) as well as the temperature coefficient n commonly used to convert pressure broadenings at the desired temperature with the following relation:

$$\gamma(T_2) = \left(\frac{T_1}{T_2}\right)^n \gamma(T_1)$$

By combining the temperature dependence and the pressure broadening coefficient, the NO₂ absorption cross sections can be computed at any temperature between 220 and 294 K and pressure, with an accuracy better than or equal to 4%, which is of the order of the uncertainty given in most of the literature data. One clear advantage of using the parameterisation of cross sections is the limitation of the noise level in the simulated spectrum [Vandaele *et al.*, 2003a]. All the data are available upon request or can be downloaded from the IASB-BIRA website (<http://www.oma.be/BIRA-IASB/Scientific/Topics/Lower/LaboBase/Laboratory.html>).

The quality of seven NO₂ cross sections dataset available in the literature was assessed by studying the influence of the cross-section choice on retrievals of 3 minor stratospheric constituents NO₂, BrO, OCIO from FT ground-based UV-Visible measurements (Harestua, Norway). In particular, we looked at the concentration RMS errors and at the amplitude of the residual structures remaining after the fit [Vandaele *et al.*, 2003c]. Variations of the retrieved NO₂ slant columns up to 17% have been observed, which can be directly related to discrepancies between the cross-sections themselves. The impact on the BrO retrieval is most important during the summer with slant columns differences up to 20%. The lowest impact on the winter BrO column is due to the lowest abundance of the NO₂ in the winter. OCIO slant columns change by less than 8% during the winter season. However, some cross-sections lead to non-zero OCIO values in the summer, when no OCIO is expected. These results point out the complexity of choosing one cross-section dataset rather than another.

To sum up, this extensive and long-term study concerning the NO₂ molecule ended by providing NO₂ absorption cross-sections at two temperatures (220 and 294 K) from 15000 to 42000 cm⁻¹ with an accuracy of 3.6-5.0%. These data were recommended by J. Orphal after a critical review effort [Orphal, 2003] and were internationally recognized by their insertion in the 2000 edition of HITRAN database (<http://cfa-www.harvard.edu/hitrان>) [Rothman *et al.*, 2003]. An empirical model able to reproduce temperature and pressure effects within 4% was also built.

5.4. Oxygen and its collision complex

The oxygen molecule and its O₂-X collision-induced (with X= O₂, N₂, Ar) absorption was extensively studied from the UV to the NIR during the ESAC I period, leading to several contributions reported in the ESAC I final report. Some advances have been made during ESAC II.

First, the re-examination of our best signal-to-noise spectra in the UV Herzberg bands region leads to the detection of very weak ¹⁶O₂ lines and the determination of new spectroscopic parameters [Mérienne *et al.*, 2001]. The list is available in the Journal of Molecular Spectroscopy supplementary material archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

Second, O₂-O₂ and O₂-N₂ collision-induced bands were examined in more detail in the visible and NIR regions. After having extracted the a¹Δ_g + a¹Δ_g (0,0) and the X³Σ⁻_g + a¹Δ_g (0,0) bands, centred at 15870 and 7900 cm⁻¹ respectively, the analysis was extended on the whole spectral range from 7000 to 30000 cm⁻¹, as illustrated in Figure 5.4-1. The Figure also shows that the agreement with literature data is reasonably good, given the high uncertainties of those measurements. The bands integrated absorption cross-sections show discrepancies of 15% for most bands, reaching up to 50% for the 3 weakest bands [Hermans *et al.*, 2003]. These results underline the difficulty of obtaining accurate values of diffuse absorbing features underlying stronger structured absorptions [Vandaele *et al.*, 2003b].

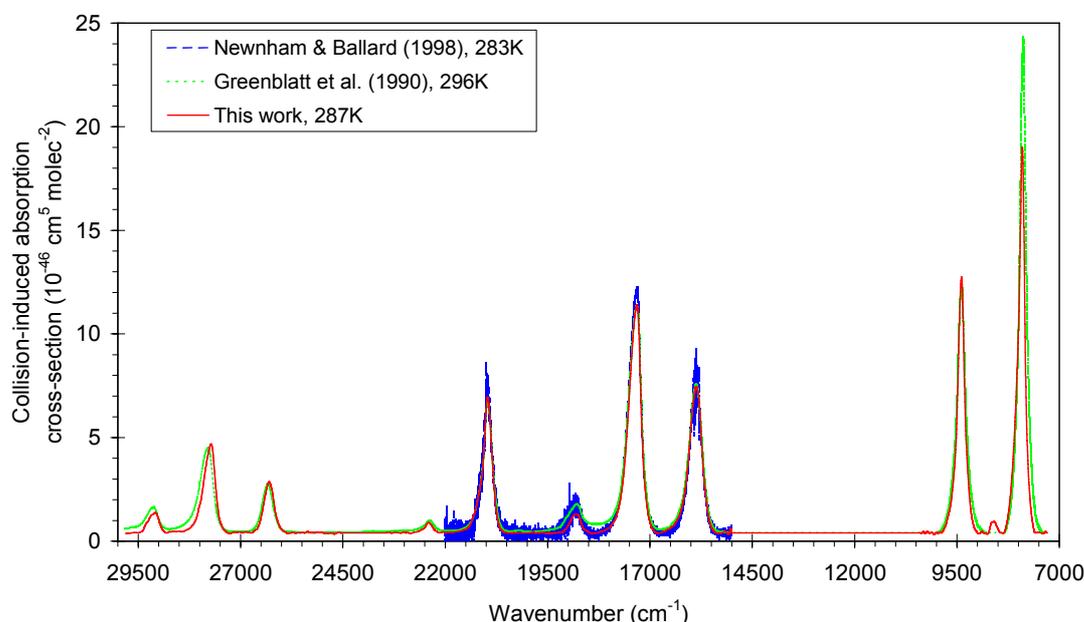


Figure 5.4-1: The O₂-O₂ collision-induced absorption cross-section at room temperature in the visible-NIR range, and comparison with literature data.

5.5. Formaldehyde

Having both an atmospheric and a spectroscopic interest as the above cited molecules, the formaldehyde (H_2CO) also needs improvements in the knowledge of its spectroscopic parameters. Available literature data suffer from a lack of resolution, a limited spectral range, and some uncertainty in the temperature dependence. H_2CO was tentatively recorded simultaneously in the UV-Vis and IR regions, as described in experiment n°5 reported in Table 5.1-1. In addition to formaldehyde, the IR spectra contained large absorption bands identified to the trioxane gas phase $(\text{H}_2\text{CO})_3$ (the cyclic trimer of formaldehyde) present in the absorption cell. Both contributions could be separated in the IR, by using spectra recorded at different pressures, and the formaldehyde absorption cross section could then be derived in the UV-visible. These preliminary results are presented in Figure 5.5-1 [Daumont *et al.*, 2003].

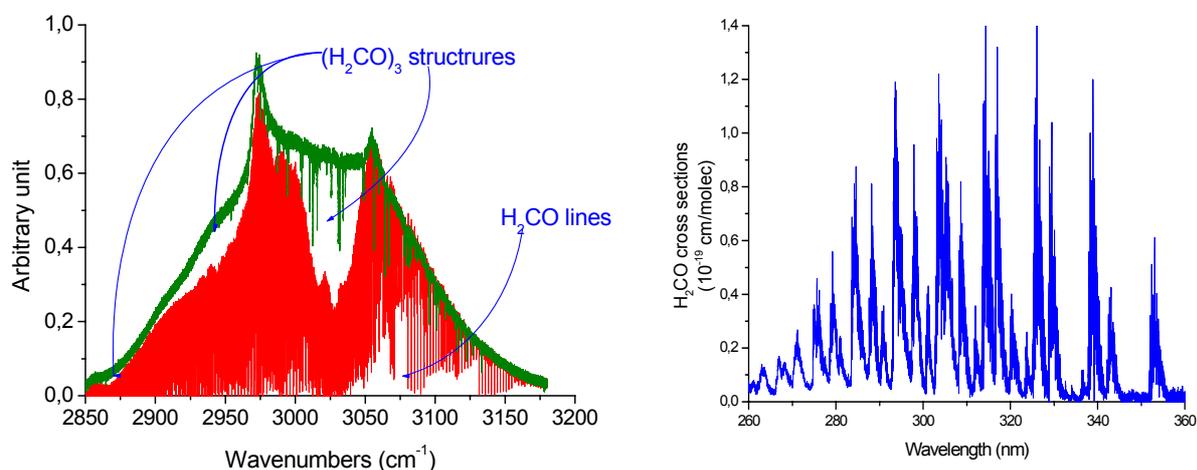


Figure 5.5-1: (left) Raw IR spectrum of formaldehyde and trioxane (right) UV-Visible absorption cross section of formaldehyde.

6. VALORISATION OF THE ESAC II RESEARCH

In addition to participation of the consortium to many symposia, workshops, and to the publication of ESAC-II related results in international scientific journals, it is worth repeating that significant ESAC-II results have been integrated in national, European and international assessments or reports which are important means to further disseminate these products to the scientific community, and to decision makers (see Section 6.3). During the project, the ESACII Website (<http://www.oma.be/ESACII/Home.html>) has been updated regularly, to inform the community about the achieved progress. Information about ESACII has been integrated in the brochures distributed by Belgian Science Policy, and in the National Reports for the WMO/UNEP Ozone Research Managers Meetings.

6.1. Contributions to data validation

- Stratospheric NO₂ data as measured by major components of the global observing system have been intercompared and integrated using a frequency-domain method developed at BIRA-IASB. Based on the harmonic decomposition of the spatial and temporal features of this trace gas on the global scale, this new technique allows detailed investigation of the geophysical consistency of two data records despite significant differences in latitude/time/altitude sampling and sensitivity. More classical direct comparisons were conducted, as well as in-depth studies in order to validate the new technique. The harmonic study concludes to a reasonable agreement between SPOT-4 POAM-III and UARS HALOE satellites, and the ground-based network of NDSC UV/Vis DOAS spectrometers. SPOT-3 POAM-II satellite data have a small bias compared to POAM-III. GOME satellite data agree in case of no tropospheric pollution. SAGE-II satellite v5.94 data are found to overestimate dramatically the other data sets by at least 30%. The agreement improves progressively with SAGE-II v6.0, v6.1 and v6.2, nevertheless, an overestimation persists in the lower stratosphere. An interesting finding is that, despite some disparity in annual mean, all sensors capture similarly geophysical cycles like the annual variation (AO), the quasi-biennial oscillation (QBO) and their meridian dependence. Relying on those results, the harmonic parameterisation technique has been used once again to derive a unified climatology of stratospheric NO₂ that takes advantage of the complementarities offered by the different sensors, sounding strategies and orbits. This climatology has been recognised as a major contribution to the next COSPAR Reference Atmosphere (CIRA).
- The ground-based measurements from DOAS and FTIR instruments have contributed to the geophysical validation and maturation of satellite data of major interest, through both individual studies at the stations and pseudo-global studies using the NDSC network as a whole. Results were presented at several ENVISAT Validation

Workshops (December 2002 and May 2003) as well as dedicated SCIAMACHY and MIPAS validation meetings.

- O₃ column data from Harestua and Jungfraujoch have been used to establish and improve the long-term and global consistency of satellite column data from GOME, Earth Probe TOMS, and ENVISAT SCIAMACHY. For the two first satellites, upgraded to versions 4.0 and 8 respectively in the course of the project, a delta validation has led to the conclusion that both sensors have reached now an acceptable quality level for accurate long-term trend detection: the mean agreement from 60°N to 60°S falls to within the 1% level and high long-term stability has been demonstrated. First SCIAMACHY data demonstrated good ozone monitoring capabilities, but also major problems for which solutions have been identified. Ground-based studies have pointed out several issues related to the absorption cross-sections and the air mass factors used in the SCIAMACHY retrievals. Currently, the latest and successful version 4.0 of the GOME Data Processor is being adapted to SCIAMACHY spectra and reprocessed data with this new version should be available in 2006.
- NO₂ column data from Harestua and Jungfraujoch have been instrumental in establishing the long-term and global consistency of satellite column data measured by GOME and SCIAMACHY, and derived from satellite profiles measured by HALOE, SAGE-II, POAM-III and ENVISAT MIPAS. NO₂ is a quite difficult molecule owing to large spectrum of intense variations (diurnal cycle, short-term fluctuations, meridian structures, annual cycle etc.) Therefore advanced comparison and analysis techniques have been developed. For MIPAS, an additional problem is that the accuracy of the limb emission NO₂ profile degrades rapidly below 27 km. To enable comparisons with ground-based column data despite the lack of 10% to 40% of the stratospheric column in MIPAS data, a new analysis technique using BASCOE assimilation results has been developed, demonstrating the high capability of MIPAS to detect geophysical cycles as well as NO₂ enhancement in the upper stratosphere by solar proton events. For SCIAMACHY, similar conclusions apply as for ozone: good capabilities, but the new algorithm version is awaited for quantitative value. SAGE-II overestimations have already been mentioned. For other satellites, stratospheric columns derived from profile measurements capture all geophysical signals observed from the ground. The absolute agreement is more an issue as 15% appears to be the lowermost limit for most cases.
- The ozone data obtained at Ukkel (columns from spectrophotometers as well as profiles from balloon soundings) are exchanged for use of the validation of satellite data (SCIAMACHY, MIPAS, GOMOS aboard the ENVISAT satellite). KMI-IRM also participates in the ozone SAF of EUMETSAT for the validation of ozone profiles obtained with present and future satellite instruments.
- Several specific calibration/validation campaigns in support of space sensors have taken place during the last four years. A special coordinated effort has been devoted to intercomparisons of ground-based FTIR (and other) measurements with

observations performed by ENVISAT instruments (MIPAS, SCIAMACHY), MOPITT (CO), ACE (HCl and ClONO₂), HALOE (HCl and HF),...

- The ACE-FTS instrument was launched in August 2003 and has been in "post commissioning" operation since February 2004 [Bernath *et al.*, 2005]. Scientific and validation papers using the first "Version 1" of level 2 data have been published recently in a GRL special issue. In particular, a study dealing with comparisons between stratospheric columns of HCl and ClONO₂ measured in 2004 by ACE and by ground-based FTIR instruments operated at five northern latitude NDSC sites has been led by ULg [Mahieu *et al.*, 2005]. Main conclusions were that: (i) ACE is able to identify for both targeted gases distribution features characteristic of geographical, dynamical, seasonal and chemical changes occurring in the atmosphere; (ii) excellent agreement was found when considering the sets of coincident measurements obtained around the Thule site (76.5°N), with mean partial column ratio (ACE/Thule) equal to 1.04 and 0.99 respectively for HCl and ClONO₂; (iii) good agreement is generally found for other sites, even if systematic differences between some data sets deserve further investigations based on additional coincident ACE "Version 2.2" and ground-level remote FTIR measurements.

6.2. Contributions to geophysical and spectroscopic databases

- All ozone and UV observations are stored in local data files and in a local relational database (Oracle) where they can be consulted together with all the other data available at the institute. The ozone profiles are also transferred systematically to the NADIR database at NILU (Norway). The data are used there among others for MATCH campaigns [see e.g. Rex *et al.*, 2002] and for the validation of satellite data.
- Ozone columns and profiles are also stored in the database of the world ozone and ultraviolet data centre of WMO, managed by Meteorological Services Canada in Toronto (http://www.woudc.org/index_e.html). Data stored in this database are world-wide used for many atmospheric studies. Also near real-time data are exchanged to enable the production of ozone maps (http://www.woudc.org/data/OzoneMaps_e.html), which can be used to plan campaigns. Ukkel has the status of complementary NDSC station for ozone (<http://www.ndsc.ncep.noaa.gov/>) and therefore the data are also stored in NDSC database.
- The ozone data are also exchanged with the ENVISAT validation team (the TASTE project).
- Building and maintenance of a local spectroscopic database: <http://www.ulb.ac.be/cpm> and <http://www.oma.be/BIRAIASB/Scientific/Topics/Lower/LaboBase/Laboratory.html>.
 - The absorption cross-sections have been distributed to scientists from USA, Japan, France, Germany, Netherlands and UK, including ESAC II users.

- Insertion of NO₂ and H₂O spectroscopic data in the two main international HITRAN and GEISA databases (<http://cfa-www.harvard.edu/hitrان> and <http://ara.lmd.polytechnique.fr/>) [Rothman *et al.*, 2003; Rothman *et al.*, in press; Jacquinet-Husson *et al.*, 2003].
 - The atmospheric detection of water dimers that was published in the Science Journal [K. Pfeilsticker *et al.*, 2003], was revealed by fitting the water monomer atmospheric absorption to a synthetic spectrum generated from our spectroscopic parameters.
 - The water vapour line parameters in the 16600-17200 cm⁻¹ window have been used to retrieve water columns and profiles from GOME (Global Ozone Monitoring Experiment) satellite observations [Lang *et al.*, 2002].
- Contribution of the ULB group to the 2003 edition of the GEISA/IASI spectroscopic database [Jaquinet-Husson *et al.*, 2005]. Introduction of SO₂, NO₂, and O₂ absorption cross-sections in the « science-softCon UV/Vis Spectra Data Base » (<http://www.uv-spectra.de/>), for which A.C. Vandaele has been appointed editor responsible for the nitrogen oxides (NO, NO₂, N₂O, NO₃, N₂O₄, N₂O₅) and hydrogen oxygen species (HO₂, H₂O₂, H₂O, O₂, O₃).
- Consistent data sets archived at the NDSC database (NOAA-Washington, <ftp://ndsc.ncep.noaa.gov>) have been updated on an annual basis, total column time series of HCl, ClONO₂, HF, COF₂, HNO₃, NO, NO₂, CCl₂F₂, CHClF₂, O₃ and N₂O cover the 1989-2004 time frame. Within the frame of ENVISAT validation activities, specific retrievals of HNO₃, NO, NO₂, O₃, CO, CH₄, N₂O and CO₂ have been performed and related results have been archived using the hdf format at the ENVISAT CAL/VAL database (<http://nadir.nilu.no/calval>).
- The all set of data obtained by IASB-BIRA is stored in a local database accessible to all applicants. Moreover the data are submitted to the EUVDB (European UV Database) where quality control and quality insurance tests are performed. Site audit performed in 2002 is accessible on the web: (<http://www.muk.uni-hannover.de/~martin/database.html>). Instrument comparison report can be found on: <http://lap.physics.auth.gr/qasume/EvaluationsDetails.asp?id=33#>.
- Finally the IASB-BIRA UV station in Ukkel is presently under evaluation to be included in the NDSC UV network.

6.3. Recognition and valorisation of expertise through memberships of international committees and participation to important international studies and projects.

- The long-term expertise with the ozone soundings at KMI-IRM was used to collaborate in a WMO/GAW group to define standard operating procedures for ozone sonde operators.

- H. De Backer is member of the Brewer Science advisory group of WMO/GAW to assess the operation of the spectrophotometers in the network. He is also member of the Regional Brewer Science Group of Europe who monitors the calibration level of the instruments in Region VI (Europe) of WMO.
- Within the COST713 action "UV forecasting" (1996-2001), H. De Backer was member of the management committee and leader of workgroup 1 (Data).
- Within the COST726 action "Long term changes and climatology of UV radiation over Europe" (2004-2008), H. De Backer is member of the management committee and leader of workgroup 1 (Data).
- J-C. Lambert is:
 - The Belgian national coordinator in the SCIAMACHY Validation and Interpretation Group (SCIAVALIG) and the co-author of several documents regarding SCIAMACHY validation and exploitation.
 - Co-chairman of the Satellite Working Group of the NDSC Steering Committee.
 - Member and the NDSC Representative of the Committee on Earth Observation Satellites's Atmospheric Chemistry Subgroup (CEOS/ACSG).
- P.C. Simon has been co-chairman of the NDSC Steering Committee between 2003-2005.
- M. Van Roozendael is Co-chairman of the NDSC UV-Vis Working Group since December 2003.
- M. De Mazière has been elected co-chairman of the NDSC IRWG in November 2004, to become effective in 2006.
- M. De Mazière has been member of the EORCU Vintersol Core Group (2002-2004); contributions to the 'Vintersol Planning Document' and the Vintersol brochures.
- M. De Mazière is member of the EC Atmospheric Science Panel (2003→)
- M. De Mazière has contributed several times to the evaluation and ranking of research proposals at the EC, e.g., in March 2001, in the area 'Stratospheric Ozone', and in 2003, in the field of Global Observation and Forecasting Systems (call 2003 Global-2 Area 1.6.3.VI.1).
- J-C. Lambert was member of the Scientific Organizing Committee of the NDSC Symposium 'Celebrating 10 years of atmospheric research', Arcachon, Sept.24-27, 2001.
- ESACII partners have been solicited regularly for participation in EU projects (e.g., GEMS, SCOUT-O3, Evergreen, QUILT, NOVAC, GMES-GATO, Geomon (submitted), etc.), often with responsibilities as coordinator (e.g., UFTIR) or task leader.

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- M. Van Roozendael has participated to the European Commission Assessment 'European Research in the Stratosphere 1996-2000. Advances in our understanding of the ozone layer during THESEO', Directorate-General for Research, Environment and sustainable development programme, EUR 19867, 2001.

6.4. Lectures; Contributions to public manifestations and publications edited by the Belgian Science Policy

- M. De Mazière and M. Van Roozendael have lectured at the ICTP Course on 'Inverse methods in Atmospheric Science', (Trieste, October 1-12, 2001), with lectures entitled 'The empirical Optimal Estimation Method applied to the inversion of FTIR atmospheric remote sensing data', and 'DOAS', respectively.
- M. De Mazière has given a lecture entitled 'Ozon in al zijn facetten' as a contribution to the course 'Topics of Global Change' (coördinated by Prof. R. Ceulemans) at the 'Instituut voor Milieukunde' of the University of Antwerp, in the years 2004 and 2005.
- M. De Mazière was session chairman at the 'Studiedag: ozon in de troposfeer', VITO and PPS Science Policy, Brussels, June 10, 2004.
- Professeur R. Colin held several general public conferences about atmospheric pollution problems and climate changes in different places in Belgium (Nivelles, Wavre, Brussels, Arlon, Tubize).
- M. Carleer gave a lecture about the important role of the water molecule in the atmosphere to Atmospheric Physics students at the University of Toronto, Canada.
- KMI-IRM and BIRA-IASB participated in 2001 to the event "Space for you" for secondary school students. Presentations about the ozone issues in general were given. Also the related activities at both institutes were highlighted.

- Seminars:
 - "L'ozone Atmosphérique" was presented in the series of seminars of the "Société Royale Belge d'Astronomie, de Météorologie et de Physique du Globe (SRBA)" on 23 March 2002 in Brussels.
 - "Aerosol Optical Depth Retrieval from the Brewer Measurements from 1984 to 2002", was given by Anne Cheymol in the series of seminars of KMI-IRM on 15 October 2003 in Brussels.
 - "Invloed van meteorologische parameters op ozonconcentraties in de grenslaag", was given by Andy Delcloo in the series of seminars of KMI-IRM on 17 December 2003 in Brussels.
 - 'Trace gas measurements at the Jungfraujoch by Fourier transform infrared and UV-Visible spectrometry', Jan. 16, 2001, at the Institut für Meteorologie und Klimaforschung, Forschungszentrum Karlsruhe, by M. De Mazière.
 - 'Integrated Use of the Global Monitoring System for Atmospheric Composition', Nov. 9, 2001, at the University of Bremen (IFE), by J.-C. Lambert.
- An explanation about the activities in the field of atmospheric ozone at KMI-IRM was given for a group of visitors (28 April 2003).
- On different occasions questions of students and other interested people (incl. press) were answered by ESACII researchers.
- M. De Mazière and H. De Backer have contributed to the 2006 calendar of 'Natuur en Techniek', with a week on 'Stratospheric Ozone'.
- The UV Index is forecasted and disseminated every day in the media. Since 2002 the forecasted UV index is available on the Internet web-site of KMI-IRM, together with the observed values for that day. Background information for the interpretation of the UV index is available of the web-site of the ozone/uv group (<http://ozone.meteo.be>).
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- Development, Validation and Exploitation of ERS-2 GOME Satellite Data: Overview and Perspectives for ENVISAT, J.-C. Lambert, M. Van Roozendael, M. De Mazière, in Space Scientific Research in Belgium, Volume 3: Earth Sciences, Part III, 1994-2000, 47-66, 2002.

ACRONYMS

BR	Brussels-Reims
DOAS	Differential Optical Absorption Spectroscopy
ESA	European Space Agency
EORCU	European Ozone Research Coordinating Unit
FT	Fourier Transform
FTS	Fourier Transform Spectrometer
FTIR	Fourier Transform Infrared
GEISA	Gestion et Etude des Informations Spectroscopiques Atmosphériques
GSMA	Groupe de Spectrométrie Moléculaire et Atmosphérique
HITRAN	High Resolution TRANsmission
IASB- BIRA	Institut d'Aéronomie Spatiale de Belgique - Belgisch Instituut voor Ruimte Aeronomie
IGBP	International Geosphere-Biosphere Programme
IPCC	Intergovernmental Panel on Climate Change
IR	Infrared
KMI-IRM	Koninklijk Meteorologisch Instituut van België – Institut Royal Météorologique
NIR	Near-Infrared
NDSC	Network for Detection of Stratospheric Changes
RMS	Root Mean Square
SPARC	Stratospheric Processes And their Role in Climate
SZA	Solar zenith angle
ULB	Université Libre de Buxelles
ULg	Université de Liège
UV	Ultraviolet
Vis	Visible
WCRP	World Climate Research Programme
WMO/UNEP	World Meteorological Organization/United Nations Environment Programme

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**ANNEX1:
Proceedings & Theses**

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