

**Annual Report
Progress Through March 31, 1997**

**NASA Grant NAGW-2541
U. S. Participation in the GOME and SCIAMACHY Projects**

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Introduction

This report summarizes research done under NASA Grant NAGW-2541 from April 1, 1996 through March 31, 1997. The research performed during this reporting period includes development and maintenance of scientific software for the GOME retrieval algorithms, consultation on operational software development for GOME, consultation and development for SCIAMACHY near-real-time (NRT) and off-line (OL) data products, and development of infrared line-by-line atmospheric modeling and retrieval capability for SCIAMACHY. SAO also continues to participate in GOME validation studies, to the limit that can be accomplished at the present level of funding. The Global Ozone Monitoring Experiment was successfully launched on the ERS-2 satellite on April 20, 1995, and remains working in normal fashion. SCIAMACHY is currently in instrument characterization. The first two European ozone monitoring instruments (OMI), to fly on the Metop series of operational meteorological satellites being planned by Eumetsat, have been selected to be GOME-type instruments (the first, in fact, will be the refurbished GOME flight spare). K. Chance is the U.S. member of the OMI Users Advisory Group.

GOME and SCIAMACHY Studies Through March 1997

The research at the SAO for the GOME and SCIAMACHY projects includes development and maintenance of scientific software for the GOME retrieval algorithms, advising and assisting in the development of GOME operational software, participation in GOME validation and science studies, sensitivity and instrument studies to help finalize the definition of the SCIAMACHY instrument (now completed), completion of the SCIAMACHY study to produce the first version of the Scientific Requirements Document for Data and Algorithm Development (included as Appendix A to this report), development of scientific software for SCIAMACHY retrievals, and consultation on the development NRT and OL operational data processing and data products.

GOME

The development of the scientific code that implements the GOME retrieval algorithms and their realization as the first release of operational processing code was finished. Following the end of the GOME commissioning phase (March 1996) and the initial validation of the operational retrieval algorithms, the first official release of GOME level 2 products (total ozone columns) took place in July 1996. SAO GOME studies this year include the following items:

- Guiding the development of GOME Level 0-1 and 1-2 operational software through extensive collaboration with the DLR.
- Cloud studies, including investigation of fitting schemes and analysis of uncertainties due to various error sources, including line parameters of O₂. These resulted in production of the prototype operational algorithm for GOME cloud correction which has now been implemented in the Level 1 operational software.
- Substantial improvements to the GOMEware for thorough scientific testing of GOME algorithms, including those that have been implemented initially in the operational framework at DLR. This includes the implementation of the SBUV code in the GOMEware, and its testing for a variety of simulated GOME measurements.
- The GOMETran finite difference forward model has been fully integrated and is now used in various modeling contexts.
- Participation in GOME validation and scientific studies. Note that the validation studies include ozone profiles and tropospheric ozone abundances, which are being produced as off-line scientific products.

- Collaboration on the development of the DOAS method as the operational procedure for GOME Level 1-2 processing to produce O₃ columns from GOME. This collaboration includes code development, measurement window selection, and a number of related issues.
- Changes to operational code for GOME Level 0-2 processing, to adjust for post launch conditions and to correct initial deficiencies.
- Continuing participation in GOMETran forward model development, in collaboration with the University of Bremen.
- Spectroscopic and aerosol database development, including the production of an improved database of molecular parameters for the visible O₂ A band (now published).
- Radiative transfer studies related to wavelength calibration and spatial and spectral aliasing, including development of an improved solar reference spectrum for wavelength-specific applications (now published).
- Improved determination of the wavelength-dependent Rayleigh scattering cross section (now published).
- Improved molecular parameters for the Ring effect through molecular physics studies employing the best currently available molecular data; improved atmospheric cross sections describing the Ring effect (now published; the last three items are included in “Ring Effect Studies: Rayleigh Scattering, Including Molecular Parameters for Rotational Raman Scattering, and the Fraunhofer Spectrum,” included as Appendix B to this report).
- Participation in the ESA cloud and aerosol *ad hoc* study group to produce cloud and aerosol data products from GOME.
- Guiding and advising work on operational processor updates and reprocessing of GOME data. This includes, for example, the future use of the TOMS Version 7 ozone climatology in GOME data processing.

SCIAMACHY

SCIAMACHY is a joint German/Netherlands/Belgian program, with scientific participation from other European countries and, in the U.S., the SAO. It is included for launch aboard the ESA Envisat-1, currently planned for 1999.

The SCIAMACHY Science Advisory Group (SSAG) was formed, including K. Chance of the SAO as a U.S. member and head of the Data and Algorithm Subcommittee, J. Geary of the SAO as a U.S. member and advisor on instrument and detector issues, and R. Spurr as the third U.S. member and organizer and chair of the GOME/SCIAMACHY Scientific Working Sessions. The SSAG has met several times during the past year in order to address the many issues involved in the development of SCIAMACHY. SAO SCIAMACHY studies this year include the following items:

- Finalization of the SCIAMACHY band definitions and detector selection criteria; synthetic retrieval studies for atmospheric spectroscopy in the infrared contributing to these definitions.
- Chairing the scientific working subgroup for Algorithm Development and Data Usage; Organizing and chairing the joint GOME/SCIAMACHY Scientific Working Sessions, now in their third year.
- Heading the development, compilation, and production of the Scientific Requirements Document for SCIAMACHY Data and Algorithm Development (Appendix A to this report).
- Radiative transfer studies, including development of line-by-line modeling capability for the infrared and visible and ray tracing for the limb and occultation measurement geometries, all underway during this year. The issue of properly combining limb and nadir measurements must be addressed in conjunction with the development of the SCIAMACHY observational strategy. This is being addressed in the context of the Algorithm Development and Data Usage subgroup.
- Development of the Basic Infrared Absorption Spectroscopy (BIAS) technique for application to the SCIAMACHY infrared channels.
- Extension of GOME software development to SCIAMACHY, now well underway. Existing GOME databases extended in wavelength where appropriate to near infra-red. New line spectroscopic data sets compiled for SCIAMACHY channels 7 and 8.
- Participation in the definition of NRT and OL data products for SCIAMACHY, including close collaboration with the DLR in the generation of SCIAMACHY NRT specification documentation.

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A Scientific Requirements Document for Data and Algorithm Development

Scientific Requirements Document for SCIAMACHY Data and Algorithm Development

March 1997

Contents

1	Executive Summary	1
1.1	Summary of progress	1
1.2	Future development	2
2	Introduction	3
2.1	A brief history of SCIAMACHY	4
2.2	Mission scientific objectives	4
2.2.1	Primary mission objectives	5
2.2.2	Secondary mission objectives	5
2.3	Scope of this scientific requirements document and of the Algorithm Development and Data Usage Subgroup activities	6
2.4	Prioritized scientific issues and applications	7
2.4.1	Chemical and physical processes in the atmosphere	8
2.4.2	Modeling of transport and chemistry	11
2.4.3	Aerosols	12
2.5	Executive summary of GOME studies relevant to SCIAMACHY data and algorithm issues	13
2.5.1	Radiative transfer models	13
2.5.2	Retrieval algorithms	13

2.5.3	Databases	14
2.5.4	The software framework GOMEware	15
2.5.5	The GOME Instrument Simulator	16
2.5.6	Error analysis of DOAS and optimal estimation algorithms	16
3	Targeted Atmospheric Constituents and Geophysical Parameters	17
3.1	Retrieval priorities for atmospheric chemistry	17
3.2	Targeted constituents in the various channels	18
3.3	Targeted constituents from different viewing geometries	18
4	Data Product Level Definitions	19
5	Requirements for SCIAMACHY Level 1b Data Processing	19
6	Requirements for SCIAMACHY Level 2 Data Processing	20
6.1	Forward models	21
6.1.1	Models specific to occultation measurements	21
6.2	Spectroscopic databases	22
6.2.1	Introduction	22
6.2.2	SCIAMACHY database	23
6.2.3	Recommendations	25
6.3	Aerosols	26
6.4	Geophysical data	26
6.5	Retrieval algorithms	29
6.5.1	Gases	29
6.5.2	Aerosols	30
6.5.3	Clouds	31
6.5.4	Spectral reflectance	31
6.6	Product confidence data	32

7	Requirements for SCIAMACHY Higher Level Data Processing	32
7.1	Definitions	32
7.2	Availability of level 2 data	32
7.3	Level 3 data processing	33
7.3.1	Gridding, interpolation, and projection	33
7.3.2	Resolution of level 2 data	33
7.3.3	Column density maps	34
7.3.4	Profile maps	34
7.3.5	Visualization	34
7.3.6	Time series	34
7.4	Value-added data processing	35
7.4.1	Dynamical models and data assimilation	35
8	SCIAMACHY Data Products	36
A	Algorithm Development Activities	38
A.1	German activities	38
A.1.1	ife Bremen	38
A.1.2	DLR	39
A.2	Netherlands activities	40
A.2.1	SRON	40
A.2.2	KNMI	40
A.2.3	Other institutes	41
A.3	Belgian activities	41
A.4	International collaboration	42
A.4.1	U.S.A	42
B	References	42

1 Executive Summary

SCIAMACHY presents a particular challenge for algorithm development because of the tremendous wavelength range of its measurements and its capability to measure in the nadir, in limb viewing, and to perform solar and lunar occultations. SCIAMACHY was noted from the beginning as a very ambitious project because of these capabilities and because of the technical challenge of producing such an instrument. At the present time the technical challenge has largely been met. It has also become increasingly common in the atmospheric community to develop instruments with comparably large ranges of capabilities.

1.1 Summary of progress

A substantial amount of the development necessary for SCIAMACHY algorithm development has been accomplished. This is partly due to the development undertaken for the Global Ozone Monitoring Experiment (GOME), much of which can be adopted directly, as well as SCIAMACHY-specific studies that are underway. Progress to date includes the following:

- Forward modeling: this includes consideration of technical aspects of radiative transfer modeling and data analysis, such as wavelength calibration and Ring effect correction.
 - GOMETran multiple scattering code, nadir geometry
 - AMFtran single scattering code, nadir geometry
 - DAK multiple scattering code, including polarization
 - GOMESim code, including extensive surface properties
 - Implementation of additional models from other sources for SCIAMACHY testing (Disort, Modtran, Fascode, Interlope, Dave code)
- Retrieval techniques
 - Differential Optical Absorption Spectroscopy (DOAS)
 - Optimal estimation
 - GOME Initial Cloud Fitting Algorithm (ICFA)
 - Nonlinear least-squares fitting of line-by-line spectra (Interlope)
- Databases
 - Cross sections and line parameters for gaseous absorption
 - Solar spectra
 - Ring effect spectra, measured and calculated
 - Cloud properties

- Aerosol properties
- Topography
- Ground and sea-surface reflectance

1.2 Future development

Substantial work remains to be done to permit the full scientific use of the data to be obtained from SCIAMACHY. This includes both work that would apply to GOME but has not yet been completed and work applicable to the extended wavelength range of SCIAMACHY and its additional viewing modes. The necessary research includes:

- Radiative transfer modeling
 - Ability to calculate in spherical geometry
 - Extension to limb and occultation measurement geometries
 - Extension to infrared region
 - * Inclusion of thermal radiation
 - * Range of refractive indices
 - * Line-by-line code/ESFT and other approximations
- Retrieval techniques
 - Global fitting for limb and occultation geometries
 - Combining limb and nadir measurements
 - Height-resolved retrievals from nadir measurements: O₃, H₂O, CH₄
 - Aerosol and cloud retrievals
- Databases
 - Cross sections and line parameters for gaseous absorption extended to 2.4 μm
 - Solar spectra to 2.4 μm
 - Cloud properties
 - Aerosol properties
 - Infrared ground and sea-surface reflectance
- Interfacing with operational processing
- Planning for validation exercises

2 Introduction

SCIAMACHY is a joint project of Germany, The Netherlands, and Belgium for atmospheric measurements. SCIAMACHY has been selected by the European Space Agency for inclusion in the list of category 3 instruments (instruments for scientific and application Earth observation research) for the Envisat-1 polar platform, to be launched in 1999. The SCIAMACHY program is currently in progress under the supervision of the SCIAMACHY science team, headed by Co-Principal Investigators Professor J. P. Burrows (University of Bremen, Germany) and Dr. Albert P.H. Goede (Space Research Organization of the Netherlands).

SCIAMACHY is an instrument designed to measure both tropospheric and stratospheric abundances of a number of atmospheric constituents, with particular emphasis on the troposphere. It is comprised of a spectrometer and telescope system which observes transmitted, reflected and scattered light from the atmosphere in the ultraviolet, visible and near infrared wavelength regions. The spectrometer is equipped with state of the art 1-dimensional photodiode array detectors which allow on-chip integration of the collected photons. This allows very small optical absorptions to be detected. The appropriate combinations of gratings and array detectors enables atmospheric spectra to be recorded at a relatively high resolution (0.2-0.5 nm) over the range 240-1700 nm and in selected regions between 2.0 and 2.4 μm . The high spectral resolution and enormous wavelength coverage intrinsic to SCIAMACHY and its predecessor, GOME, made possible by advances in array detectors, differentiates it from previous satellite remote sensing using ultraviolet or visible spectroscopy (*e.g.*, SBUV/TOMS or SME). Consequently, much more information is retrievable from SCIAMACHY measurements than has been possible with the present generation of instruments.

For the majority of each orbit, SCIAMACHY obtains atmospheric spectra in limb and nadir viewing, where the nadir swath is selected from a range of widths allowing for tradeoff between global coverage and small scale measurements. During sunrise, solar absorption measurements are made over northern latitudes. Over southern latitudes, lunar absorption measurements are made. This data enables the amount and spatial distribution of trace gases to be determined. From the intensity of the scattered light as a function of wavelength, the aerosol loading of the atmosphere is also measured.

SCIAMACHY observations yield information about both tropospheric and stratospheric constituents. The following species are measured:

- in the troposphere - O_3 , O_2 , O_4 , N_2O , NO_2 , H_2CO , CO , CO_2 , CH_4 , H_2O and aerosols and, in polluted conditions, SO_2 ;
- in the stratosphere - O_3 , O_2 , NO , NO_2 , NO_3 , CO_2 , CH_4 , H_2O , ClO , OCIO , BrO , aerosols, stratospheric haze and clouds, and, possibly, H_2CO and CO .

The measurements obtained from SCIAMACHY enable a wide range of phenomena, both natural and anthropogenic in origin, which influence atmospheric chemistry and, consequently, the climate to be investigated:

- troposphere - biomass burning, biogenic emissions, pollution episodes over populated regions, lightning production of oxides of nitrogen, Arctic haze, forest fires, dust storms, industrial plumes;
- stratosphere - ozone chemistry, including a special emphasis on the “ozone hole”, volcanic events, and solar proton events.

2.1 A brief history of SCIAMACHY

The SCIAMACHY project draws its inspiration from several satellite experiments that have provided atmospheric constituent measurements (*e.g.*, SBUV/TOMS [Heath *et al.*, 1975], SAGE [McCormick *et al.*, 1979], and SME [Barth *et al.*, 1983]), and the development of differential optical absorption spectroscopy (DOAS) for the measurement of gas phase concentrations in the troposphere and stratosphere [Platt *et al.*, 1979; Noxon *et al.*, 1979].

It was submitted by Dr. J. P. Burrows, then of the Atmospheric Chemistry Division of the Max Planck Institute for Chemistry, in response to the ESA announcement of opportunity for experiments to fly on board the Polar Platform Element of the Columbus Program, in 1986. SCIAMACHY has now been selected by the European Space Agency for inclusion in the list of category 3 instruments (instruments for scientific and application Earth observation research) for the ESA polar platform Envisat-1.

In 1990, ESA selected the Global Ozone Monitoring Experiment (GOME) as an instrument that would concentrate on measurements in the ultraviolet and visible portions of the spectrum covered by SCIAMACHY, in the nadir geometry, in order to improve the global measurement of ozone and a number of related constituents. GOME is currently flying on the ERS-2 satellite, launched in April, 1995. The success of GOME has allowed some aspects of the planned SCIAMACHY observations to be tested in a crucial manner in advance of the full SCIAMACHY development.

2.2 Mission scientific objectives

The SCIAMACHY instrument fulfills a general need in atmospheric science for greatly improving the state of tropospheric constituent measurements, particularly of pollutants, while also providing measurements of an important suite of stratospheric gases. They provide data on the chemistry associated with: (1) Biogeochemical cycles. This includes the chemistry involved in acid precipitation and deposition, through measurements of carbon, nitrogen, and (with limits) sulfur species, and the global distribution and transport of tropospheric gases and aerosols, through continuing global measurements of a number of tropospheric gases, including O₃ and CO, and aerosols. (2) Atmospheric processes. Simultaneous measurements of stratospheric and tropospheric gases provide information on the chemical and dynamic coupling of the troposphere and stratosphere and improve the quantitative understanding of O₃, including anthropogenic perturbations in both the troposphere and stratosphere.

2.2.1 Primary mission objectives

The primary scientific objective of SCIAMACHY is the global measurement of trace gases in the troposphere and stratosphere. SCIAMACHY retrieves the atmospheric amounts of trace gases from observations of transmitted, back scattered and reflected light from the atmosphere in the wavelength range between 0.24 and 2.4 μm . On Envisat, SCIAMACHY aims to obtain global coverage within 3 days at the equator and more rapidly at higher latitudes.

In the A.O. Proposal (1988), the following gases were targeted for measurement:

O₂, O₃, O₄, NO, NO₂, NO₃, CO, CO₂, H₂CO, CH₄, H₂O, SO₂ and possibly ClO and OClO.

As a result of the sensitivity analysis performed during the Phase A Study, N₂O, BrO and O₂(¹ Δ_g) have been added to the target list. In addition, the OClO and ClO measurements have been further investigated and, under ozone hole conditions both are observable. The list of target molecules for SCIAMACHY at the end of Phase A is thus:

O₂, O₂(¹ Δ_g), O₃, O₄, NO, NO₂, NO₃, N₂O, H₂CO, SO₂, CO, CO₂, CH₄, H₂O, BrO, ClO, and OClO.

2.2.2 Secondary mission objectives

Aerosol and cloud measurements From the dependence of the scattered light intensity on wavelength, the atmospheric aerosol abundance can be determined from SCIAMACHY observations. Aerosol scattering has a first order wavelength dependence (Mie Scattering $\sim \lambda^{-1}$), whereas molecular scattering has a fourth order wavelength dependence (Rayleigh Scattering $\sim \lambda^{-4}$). The large wavelength range of SCIAMACHY makes it ideally suited to the determination of atmospheric aerosol. In addition the polarization measurements made by SCIAMACHY will assist in the analysis of aerosol abundance. The nadir and limb viewing strategies of SCIAMACHY yield global aerosol total column amount and stratospheric profiles. This enables the stratospheric and tropospheric abundances to be estimated.

In nadir viewing the O₂, O₄ and CO₂ absorptions will enable the penetration depth of light in the atmosphere and therefore the cloud top height to be estimated. In addition the spectral reflectance (*i.e.* albedo) in the range 0.33-2.4 μm enables the cloud cover to be estimated. The following cloud physical parameters can be determined by SCIAMACHY: optical thickness; thermodynamic phase; average particle size; cloud top altitude.

Polar Stratospheric Clouds (PSCs) were first discovered by SAGE and will be readily measured by SCIAMACHY. These particles play a very important role in the ozone hole depletion mechanism. There are at least two distinct types of PSC and SCIAMACHY will distinguish between them.

Stratospheric aerosol measurements also include background aerosol and Junge layer; tropospheric aerosols include clouds, sand winds, and soot from forest fires.

Pressure and temperature measurements Stratospheric density/pressure profiles along the limb can be determined from the limb and occultation profiles of the well mixed gases O₂ and CO₂. There

are two methods to determine temperature profiles: (a) stratospheric density profiles are readily inverted to yield stratospheric temperature profiles; (b) via the Boltzmann distribution of the CO₂ vibrational-rotational features.

In cloud free conditions the surface pressure can be determined from the O₂ and CO₂ total column measurements in nadir viewing.

Land and ocean measurements SCIAMACHY is able to monitor broad surface absorptions in the range 0.33-2.4 μm . These measurements are relevant for the Ocean and Land-Usage scientific communities. However the spatial resolution of SCIAMACHY in nadir viewing ($\geq 25 \times 25 \text{ km}^2$, dependent on data rate considerations) is not as high as that of dedicated imaging devices such as SPOT. Nevertheless SCIAMACHY will provide useful global information on the surface spectral reflectance in the range 0.33-2.5 μm for large scale processes.

Oceanographic measurements: ocean color can be determined from broad-band visible absorptions under cloud free conditions. This can be used to estimate the abundance of near surface phytoplankton biomass, which in turn is correlated to water column primary productivity. An example of a large scale event to be studied is the El Niño-southern oscillation phenomenon in the pacific ocean, which is thought to have a large impact on global weather patterns.

Terrestrial measurements: the surface spectral reflectance will be measured in cloud free areas by SCIAMACHY: Broad-band absorption due to the presence of chlorophyll in plants will be measured. This enables the following parameters to be determined globally at low spatial resolution: vegetation index and ground classification and state (desert etc.). This leads to knowledge about deforestation and the extent of biomass burning in savannah regions which are extremely important parameters in global change.

Studies of the usefulness of SCIAMACHY observations for these applications and synergism with other instruments (*e.g.*, dedicated surface instruments such as MERIS) chosen for Envisat will be undertaken in the future (some suggestions exist in the A.O. Proposal). The use of SCIAMACHY for these applications may have become more important since the SCARAB instrument has been de-selected.

Additional measurements The observations made by SCIAMACHY are also of interest to scientists studying the earth's radiation budget. There is currently a long-term satellite program (the earth radiation budget experiment ERBE) focussed on this issue. However the sensors typically have much lower spectral resolution than SCIAMACHY in the range 0.24-2.4 μm . SCIAMACHY spectral observations, in conjunction with model calculations, should contribute significantly to radiation budget studies.

2.3 Scope of this scientific requirements document and of the Algorithm Development and Data Usage Subgroup activities

The present document has been developed under the guidance of the SCIAMACHY Science Advisory Group to fulfill several needs that are necessary for the proper development of the SCIAMACHY instrument and a data processing and dissemination program, in order to maximize the scientific output

from SCIAMACHY. The ongoing work of this subgroup is largely the continuation and extension of that undertaken in conjunction with the development of this document. Scientific needs will iterate as progress is made in their understanding and as new problems in atmospheric science come to light. The purposes of the subgroup, as reflected in this document, include:

- Recommending research activities, and levels of staffing and funding for those activities, to funding agencies. This will include recommendations on instrument testing and validation activities, made in collaboration with the respective subgroups, insofar as they affect the error assessment of data products.
- Providing scientific advice for the purpose of refining the SCIAMACHY instrument requirements. This includes advice on the needs and desires for particular atmospheric measurements, the required precisions and accuracies for these measurements, and the tradeoffs between conflicting measurements, and between measurements and instrumental complexity.
- Providing scientific advice as input to the SCIAMACHY calibration and characterization. Determination of instrument characteristics has an intimate effect on the ability to retrieve atmospheric constituents. This document will serve as an interface between data and algorithm issues and the related calibration and characterization needs.
- Recommending the scientific component of data product definitions.
- Guiding the development of operational algorithms. The scientific requirements for operational software, much of the detailed atmospheric physics, and in many cases the coding of the physics at a pre-operational level are done as part of the SCIAMACHY science development.
- Guiding the development of higher level data products. As in the previous item on operational algorithms, in many cases the scientific studies done in the context of this group's activities have direct utility for level 3 and higher data products.
- Detailing which auxiliary data are necessary for the production of both scientific and operational data products.
- Recommending certain activities as part of the planning for the Envisat-1 program, in order to maximize to scientific usefulness of SCIAMACHY.
- Performing further research as required by the SCIAMACHY Scientific Advisory Group.

2.4 Prioritized scientific issues and applications

Over the last 100 to 150 years significant changes have occurred in the composition of the atmosphere. These changes, which are anthropogenic in origin, may well have far-reaching consequences for the climate on earth. They may also seriously affect our ecosystem in many other ways. There is considerable uncertainty about the composition of the atmosphere and the chemical interactions between the various constituents of the atmosphere. A problem in determining the details of the composition is that the

concentrations of the trace gases of interest are very low (the mixing ratios of most constituents are of the order of 10^{-6} or less). By getting to know more about the changes in the composition of the atmosphere we may be able to exert greater control over the possible effects of these changes.

A comprehensive program of observations can reduce our uncertainty about the composition of the atmosphere. In addition, model calculations will make a valuable contribution to the analysis and interpretation of the observations. Because of improved computer facilities we now have very advanced models which are able to simulate not only the physics and dynamics of the atmosphere but also a large number of complex chemical reactions between the various constituents of the atmosphere. The calculations make it possible for us to analyze how the atmosphere responds to changes in its chemical composition. Model results, of course, have to be tested rigorously against independent observations. By using the various observational techniques now available we should be able to obtain a fairly complete picture of the various processes that occur in the atmosphere. In practice, however, it will not be possible to observe all processes completely. We expect that further progress will depend largely on the synthesis of model calculations and observations.

SCIAMACHY will be put into orbit in 1999. It will take measurements of the sunlight that is reflected by the earth and by the atmosphere, providing high quality determinations of the composition of the atmosphere for a number of years. Thus it will play a very important role in unraveling the chemical composition of the atmosphere.

2.4.1 Chemical and physical processes in the atmosphere

Ozone (O_3) The chemistry of the boundary layer and the free troposphere differs markedly from that of the stratosphere. Therefore we give separate descriptions of chemical reactions of ozone in the stratosphere and in the troposphere.

Tropospheric ozone Whereas the amount of stratospheric ozone is declining, the concentration of tropospheric ozone is increasing due to emissions of nitrogen dioxide and hydrocarbons. This increase is undesirable because tropospheric ozone has a harmful effect on the environment. Tropospheric ozone forms mainly in the atmospheric boundary layer, on a local to regional scale. To study the ozone cycle in that layer we currently have to rely mainly on observations made on the ground or from airplanes. The influence that regional air pollution has on the chemical composition of the free troposphere is partly determined by the exchange between the boundary layer and the free troposphere. Satellite measurements of, for instance, nitrogen compounds in the troposphere will give us more information about tropospheric ozone formation.

Stratospheric ozone The ultraviolet radiation that is harmful to man and the environment (wavelength <320 nm) is strongly absorbed by the ozone in the stratosphere. 90% of the total atmospheric ozone is in the stratosphere, the maximum concentrations being at altitudes between 20 and 30 km. Ozone is formed by the short-wave ultraviolet photolysis of oxygen (wavelength <242 nm). It is removed by dissociation by long-wave ultraviolet radiation (wavelength between 240 and 300 nm), chemical re-

actions with molecules of natural and anthropogenic origin (hydrogen, nitrogen, chlorine, and bromine oxides) and transport to the troposphere.

The ozone concentration therefore depends strongly on the solar radiation and varies considerably with season and latitude. There is increasing evidence that the ozone shows not only periodic variation but also a general declining trend. The hole in the ozone over Antarctica, caused mainly by anthropogenic chlorine and bromine emissions, is the most striking example of this.

Modern satellite sensors have proved capable of measuring the horizontal distribution of ozone on regional and global scales. These measurements can be used to study the horizontal transport of ozone. To analyze the vertical transport, one needs to measure the vertical distribution of ozone as well. Since this has been done only sporadically, one can obtain only a fragmentary picture of the 3-dimensional distribution of ozone.

To study ozone chemistry one also needs to take measurements of halogen compounds, such as ClO, OClO, and BrO. To date, very limited measurements of stratospheric OClO and BrO have been made, giving only a fragmentary picture of their impact on ozone chemistry on regional and global scales.

Because the SCIAMACHY instrument can be calibrated in flight during its operational mission it should be possible to use the SCIAMACHY data to determine the long-range trend (*i.e.* over several years) for ozone within an error margin of 1%. Because the instrument works in both nadir and limb scanning modes, it should be possible to use SCIAMACHY measurements to reconstruct the 3-dimensional structure of the ozone distribution. Because the instrument has high spectral resolution over a wide spectral range, the data it yields should enable us to determine the atmospheric concentration of a number of compounds involved in ozone chemistry. Clearly, the SCIAMACHY data are going to play a very important role in further studies of atmospheric ozone.

Carbon monoxide (CO) SCIAMACHY measurements will provide global information on the production of CO from the use of fossil fuels and from biomass burning. CO is the major reactant with OH in the background troposphere. Thus, SCIAMACHY measurements of the CO distribution will provide an improved understanding of the odd hydrogen and organic photochemistry of the troposphere.

Nitrous oxide (N₂O) The release and uptake of nitrogen-containing trace gases by ecosystems have important implications for atmospheric composition and nutrient fluxes and cycling. Nitrous oxide, a significant greenhouse gas with a long atmospheric lifetime, is the most important agent in natural ozone destruction in the stratosphere and has been increasing in atmospheric concentration at the rate of about 0.25% per year. Nitrous oxide is formed in soils by both nitrification and denitrification processes in both natural and agricultural ecosystems.

Methane (CH₄) The concentration of methane is increasing in the atmosphere at a rate of about 1% per year and has approximately doubled in the past few hundred years. Though the increase has flattened off in recent years for as yet uncertain causes, methane is an important greenhouse gas that, on a molecule-for-molecule basis, is about 20 times more effective than carbon dioxide in trapping heat.

In addition to its role as a greenhouse gas, methane is an important sink for the hydroxyl radical in the atmosphere.

Depending on atmospheric nitrogen oxide concentrations and other chemical parameters, methane increases can change the atmospheric concentrations of the hydroxyl radical and hence change the atmospheric lifetimes and concentrations of several important gases, which would lengthen the time over which a species like methane contributes to radiative forcing of the climate system. Also, methane is an important source of water vapor in the stratosphere, and increases in stratospheric water vapor can have other significant global consequences. The mechanism of methane production is fairly well known and results from anaerobic microbiological processes in wetlands, rice fields, and ruminants.

The major research activities focus on the following.

- Process studies that relate methane production, consumption, and fluxes to environmental parameters, including human activities such as burning and livestock farming.
- Improved instrumentation for the direct measurement of methane fluxes over small- and large-scale regions must be developed in order to improve our understanding of the relationship between fluxes and ecosystem processes and dynamics.
- In order to fully understand the atmospheric methane cycle, improved estimates of the atmospheric oxidation by the hydroxyl radical must be obtained. This requires a more complete understanding of atmospheric photochemistry than is currently available. Specifically, it is necessary to either directly or indirectly determine the concentration of OH in the atmosphere and the chemical processes that control this concentration. The methane increase should be considered in relation to OH concentrations (and hence a changed oxidizing capacity of the atmosphere) through changes in the atmospheric concentrations of OH sinks.

The hydrological cycle Although SCIAMACHY is not designed specifically for studying the hydrological cycle, the measurements it takes can be very useful in this respect. The cycle plays an important role in the greenhouse effect. The carbon dioxide concentration increases as a result of the burning of fossil fuels. Because of the strong absorption of thermal radiation from the earth this increase in carbon dioxide disturbs the radiation balance at the top of the troposphere. If this initial disturbance is coupled to the hydrological cycle this could lead to a rise in the temperature of the atmosphere on a global scale. So far little is known about the relation between the radiation balance and the hydrological cycle. Current satellite sensors are able to detect the horizontal distribution of water vapor and clouds. These data are used to check the accuracy of climate models. Because there is a lack of accurate measurements of water vapor concentrations in the top layers of the troposphere (made in combination with measurements of the radiation budget) the relation between the two processes is not understood.

When the SCIAMACHY measurements with their high resolution are supplemented by measurements made by other sensors on board the ENVISAT satellite it should be possible to study the vertical distribution of water vapor in great detail. Because of its relatively poor spatial resolution the instrument is less suitable for analyzing the influence of clouds on aspects such as the chemical composition and the radiation balance of the atmosphere. However, the quantification and the identification of sub-pixel clouds

and cloud height with the help of SCIAMACHY data are important for the development of retrieval methods for tropospheric trace gases.

Carbon dioxide (CO₂) Atmospheric carbon dioxide concentrations have been rising at rates apparently faster than ever before in the earth's history. During the last decade, these increases have been associated with increasing amplitude of the annual cycle of atmospheric carbon dioxide and possibly surface air temperature of the Earth. It is essential to know the causes and effects of the accelerated rate of increase in atmospheric carbon dioxide, because it is a radiatively active greenhouse gas that has contributed to global warming and will continue to do so and because it has direct effects on ecosystems. More specifically:

- Why don't the perceived sources and sinks match the interhemispheric carbon dioxide studies? Much is known about the major sources and sinks for carbon dioxide and the global pattern of carbon dioxide transport in the atmosphere, but currently the perceived sources and sinks for carbon dioxide do not match the interhemispheric carbon dioxide gradient.
- What is the effect on climatic change of episodic events such as biomass burning, the amount of carbon released, the resultant change in vegetation, and consequent changes in albedo, evapotranspiration, and plant production? These effects should be addressed with satellite monitoring of disturbances such as fires and then related to surface moisture, temperature, and biomass.
- What are the pools of biomass and soil carbon, net primary production, and ecosystem respiration in the world's ecosystems? New data must be acquired by remote sensing of surface temperature, surface moisture, atmospheric water vapor concentration, and indicators of vegetation production and biomass.

2.4.2 Modeling of transport and chemistry

Global methods of the atmosphere deal with transport phenomena (dynamics) and the chemical composition. They therefore have to contain both a chemical and a meteorological module. The chemical part includes a number of reaction chains transformed into differential equations: for the study of air pollution, more than 50 substances and 150 reactions between these substances are investigated. The meteorological module provides a description of the transport processes and of the energy and radiation budget in the atmosphere. So far, little is known about the mechanism of vertical transport, namely the exchange between the troposphere and the stratosphere. The simplest chemical models give a description of the vertical distribution of trace gas compounds and describe the transport in the form of a turbulent diffusion equation. Details of the chemistry can be incorporated in these models and in this equation.

Two dimensional models (depicting height and latitude) make it possible to describe the dynamics (circulation) of the zonally averaged atmosphere. They are a compromise between detailed dynamical and detailed chemical processes.

Global circulation models describe the 3-dimensional physical and dynamical state of the atmosphere. At present various attempts are being made to find a way of integrating meteorological and chemical

models. Limited computer capacity is still a restricting factor in this kind of research. The spatial and time resolution of the models varies considerably. They vary from 100 to 5000 m in height and between 1 and 24 hours in time. "Sub-grid processes" (processes that occur on smaller spatial or temporal scales than those of the model) have to be described in the model by means of parameterizations. In the near future 3-dimensional models will be developed which will be able to describe the chemical and dynamical processes in the troposphere and the stratosphere (*e.g.*, within the framework of GLOMAC). The horizontal resolution of these models will be 20-1000 km and the vertical resolution will be about 0.5 -1 km. Trace gas measurements are of fundamental importance in the development of these models. They prescribe the starting conditions and validate the results.

2.4.3 Aerosols

Aerosols can affect local, regional, and global air quality. The roles they play in atmospheric processes can also affect weather and climate. In the following, several important scientific issues associated with atmospheric aerosols are discussed:

Radiative properties of atmospheric aerosol The scattering and absorption of atmospheric aerosols in the visible and infrared spectral region can directly impact the radiation budget of the Earth-atmosphere system. The complex dependence of aerosol radiative properties on composition, shape, size distribution, and abundance presents the major obstacle to the understanding of their impact on climate. Both tropospheric and stratospheric aerosols can be important in radiative forcing of climate. In the stratosphere, concentration of aerosols can increase significantly after a major volcanic eruption, thereby producing large perturbation to the net radiative balance of the Earth.

Cloud-aerosol interactions Since cloud droplets form through condensation of water vapor on cloud condensation nuclei, *i.e.*, aerosol particles, aerosols can modify the microphysical properties of clouds, affecting their radiative properties. A strong aerosol-enhancing albedo relation has been observed in the wake of ship-stack effluents. Hence, a global increase in tropospheric aerosol loading has the potential to increase the albedo of the planet.

Biomass burning aerosols in the tropics Biomass burning in the tropics generates large quantities of smoke particles and trace gases which could affect atmospheric chemistry and global climate. The radiative, physical, and chemical properties of smoke aerosols are still not well known.

Arctic aerosols and polar stratospheric clouds Concentrations of anthropogenic aerosols have increased significantly in the northern-most latitudes. These aerosols are predominantly composed of sulfates, black carbon, and organic carbon. They are effective in perturbing the radiation balance in the underlying high-albedo Arctic region. Polar stratospheric clouds are known to play an important role in the development of the springtime Antarctic ozone hole by perturbing the normal stratospheric chemical balance and by catalyzing heterogeneous chemical reactions which liberate reactive chlorine for catalytic

ozone destruction. Similar processes could lead to ozone destruction in the Arctic over smaller temporal and spatial scales than those typical of the Antarctic.

2.5 Executive summary of GOME studies relevant to SCIAMACHY data and algorithm issues

GOME is a reduced version of the SCIAMACHY instrument, so that many of the software tools developed for GOME and much of the experience gained with GOME can be applied to SCIAMACHY.

2.5.1 Radiative transfer models

A number of radiative transfer models have been used in GOME studies, including the development of the GOME operational processing algorithm. Codes developed by the members of the GOME Scientific Advisory Group (GSAG) include: the GOMEtran finite-difference multiple scattering code, to be used in the second generation of GOME operational processing; the AMFtran single-scattering code, used for the initial operational algorithm in conjunction with multiple scattering look-up tables generated using GOMEtran; the DAK multiple scattering code, which includes polarization; and the GOMEsim code, which includes several special features for the investigation of surface conditions.

Additional models that have been used by GOME investigators for a number of applications include Lowtran/Modtran, Disort, Interlope, and the Dave radiative transfer code used by the SBUV/TOMS investigators.

2.5.2 Retrieval algorithms

Gases The Differential Optical Absorption Spectroscopy (DOAS) method has been selected as the first operational GOME retrieval algorithm to derive total column amounts of O₃ and NO₂. Later versions of the algorithm will use the Optimal Estimation technique. This will include, in the near future, the retrieval of the ozone profile. Optimal estimation is also being used by several research groups for the retrieval of scientific data products from GOME. Additionally, the retrieval methods used for analysis of SBUV and TOMS data, which include optimal estimation in the latest versions, have been available for GOME data analysis studies.

Clouds The GOME Initial Cloud Fitting Algorithm (ICFA) uses a linear fit to absorption templates in the O₂ A band for retrieval of cloud coverage. More sophisticated methods, which might include the use of the Polarization Measuring Device (PMD) information are currently under development.

Aerosols A GOME aerosol optical thickness algorithm is currently being developed. It is based on fitting to minimize the differences of spectral radiances including aerosol contributions calculated using GOMEsim and those measured with GOME.

2.5.3 Databases

The following databases have been selected for the operational GOME software following recommendations of the GOME Data and Algorithm Group.

Gas absorption parameters Absorption cross section measurements are available for O₃, O₄, NO₂, NO₃, ClO, OClO, BrO, H₂CO, and SO₂ from a number of sources, including measurements of O₃ and NO₂ with the GOME breadboard and flight models. An improved set of line parameters was developed for the O₂ A band specifically for GOME [Chance, 1996]. Line parameters for H₂O are currently from the Hitran database.

Aerosol parameters The parameters currently available are the Lowtran database for aerosol loading, spectral dependence of extinction, and scattering phase functions. These are supplemented by new results, including extinction and scattering coefficients, single scattering albedos, phase function moments, and asymmetry factors for six basic aerosol types which have been recommended by WMO to be mixed additively in a weighted form to obtain the aerosol most suitable for a given geolocation and time of the year [WMO, 1983].

Cloud spectral parameters Clouds are described in the operational software database by bi-directional cloud top reflectances for a number of incident and reflected zenith angles from 0° to 90° and relative azimuth angles from 0° to 180°. Reflectances are given for eight different cloud types and at 25 wavelengths across the GOME range. The cloud top reflectivity is supplemented by tables for the escape function, which accounts for light which penetrates into the cloud and leaves it again, developed by the University of Bremen.

As an alternative to their description as reflecting surfaces, clouds can be treated as particle layers with high optical density. In this case their description requires spectral parameters similar to the ones for aerosols, *i.e.*, profiles of extinction and absorption coefficients, asymmetry parameters, and the phase function moments, derived from Mie calculations. These parameters will be implemented in the operational DLR software for the same eight cloud types and at 25 wavelengths across the GOME range from 200 nm to 800 nm.

Surface parameters Topography is available as a global database derived from the U.S. National Oceanographic and Atmospheric Administration (NOAA), which has been degraded from the original 5 arc-second resolution to a 1° × 1° grid.

At present a database for a bi-directional surface reflectance which includes the dependence on the angles of incidence and reflection is available only over the ocean. The results have been obtained from a sea glitter reflectance model developed at IMGA/CNR [Guzzi and Cervino, 1992]. Values are given for 30 incident solar zenith angles, 25 wavelengths in the GOME range, and 5 wind speeds.

A geographically coded global data set for the albedo is used in the operational software: The earth's surface is classified into 31 surface types on a $1^\circ \times 1^\circ$ grid, with a single albedo value for each surface type. An alternative data set available for testing purposes includes five land surface types where the wavelength dependent albedo is given at 86 wavelengths across the GOME range for each surface type. These data are not geographically coded.

Atmospheric constituent profiles Vertical profiles of atmospheric pressure, temperature and trace gases concentrations are from a two-dimensional atmospheric chemo-dynamical model of the Max Planck Institute for Chemistry in Mainz, Germany [Brühl, 1992]. Profiles are given for 34 pressure levels between 0 and 61 km and 18 latitude zones. Monthly pressure and temperature, and seasonal trace gas concentrations are given. Trace gases include O_3 , NO, NO_2 , NO_3 , ClO, OClO, BrO, and H_2CO .

This database is supplemented by six scenarios from an AFGL database [Anderson *et al.*, 1986]. The scenarios are for the tropics, midlatitude winter and summer, Antarctic winter and summer, and the U.S. Standard Atmosphere. They are given from 0 to 120 km for pressure, temperature, O_3 , NO, NO_2 , ClO, H_2CO , SO_2 , and H_2O . They are especially used to complement the MPI profiles, which cover only altitudes up to 61 km. Both the MPI and the AFGL profiles describe “unperturbed” atmospheric conditions.

Additionally, eight “special” scenarios which are representative for different perturbed atmospheric compositions corresponding to ozone hole conditions (day-time and night-time), biomass burning, perturbations following volcanic eruptions, polar stratospheric clouds, industrial pollution, twilight conditions, and a so-called worst case (for the retrieval of ozone) scenario have been developed for GOME test purposes.

Solar spectra Available solar spectra include: The Lowtran solar spectrum (174 to 352 nm at 10 cm^{-1} resolution and 347 nm to $2.5\ \mu\text{m}$ nm at 20 cm^{-1} resolution), and a solar reference spectrum from 230-800 nm, at 0.01 nm resolution, derived from measurements of Hall and Anderson [1991] and Kurucz *et al.*, [1984] re-calibrated in vacuum wavelength [Chance and Spurr, 1996].

Ring spectra Ring effect spectra for the analysis of GOME measurements have been measured using the GOME flight model, and have been calculated by the University of Bremen, the University of Heidelberg, and the SAO [ESA, 1996; Chance and Spurr, 1996].

2.5.4 The software framework GOMEware

GOMEware is a program to simulate and analyze atmospheric spectra in the ultraviolet, visible and near infrared bands for wavelengths from 240 to 790 nm. It is especially intended to facilitate studies related to the GOME instrument, but is not limited to those functions. The development of GOMEware has substantially slowed lately, mainly due to funding limitations. Therefore, it has not been possible yet to accommodate the most recent modifications for radiative transfer models and retrieval algorithms which have been developed and tested off-line.

The current version of GOMEware includes three different radiative transfer models, Lowtran and plane-parallel versions of Disort and GOMETran. With respect to retrieval algorithms the SBUV retrieval procedure is included, an early version of Optimal Estimation and an incomplete version of the DOAS algorithm. Databases for molecular absorption include the gases O₃, O₂, O₄, NO₂, NO₃, BrO, ClO, OClO, H₂CO, H₂O and SO₂. Aerosol phase functions can be described by either Mie calculations or Henyey-Greenstein factors. A large selection exists for atmospheric trace gas and aerosol compositions, including perturbed atmospheric conditions such as ozone hole, biomass burning, tropospheric pollution or volcanic events. Databases for clouds have not been prepared yet. The desired viewing geometry can be either set explicitly or derived from a satellite propagator for ERS 2. Signals as measured with GOME can be simulated with the GOME instrument simulator using radiances calculated with either of the radiative transfer models. GOMEware is described in a Users Guide [Lavagnino, 1993].

2.5.5 The GOME Instrument Simulator

The purpose of the GOME Instrument Simulation Software (GISS) is to simulate and analyze the performance of the instrument in terms of signal transmission and noise, depending on various input and characterization data which can be changed by the user [Slijkhuis, 1994]. More recently, the SCIAMACHY Instrument Simulation Software (SISS) has been developed as well.

The program uses a "travelling spectrum" approach, where the input spectrum travels through the instrument and is modified each time it encounters optical/electronic components. This approach allows easy analysis of the influence on the output caused by a certain component (by changing its characterization data), and it is well suited for signal-to-noise calculations.

From a user-supplied (polarized) input radiance or irradiance spectrum the program calculates output signals and signal-to-noise ratios, taking into account polarization-dependent transmission/reflection of optical components, spectral degradation (using a user-supplied slit function), stray light (uniform, user-supplied magnitude), detector pixel binning, detector quantum efficiency and leakage current, electronic amplification and ADC conversion. Simulations can be performed for various instrument modes, including calibration modes.

The first versions of the software used the MATHCAD environment. To overcome memory and CPU limitations the package has been written in FORTRAN-77, with an interface to the PV-WAVE graphical package for display of the results. Configuration control will be carried out under SRON responsibility. Test and validation of the SISS is carried out by various users (*e.g.* ife Bremen). The package will be distributed by ESTEC.

2.5.6 Error analysis of DOAS and optimal estimation algorithms

Since 1992 ESA has been funding a study concerned with the retrieval of atmospheric constituents from space-borne ultraviolet and visible spectrometers. The first two-year phase of this study prepared and/or developed potential methods to derive column amounts and profiles from GOME data. Investigated methods were DOAS, Optimal Estimation, and FURM. The results of this work, which was focused on

the provision of suitable software tools and a preliminary assessment of retrieval accuracy, are summarized in Burrows *et al.*, [1994]. The study continued in 1994 with a second phase which was dedicated to a thorough error assessment of the operational DOAS algorithm and to a further development of Optimal Estimation for O₃ profile retrievals.

3 Targeted Atmospheric Constituents and Geophysical Parameters

SCIAMACHY measurements rely on the observation of the solar radiation, which is transmitted, reflected or scattered through the atmosphere. At the spectral resolution of SCIAMACHY, characteristic spectral features of a number of molecules can be measured. SCIAMACHY channels 1 to 6 cover the entire spectrum from 240 to 1700 nm, which corresponds to the first atmospheric window. Channels 7 and 8 cover selected regions between 2 and 2.4 μm in the third atmospheric window. To minimize the number of channels, no measurements are currently planned in the second atmospheric window between 1.7 and 1.9 μm .

SCIAMACHY has three measurement geometries: nadir observing, viewing the earth's limb in scattered light, and solar and lunar occultations. In nadir observation alone, profile information is determinable in some cases by differential penetration of backscattered light at different wavelengths (as in TOMS/SBUV), and by the variable temperature structure of some molecular absorptions. Height resolution from nadir measurements is limited to 8-10 km from differential penetration and ~ 5 km in favorable cases using temperature structure. Height resolution in limb viewing is ~ 3 km, limited by the weighting functions for limb scattering and by the spacecraft stability. Height resolution is 2.5 km minimum for occultations, limited by the IFOV of the instrument.

3.1 Retrieval priorities for atmospheric chemistry

The SCIAMACHY instrument provides a unique opportunity for simultaneous atmospheric measurements of multiple species relating to potentially critical processes. The scientific drivers for the SCIAMACHY measurements reflect this capability. The prioritized scientific measurements are:

1. Simultaneous measurements of tropospheric constituents related by pollution chemistry: O₃, CO, N₂O and CH₄ in nadir viewing.
2. Resolution of tropospheric and stratospheric amounts of photochemically-active species by sequential nadir-limb measurements: CO, CH₄, N₂O, and O₃.
3. Stratospheric and tropospheric aerosols.
4. Height-resolved studies for halogen loading in polar regions by limb viewing: BrO, OClO, and NO₂.

3.2 Targeted constituents in the various channels

Channel 1: 240-314 nm. Due to the fall-off in the solar source function and the absorption due to O₃, light levels are relatively small in this channel which is used to observe the O₃ Hartley band maximum and the NO γ -band emission. (Under high ClO and low O₃ conditions the strongest ClO absorptions may also be observed).

Channel 2: 309-405 nm (UV-B and UV-A radiation). A variety of molecules have banded absorption features in this region: O₃, O₄, NO₂, ClO, OCIO, BrO, SO₂, and H₂CO.

Channel 3: 400-605 nm. The following molecules have identifiable banded visible absorption features: NO₂, NO₃, OCIO, H₂O, O₂, O₃, and O₄.

Channels 4 and 5: 590-810 nm and 790-1055 nm. The following species absorb significantly in this region NO₃, O₃, O₂, O₄, and H₂O. Channel 5 is also a primary aerosol channel.

Channel 6: 1000-1700 nm. This is a primary aerosol channel. Features due to O₂(¹ Δ_g), O₄ and H₂O may also be observed.

Channel 8: 1940-2040 nm. This region is specifically chosen for CO₂ measurements. H₂O also absorbs in this region.

Channel 8: 2265-2380 nm. Absorptions due to CO, CH₄, N₂O and H₂O are observed in this atmospheric window.

3.3 Targeted constituents from different viewing geometries

Nadir observations: Total column amounts of O₃, O₂(¹ Δ_g), O₄, O₂, CO, H₂O, CH₄, CO₂, NO₂, N₂O, H₂CO, SO₂, ClO, OCIO, and BrO; stratospheric profiles of O₃, the column of NO above the ozone layer; tropospheric profiles or columns of O₃, CO, H₂O, CH₄, CO₂, N₂O. Stratospheric profile information, discrimination between stratospheric and tropospheric columns, and, in some cases, tropospheric profile information is derived from the temperature dependences of the absorption features.

Limb viewing observations: Stratospheric profiles of O₃ (20-50 km), O₂(¹ Δ_g) (50-90 km), O₂ (20-50+ km), CO (20-35 km), H₂O (20-53 km), CH₄ (20-40 km), CO₂ (20-50+ km), NO (40-140 km), NO₂ (20-40 km), N₂O (20-35 km), BrO (20-25 km under normal conditions; 20-30 km under ozone hole conditions).

Solar/lunar occultations: Stratospheric profiles of O₃ (15-50 km), O₂(¹ Δ_g) (below 50-90 km), O₂ (15-50+ km), CO (15-35 km), H₂O (15-53 km), CH₄ (15-40+ km), CO₂ (15-50+ km), NO₂ (15-40 km), N₂O (15-35 km), BrO (15-35 km under normal concentrations). Occultations are more infrequent than limb scattering observations, and are limited to latitudes of 50-80°, but provide the most sensitive and precise profile retrievals.

Tropospheric amounts from limb-nadir subtraction: tropospheric columns of O₃, CO, H₂O, CH₄, CO₂, NO₂, N₂O.

4 Data Product Level Definitions

- Level 0: SCIAMACHY reformatted data delivered in compatible format
- Level 1b: geolocated, engineering calibrated radiances
- Level 2: geolocated, calibrated concentrations
 - Gases, aerosols, and cloud products
 - Nominally based on SCIAMACHY and associated auxiliary data
 - Optionally (multi-sensor product) based on SCIAMACHY, other instruments flying on Envisat, and auxiliary data
- Level 3: interpolated and temporally-averaged data
- Value added products: other products derived from SCIAMACHY level 1, 2, or 3 products and merged with additional data (*e.g.*, assimilation in models, advection using wind fields).

5 Requirements for SCIAMACHY Level 1b Data Processing

SCIAMACHY level 0 data is converted into level 1b calibrated radiances by applying calibration algorithms using parameters from the calibration database.¹ Calibration parameters are determined pre-flight and updated regularly during the mission using data obtained in the SCIAMACHY calibration modes. The calibration parameters form a complete “calibration database,” maintaining continuity over the lifetime of the mission. The required elements for level 1b processing include:

1. Modeling of the solar spectrum and radiation transport, including:
 - (a) Changes in terrestrial albedo, surface studies (including topography and BRDF); lunar albedo measurements, averaging over IFOV, lunar phase
 - (b) Changes in the solar spectrum, as measured in solar spectra taken by SCIAMACHY for calibration (using cross-correlation with reference Fraunhofer spectrum)
2. Modeling of the quantity actually measured by each pixel in the detector arrays and conversion into equivalent radiance values, including:
 - (a) Telescope field of view, vignetting, lunar filling function
 - (b) Modulation transfer function, line/point spread function
 - i. Optical efficiency vs. wavelength, and its polarization dependence (especially at crossover points)

¹By level n processing we mean: processing level $n - 1$ data to produce level n data. The term “level n and higher processing” will be sometimes be abbreviated as “level $n+$ processing”.

- ii. Stray light
 - iii. Pixel effects - blooming, cross-talk, finite size, memory effects
 - iv. Pixel and optics changes - drift, temperature effects (thermal gradients)
 - v. Gain versus wavelength, temperature
- (c) Ageing effects, including their identification from measurements and the use of calibration data to correct them, diffuser plate characteristics versus time, contamination
 - (d) Optical depth in pixel averaging (especially detector I)
 - (e) Doppler effect in the measured spectrum due to spacecraft motion
 - (f) Detector noise, photon noise, microphonic and microthermal contributions to noise/dark current (track 1 - additive dark current spectrum), electronic pickup (EMI)
 - (g) ADC effects, including nonlinearity, missing codes, digitization noise
 - (h) Defective pixels, cosmic ray effects
 - (i) Telemetry errors
 - (j) Wavelength, intensity, and polarization calibration (including thermal drift), interpolation of calibration in time

The modeling will include extensive feedback from calibration/characterization and instrument model studies. The algorithm requires the conversion of the measured quantities into radiances as part of the level 0→1 processing of the data.

- 3. Geophysical parameter inputs, data registration
 - (a) Time and location of subsatellite point and, in case of limb/occultation, tangent point
 - (b) Orbital parameters
 - (c) Sun and moon ephemeris data
 - (d) SCIAMACHY requires that the wavelength-dependent albedo and aerosol distributions be known for constituent retrievals. It may be possible to determine these from the SCIAMACHY data itself to the required accuracy.
- 4. Error analysis

6 Requirements for SCIAMACHY Level 2 Data Processing

The largest uncertainties in the 1-2 processing will be from uncertainties in the inputs to the forward modeling, including albedo functions, cloud models, scattering models, and scattering cross sections. The modeling studies will provide substantial feedback to the instrument characterization requirements (including molecular absorption and aerosol scattering cross sections).

6.1 Forward models

The forward modeling for SCIAMACHY operational processing will likely be a parameterized look-up scheme based on calculations from a validated multiple-scattering forward model such as GOMETran. This may include a look-up form of multiple scattering and albedo correction such as that currently employed in the TOMS/SBUV algorithms. During model testing, at least, it will be necessary to include models with polarization, such as the currently-available DAK (KNMI) and GOMESim (IMGA) models, and the Dave-Mateer code used in the TOMS/SBUV forward modeling. The forward modeling will include ray-tracing and will calculate absorption and scattering using the databases as detailed below in this section.

Aspects of modeling studies that need to be included in scientific and, later, operational development include:

- The forward model(s) must be extended to include rapid line-by-line calculations and, in favorable cases, the use of exponential sum fitting coefficients or band models.
- The forward models must include thermal radiation in the infrared.
- Modeling studies will need to include the effects of averaging over the IFOV.
- Modeling studies will need to include the effects of averaging over the lunar phase.
- The Ring effect: corrections for rotation Raman scattering in Fraunhofer and molecular absorption structures.
- The change in index of refraction over the enormous wavelength range measured by SCIAMACHY must be considered in ray tracing studies.
- Limb issues: source function; radiative transfer models; global fitting.
- Occultation issues: sampling over solar disk; global fitting.
- Cloud and haze models, cirrus, avoidance of glint and halos.
- Extension of atmospheric modeling to the limb geometry.

6.1.1 Models specific to occultation measurements

Atmospheric refraction model An atmospheric refraction model describing the apparent changes in shape of the solar or lunar disk as view from the spacecraft platform at different tangent heights in the atmosphere must be used in the forward modeling for both scientific and operational development. The model can be constructed from ray tracing calculations using prescribed temperature and pressure profiles.

Solar and lunar limb darkening profiles; lunar albedo Solar limb darkening profiles at the measurement wavelengths of the SCIAMACHY instrument will be needed for calibration of the solar occultation measurements and for the detection of sun spots on the solar limb curves. The lunar albedo map being produced by USGS will be useful for processing the lunar occultation measurements. Lunar limb darkening will also need to be modeled.

6.2 Spectroscopic databases

6.2.1 Introduction

In order to retrieve geophysical parameters (P, T, concentration profiles, etc.) from the SCIAMACHY measurements, a detailed knowledge of the spectroscopic properties of all the species absorbing significantly in the spectral domains covered by SCIAMACHY will be required. Since SCIAMACHY is a rather high resolution experiment (up to 0.25 cm^{-1} in the infrared) the line structure of the spectra, when it exists, will be observed. This means that it may be necessary to perform line-by-line calculations. Moreover, even if band models or exponential sum fitting coefficients are used, it will be necessary to validate them through comparisons with line-by-line calculations.

Spectral parameters The spectral parameters needed for the retrievals are not the same when dealing with spectra of lines as they are when dealing with continua. However, it is worth stressing that, since the atmospheric temperature is varying (over approximately 180-300 K), in both cases it is essential to know precisely the temperature dependence of the spectral parameters. Their pressure dependences will also need to be considered.

Spectra of lines For those spectra which are produced by rather light species (H_2O , CH_4 , CO_2 , O_3 , etc.) the relevant spectral line parameters are:

- Line positions and their pressure shifts.

These can be calculated using modern quantum-mechanical models. However, all important molecular parameters must come from laboratory measurements using high-resolution spectroscopy. Generally, every line has an individual set of quantum numbers for its assignments.

- Line intensities at a given temperature, together with the lower energy levels of the transitions and the partition functions of the molecules, in order to calculate the temperature dependences.

While the temperature dependence of the individual line intensity is easy to calculate provided that the quantum mechanical assignment is correct (*i.e.* the lower state's energy is known), line intensities also need to be measured in accurate high-resolution spectroscopic experiments, and may vary in value and precision among experiments.

- Air broadening coefficients and their temperature dependences.

Self broadening coefficients could be necessary as well, at least for tropospheric molecules such as H₂O, whose self broadening coefficients are much larger than air broadening coefficients; for all broadening coefficients, high-precision laboratory experiments are needed.

- Line mixing effects, which must be considered in the case of “piling-up of lines.”
These latter effects are important mainly in Q branches, *i.e.*, superpositions of many lines forming one strong absorption peak.

Continua One deals here with unresolved spectra of species which do not exhibit individual lines but, rather, continuous absorptions. These could be either “real” continua (electronic transitions leading to dissociation of the molecule, induced spectra of O₂ and N₂, H₂O continuum, aerosols, clouds) or “pseudo” continua (electronic spectra of molecules where slow dissociation occurs due to intra-molecular energy transfer or line spectra of heavy molecules where the density of lines is larger than their widths). Note that in the ultraviolet and visible, in many cases, the resolution of reference spectra currently known from laboratory experiments is not limited by the molecular spectra but by the resolution of the instruments used when recording these spectra.

For either case the relevant spectral data are:

- Absorption cross sections measured at much higher resolution than that of SCIAMACHY; this is important because the cross sections need to be convolved with SCIAMACHY’s instrument function before they can be considered as appropriate for data processing;
- Their temperature dependences in the relevant range (180-300 K);
- Their pressure dependences, when this is relevant.

6.2.2 SCIAMACHY database

Spectroscopic databases already exist (*e.g.*, Hitran) but one may find them not well adapted to SCIAMACHY for the following reasons:

- It is sometimes difficult to assess the quality of their data, which is a main concern as far as the accuracy of the retrievals is concerned;
- Their updates are not usually very frequent;
- They contain much more data than required for SCIAMACHY; *e.g.*, Hitran covers a much larger spectral range than SCIAMACHY, and only a small sub-set of the data is useful for the SCIAMACHY data processing.

Therefore, it is important to review the current status of existing spectroscopic databases with respect to the SCIAMACHY target molecules and spectral regions; however this is a considerable task and will also in future be a constantly evolving process.

It is neither possible nor reasonable to give in this section a detailed description of the accuracy of the existing spectral line parameters for all the spectral bands of all the atmospheric species of interest. However one can make the following general comments (see Table 1 for an overview of the line-by-line situation, and Table 2 for estimates of the quality of cross section data):

Line positions and intensities

1. **H₂O** H₂O absorbs in several channels of the SCIAMACHY experiment. In channel VIII, the spectral line parameters provided in Hitran are mainly calculated values. These calculations were based on a small number of measured intensities, not including transitions with $\Delta K_a \geq 3$. As a consequence, the corresponding lines are poorly predicted (an error in their intensities of a factor 2 is possible), but they are weak lines. For the other channels (III-VII) the data are from experimental measurements and the intensity accuracy depends on the origin of the data. Also, it is worth noting that since no systematic calculation developed for fitting these available data was performed, some lines or bands could be missing. It is certainly true that for H₂O, the status of the existing databases is not very satisfactory with respect to the precision needed for SCIAMACHY.
2. **CO** CO is, from the spectroscopic point of view, a simple molecule and it has been precisely studied. In the case of SCIAMACHY, given the resolution, it is likely that the contribution to the absorption of the atmospheric and of the solar CO will be mixed. This problem has to be addressed, as noted in previous sensitivity studies for the infrared channels of SCIAMACHY.
3. **CO₂** The data for CO₂ (channel VII) are a mixture of experimental results (when they are available) and of calculations (Direct Numerical Diagonalization method, DND). As a consequence one may estimate that, depending on the band, the accuracy of line intensities may vary from 5 to 30%. Line positions are available with precision sufficient for SCIAMACHY.
4. **N₂O** The situation for N₂O is analogous to that of CO₂ except the fact that no systematic calculation by DND was performed. As a consequence the consistency and the accuracy of the data is of lower quality. This means that new laboratory measurements would be of great value to improve the current knowledge of N₂O line parameters with respect to the SCIAMACHY database.
5. **CH₄** Channel VIII corresponds to the so-called octad region, where the eight bands $3\nu_4$, $2\nu_4 + \nu_2$, $\nu_1 + \nu_4$, $\nu_3 + \nu_4$, $\nu_4 + \nu_2$, $\nu_1 + \nu_2$, $\nu_2 + \nu_3$ and $3\nu_2$ appear. No systematic spectroscopy of this spectral region has been performed; the available data are only experimental. As a consequence no systematic assessment can be made on the precisions and it must be recognized that many lines are still unidentified or missing. This is a major problem when the temperature dependence of the CH₄ line intensities needs to be known.
6. **O₂** The line parameters for the $\Delta v = 0$ A visible band of the $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ electronic transition have been re-evaluated for use in GOME cloud fitting [Chance, 1996]. Intensities are now known to 2% and line widths over the atmospheric temperature range to 3%. The higher vibrational bands of this electronic transition (B band, etc.) are less well-determined. Proper modeling will need to compensate for the formation of the O₂-O₂ collisional complex.

Broadening coefficients Broadening coefficients are needed because, for accurate retrieval of concentration profiles from the near infrared channels, they strongly influence the data processing. However, laboratory measurements of line profiles are very difficult and time-consuming. Thus, the situation for the air broadening coefficients is much less satisfying than for the line positions and intensities. Indeed, very few measurements have been performed in the spectral regions of interest for SCIAMACHY. The line broadening coefficients are usually extrapolated, through calculations, from lower lying bands. One problem lies in the fact that the theoretical models are not sophisticated enough to provide precise broadening coefficients for higher harmonics involved in combination bands, and that usually it is then necessary to perform some type of scaling. The situation is even worse for the temperature dependences of these coefficients and for the self broadening coefficients. To the extent that SCIAMACHY will contribute to tropospheric chemistry, this is a very important aspect of the spectroscopic database.

Isotopic variants In the SCIAMACHY spectral regions of interest, comparatively little study has been done on the spectroscopic properties of the minor isotopic variants, such as ^{13}CO , $^{13}\text{CO}_2$, $^{15}\text{N}_2\text{O}$, $^{13}\text{CH}_4$, H_2^{18}O etc. This means that laboratory measurements and spectroscopic studies are still to be done for almost all such species. Consideration of the selection of microwindows for retrieval purposes (see *Recommendations*, below), very important for the minor isotopic variants if it is determined that significant scientific information can be obtained from isotope studies, is thus problematical.

Continua Many studies exist for important continuum absorption spectra, such as O_3 , NO_2 , etc. However, the relative and absolute agreement of the data is very often not enough for the SCIAMACHY data processing. Because of the importance of this issue, it is recommended that the actual status of published data on continua be assessed in a separate document. This should be based on previous studies for the Global Ozone Monitoring Experiment. However, new data have been published and need to be included in the comparisons.

6.2.3 Recommendations

It is necessary to implement a database dedicated to SCIAMACHY with subsets corresponding to the microwindows chosen either for simulation or for operational retrievals; obviously, the improvement of spectroscopic parameters should first concentrate on the microwindow regions, and on the range of pressures and temperatures corresponding to the atmospheric measurements. It is recommended that this SCIAMACHY database should be updated in a regular way with the most accurate spectroscopic data available for the target molecules. For cross section measurements, laboratory data should be obtained at much higher spectral resolution than that of SCIAMACHY. It is also strongly suggested that, once the database is implemented, it be kept under strict configuration control: for meaningful comparisons of retrievals it is indeed of the utmost importance to know precisely which spectral data have been used. (Note: for operational retrievals, the database would presumably automatically be under configuration control.) Finally, great attention must be given to attaching realistic errors to all spectral parameters. Figure 1 presents a schematic of a possible strategy to implement a database dedicated to SCIAMACHY with the conditions recommended here:

- Implement a database for SCIAMACHY.
- Define and implement a subset of this database for the microwindows used in the operational retrievals.
- Update the SCIAMACHY database in a regular way with new spectroscopic data.
- Maintain under configuration control.
- Assess the quality of the spectral parameters of molecules in the microwindows dedicated to their retrievals. It is very important to define through simulations the microwindows of interest for the retrievals, starting from an existing database (Hitran for example). Once this is done, a careful and critical analysis of the quality of the spectral parameters of interest should be performed with, in parallel, a study of the influence of these parameters on the retrieved quantities. In this way improvements to be made will be defined allowing implementation of the necessary spectroscopic studies.

6.3 Aerosols

Cross sections and phase functions appropriate to various climatologies to be encountered are required. The SCIAMACHY measurements of atmospherically scattered light will require a particularly strong interface to recursive database updating. The scattering database includes catalogued scattering cross sections and phase functions, including those in Lowtran, and those developed under ESA-sponsored scattering studies and derived from SAGE II measurements. It also includes vertical distributions of aerosols in the atmosphere.

Spectral signatures from soot, ice crystals, sand storms, etc. are needed.

6.4 Geophysical data

- Changes in terrestrial albedo, surface studies (including topography and BRDF); lunar albedo measurements (USGS lunar studies will be applicable here).
- Pressure and temperature fields.

FIGURE 1

Schematic of a strategy to implement a database dedicated to SCIAMACHY

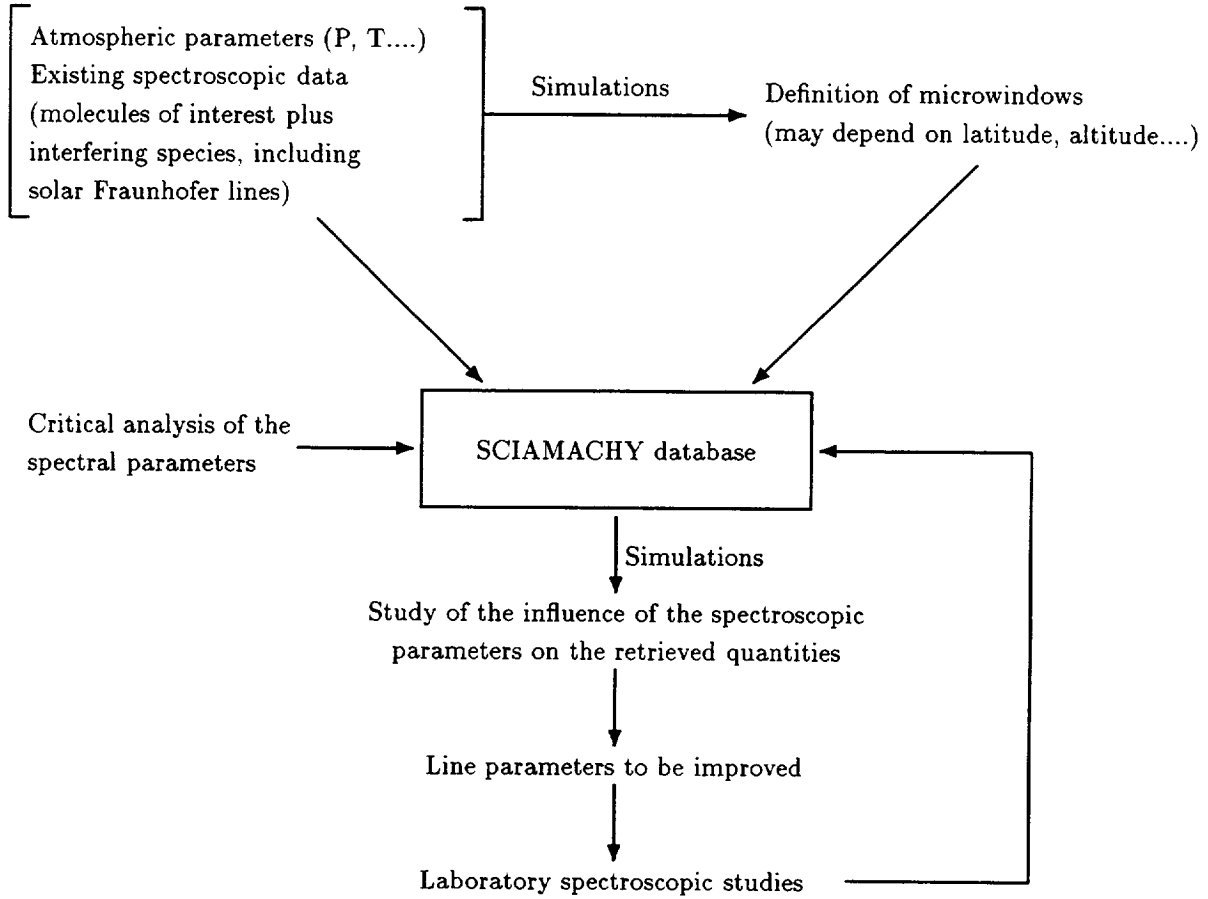


TABLE 1. Estimated errors in line intensities

Molecule	Spectral region	Relative accuracy, comments
H ₂ O	2.3 μm (channel VIII)	5-60% depending on the line. $\Delta K_a \geq 3$ line intensities poor.
	1.5-0.45 μm (channel III-VII)	Observed intensities. Precision 5-40% depending on the spectral region. Weak lines missing.
CO	2.3 μm (channel VIII)	10% Interferences with solar CO to be properly considered.
CO ₂	2 μm (channel VII)	5-30% Mixture of observations and calculations (DND method).
N ₂ O	2.5 μm (channel VIII)	5-40% Mixture of observations and calculations (effective method).
CH ₄	2.3 μm (channel VIII)	5-40% Observations available. Calculations to be done. Weak lines missing. Some lines not assigned.
O ₂	762 nm (channel IV)	2% Higher vibrational bands need work.

TABLE 2. Estimated errors in cross sections

Molecule	Spectral region	Relative accuracy, comments
O ₃	220-300 nm (channels I-II)	Hartley band; 2% accuracy, low temperature dependence
	300-360 nm (channel II)	Huggins bands; 2% accuracy, high temperature dependence, well-determined
	400-700 nm (channels III-IV)	Chappuis bands; 2% accuracy, modest temperature dependence, well-determined
O ₂	200-242 nm (channel I)	Herzberg continuum; 10% accuracy; small correction on O ₃
O ₄	343-1065 nm (channels II-VI)	O ₂ -O ₂ collision complex; 10% accuracy; OK for O ₃ correction, improved P,T dependence needed to use as cloud diagnostic
H ₂ CO	250-360 nm (channels I-II)	<10%
SO ₂	270-314 nm (channels I-II)	2.4%
NO ₂	310-570 nm (channels II-III)	3% for cross sections vs. temperature; higher resolution measurements needed
NO ₃	300-700 nm	>10% for peaks at 623, 662 nm; observable in channel IV
ClO	220-320 nm (channels I-II)	10%
OCIO	240-480 nm (channels I-III)	10%
BrO	312-385 nm (channel II)	7%
OH	282-308 nm (channels I-II)	3%
NO	227-280 nm (channel I)	γ bands; 5%

6.5 Retrieval algorithms

6.5.1 Gases

SCIAMACHY gas concentrations and, where applicable, altitude profiles will be retrieved using an optimal estimation (OE) iterative least-squares fitting procedure. OE has evolved to be the method of choice in inversions of many satellite measurements, including SBUV ozone profiles, chiefly because of its

ability to properly include *a priori* information to stabilize otherwise ill-posed inversion problems. Note that some former distinctions between methods have begun to blur as, for example, optimal estimation retrieval techniques are applied to measurements of highly-structured spectra. The necessary OE procedure is under development for the nadir geometry in the context of the GOME scientific and operational algorithm development, so that much work will directly transfer. Additional work remains to be done, however, particularly for SCIAMACHY measurements in the limb and occultation geometries. Specific items that scientific inversion studies for SCIAMACHY gas retrievals must address include:

- Microwindow selection, including target and interfering species, Ring effect, and nonlinearity in the measured spectra due to Rayleigh scattering at high solar zenith angles and intense absorption by interfering species (*e.g.*, for ClO or SO₂ obscured by O₃).
- Implementation of the global fitting inversion procedure [Carlotti, 1988] for limb and occultation geometries. This procedure uses all the radiance measurements as input, to solve for the vertical profiles for all species, and also allows for the use of *a priori* information.
- Retrieval of pointing information from SCIAMACHY spectra (*e.g.*, from CO₂ or O₂ lines). It may be possible to determine the pointing more accurately from the spectra themselves than from instrument and spacecraft pointing data.
- Improved cloud correction for gas retrievals.
- Protocols for obtaining the maximum realistic profile information from measurements and for retrieving at lower altitude resolution when the data are less than optimum.
- Closure problems, non-zero residuals (*e.g.*, background from stray light, noise floor).
- Inhomogeneity of scene.
- Inclusion of aerosol influences.
- Inclusion of error budget in data products.

6.5.2 Aerosols

Limb and occultation aerosol measurements The retrieval of aerosol vertical profiles from limb and occultation measurements will be performed in parallel to the gaseous species retrievals. The spectral intervals studied will be corrected for gaseous effects, and will emphasize windows where gaseous extinction is expected to be weak, for example at 380, 450, 520, 700, 800, 1000, 1550 and 2200 nm. SCIAMACHY aerosol retrievals present commonalities with the SAGE retrieval procedure, allowing continuity of the two aerosol data series.

The aim of this retrieval is the determination of the vertical distributions of size and density of the aerosols. The SCIAMACHY spectral coverage can also be used, after careful gas retrieval, to determine the composition of the aerosols. The wavelength coincidence between the ultraviolet sulphate, SO₂ and

ozone spectra, and between the nitrate and NO₂ spectra, does not allow this possibility to be used at the lower spectral resolution of SAGE II.

Limb radiance data inversion is an ill-posed problem for which a number of different solutions have been proposed. The use of *a priori* information in an optimal estimation or global fitting scheme may be appropriate for aerosol retrieval as well as gas retrieval. Full use of the wide SCIAMACHY spectral interval and of its resolution permits a more extensive approach to aerosol retrieval than has been used in previous treatments. A useful test of aspects of the SCIAMACHY aerosol retrieval could be made using the results from the MARS96 mission where several limb sounding instruments will be active in the aerosol-dominated Martian atmosphere.

6.5.3 Clouds

SCIAMACHY can play a unique role in cloud studies, because it is designed to detect near infrared absorption by water and ice clouds in channel 6. Water and ice each have a broad absorption band near 1.6 μm , but the band shapes are different. Therefore, discrimination between the two phases of water will be possible. By combining the reflectivity of clouds at non-absorbing wavelengths in the visible with the reflectivity at absorbing wavelengths in the near infrared, the cloud optical thickness and particle size can be found.

Near infrared absorption is thought to be one of the possibilities to explain the so-called anomalous absorption by clouds. SCIAMACHY could contribute significantly to cloud-radiation studies, since it measures almost all shortwave radiation. Combined with cloud properties derived from specific wavelengths, such as optical thickness, particle size, and cloud top height, the integrated shortwave radiation from SCIAMACHY would be an important product for cloud studies.

Substantial work is in progress to determine cloud data products from the GOME instruments, using both the spectroscopic measurements and the higher spatial resolution PMD measurements. Much of this development should be directly applicable to SCIAMACHY nadir measurements. The infrared extension of SCIAMACHY provides obvious advantages in greater wavelength coverage and for the use of H₂O and CO₂, in addition to O₂, as spectroscopic probes of light penetration into the atmosphere.

6.5.4 Spectral reflectance

Surface spectral reflectances are additional valuable data products that could potentially be derived from SCIAMACHY measurements. The advantage of SCIAMACHY for the generation of surface spectral reflectances is the fact that correction for atmospheric absorption can be done accurately, since SCIAMACHY measures all relevant trace gases. The disadvantage is that the SCIAMACHY ground pixels are relatively large, so that not many cloud-free scenes will be available except over desert areas. The effect of tropospheric aerosols complicates the atmospheric correction, since they cannot be easily distinguished from surface reflection. However, with the wide wavelength range of SCIAMACHY, the spectral signatures of surfaces and aerosols can, hopefully, be separated. The work in this field is at a very early stage.

6.6 Product confidence data

Within the extraction of the geophysical quantities, confidence data permitting the assessment of the quality of the retrieval process will be produced. Examples include convergence criteria and covariance matrices from the fitting process. The product confidence data shall be included as part of the product.

7 Requirements for SCIAMACHY Higher Level Data Processing

7.1 Definitions

In this section we will describe the requirements for level 3 and higher (3+) data processing. The aim of level 3 and higher data processing is to make the SCIAMACHY measurements more ready for use by researchers who are not familiar with the SCIAMACHY instrument. In addition, higher level data products (especially images) are useful to present results to the public and to policy makers. It is important to stress that higher level data processing depends on the availability of level 2 data, which emphasizes the importance of SCIAMACHY retrievals.

We use the following definitions of data product levels:

- Level 2 data products: geolocated, calibrated geophysical quantities on the observational grid
- Level 3 data products: interpolated and temporally-averaged data
- Value-added data products: level 2 data augmented and interpolated using external data (*e.g.* meteorological data or data from other satellite instruments).

This data level nomenclature also holds when level 1 data are used as input data for level 3+ processing. For example, spectral reflectance maps of the Earth can be called a level 3 product. In the following, however, we will focus on higher level processing of level 2 data.

Level 3 data can be seen as data interpolated without using any additional information. From GOME experience, we expect that the addition of meteorological information in value-added processing through the assimilation of level 2 data in a dynamic atmospheric model will yield more useful results (see issues in Section 2.4).

7.2 Availability of level 2 data

The level 3+ data processing discussed here assumes the availability of a number of level 2 data products, particularly column densities and concentration profiles. These include:

- Column densities of O₃, H₂O, CO, CH₄, NO₂, SO₂, and aerosols.
- Profiles of O₃, NO₂, H₂O, and aerosols.

The column densities are derived from nadir mode measurements. The profiles can be derived from the nadir mode or the limb mode. In the nadir mode the profile information will be mainly limited to O₃. In the limb mode the profiles of more gases will be available, but the altitude range will be mainly limited to the stratosphere. The combination of nadir and limb profiles can be regarded as a level 3 product, but it may also be a level 2 product when the retrieval algorithm combines level 1 data from nadir and limb. As an intermediate product between column densities and profiles, a division between tropospheric and stratospheric column densities would be important for scientific studies.

7.3 Level 3 data processing

7.3.1 Gridding, interpolation, and projection

SCIAMACHY has a maximum swath width of 960 km, implying a global coverage in 3 days (with a large pixel size). This means that there would be large holes if the level 2 data are plotted for one day on a global map. If level 2 data at a certain point in space and time are not available, there must be an option to fill this data gap by interpolation in space and time from available data. Possible interpolation schemes include linear and cubic spline.

In level 3 data processing, gridding (or binning) of the data is an essential step. A standard grid should be defined, which could be common to other Envisat instruments.

The gridded data must be projected on the globe. Geographic projection options could include:

- Conformal projection (*e.g.* Mercator, polar or tilted stereographic);
- Equal-area projection (homolographic);
- Planet's view.

The time of measurement of a certain quantity is only present in the level 2 data - after interpolation in the level 3 data processing this information is lost. Therefore, for some important quantitative applications the most reliable data set will be the level 2 data. For example, the use of SCIAMACHY data in chemical models will be done using both level 1 and level 2 data products. We may anticipate that the chemical models at the end of this century will be intelligent enough to assimilate level 2 data. For these users, fast delivery of the data (within a few hours of acquisition) will be more important than level 3 presentation.

7.3.2 Resolution of level 2 data

The preferred horizontal resolution of the level 2 data for higher level processing depends on the application. For climatological and atmospheric chemistry trend studies, accurate columns and profiles for small pixels (minimum 30×25 km²), implying partial coverage, are preferred. For the observation of short-

living phenomena or the global transport of atmospheric species, intermediate or large pixels (maximum $240 \times 25 \text{ km}^2$), implying total coverage in 3 days, are preferred.

Since the exact form of a level 3 data product will vary from application to application, and from user to user, we suggest the development of an interactive (“do-it-yourself”) level 3 processing software package, so that each user can make his/her own data product with varying resolution in time and space.

7.3.3 Column density maps

A global image of the total column density of a selected trace gas is a basic product at level 3. Making such an image requires the following steps:

- Mapping the data of several orbits, acquired within a certain time interval (*e.g.* one day), to a standard grid.
- Interpolation in space of gridded level 2 data (filling the gaps).
- Displaying the data in a convenient geographic projection with land contours.

The magnitude of column density can be represented by colors or isolines.

7.3.4 Profile maps

An atmospheric profile map is the basic product. A first step towards profile mapping is the production of a global image of the tropospheric and stratospheric column densities of a selected trace gas.

To obtain a global view of profiles one has the problem of projecting 3D data to a 2D plane. One solution is to provide adjacent global images of the column densities in selected layers: *e.g.* 1000-800 hPa, 800-500 hPa, 500-300 hPa, 300-150 hPa, and 150-0 hPa.

7.3.5 Visualization

To fully exploit the SCIAMACHY level 2 data, which are columns and profiles of various trace gases, one needs *visualization tools* to get a qualitative impression of all data. Then, if an interesting region has been found, one can zoom-in for quantitative analysis. To visualize global columns, one would like to rotate the entire Earth image to have a global view.

To visualize the 3D data, *i.e.* the profiles on a global scale, one would need a visualization tool to “fly” through 3D space to see trace gas 3D variations (*e.g.* ozone holes or blobs).

7.3.6 Time series

Time series are essential for climatological studies. Therefore, for time series all archived data should be accessible. For quantitative trend analysis, images are less useful - level 2 data will be used directly. The main options are:

- A times series of global images in a specific geographic projection.
- A times series of a certain quantity (column or profile) at a specific location.

7.4 Value-added data processing

7.4.1 Dynamical models and data assimilation

Dynamical models Validated satellite measurements and ground-based measurements of trace gases are essential for understanding their dynamical and chemical behavior, for studying the ozone hole phenomena, for detecting trends in trace gas distributions, and for determining their climatologies. Global coverage of satellite measurements is important for most of these studies. Global total ozone, ozone profile, and other trace gas measurements are performed by SCIAMACHY so that monitoring of their distribution is possible on a daily basis. However, the trace gas maps are often hampered by missing data. For example, ozone measurements by TOVS are subject to retrieval problems in the presence of clouds and ozone maps measured by SBUV and GOME (and, in the future, SCIAMACHY) are hampered by a limited swath width. In these cases, only sparse data are obtained and it is often difficult to characterize general features in the ozone distribution. Another fundamental problem with the use of data from polar orbiting satellites is that spatially adjacent observations may not be taken nearly simultaneously in time. Using data assimilation and advection techniques, it is possible to perform a sophisticated interpolation and one can cope with the incomplete space-time distribution of satellite data.

Dynamical models describe the transport of trace gases in the atmosphere using advection techniques and can produce maps of, *e.g.*, total ozone at any given time. Meteorological data are needed to feed these kinds of off-line dynamical models. They can be obtained from the European Centre for Medium Range Weather Forecasts (ECMWF). Three-dimensional fields of temperature, pressure, wind, and humidity are available. The data resolved at different pressure levels are available with a maximal horizontal resolution of $0.5^\circ \times 0.5^\circ$.

Data assimilation By extending dynamical models with data assimilation it is possible to obtain maps of, *e.g.*, ozone data at a specific time. This is in contrast to a level 3 global image product which consists of data measured at different times. Data assimilation techniques have now been used extensively in meteorology for several years. In data assimilation, satellite observations of, *e.g.*, ozone are fed into the model and weighted with the model-calculated ozone values in order to obtain the best available description of the atmosphere, and make optimum use of the data. Incorporating data assimilation will lead to a good description of the atmosphere and enable analyses and forecasts of ozone which are consistent with all available real-time measurements of ozone and are also consistent with all available dynamical information.

Validation of satellite data using data assimilation models Ground-based measurements are generally taken at different times and geographical locations than the satellite measurements and are therefore less suited for direct comparison. Also, satellite measurements usually represent averages over a

large area, whereas conventional measurements represent local values, which makes the two not directly comparable. Advection and assimilation models, which retain the dynamical information on ozone, make it also possible to use non co-located ground-based and satellite measurements for validation. Moreover, data assimilation offers the possibility to identify ground stations which deliver controversial data by comparison with observations of a satellite instrument. Furthermore, models extended with data assimilation also produce statistical information on the quality of instruments and observations.

Value-added products using meteorological data By feeding data into data assimilation and advection models, a dynamical form of interpolation is performed, taking into account the dynamical (meteorological) behavior of ozone. This is, in fact, a physically correct interpolation method using the irregularly (in space and time) distributed satellite data. The so-obtained global ozone maps can be produced at any specific time and are consistent with the current dynamical situation. These assimilated maps are of tremendous benefit for atmospheric research, climatology studies, and political needs.

8 SCIAMACHY Data Products

Level 2 data products, which may be further processed into level 3 and value-added products, will be available from two streams of processing: (1) Near real-time (NRT) data products will be available for a limited set of constituents within a few hours of spectrum acquisition. These will be processed using climatological preprocessing to supply the necessary ancillary data, so that they will be available for customers requiring fast delivery. One of the planned NRT products (CH_4) is listed as “secondary” since it is necessary to include it in the fitting for CO and N_2O . NRT processing will employ look-up tables for radiative transfer rather than operational running of the models. (2) Off-line data products will be produced using improved ancillary data that becomes available after spectrum acquisition, *e.g.*, analyzed temperature and pressure fields. In off-line processing, the radiative transfer model may be used operationally, depending on the results algorithm development and refinement studies. Special data products are those which will be made available under certain climatological conditions, *e.g.* volcanic eruptions, ozone hole conditions, or heavy tropospheric pollution.

TABLE 3. SCIAMACHY Level 2 Data Products

	Nadir UV/Vis	Nadir IR	Nadir UV/Vis/IR	Limb UV/Vis	Limb IR	Limb UV/Vis/IR
Near Real- Time	O ₃ NO ₂	H ₂ O N ₂ O CO CH ₄ ¹	Clouds Aerosol			
Off- Line	O ₃ NO ₂ BrO	H ₂ O N ₂ O CO CO ₂ CH ₄ P,T	Clouds Aerosol	O ₃ NO ₂ BrO	H ₂ O N ₂ O CO CO ₂ CH ₄ P,T	Aerosol
Special	OCIO SO ₂ H ₂ CO					

¹“secondary” product (see text)

A Algorithm Development Activities

A.1 German activities

A.1.1 ife Bremen

The overall goal at ife is development of the radiative transfer research tool SCIAtran++, based on experience with the development of GOMETran++. GOMETran++, the radiative transfer research tool to be used in the GOME operational data processing chain, will be the core of SCIAtran++. SCIAtran++ will include:

- **Radiative transfer codes for nadir, limb, occultation and ground-based geometries**
 - Nadir: Extension of GOMETran/GOMETran++ to the infrared spectral range
 - * implementation of IR band models/ESFT code for the trace gases H₂O, CO, CO₂, N₂O, CH₄ (based on experiences with GOMETran O₂ A band studies)
 - * implementation of thermal and non-thermal IR emission
 - * DOAS nadir in the Infrared; algorithms and validation of the code by ground-based measurements (based on UV-Vis DOAS experience with GOME and ground-based measurements)
 - * IR features of clouds and aerosols
 - * nadir retrieval studies (FURM)
 - Radiative transfer model for limb geometry
 - * development of an accurate and efficient radiative transfer code for the limb geometry
 - * validation of the algorithms
 - * limb retrieval studies (FURM)
 - P-T profile retrieval study for NRT data processing
 - * study and comparison of different P-T retrieval strategies (O₂, CO₂ absorption, Rayleigh scattering)
 - Limb DOAS development for NRT data processing
 - * development of a DOAS-type algorithm for limb measurements
 - * validation of the algorithm by comparison with accurate radiative transfer calculations
 - Occultation (Sun/Moon):
 - * implementation of an accurate and efficient radiative transfer code for the occultation measurements
 - * validation of the code by ground- and space-based measurements
- **Cross section, aerosol and cloud databases**
- **Atmospheric constituent climatologies**

A.1.2 DLR

Activity at DLR will center on the operational implementation of SCIAMACHY Data Processing (SDP) Algorithms. This covers two main phases:

- **Algorithm specification of the SCIAMACHY ground processing segment, for both the off-line and the near real-time processors**
 - Specification of SDP performance and computation resource requirements
 - Input and output data definitions, parameter data lists
 - Functional composition, basic mathematical and physical models
 - Scheduling for operational prototype installation and testing
 - Initial specification documentation
- **Implementation of operational algorithm prototypes (off-line SDP only)**
 - Construction of architectural designs for the 0 to 1b and 1b to 2 processing chains
 - Definition of detailed software requirements for the 0 to 1b and 1b to 2 processing chains
 - Product definition and formatting of SCIAMACHY Level 1b and Level 2 Data Products
 - Input and output file specifications and read/write interface modules
 - Transposition of scientific code into compatible algorithm components for the system prototypes
 - Compilation and maintenance of operationally compatible reference/climatological and calibration/characterization data sets
 - Construction of interface modules for algorithm components and auxiliary data sets, and integration of components and interfaces into processor system chains
 - Development of appropriate software tools for module, component and system testing of SDP (display tools, error handling, detailed output, test data package)
 - Construction of SCIAMACHY Level 1 data packages for end-to-end system testing. This includes radiative transfer modeling and the use of the SISS as provided by SRON/NIVR and maintained by SRON.
 - Execution of an extensive battery of tests to validate algorithms before the launch, including widespread use of GOME data
 - Production of documentation covering all phases of operational algorithm development
 - Participation in data product validation activities during the commissioning phase and after
 - Ongoing role as major consultant to industry in the development of the SCIAMACHY NRT processors
 - Close consultation with DLR colleagues working on operational GOME algorithm developments

A.2 Netherlands activities

A.2.1 SRON

- **Ozone profile retrieval**

Methods are being studied at SRON, in cooperation with KNMI (the PROGRES project), for the retrieval of profiles of ozone (and other trace gases) from GOME data, in view of preparing for similar retrievals from SCIAMACHY data. Various retrieval methods are being studied, *e.g.*, global fitting and optimal estimation. At this stage, MODTRAN is used as a forward model, permitting the study of the influence of various atmospheric parameters. The use of the GOME/SCIAMACHY instrument simulator, developed at SRON, permits the inclusion of instrumental parameters in the retrieval process. It also enables assessment and possibly correction of instrumental systematic errors.

- **Simultaneous retrieval from nadir and limb measurements**

SRON is studying the possibilities of combining results from nadir and limb measurements of the same air volume into one single retrieval process. Preliminary results indicate that errors on retrieved trace gas concentrations can improve considerably using this combined approach.

- **Off-line data products**

In a continuation of earlier work on the sensitivity of SCIAMACHY for CO and CH₄ detection, an off-line algorithm for a CO data product is being developed.

A.2.2 KNMI

Retrieval studies

- Development of the DAK radiative transfer model, which includes multiple scattering of polarized light in the Earth's atmosphere by molecules, aerosols, and clouds, as well as reflection by surfaces.
- Inclusion of the correlated k-distribution method in DAK, to account for strong absorption bands (like the O₂ A-band)
- Development of ozone profile retrieval based on DAK and instrument simulation software (with SRON).
- Polarization-correction algorithm development based on DAK polarization modeling.
- Use of PMDs for scene identification and cloud cover estimation.
- Use of GOME data for retrieval of spectral surface albedo for various surface types.

Data assimilation and dynamical modeling

- **2D advection and assimilation model AMK**

The AMK model is a two-dimensional (latitude/longitude) global model with a uniform horizontal resolution of $110 \times 110 \text{ km}^2$ (Levelt et al., 1996). It is an off-line model which advects total column ozone with a pre-calculated wind field, obtained from ECMWF. With the AMK model a dynamical interpolation can be performed and global ozone maps can be obtained every day.

- **3D Chemical Tracer Model CTMK**

This model gives a 3D description of the atmosphere. The model is coupled to ECMWF meteorological data and contains a chemistry module and an ozone climatology. With CTMK it will be possible to make dynamically consistent three-dimensional (ozone) maps of SCIAMACHY profile data.

A.2.3 Other institutes

At TNO/FEL, aerosol retrieval development is ongoing, and being applied to GOME data. An advanced aerosol model is coupled to the DISORT radiation scheme to derive the aerosol optical thickness and aerosol type from the spectral reflectance of cloudless scenes over ocean. The reflectance of the ocean itself is taken into account in detail.

At the Free University of Amsterdam (VUA) basic radiative transfer model development takes place. The so-called GAP model is being developed, which includes multiple scattering of polarized light, and which is the kernel of the DAK model of the KNMI. Also at VUA, laboratory measurements of cross-sections of O_2 and H_2O are being performed, using a novel laser technique (cavity ring-down spectroscopy).

A.3 Belgian activities

Belgian scientists will work in close co-ordination with the KNMI for interpretation and treatment of the SCIAMACHY PMD data. Specific studies include:

- **Validation of polarization data** through studies involving other projects, such as flights of stratospheric balloon instruments in co-operation with the Laboratoire d'Optique Atmosphérique de Lille (LOA).
- **Studies of synergy between GOME, POLDER and SCIAMACHY.** This program includes an accepted proposal for validation of the POLDER data by GOME polarization measurements.
- **Specific studies of the SCIAMACHY infrared channels** using direct models, on the basis of the experience developed at the Belgian Institute for Space Aeronomy.

A.4 International collaboration

A.4.1 U.S.A

The SCIAMACHY algorithm research at the Smithsonian Astrophysical Observatory contributes to a number of the elements that must be addressed for comprehensive analysis of SCIAMACHY measurements. These include:

- **SCIAMACHY mission planning**
 - Mission scenario studies, including updates of optimized limb and nadir measurement strategies
- **SCIAMACHY algorithm development**
 - Radiative transfer studies
 - * extension of radiative transfer models used for GOME studies to infrared wavelengths out to 2.4 μm
 - * incorporation of line-by-line code in radiative transfer models
 - * comparisons of line-by-line code with exponential sum fitting and other band model code
 - * participation in the development of modeling to deal with limb and occultation geometries
 - * generation of retrieval software to be used in conjunction with radiative transfer modeling
 - * preparation of ozone climatology data base
 - * investigation of aliasing effects
 - * wavelength calibration study
 - Database issues
 - * extension of existing GOME databases to SCIAMACHY range, including new trace gas species
 - * development of cloud and aerosol models to generate additional databases
 - * generation and compilation of appropriate spectroscopic line data
- **SCIAMACHY data product definition**
 - Participation in the specification of standard SCIAMACHY Level 1 and 2 data products
 - Consultation on the final definition of SCIAMACHY near real time (NRT) products

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B Ring Effect Studies: Rayleigh Scattering, Including Molecular Parameters for Rotational Raman Scattering, and the Fraunhofer Spectrum

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**RING EFFECT STUDIES: RAYLEIGH SCATTERING, INCLUDING
MOLECULAR PARAMETERS FOR ROTATIONAL RAMAN
SCATTERING, AND THE FRAUNHOFER SPECTRUM**

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Ring effect studies: Rayleigh scattering, including molecular parameters for rotational Raman scattering, and the Fraunhofer spectrum

K. Chance and R.J.D. Spurr

Abstract

Improved parameters for the description of Rayleigh scattering in air and for the detailed rotational Raman scattering component for scattering by O₂ and N₂ are presented for the wavelength range 200-1000 nm. These parameters enable more accurate calculations to be made of bulk molecular scattering and of the "Ring effect" for a variety of atmospheric radiative transfer and constituent retrieval applications. A solar reference spectrum with accurate absolute vacuum wavelength calibration, suitable for convolution with the rotational Raman spectrum for Ring effect calculations, has been produced at 0.01 nm resolution from several sources. It is convolved with the rotational Raman spectra of O₂ and N₂ to produce an atmospheric Ring effect source spectrum.

1 Introduction

The phenomenon that has come to be known as the Ring effect was first noted by Grainger and Ring¹ as a "filling in" (broadening and reduction of depth) of solar Fraunhofer lines when viewed from the ground in scattered sunlight. Various processes have been proposed as contributing to the effect, including scattering with fluorescence from aerosols and from the ground.^{2,3} However, the predominance of molecular scattering as the major cause was established by Kattawar *et al.*,⁴ who analyzed the Ring effect contributions from rotational Raman scattering and inelastic Rayleigh-Brillouin scattering. The Rayleigh-Brillouin component is not of primary importance in satellite-based UV-visible backscatter measurements, for which the present work is undertaken, and it is not analyzed here. The atmospheric scattering situation is nicely defined by Young:⁵ "To summarize: molecular scattering consists of Rayleigh scattering and vibrational Raman scattering. The Rayleigh scattering consists of rotational Raman lines and the central Cabannes line. The Cabannes line is composed of the Brillouin doublet and the central Gross or Landau-Placzek line. None of the above is completely coherent. The term 'Rayleigh line' should never be used." Note that the vibrational Raman contribution results in lines so widely separated from the frequency of the incoming light that they are not normally considered part of the Ring effect, although in recent applications the Ring effect has developed a somewhat broader definition that includes substantial interfering structure in observations, rather than the initial effect which was limited to the broadening of partially-resolved lines.

Understanding the Ring effect has become more important in recent years with the increase in ultraviolet and visible spectroscopic observations of the Earth's atmosphere from the ground^{6,7} and from satellites.⁸⁻¹² In order to retrieve abundances of trace species from such observations it is necessary to take the Ring effect into account. Methods have been developed to do so by pragmatic means - by measuring the polarization of scattered sunlight,⁶ and by modeling of the effect directly from molecular scattering processes.^{7,10} It has been proposed to use the Ring effect with selected Fraunhofer lines (in particular, the Ca II H and K lines) to determine cloud parameters in conjunction with satellite-based observations of O₃.¹¹ Joiner *et al.*¹⁰ also determined that the contribution to the Ring effect from the Rayleigh-Brillouin scattering process is negligible for most geometries used in satellite observations.

The use of visible bands of O₂, in particular the 762 nm A band, for determination of cloud parameters is being developed for proposed and existing satellite instruments which monitor the atmosphere with emphasis on tropospheric measurements.¹³ This includes the European Space Agency's Global Ozone

Monitoring Experiment (GOME) and the upcoming SCanning Imaging Absorption spectroMeter for Atmospheric CHartography (SCIAMACHY). The Ring effect has a substantial influence on such observations; work is underway in our institution to refine and model the effects. In this case, the effect is due to inelastic scattering in molecular absorption lines themselves, rather than in the solar Fraunhofer lines. Similar effects have been noted for the detailed retrieval of trace species including O₃ and NO₂.^{6,7,12,14}

The present work is part of an ongoing effort to quantify the Ring effect for atmospheric radiative transfer modeling, with application to satellite- and ground-based measurements, and to apply it to particular cases such as the detailed absorption in the visible O₂ bands, the retrieval of tropospheric O₃ from UV measurements, and retrievals of trace photochemically-active gases. Much of the previous modeling work^{7,10,15} has relied on the development of molecular parameters for N₂ and O₂ by Penney *et al.*;¹⁶ only one study¹⁰ has used the updated dynamic polarizability anisotropies as developed by Bates.¹⁷ Previous work has largely ignored the complication of the rotational Raman spectrum of O₂ caused by the electronic spin angular momentum in the $^3\Sigma_g^-$ ground state and the issue of pressure broadening of the rotation Raman lines. In this publication we update the molecular parameters and the scattering with respect to the solar Fraunhofer spectrum using the best currently available laboratory and field data and theoretical studies of which we are aware. This provides: An updated expression for Rayleigh scattering by air; expressions for the wavelength-dependent polarizability anisotropies of O₂ and N₂; accurate Placzek-Teller coefficients (the state-dependent factors in the line intensities) for O₂ rotational Raman lines (the Placzek-Teller coefficients of Penney *et al.*¹⁶ for N₂ are correct as given); a tentative set of pressure broadening coefficients for the O₂ and N₂ rotational Raman lines; a solar reference spectrum for convolution with calculated Ring cross sections; and a convolved Fraunhofer-rotational Raman source spectrum for fitting of atmospheric spectra. The tables and spectra are not included here due to size limitations. They are available from the authors.

2 Rayleigh Scattering

To examine the detailed Rayleigh and rotational Raman scattering properties, including their relative intensities and the scattering phase functions, we begin with Table I of Kattawar *et al.*⁴ This table describes the relative intensities and angular behaviors for the Rayleigh-Brillouin and rotational components, and their sum. They are given for various input polarizations, including unpolarized light (the predominant contribution for many atmospheric observations, where single scattering is the major contributor to the Ring effect). For unpolarized light, the depolarization ratios (defined in each case as the ratio of the horizontally-polarized component to the vertically-polarized component at 90° scattering angle) may be determined directly. Table I of Kattawar *et al.*⁴ is reproduced here as Table 1, with the addition of the depolarization ratios, for the three cases: Rayleigh-Brillouin (the central Cabannes component, *C*); rotational Raman (the wings, *W*); and the sum of the two (*T*, for total). The phase functions for scattering may also be derived for each case. They are (normalized over solid angle to 1):

$$\begin{aligned}\Phi_0^C &= \frac{3}{160\pi} \left[\frac{(180 + 13\epsilon) + (180 + \epsilon) \cos^2\theta}{18 + \epsilon} \right] \\ \Phi_0^W &= \frac{3}{160\pi} (13 + \cos^2\theta) \\ \Phi_0^T &= \frac{3}{80\pi} \left[\frac{(45 + 13\epsilon) + (45 + \epsilon) \cos^2\theta}{9 + 2\epsilon} \right]\end{aligned}\tag{1}$$

where $\epsilon = (\gamma/\bar{\alpha})^2$, γ is the anisotropy of the polarizability, and $\bar{\alpha}$ is the average polarizability. In each case, the phase function is given in terms of the *respective* depolarization ratio ρ_0^X ($X = C, W, T$) by:

$$\Phi_0^X = \frac{3}{8\pi} \left[\frac{(1 + \rho_0^X) + (1 - \rho_0^X) \cos^2\theta}{2 + \rho_0^X} \right].\tag{2}$$

The Rayleigh scattering cross section at standard temperature (273.15 K) and pressure (1 atmosphere) is given by

$$Q_R = \frac{32\pi^3(n-1)^2 F_K}{3N_0^2 \lambda^4} \quad (3)$$

where n is the index of refraction, F_K is the King correction factor,¹⁸ N_0 is Loschmidt's number ($2.686763 \times 10^{19} \text{ cm}^{-3}$), and λ is the wavelength. The King correction factor is given by

$$F_K = 1 + 2 \left(\frac{\gamma}{3\bar{\alpha}} \right)^2 = \frac{6 + 3\rho_0^T}{6 - 7\rho_0^T} = 1 + \frac{2\epsilon}{9}. \quad (4)$$

The average polarizability can be determined from the relation

$$|\bar{\alpha}|^2 = \frac{(n-1)^2}{4\pi^2 N_0^2}. \quad (5)$$

3 Molecular Parameters

3.1 Rayleigh scattering cross sections

The major source of improved data for the indices of refraction of O_2 , N_2 , and air versus wavelength, the King correction factors, and the anisotropies of the polarizabilities, is Bates¹⁷. He presents a comprehensive review of both measurements and theoretical calculations and derives a data set that is demonstrated to be better than 1% for all data and parameterizations utilized in the present work.

Bates' Table 1 gives refractive indices, Rayleigh scattering cross sections, and King correction factors versus wavelength for air from 200-1000 nm. We find that the following Edlén-type expression fits the index of refraction data to better than 0.1% for all values:

$$(n_{air} - 1) \times 10^4 = 0.7041 + \frac{315.90}{157.39 - \sigma^2} + \frac{8.4127}{50.429 - \sigma^2} \quad (6)$$

where $\sigma (\mu\text{m}^{-1}) = 1/\lambda (\mu\text{m})$. The Rayleigh cross sections are reproduced to 0.3% rms (worst case, 0.5%) over the full 0.2-1.0 μm range by the expression

$$Q_R \times 10^{24} (\text{cm}^2) = \frac{3.9993 \times 10^{-4} \sigma^4}{1 - 1.069 \times 10^{-2} \sigma^2 - 6.681 \times 10^{-5} \sigma^4}. \quad (7)$$

Nicolet¹⁹ gives an expression for fitting the data of Bates to 0.5% over the 0.2-0.55 μm range; the present expression is slightly more accurate and extends over a larger wavelength range (also see Bucholtz²⁰). The King factor and depolarization ratio for any choice of wavelength within the 0.2-1.0 μm range can be accurately determined from the previous two equations.

3.2 Polarizability anisotropies

The previous expansions are for air, including standard amounts of Ar and CO_2 . For rotational Raman cross sections, we will limit the calculations to O_2 and N_2 . Bates gives segmented representations for the indices of refraction of O_2 and N_2 versus wavelength and expansions for the respective King correction factors. Tables giving the King correction factors, values of $\sqrt{\epsilon}$, index of refraction $\bar{\alpha}$, and γ for O_2 and N_2 have been derived in the present study. γ_{O_2} values from these data are fitted to 0.6% rms over this wavelength range (1% worst case) by:

$$\gamma_{\text{O}_2} \times 10^{24} = 0.07149 + \frac{45.9364}{48.2716 - \sigma^2}. \quad (8)$$

The γ_{N_2} values are fitted to 0.02% rms (0.04% worst case) by:

$$\gamma_{\text{N}_2} \times 10^{25} = -6.01466 + \frac{2385.57}{186.099 - \sigma^2}. \quad (9)$$

These equations should be considered merely as phenomenological fits over the particular wavelength range, rather than trying to attach physical importance to (for example) the negative value of the constant term in the N_2 equation. They should not be extrapolated to outside the 0.2 - 1.0 μm range.

3.3 Basic spectroscopy

The ground state of O₂ is ${}^3\Sigma_g^-$; it has significant electronic structure in both its magnetic dipole rotational spectrum and its rotational Raman spectrum. Rotational Raman spectra of both O₂ and N₂ have previously been approximated by simple expansions in the lowest rotational parameters (for positions) and by using T/c_2B_0 for the rotational partition functions. Very precise data are now available for the term energies, allowing line positions and Boltzmann factors to be accurately and rapidly calculated. The use of term values from the current HITRAN listing²¹ allows for calculations of line positions to 0.0001 cm⁻¹ accuracy, and for highly accurate calculation of the statistical partitioning.

3.4 Placzek-Teller coefficients

Cross sections for rotational Raman scattering are given by

$$Q_{N,N'}^W(\text{cm}^2) = \frac{256\pi^5}{27(\lambda')^4} \gamma^2 f_N c_{PT}(N, J, N', J'), \quad (10)$$

where f_N is the fractional population in the initial state. The quantum state-dependent factors in the cross sections $c_{PT}(N, J, N', J')$ are commonly known as ‘‘Placzek-Teller coefficients’’ from the initial derivations.²² These factors are given for a molecule in a Σ electronic state with one electronic spin angular momentum, in the Hund’s case b coupling scheme (electron spin coupled to rotational angular momentum), by

$$c_{PT}(N, J, N', J') = (2N+1)(2N'+1)(2J'+1) \begin{pmatrix} N & L & N' \\ 0 & 0 & 0 \end{pmatrix}^2 \left\{ \begin{matrix} N & L & N' \\ J' & S & J \end{matrix} \right\}^2 \quad (11)$$

where J is the total angular momentum, S is the electronic spin angular momentum (1 for O₂ and 0 for N₂), and L is the component of the 2nd rank polarizability tensor responsible for the interaction. $L = 0$ for the isotropic part of the polarizability (the Cabannes component) and $L = 2$ for the anisotropic part of the polarizability (Raman scattering). The standard definitions for 3- j and 6- j coefficients are used. Two near equivalents to this equation give the formula for ‘‘line strengths’’ which include the initial state degeneracy.^{23,24} For $S = 0$ (i.e., N₂), eq. 11 reduces to the result of ref. 16, eq. 7:

$$\begin{aligned} c_{PT}(J \rightarrow J+2) &= \frac{3(J+1)(J+2)}{2(2J+1)(2J+3)} \\ c_{PT}(J \rightarrow J) &= \frac{J(J+1)}{(2J-1)(2J+3)} \\ c_{PT}(J \rightarrow J-2) &= \frac{3J(J-1)}{2(2J+1)(2J-1)}. \end{aligned} \quad (12)$$

This derivation gives correct Placzek-Teller coefficients for N₂, but approximates those for O₂ by treating it as a pure Hund’s case b molecule. At low N and J , the departures from the pure coupling case due to the electron spin-rotation interaction are enough to significantly affect the spectrum.^{23,25} In the classic study of the O₂ ground state, Tinkham and Strandberg²⁶ include the correct eigenvectors of the secular determinant for levels up to $J = 26$ in the case b basis set (their Table V and equation 54). Above this level the molecule is described by case b behavior to a very high degree of accuracy. For $J = 0$ and all odd J levels the case b description is exact. For even J levels, $J \neq 0$, the transformation from case b basis functions $\phi_{N,J}$ to eigenfunctions $\Psi_{N,J}$ is given by

$$\begin{aligned} \Psi_{J-1,J} &= b_J \phi_{J-1,J} - d_J \phi_{J+1,J} \\ \Psi_{J+1,J} &= d_J \phi_{J-1,J} + b_J \phi_{J+1,J}. \end{aligned} \quad (13)$$

The b_J and d_J values from Ref. 26 are used here to calculate correct Placzek-Teller coefficients for values up to $J = 10$, above which the corrections become completely negligible. An almost identical result was

determined by Altmann *et al.*²⁷ who calculated eigenvectors for the secular determinant and molecular parameters given in the slightly earlier work of Mizushima and Hill.²⁸ The database calculated using the corrected eigenvectors is prepared with an intensity cutoff to include all rotational Raman lines with intensities at 296 K within 0.1% of the strongest line. Because of the mixing of states, this now includes two $\Delta N = 4$ transitions. Figure 1 gives rotational Raman cross sections for N_2 and O_2 calculated for a temperature of 250°K and an excitation wavelength of 440 nm, appropriate to investigations of the effect of the Ring effect on retrievals of atmospheric NO_2 concentrations.

3.5 Pressure broadening coefficients

The capital letter Γ is used here to denote the half-width at half-maximum pressure broadening coefficient to distinguish it from the γ used for anisotropy of polarizability. The best existing measurements of pressure broadening for the rotational Raman lines are from Jammu *et al.*²⁹ These authors note some evidence that the unresolved Q branches of vibrational Raman bands seem to broaden less than lines due to ordinary dipole transitions, but that the rotational Raman lines broaden comparably to dipole transitions. They present self-broadening measurements for N_2 , O_2 , CO_2 , and CO , as well as He and Ar broadening of N_2 , O_2 . All measurements were made at room temperature. Given the experimental conditions (very high pressures, modest spectral resolution) and the lack of air-broadening measurements, temperature dependences, and a tabulation of the J -dependent N_2 broadening coefficients, it was decided not to use these measurements as the basis for broadening in the present data set.

For O_2 , the HITRAN92 values corresponding to rotational transitions of the same ΔN are initially adopted.²¹ Where multiple corresponding transitions exist, the pressure broadening coefficients are averaged. For the two $\Delta N = 4$ transitions, the averages of the values for lines connecting the upper and lower states are taken. The resulting pressure broadening coefficients are multiplied by 1.185, which is the average result for the ratio of measured air pressure broadening coefficients for O_2 magnetic dipole rotational transitions to those given in HITRAN (see ref. 30 for an explanation of this correction). For N_2 , pressure broadening values for the corresponding quadrupole lines of the vibrational fundamental are adopted. Values determined for the pressure broadening coefficients of both O_2 and N_2 are at 296 K. The temperature dependence should be calculated using the recommended HITRAN92 coefficient of $n = 0.5$ for N_2 lines²¹ and a value of $n = 0.72$ for O_2 lines,³⁰ through the relation

$$\Gamma_T = \Gamma_{296} \times \left(\frac{296}{T} \right)^n \quad (14)$$

4 Solar Reference and Ring Source Spectra

A solar reference spectrum for the range 230-800 nm, at 0.01 nm resolution, has been determined by combining ground-based measurements³¹ and balloon measurements.³² Both spectra were converted to vacuum wavelengths. The balloon data were re-calibrated in wavelength using 20 selected atomic reference lines. The spectra were re-sampled at even 0.01 nm increments, employing a triangular filter of 0.01 nm half-width at half-maximum, and linearly merged over the 300-305 nm wavelength range. The result is a reference spectrum in vacuum wavelengths accurate to better than 0.001 nm above 305 nm and 0.002 nm below 300 nm. This spectrum was created specifically for GOME applications, in particular wavelength calibration studies and calculation of Ring effect contributions to GOME measurements. A sample of this Fraunhofer reference spectrum is given in Figure 2 (a); in Figure 2 (b) it has been convolved with a Gaussian slit function having a half-width at 1/e intensity of 0.212 nm, appropriate to the GOME instrument in this wavelength range. The solar spectrum, with GOME slit function, has been convolved with the rotational Raman cross sections described here, to create a Ring effect source spectrum for fitting of GOME data. The same wavelength portion of this Ring effect source spectrum is shown in Figure 2 (c). The units are those of cross sections times photons, corresponding to the Ring effect scattering source per air molecule at 250°K. In Figure 2 (d) the ratio of the Ring effect source spectrum to the Fraunhofer spectrum has been taken and a cubic polynomial, fitted to the region presented in the figure, has been subtracted off, for comparison with differential Ring effect spectra determined in previous studies. Atmospheric Ring spectra have been determined by several groups from polarized spectroscopic

measurements of the zenith sky at high solar zenith angles. Measurements at polarizations parallel and perpendicular to the single-scattering plane are combined in similar formulations to obtain effective Ring effect cross sections.^{6,7,12,14} For a single-scattering Rayleigh atmosphere this procedure could yield the rotational Raman cross sections directly. In practice, because of Mie and multiple Rayleigh scattering, what is determined is the ratio of the rotational Raman spectrum to the solar Fraunhofer spectrum. This may be confirmed by comparing Figure 2 (d) with the results of the above studies. Atmospheric radiative transfer calculations of Ring spectra^{7,12,14} also determine this quantity. It is distinct from the “filling in” calculated by Joiner *et al.*,¹⁰ who include both the rotational Raman source term and the Cabannes loss term in their calculations. The use of the ratio of rotational Raman to Fraunhofer has proved useful in fitting atmospheric spectra for minor constituent abundances; it is a good approximation to the quantity needed for Ring effect correction in some fitting techniques and measurement geometries. However, its use has limitations due to the distortion of the rotational Raman spectrum and its constant ratio to the Fraunhofer spectrum. The rotational Raman spectrum and Fraunhofer spectrum determined in this study should be more generally applicable to fitting of atmospheric spectra obtained from various measurement geometries, including satellite-based measurements.

5 Conclusions

The complete Rayleigh with rotational Raman scattering database as described in the previous sections is available from the authors. It includes: N₂ and O₂ term values and statistical partitioning (tables including the quantum numbers and term energies for O₂ and N₂ up to states allowing for partitioning to better than 0.01% accuracy and Boltzmann factors with nuclear spin degeneracies, g_N); tables giving the King correction factors, values of $\sqrt{\epsilon}$, where $\epsilon = (\gamma/\bar{\alpha})^2$, index of refraction $\bar{\alpha}$, and γ for O₂ and N₂; Placzek-Teller coefficients, with examples of cross-sections; pressure broadening coefficients; the solar reference spectrum derived above; the convolved solar and rotational Raman spectrum (Ring effect source function “cross section” calculations). This database is a summary of the best available relevant data that were found in the literature, and the calculations performed in this study. One item not included here is the additional broadening due to Rayleigh-Brillouin scattering.⁴ For the rotational Raman lines, this will provide an extra source of broadening, although the extent of the broadening is within the uncertainties in the pressure broadening for scattering in the troposphere. The effect of Rayleigh-Brillouin scattering for the filling in of the central Cabannes line for narrow Fraunhofer lines might be significant for some satellite measurement conditions and will be a topic for future investigations.

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TABLE 1. Relative Rayleigh and Raman Scattering Intensities
 Mostly from Kattawar *et al.*, 1981

V polarization in	H polarization in	Sum (natural light in)
Rayleigh-Brillouin		
${}^V C_V = 180 + 4\epsilon$	${}^H C_V = 3\epsilon$	${}^0 C_V = 180 + 7\epsilon$
${}^V C_H = 3\epsilon$	${}^H C_H = 3\epsilon + (180 + \epsilon) \cos^2\theta$	${}^0 C_H = 6\epsilon + (180 + \epsilon) \cos^2\theta$
${}^V C_0 = 180 + 7\epsilon$	${}^H C_0 = 6\epsilon + (180 + \epsilon) \cos^2\theta$	${}^0 C_0 = (180 + 13\epsilon) + (180 + \epsilon) \cos^2\theta$
		$\rho_0^C = 6\epsilon / (180 + 7\epsilon)$
Raman		
${}^V W_V = 12\epsilon$	${}^H W_V = 9\epsilon$	${}^0 W_V = 21\epsilon$
${}^V W_H = 9\epsilon$	${}^H W_H = 9\epsilon + 3\epsilon \cos^2\theta$	${}^0 W_H = 18\epsilon + 3\epsilon \cos^2\theta$
${}^V W_0 = 21\epsilon$	${}^H W_0 = 18\epsilon + 3\epsilon \cos^2\theta$	${}^0 W_0 = 39\epsilon + 3\epsilon \cos^2\theta$
		$\rho_0^W = 6/7$
Sum		
${}^V T_V = 180 + 16\epsilon$	${}^H T_V = 12\epsilon$	${}^0 T_V = 180 + 28\epsilon$
${}^V T_H = 12\epsilon$	${}^H T_H = 12\epsilon + (180 + 4\epsilon) \cos^2\theta$	${}^0 T_H = 24\epsilon + (180 + 4\epsilon) \cos^2\theta$
${}^V T_0 = 180 + 28\epsilon$	${}^H T_0 = 24\epsilon + (180 + 4\epsilon) \cos^2\theta$	${}^0 T_0 = (180 + 52\epsilon) + (180 + 4\epsilon) \cos^2\theta$
		$\rho_0^T = 6\epsilon / (45 + 7\epsilon)$

FIGURE CAPTIONS

Figure 1 Rotational Raman cross sections for (a) N_2 and (b) O_2 calculated for a temperature of $250^\circ K$ and an excitation wavelength of 440 nm, appropriate to investigations of the effect of the Ring effect on retrievals of atmospheric NO_2 concentrations. The cross sections in this figure do not include the relative abundances of N_2 and O_2 in air.

Figure 2 (a) A sample of the Fraunhofer reference spectrum determined in this study; (b) The same Fraunhofer spectrum, convolved with a Gaussian slit function having a half-width at $1/e$ intensity of 0.212 nm, appropriate to the GOME instrument in this wavelength range; (c) the Fraunhofer spectrum of (b), convolved with the rotational Raman cross sections to create a Ring effect source spectrum. The units are those of cross section \times photons, corresponding to the Ring effect scattering source per air molecule at $250^\circ K$; (d) the ratio of the Ring effect source spectrum given in (c) to the Fraunhofer spectrum of (b), with a cubic polynomial subtracted off. This spectrum closely corresponds to the Ring effect spectrum used in previous studies for atmospheric spectrum correction, as discussed in the text.

