



**STRATOSPHERIC AEROSOL CLIMATOLOGY
FROM SAGE II AND OBSERVATION OF ITS
DERIVER, CARBONYL SULFIDE, OVER
EQUATORIAL AFRICA**

By
MILKESSA GEBEYEHU HOMA

SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE IN PHYSICS

AT
ADDIS ABABA UNIVERSITY
ADDIS ABABA, ETHIOPIA
JULY 2010

ADDIS ABABA UNIVERSITY
DEPARTMENT OF
PHYSICS

Supervisor:

DR. GIZAW MENGISTU

Examiners:

DR. FELEKE ZEUGE

PROF. A.V. GHOLAP

ADDIS ABABA UNIVERSITY

Date: **JULY 2010**

Author: **MILKESSA GEBEYEHU HOMA**

Title: **STRATOSPHERIC AEROSOL CLIMATOLOGY
FROM SAGE II AND OBSERVATION OF ITS
DERIVER, CARBONYL SULFIDE, OVER
EQUATORIAL AFRICA**

Department: **Physics**

Degree: **M.Sc.** Convocation: **July** Year: **2010**

Permission is herewith granted to Addis Ababa University to circulate and to have copied for non-commercial purposes, at its discretion, the above title upon the request of individuals or institutions.

Signature of Author

THE AUTHOR RESERVES OTHER PUBLICATION RIGHTS, AND NEITHER THE THESIS NOR EXTENSIVE EXTRACTS FROM IT MAY BE PRINTED OR OTHERWISE REPRODUCED WITHOUT THE AUTHOR'S WRITTEN PERMISSION.

THE AUTHOR ATTESTS THAT PERMISSION HAS BEEN OBTAINED FOR THE USE OF ANY COPYRIGHTED MATERIAL APPEARING IN THIS THESIS (OTHER THAN BRIEF EXCERPTS REQUIRING ONLY PROPER ACKNOWLEDGEMENT IN SCHOLARLY WRITING) AND THAT ALL SUCH USE IS CLEARLY ACKNOWLEDGED.

To My Father.

Table of Contents

Table of Contents	vii
List of Figures	viii
Abstract	xi
Acknowledgements	xiii
Introduction	1
PART I	4
1 The Atmosphere	5
1.1 The Atmospheric Constituents	5
1.2 The Atmospheric Structure	6
2 Radiative Transfer in the Atmosphere	9
2.1 Extinction and Emission	9
2.2 Optical Depth	10
2.3 Radiative Transfer Equation in stratified Atmosphere	12
3 Retrieval of Aerosol Size Distribution from Extinction Data	15
3.1 Retrieval Method	16
4 Principle of Remote Sensing and Retrieval Method	20
4.1 Interaction between Matter and Radiation	20
4.2 Line Shape and Width of Spectra	26
4.3 Retrieval Method	29
PART II	33
5 Atmospheric Aerosols	34
5.1 Aerosols Background	34
5.2 Sources and Removal of Atmospheric Aerosols	35

5.2.1	Sources of Atmospheric Aerosols	35
5.2.2	Removal of Atmospheric Aerosols	39
5.3	Aerosol Size Distribution	41
5.3.1	The Jung distribution	41
5.3.2	Lognormal distributions	42
5.4	Optical Properties of Aerosols	43
6	Scattering by Small Spherical Particles	46
6.1	Mie Scattering	47
7	Aerosol's Role in Atmospheric Energy Balance	50
7.1	Distribution of Insolation Outside the Atmosphere	51
7.2	Climate Impact of Aerosols	54
8	Results and Discussion	56
8.1	Vertical and spectral distribution of stratospheric aerosols	56
8.2	Time series of annual mean column AOD	65
8.3	Size distribution of stratospheric aerosols	66
PART III		69
9	FTIR Spectrometer set up in Addis Ababa	70
9.1	FTIR Components	71
9.1.1	Solar Tracker	71
9.1.2	Optical Devices	72
9.1.3	Detectors	73
9.1.4	Scanner	74
9.1.5	IR Source	74
9.1.6	Electronics Unit	75
10	FTIR Spectrometer Principle	76
10.1	Ideal Fourier Transform Spectrometer	76
10.1.1	Discrete Fourier Transform	81
10.2	Real FT Spectrometer	83
10.2.1	Apodization and ILS	83
11	Measurement of Carbonyl Sulfide over Addis Ababa	90
11.1	Carbonyl Sulfide (OCS): background and chemistry	90
11.2	OCS Spectral Signature in mid-infrared	93
11.2.1	Microwindow Selection	93
11.2.2	Error Analysis	94
11.2.3	Retrieval of OCS from FTIR Observation	97
11.2.4	Time series of carbonyl sulfide	101
11.2.5	Correlation between <i>OCS</i> , <i>CO</i> ₂ and <i>O</i> ₃	105

11.2.6 Distribution, Total mass and Life time of OCS in the Atmosphere .	108
PART IV	111
12 Conclusions	112
12.1 The climatology, microphysical and optical properties of stratospheric aerosols	112
12.2 Observation of carbonyl sulfide over Addis Ababa	114
Bibliography	117

List of Figures

1.1	Vertical Structure of the Earth's Atmosphere [9].	7
2.1	Schematic presentation of the total energy transformation by a volume element.	9
2.2	Geometry for plane parallel atmosphere.	12
4.1	Simultaneous transitions in vibrational and rotational energies	26
5.1	Severe dust storm near Cairo, 2 May, 1997.	36
5.2	Mount St. Helens volcanic eruption in July 22,1980.	37
5.3	Schematic of stratospheric aerosol lifecycle [27]	40
6.1	Scattering by spherical particle.	47
6.2	Mie extinction efficiency for different values of imaginary refractive indices [13].	49
7.1	The spectrum of the solar radiation outside and below the atmosphere of the Earth. The gases responsible for absorption are indicated. The solid line is a black body emission at $5250^{\circ}C$	51
7.2	Relationship of the solar zenith angle θ_0 to the latitude λ , the solar inclination δ , and the hour angle h . The ϕ here denotes the azimuthal angle of the sun from the south.	53
8.1	Seasonal variation of temperature profile over Ethiopia.	57
8.2	Vertical distribution of aerosol extinction value during measurement period at 386 nm.	58
8.3	Seasonal variation of column AOD values at 386 nm.	59

8.4	Vertical distribution of aerosols extinction value during measurement period at 452 nm.	60
8.5	Seasonal variation of column AOD values at 452 nm.	60
8.6	Vertical distribution of aerosol extinction value during measurement period at 525 nm.	61
8.7	Seasonal variation of column AOD values at 525 nm.	61
8.8	Vertical distribution of aerosols extinction values during measurement period at 1020 nm.	62
8.9	Seasonal variation of column AOD values at 1020 nm.	63
8.10	Annual mean column AOD at different channels.	65
8.11	Monthly mean aerosol size distribution function for the years 1985, 1989, 1991, 1993, 1997 and 2004.	67
9.1	The FTIR measurement site in Addis Ababa.	71
9.2	The IFS120M instrument optical set up in Addis Ababa.	73
10.1	Schematic diagram of IFS120M working principle.	76
10.2	Monochromatic (a) and polychromatic (b) source interferograms [49]. . . .	80
10.3	Instrumental Line Shape with Boxcar apodization function.	84
10.4	Retrieved ILS of the IFS120M in Addis Ababa	86
10.5	Evolution of Modulation efficiency loss	87
10.6	Evolution of Phase error	88
10.7	The measured and simulated transmittance spectral fit from HBr cell measurement (upper panel) and the corresponding residual spectra between the measured and calculated spectra (lower panel) for the date of 01 June, 2009	89
11.1	Random (left panel) and systematic (right panel) errors of OCS on 27 th Jan., 2010.	95
11.2	The measured and calculated spectra.	97
11.3	Averaging Kernel for selected heights.	98
11.4	Retrieved profile of OCS.	99
11.5	Variation of OCS VMR with time at 13 km	100
11.6	Partial and integrated columns of OCS on the 27 th of January, 2010. . . .	100

11.7	Time series of the total column OCS.	102
11.8	Time series of the vertical profile of OCS.	103
11.9	Time series of total column and vertical profile of OCS for January, 2010. .	104
11.10	Time series of Tropospheric and Stratospheric total column OCS	105
11.11	Relationship between atmospheric <i>OCS</i> and CO_2	106
11.12	Relationship between stratospheric <i>OCS</i> and O_3	107

Abstract

The issues of climate change and its causes have become agenda of different governmental and non-governmental discussions. The major atmospheric components responsible for climate change are particulate matters (aerosols) and trace gases (mainly anthropogenic green house gases). The stratospheric aerosol climatology over Ethiopia from SAGE II data and carbonyl sulfide (OCS) measurement from FTIR spectrometer over Addis Ababa are discussed in this thesis. The vertical profiles of aerosol extinction over Ethiopia were analyzed and the result shows seasonal variation of stratospheric aerosol distribution over Ethiopia. The total column stratospheric aerosol also shows seasonal variation with maximum value attained during Spring and minimum during Summer. The annual mean value of total column AOD is observed to be steadily increasing from 1984 to 2005, which revealed the increasing trend of stratospheric aerosols of both fine and course mode particles. Results from the monthly mean stratospheric aerosol size distribution show that the number density is maximum for months of maximum AOD values as expected however the observed trend is not significant. The Bruker IFS120M was installed at tropical site located in Addis Ababa, Capital of Ethiopia ($9^{\circ}1'$, $38^{\circ}76'$, 2443 m.a.s.l.) and has been continuously operating since May, 2009. Nearly regular cell (HBr cell) measurements were taken using laboratory source to monitor the alignment of the instrument and its stability over time. The analysis of cell measurement using LINEFIT (LINEFIT12) software has indicated the performance of the instrument is very good. The data measured between May, 2009 to April, 2010 were analyzed and interpreted. The latest version of PROFFIT (PROFFIT95) was used to retrieve vertical profiles and total column values of carbonyl sulfide from pressure dependent broadened spectra with the help of Tikhonov-Philips regularization method. The OCS VMR observed at Addis site reaches up to 0.6 parts per billion by volume (ppbv) and the total column amount reaches up to 8×10^{19} *molecules/cm²*. The total column and vertical profile observed in our

site is greater than the same quantity reported at Izana, Spain. The tropospheric and stratospheric mass of OCS is also estimated in gram and we found it to be 4.6056 Tg and 0.3427 Tg respectively which sum up to yield of 4.9484 Tg of total mass. The atmospheric life time of OCS in our region is estimated to be 4.1236 years. Because of its longer life time in the atmosphere (as compared to other sulfur containing compounds), it is transported to the stratosphere through the tropical tropopause by different mechanisms and latter converted to form stratospheric background sulfate aerosol layer, which in turn determines the Earth's radiation budget. Random and systematic Error contribution to retrieval were analyzed and the result shows that the total error contribution due to atmospheric and auxiliary parameters is less than 10%.

Acknowledgements

First of all I would like to thank Jimma University for the sponsorship during my stay at Addis Ababa University.

I am very grateful for Dr. Gizaw Mengistu for his fatherly approach and academic assistance as my Advisor and for his guidance to make this work meaningful. I would really like to thank his humble behavior in creating opportunities to share experiences with abroad research institutes and arranging international workshops from which we gain a lot. His effort to equip students with necessary facilities is also appreciable.

My gratitude also goes to Dr. Thomas Blumenstock from KIT, for his support in the operation of the FTIR spectrometer, training on LINEFIT software and discussions on the result.

I am also grateful for Dr. Frank Hase for his patient elaboration of the retrieval code(PROFFIT), technical support, and discussion of our results.

The Institute of Meteorology and Climate Research of the Karlsruhe Institute of Technology shall also be thanked for financial support to visit the Research Center.

My thanks also extends to my senior students Wondimu Alemu and Melaku Tesfaye for their valuable support and provision of readable materials.

I am so glad to thank my wife Membere Diriba for her support in typing some parts of this thesis and encouraging me during bad circumstances I face.

Finally, I would like to thank all atmospheric physics students whom I joined in Science faculty of AAU.

Introduction

The Earth's Atmosphere is a mixture of different trace gases and very minor constituents such as aerosols. The composition of aerosols, water vapor, carbon dioxide, ozone and other minor particles is less than 1%. However, these minor constituents have been influencing the atmosphere since the beginning of the 2nd industrial revolution [1]. Atmospheric aerosols are liquid and solid particulate matters in the Earth's atmosphere. They are highly populated in troposphere. Their distribution decreases with altitude [2]. The sources of these particulate matters could be from anthropogenic and natural activities at the surface or within the atmosphere. Tropospheric aerosols are usually introduced due to strong volcanic eruptions and gas-to-particle conversions. Because of their highly dynamic nature, aerosol's spatial and temporal distribution are very difficult to predict even if it is known they are populated closer to their source area. The presence of these particulate matters in the Earth's atmosphere has significant impacts (both positively and negatively) either directly or indirectly on human activities in particular and life on Earth in general. The direct effect of aerosols is scattering and absorbing both short wave (solar radiation) and long wave (terrestrial radiation). The indirect effect of aerosols is related to their role as a cloud condensation nuclei (CCN) which modifies cloud microphysics, and concentration. This results in cloud albedo (reflectance) which contributes to Earth's shortwave albedo. Therefore, aerosols alter the Earth's climate by modulating the Earth's radiation budget [3]. According to [4] sand and dust storms have major impacts on aviation (by reducing on-root visibility), mechanical engine damage, health, agriculture and weather and climate. Aerosols can also participate in heterogeneous reactions

in the atmosphere which depends on aerosol composition. This heterogeneous reaction of aerosols is also suggested as a cause for northern and mid-latitude ozone depletion [5]. The transport of aerosol-loaded air or precursors of ozone-destroying species from the tropics, where the majority of trace gases injected into the atmosphere and enter the stratosphere, and move up to mid-latitudes may also be a cause for ozone decrease of 0.6% per year at mid-latitudes and 0.2% per year at subtropics [6]. Ethiopia is one of the East African countries. Its population is more than 70 millions. Majority of the people ($> 85\%$) live in rural area, where modern energy sources have not reached yet [7]. So, this section of the population produces energy from biomass burning which results in introduction of particulate matters like soot and ash. Ethiopia has been affected by droughts in different years which is caused by climate change. The drought might be partly due to reduction in forest cover which can be related to increase in aerosol concentration in the air [8]. However, as a developing country, Ethiopia is also undertaking different activities in industrial plantations and constructions in all parts of the country. Therefore, it is now the right time to give attention to air quality and climate change impacts. This thesis is the first to provide a long term data analysis report on aerosol for Ethiopia. The main goal of this thesis (part II) is to investigate vertical and seasonal distribution and annual mean values of aerosol optical depth over Ethiopia using the SAGE II instrument's extinction data for a period of approximately 21 years extending from Oct., 1984 to Sept., 2005. The vertical distribution of aerosols at different channels of SAGE II and spatial distribution will also be discussed. The trend of column amount AOD and the monthly mean size distribution function of aerosols for some of the selected years will be retrieved using Mie algorithm as discussed in chapter 6. In the third part of this thesis, Fourier Transform InfraRed (FTIR) spectrometer installed at Addis Ababa through a joint collaboration of Institute for meteorology and climate research (IMK) and Department of physics of Addis Ababa University is described. This instrument is widely used to measure trace atmospheric composition. It is a robust and diverse ground based instrument for detection of green

house gases and other trace gases. It is the only of its kind in Africa and as a result, it is expected to provide unique information about equatorial Africa atmospheric physics and chemistry, particularly in the context of global environmental change. Since the past few decades human activities and its cause to environmental changes has attracted attention. The global warming due to enhanced green house gases and the declination of stratospheric ozone are examples of the anthropogenic sources of environmentally non-friendly emission of gases. Most of these gases which are precursors of ozone-destroying species (or aerosol-loaded air) are injected into the atmosphere from tropics [6]. The monitoring mechanism is based on continuous measurements of these gases either from ground or space born instruments like Fourier transform spectrometer. Atmospheric OCS is known to be the highest among the background aerosol sources due to its long term atmospheric life time. The transport of this gas from troposphere to the stratosphere occurs mainly through the tropical tropopause. In the stratosphere, its photooxidation produces sulfur dioxide which latter converted to the background aerosol. The objective of the third part of this thesis is to provide a preliminary result of the first high resolution, ground based, FTIR spectrometer observation results of OCS in Africa. The structure of this thesis is such that, it has 4 parts: part-I describes the atmosphere, interaction of its constituents with radiation and remote sensing procedures based on this physics, part-II is focussed on aerosol climatology over Ethiopia using SAGE II data from satellite, part-III discusses ground-based measurement of carbonyl sulfide over Addis Ababa using FTIR spectrometer, and part-IV summarizes the results of the studies from part-II and III.

PART I

Atmospheric Physics and Mathematics of Remote Sensing

Chapter 1

The Atmosphere

1.1 The Atmospheric Constituents

The Earth's atmosphere consisting primarily of a mixture of gases also contains particles, such as aerosols and clouds [2]. The chemical composition of the atmosphere is reported in terms of the volume mixing ratio, which is the ratio between the number of molecules of that gas present in a given volume with respect to the total number of molecules present in the same volume. The Earth's atmosphere is composed mostly (99%) of nitrogen and oxygen, which are permanent gases. The remaining (i.e one percent) is made up of argon, a noble gas, liquid and solid particulate, etc. However it is just those gases and particulate matters with mixing ratio less than one percent that are responsible for some of the most important properties of the Earth's atmosphere and the climate of the planet. In turn, the climate and the environment determined by the tiny amount of these gases makes life possible on our planet [9].

Atmospheric gases are usually classified, according to their degree of concentration as permanent and variable. Gases which do not exhibit significant variations in concentrations for different locations and for a long period of time are classified as permanent [10]. These gases are listed in Table 1.1 below including their residence time in the air, as different gases have different residence times in the atmosphere.

Table 1.1. Gas composition of dry atmospheric air in the troposphere.

Type of gases	Symbol	Concentration (ppm)	Residence time
Principal gases			
Nitrogen	N_2	780000	Continuous
Oxygen	O_2	209400	Continuous
Argon	Ar	9300	Continuous
Trace gases(constant)			
Helium	He	5.2	about $2 * 10^6$ years
Neon	Ne	18	Continuous
Krypton	Kr	1.1	Continuous
Xenon	Xe	0.086	Continuous
Trace gases(variable)			
Carbon dioxide	CO_2	200 – 400	4 years
Carbon monoxide	CO	0.01 – 0.2	about 0.3 years
Methane	CH_4	1.2 – 1.5	about 100 years
Formaldehyde	CH_2O	0 – 0.1	unestimated
Nitrous oxide	N_2O	0.25 – 0.6	about 4 years
Nitrogen dioxide	NO_2	$(1 - 4.5) * 10^{-3}$	a few days
Ammonia	NH_3	0.002 – 0.02	unestimated
Hydrogen sulfide	H_2S	$(2 - 20) * 10^{-3}$	about 40 days
Sulfur dioxide	SO_2	0 – 0.02	about 5 days
Chlorine	Cl_2	$(3 - 15) * 10^{-4}$	a few days
Iodine	I_2	$(0.4 - 4) * 10^{-5}$	unestimated
Hydrogen fluoride	HF	$(0.8 - 18) * 10^{-3}$	unestimated
Ozone	O_3	0 – 0.5	about 60 days

This table is taken from [2].

1.2 The Atmospheric Structure

The atmosphere has an enormous mass, that it has a density of around 1.2 kg.m^{-3} . The other characteristic of the atmosphere is its extreme mobility. The mixing of the atmosphere is 0.2 years [11]. In the atmosphere the pressure change alters the density of

gases, and the variation of pressure with altitude can be derived from the gas laws. This is given by

$$P_z = P_0 \exp \frac{-Z}{H} \quad (1.2.1)$$

where H is called the *exponential scale height*. This useful parameter represents the change in height required to achieve a pressure drop by a factor of $\frac{1}{e}$.

The profile of the Earth's atmosphere illustrated in Fig.1.1 shows how rapidly pressure falls off with altitude. The interaction of radiation with the atmosphere leads to the thermal structure shown in Fig.1.1.

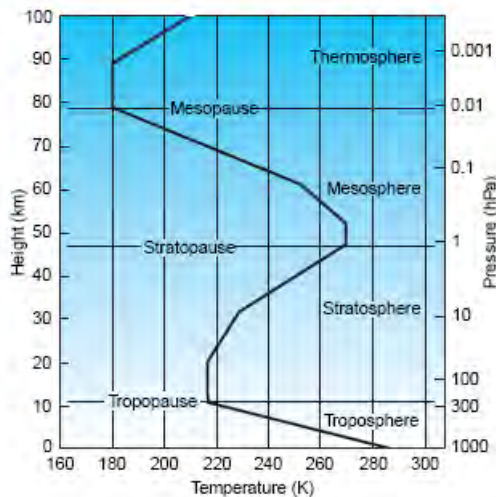


Figure 1.1: Vertical Structure of the Earth's Atmosphere [9].

The Earth's atmosphere is commonly described as a series of layers defined by their thermal characteristics. Each layer is a region where the change in temperature relative to altitude has a constant sign. The layers are called "spheres" and the boundaries between them are the "pauses". The troposphere is vertically well mixed because of the negative temperature gradient. Temperature and location of the *tropopause* vary with latitude and season. At the Equator, its mean altitude is near 17 km and the corresponding temperature is about 190 K, while in polar regions its elevation is about 8 km only and

the temperature roughly is 220 K . In contrast to the troposphere, the stratosphere is characterized by a stable layering, i.e, only weak vertical motion exists (reduction of vertical turbulent transport). This is due to the increase of temperature with height in this layer. The positive temperature gradient is a result of ozone heating, which is due to the absorption of solar ultraviolet (UV) radiation by ozone.

The *stratopause* lies at an altitude of about 48 km with a temperature of 270 K . In the mesosphere ozone heating is reduced and the temperature decreases with height up to the *mesopause* at about 85 km. Temperature once again increase in the thermosphere, where energetic solar radiation is absorbed [6].

Chapter 2

Radiative Transfer in the Atmosphere

2.1 Extinction and Emission

Matter and radiation have only two forms of interactions: extinction and emission. Lambert first proposed that the extinction (i.e, reduction) of radiation traversing an infinitesimal path ds is linearly proportional to the incident radiation and the amount of interacting matter along the path:

$$\frac{dI_\nu}{ds} = -k(\nu)I_\nu \quad (2.1.1)$$

where $k(\nu)$ is the extinction coefficient, a measurable property of the medium, and s is the absorber path length. $k(\nu)$ is proportional to the local density of the medium and is positive definite.

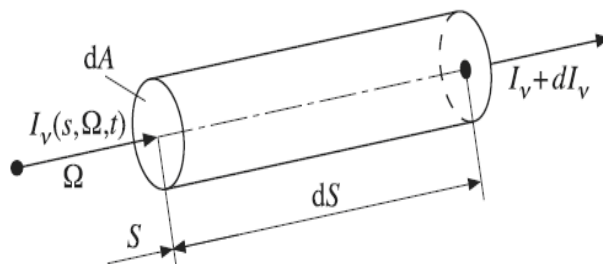


Figure 2.1: Schematic presentation of the total energy transformation by a volume element.

Extinction includes all processes which reduce the radiant intensity. These processes include absorption and scattering, both of which remove photons from the incident beam. Similarly the radiative emission is also proportional to the amount of matter along the path:

$$\frac{dI_\nu}{ds} = k(\nu)S_\nu \quad (2.1.2)$$

where S_ν is known as the source function. The source function plays an important role in radiative transfer theory. Emission includes all processes which increase the radiant intensity. These processes include thermal emission and scattering which adds photons to the beam.

Extinction and emission are linear processes, and thus additive. Since they are the only two processes which alter the intensity of radiation, they can be combined as:

$$\frac{dI_\nu}{ds} = -kI_\nu + kS_\nu \quad (2.1.3)$$

$$\frac{1}{k} \frac{dI_\nu}{ds} = -I_\nu + S_\nu \quad (2.1.4)$$

Eq.(2.1.4) is the differential equation of radiative transfer in its simplest form.

2.2 Optical Depth

Optical depth is a dimensionless parameter which quantifies the attenuation of the sun's direct beam. It is a measure of how much light do air born particles prevent from passing through a column of atmosphere. Aerosols tend to absorb or reflect the incoming sunlight, thus reduce visibility and increase optical depth. Optical depth of less than 0.1 indicates

a crystal clear sky with maximum visibility whereas the value 4 indicates the presence of aerosol so dense which is difficult to see the sun at mid-day [12].

Mathematically, we define optical depth τ between points P_1 and P_2 as:

$$\tau(z_1, z_2) = \int_{z_1}^{z_2} k dz \quad (2.2.1)$$

or, in differential form:

$$d\tau = -k dz \quad (2.2.2)$$

To gain more insight into the usefulness of the optical depth, we can express τ in terms of the aerosol mass M , rather than number concentration N . For a monodisperse aerosol of density ρ , the mass concentration is

$$M = \frac{4}{3}\pi r^3 \rho N \quad (2.2.3)$$

where r is the radius of the spherical particles. Combining the above expression with the optical depth defined in terms of the extinction k as,

$$\tau \equiv k \Delta z = \pi r^2 Q_e N \Delta z, \quad (2.2.4)$$

we obtain

$$\tau = \frac{3M \Delta z}{2r \rho}. \quad (2.2.5)$$

Thus, τ increases linearly with M for a given r . Note however, that a given mass M produces an optical depth that is inversely proportional to the radius of the particles.

2.3 Radiative Transfer Equation in stratified Atmosphere

A stratified atmosphere is one in which all atmospheric properties such as temperature, density, etc vary only vertically. We obtain the radiative transfer equation in terms of optical depth as,

$$U \frac{dI_\nu}{d\tau} = -I_\nu + S_\nu \quad (2.3.1)$$

where the photon path increment ds at polar angle θ in a stratified atmosphere is related to the vertical path increment dz by $dz = \cos\theta ds$ or $ds = U^{-1}dz$ is used in Eq.(2.1.3).

Eq.(2.3.1) is the differential form of the radiative transfer equation in a plane parallel atmosphere for all angles.

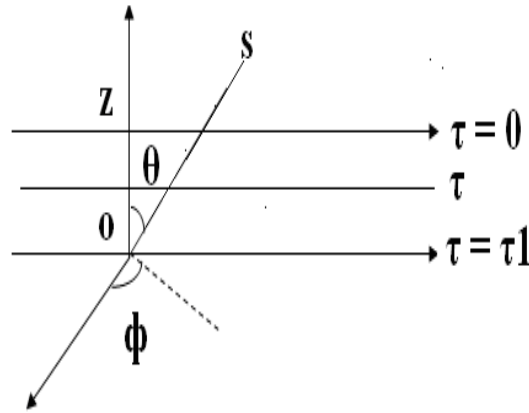


Figure 2.2: Geometry for plane parallel atmosphere.

We know that at the top of the atmosphere, sunlight is the only incident intensity from the hemisphere containing the sun; and at the surface, we have constraints on the upwelling intensity due to thermal emission or the surface reflectivity. When combined, these two hemispheric boundary conditions span a complete range of polar angle. Thus we need to decouple Eq.(2.3.1) into its constituent upwelling and downwelling radiation components

as:

$$-\mu \frac{dI_{\nu}^{-}}{d\tau} = I_{\nu}^{-} - S_{\nu}^{-} \quad (2.3.2)$$

$$-\mu \frac{dI_{\nu}^{+}}{d\tau} = I_{\nu}^{+} - S_{\nu}^{+} \quad (2.3.3)$$

Eq. (2.3.2) is defined over $0 < \theta < \frac{\pi}{2}$ and Eq. (2.3.3) is defined over $\frac{\pi}{2} < \theta < \pi$ where I_{ν}^{-} and I_{ν}^{+} are downwelling and upwelling radiance, similarly for source functions S_{ν}^{-} and S_{ν}^{+} , and $\mu = \|U\| = \|\cos\theta\|$ which is a positive definite. These are the equations of radiative transfer in slab geometry for downwelling ($0 < \theta < \frac{\pi}{2}$) and upwelling ($\frac{\pi}{2} < \theta < \pi$) intensities, respectively. The solution of radiative transfer equation (integral form) is given for upwelling radiance as [13]:

$$I_{\nu}(\tau, +\mu) = \exp\frac{-(\tau^{*} - \tau)}{\mu} I_{\nu}(\tau^{*}, +\mu) + \mu^{-1} \int_{\tau}^{\tau^{*}} \exp\frac{-(\tau' - \tau)}{\mu} S_{\nu}(\tau', +\mu) d\tau' \quad (2.3.4)$$

where τ^{*} is optical depth at the surface, τ is the optical depth at level of interest and τ' is at any intermediate level. The first term on the right hand side (RHS) is the contribution of the boundary (e.g. Earth's surface) to the upwelling intensity at level τ . This contribution is attenuated by the optical path of the radiation between the ground and level τ . The second term on the RHS is the contribution of the atmosphere to the upwelling intensity at level τ . The net upwelling emission of each parcel of air between the surface and level τ is $S_{\nu}(\tau', +\mu)$, but this internally emitted radiation is attenuated along the slant path between τ' and τ . The μ^{-1} factor in front of the integral accounts for the slant path of the emitting mass in the atmosphere. The solution for downwelling radiance is given by

$$I_{\nu}(\tau, -\mu) = \exp\frac{-\tau}{\mu} I_{\nu}(0, -\mu) + \mu^{-1} \int_0^{\tau} \exp\frac{-(\tau - \tau')}{\mu} S_{\nu}(\tau', -\mu) d\tau' \quad (2.3.5)$$

The solutions for radiative transfer equation is important for applications in remote sensing of the atmosphere, and calculation of radiative forcing.

Chapter 3

Retrieval of Aerosol Size Distribution from Extinction Data

Remote sensing is the science of obtaining information about an object, area, or phenomenon through the analysis of data acquired by a device that is not in contact with the object, area or phenomenon under investigation [14]. For instance, to survey for the existence of minerals or oils in the ground, one needs only measuring the density of the suspect area using gravimeter or send seismic waves and detect the reflected waves. Similarly for atmospheric cases, one can retrieve the physical and optical properties of atmospheric constituents by measuring radiances attenuated by the atmosphere either from ground or space based instruments.

Since Angstrom found an empirical relationship between the size of the aerosol particles and the wavelength dependence of the extinction coefficients, different scientists showed interest in the retrieval of aerosol size distributions [15].

According to [11], there are two types of inversions: direct and indirect inversion techniques. He presented the difference between the two as follows. By looking an animal and identifying its foot print is a direct inversion but looking a foot print and identifying the animal is an indirect inversion technique and it is complicated. The latter inversion type is the commonest one in retrieval of atmospheric parameters such as size distributions of

aerosols, vertical profiles of trace gases, etc. In this thesis we retrieve the aerosols size distribution from aerosols extinction data.

3.1 Retrieval Method

The aerosols size distribution (ASD) is very important parameter for characterizing the behavior of aerosols, since aerosol properties depend largely on this variable. The ASD also tells us the sources of aerosols [16, 17]. The global extinction data obtained from Stratospheric Aerosols and Gas Experiment II (SAGEII) instrument aboard on Earth's Radiation Budget Satellite (ERBS) is filtered out over Ethiopian region (i.e, $3^{\circ}N - 15^{\circ}N$ and $33^{\circ}E - 48^{\circ}E$). Then monthly mean extinction data is obtained using matlab code, at four aerosol channels of the instrument centered at 386 nm , 452 nm , 525 nm and 1020 nm . The extinction data is provided for each 0.5 km interval up to 40 km above the surface of the Earth. So we can consider the atmosphere to be stratified at 0.5 km levels. So we can calculate optical depth from,

$$\tau(\lambda) = \int_0^{\infty} \beta_e(z, \lambda) dz = \int_0^{\infty} (\beta_{sca} + \beta_{abs}) dz \quad (3.1.1)$$

where the total extinction coefficient β_e is the sum of the extinction due to absorption (β_a) and scattering β_{sca} . The aerosol optical depth (AOD) is a complex function of particles size distribution, refractive index, shape, etc. Assuming aerosols are homogeneous spheres, the equation that relates AOD and ASD is given by [16, 17] in the form of:

$$\tau(\lambda) = \int_0^{\infty} \int_0^{\infty} \pi r^2 Q_{ext}(r, \lambda, m) n(r, z) dz dr \quad (3.1.2)$$

where $n(r, z)dr$ is the height-dependent aerosol number density in the radius range r to $r + dr$, m is the complex refractive index of the aerosol particles such that the real part

represents the contribution due to particulate scattering while the imaginary quantity denotes particulates' absorption, λ is the wavelength of the incident illumination, and $Q_{ext}(r, \lambda, m)$ is the extinction efficiency factor of the atmosphere for Mie theory, in which the aerosol is assumed to consist of homogeneous spherical particles which are non dispersive over the wavelength range of the observations. Performing integration over height (entire column), Eq. (6.1.2) can be written as:

$$\tau(\lambda) = \int_0^\infty \pi r^2 Q_{ext}(r, \lambda, m) n_c(r) dr \quad (3.1.3)$$

where $n_c(r)$ is the unknown columnar aerosol size distribution, i.e, the number of particles per unit area per unit radius interval in a vertical column through the atmosphere. It is difficult to solve for $n_c(r)$ in terms of $\tau(\lambda)$ analytically in Eq.(3.1.3); so a numerical approach must be followed to separate $n_c(r)$ into two parts as $n_c(r) = h(r)f(r)$, where $h(r)$ is rapidly varying function with r and $f(r)$ is slowly varying. Upon substitution the above integral equation changes to,

$$\tau(\lambda) = \int_{r_a}^{r_b} \pi r^2 Q_{ext}(r, \lambda, m) h(r) f(r) dr \quad (3.1.4)$$

Therefore, the integral in Eq.(3.1.3) should also be replaced by summation over coarse intervals (quadratures) in r ,

$$\tau(\lambda) = \sum_{j=1}^q \int_{r_j}^{r_{j+1}} \pi r^2 Q_{ext}(r, \lambda, m) h(r) f(r) dr \quad (3.1.5)$$

where the limits of integration have been made finite with $r_1 = r_a$ and $r_{q+1}=r_b$. If $f(r)$ is assumed constant in the above equation within each coarse interval, a system of linear equations result which may be written as,

$$\mathbf{g} = \mathbf{A}\mathbf{f} + \varepsilon \quad (3.1.6)$$

where ε is an unknown error vector whose elements represent the deviation between the measurement ($\mathbf{g}_i$) and the theory ($\sum_j A_{ij}f_j$). This deviation arises from quadrature and measurement errors, as well as any uncertainties as to the exact form of the Kernel function (in this case $\pi r^2 Q_{ext}(r, \lambda, m)h(r)$). The elements of the Eq. (3.1.6) are given by,

$$g_i = \tau_i(\lambda); \quad i = 1, 2, 3, \dots p \quad (3.1.7)$$

$$A_{ij} = \int_{r_j}^{r_{j+1}} \pi r_j^2 Q_{ext}(r, \lambda_i, m) h(r_j) dr_j; \quad j = 1, 2, 3, \dots q \quad (3.1.8)$$

$$f_j = f(\bar{r}_j); \quad r_j < \bar{r}_j < r_{j+1} \quad (3.1.9)$$

where p is the number of channels, q is the number of coarse intervals of radius and $\bar{r}_j$ are the mid points of the coarse interval. Eq. (3.1.3) is a type of Fredholm integral equation of the first kind which are considered to be ill-posed (whose solutions are unstable). Among some of the techniques to tackle such problems, we employ the one suggested by Twomey as mentioned in [18], to suppress ill-posedness by imposing smoothing and non-negativity constraints on the desired size distributions. Philips (1962) mentioned in [18] that due to the ever-present error, a constraint has to be added that discriminates against such instability. So, by applying Twomey's regularization technique, the size distribution is obtained as,

$$\mathbf{f} = (\mathbf{A}^T \mathbf{A} + \gamma \mathbf{H})^{-1} \mathbf{A}^T \mathbf{g} \quad (3.1.10)$$

In Eq. (3.1.10) $\mathbf{A}$ is a Kernel matrix which is calculated from extinction efficiencies, $\mathbf{H}$ is the smoothing matrix suggested by Twomey as follows (it is restricted to 4×4 dimension

in this work since we use 4 wavelengths for aerosol detection):

$$\mathbf{H} = \begin{pmatrix} 1 & -2 & 1 & 0 \\ -2 & 2 & -4 & 1 \\ 1 & -4 & 5 & -2 \\ 0 & 1 & -2 & 1 \end{pmatrix} \quad (3.1.11)$$

$\mathbf{g}$ is the vector of optical depth values, and $\mathbf{f}$ is the size distribution array. The Lagrange multiplier γ , ensures that the algorithm will produce stable results. The Lagrange multiplier is considered to be a non-negative multiplier that weighs the smoothing constraints used to solve for the size distribution [16, 17]. The initial weighting function assumed in this thesis is the Jung size distribution given by,

$$h^0(r) = r^{-3} \quad (3.1.12)$$

By using $h^0(r)$ as initial guess, first order f^1 values are evaluated using the equation,

$$\mathbf{f}^1 = (\mathbf{A}^T \mathbf{A} + \gamma \mathbf{H})^{-1} \mathbf{A}^T \mathbf{g}. \quad (3.1.13)$$

This iteration procedure is repeated until the measured OPD comes closer to the simulated OPD, to some degree of uncertainty [19].

Chapter 4

Principle of Remote Sensing and Retrieval Method

The Earth's atmosphere is mainly a composition of trace gases. The interaction of electromagnetic radiation with matter modifies to some extent the incident wave. The medium therefore, produces a signature in the amplitude, phase, or spectral composition which depends on composition and structure of the medium. The basic principle associated with remote sensing of atmospheric constituents involves the interpretation of radiometric measurements of electromagnetic radiation in specific spectral intervals which are sensitive to some physical aspects of the medium. In this chapter, we first discuss the remote sensing of atmospheric trace gases in terms of the interaction between matter and radiation and next we discuss the interaction model and spectral analysis for the gas of interest using PROFFIT software. The radiative transfer concept has already been discussed in Chapter 3.

4.1 Interaction between Matter and Radiation

It is well discussed in Chapter 3 that radiation and matter interact only in two ways: extinction and emission. The term extinction includes absorption and scattering. In the FTIR spectroscopy, we usually consider absorption spectra. The absorption spectrum of a gas consists of a complex array of lines that correspond to transitions between the

discrete electronic, vibrational, and rotational energy levels of molecules. Vibrational and rotational-vibrational transitions occur in IR and microwave regions, while electronic transitions are stimulated by shorter wavelengths. At even higher photon energies a continuum of absorption occurs producing photodissociations and photoionization of molecules [6]. The mid-infrared absorption spectra of molecules in the atmosphere are a result of simultaneous rotational and vibrational transitions of the molecules.

Strength of Spectral Line

The line strength of a spectrum is a measure of intensity (basically in a laboratory) and it is also a measure of the strength of absorption line. The integrated absorption cross-section also defines the line strength.

$$S = \int_0^\infty \kappa(\nu) d\nu \quad (4.1.1)$$

The line strength for a transition of a molecule with permanent dipole moment of $R(m_i n_j)$ from energy level of E_m to E_n with m and n molecules per unit volume is given by:

$$S = \frac{2\pi^2\nu}{3h\epsilon_0 c} \left(\frac{N_m}{g_m} - \frac{N_n}{g_n} \right) \sum_{i,j} |R(m_i n_j)|^2 \quad (4.1.2)$$

where, g_m and g_n are the total degeneracy of the states at energy levels of E_m and E_n respectively and i and j represent the i^{th} and j^{th} energy levels of the degenerate E_m and E_n energy states. The line strength can also be expressed precisely in terms of the absorption coefficient κ_{mn} of a molecule with energy levels of E_m and E_n for radiation of frequency ν_{mn} as follows:

$$\kappa_{mn} = \frac{8\pi^2 n g_n}{3hcQ} \nu_{mn} |R(m_i n_j)|^2 (e^{\frac{-E_m}{k_B T}} - e^{\frac{-E_n}{k_B T}}) \quad (4.1.3)$$

where Q is the total internal partition function and k_B is the Boltzmann's constant.

For interaction to take place a force must act on a molecule in presence of an external electromagnetic field. The existence of such a force depends on the presence of an electric or magnetic instantaneous dipole moment. The realizability of a molecule is related to the extent to which a molecule has a permanent dipole moment or can acquire an oscillating one produced by its vibrational motion. If we consider a molecule as a rigid rotator, radiative interaction can take place only if the molecule possess a permanent dipole moment. Thus, molecules such as CO , N_2O , H_2O , OCS , HCl and O_3 interact with the field by changing their rotation vector, while homo-nuclear molecules like N_2 , O_2 , CO_2 and CH_4 do not. However, as a molecule like CO_2 vibrates, an oscillating electrical dipole moment is produced and rotational interaction can take place. Hence CO_2 and CH_4 possess vibration-rotation coupling with the incident wave. In what follows only interaction through electric dipole moments will be considered in the next subsections.

The Molecule as a Rigid Quantized Rotator

Molecules with pure dipole moment undergo pure rotational transition, this includes HCl , OCS and CO . The quantized rotational energy of a molecule associated with a rotational state J around a specific principal axis is given by,

$$E_{rot} = E_{rot,J} = \frac{h^2}{8\pi^2 cI} J(J+1) = AhcJ(J+1) \quad (4.1.4)$$

where $A = \frac{h}{8\pi^2 cI}$ is defined as a rotational constant and c is the speed of light. When the interaction between the molecule and the external field takes place a quantum of energy $\frac{h\nu}{c}$ is extracted (absorption process) or added (emission) to the external field where ν is wavenumber. The basic relation which yields this energy change is given by,

$$E' - E'' = \frac{h\nu}{c} \quad (4.1.5)$$

where E' and E'' are the two energy levels involved. A quantum selection rule dictates

that only transition among adjacent levels are allowed, that is

$$\Delta J = J' - J'' = \pm 1$$

where the value +1 applies to absorption, which increases the internal energy of the molecule and the value -1 to emission. For the case of absorption,

$$\Delta E_{rot} = 2B(J'' + 1) = 2BJ' = \nu_{rot} \quad (4.1.6)$$

The absorbed photons have energies that are individually equal to ν_{rot} in units of cm^{-1} . The aggregate effect from all the molecules in a volume is a depletion of the incident wave energy at wavenumber ν_{rot} which is observed as a spectral line.

The Molecule as Quantized Vibrator

A classical two-mass vibrator has a natural frequency $\tilde{\nu}$ which is given by,

$$\tilde{\nu} = \frac{1}{2\pi} \left(\frac{k}{m'} \right)^{\frac{1}{2}}$$

where k is the elastic force constant and m' is the reduced mass. The potential energy for this system is given by the relation,

$$E_p = 2\pi^2 m' (r - r_0)^2 \tilde{\nu}^2$$

where r_0 is the distance between the two masses at equilibrium. Quantum restrictions on vibrational energy are found by solving the time independent Schrodinger equation in one dimension. The eigenvalues defining the allowed energy levels are

$$E_v = \left(v + \frac{1}{2} \right) h \tilde{\nu} \quad (4.1.7)$$

where v is the vibrational quantum number that takes values $0, 1, 2, \dots$

$$E_v = (v + \frac{1}{2}) \frac{h}{2\pi} (\frac{k}{m'})^{\frac{1}{2}}$$

The quantum selection rule for vibrational transition allows only for which $\Delta v = \pm 1$, where the plus sign applies for transition in which the internal energy is incremented through absorption of a quantum of energy. Denoting by v' for any level except $v = 0$ and by v'' the next lower level, the transition energy is

$$\Delta E = \frac{h}{2\pi} (\frac{k}{m'})^{\frac{1}{2}} \quad (4.1.8)$$

Therefore a photon of energy $\frac{h\nu_{vib}}{c}$, where ν_{vib} denotes the wavenumber of the transition, will be absorbed if

$$\Delta E = h\tilde{\nu} = \frac{h\nu_{vib}}{c} \quad (4.1.9)$$

that is when

$$\nu_{vib} = \frac{c}{2\pi} (\frac{k}{m'})^{\frac{1}{2}}$$

The absorption by a volume of gas will result in the depletion of radiation of wavenumber ν_{vib} (or frequency $\tilde{\nu}$) which appears as an absorption line in the spectrum.

Vibration-rotational Transitions

It is already pointed out that molecules which do not have permanent dipole moment do possess oscillating dipole moments, caused by their vibrational motion, therefore rotational transition coupled to vibrational transition are possible. Transition selection rules

for many important molecules (including all diatomic molecules), require that $\Delta\nu \neq 0$ and $\Delta J \neq 0$, i.e., vibrational transitions must occur simultaneously with rotational transitions. Thus simultaneous transitions of both vibrational and rotational states are common in the atmosphere. These simultaneous transitions form what are called *combination bands* or *vibration-rotation bands*. The energy of such transitions is obtained by subtracting the lower energy state from the upper energy state,

$$\nu_R = \nu_k + B'_v J'(J' + 1) - B''_v J''(J'' + 1) \quad (4.1.10)$$

where ν_k is the energy of pure vibrational transition and J'' is the lower and J' is the upper energy state rotational quantum numbers. Substituting $\Delta J = \pm 1$ into the above equation leads to the energy spacings between the *R-branch* and *P-branch* transitions, respectively, as follows.

$$\nu_R = \nu_k + 2B'_v + (3B'_v - B''_v)J + (B'_v - B''_v)J^2 \quad (4.1.11)$$

$$\nu_P = \nu_k - (B'_v + B''_v)J + (B'_v - B''_v)J^2 \quad (4.1.12)$$

Another type of transition is a *Q-branch* which occurs when the dipole moment change of a polyatomic molecule has a component perpendicular to the principal axis of rotational symmetry, then a vibrational transition becomes possible without a rotational transition ($\Delta J = 0$). The three transitions discussed above are schematically presented in Fig.4.1.

There may be a number of absorption bands in addition to the fundamental bands of a molecule. One of these is overtone bands; these occur at frequencies which are multiples of fundamental frequencies.

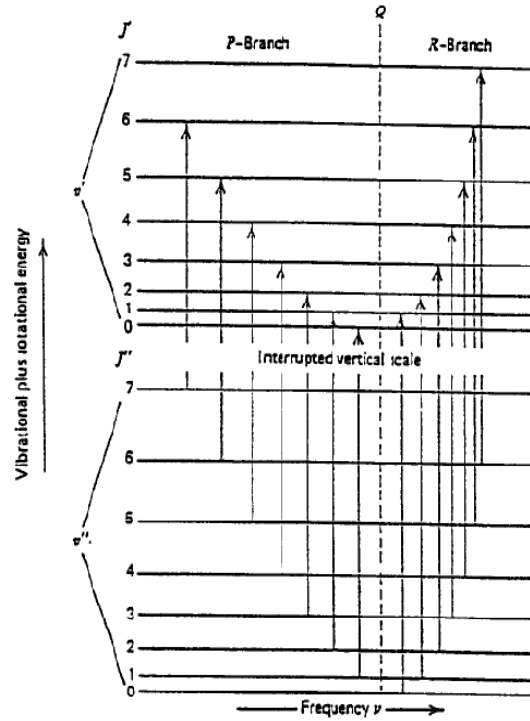


Figure 4.1: Simultaneous transitions in vibrational and rotational energies

4.2 Line Shape and Width of Spectra

Three physical phenomenon occur in the atmosphere and (elsewhere) which produce broadening of the absorption lines of the molecules. Additionally in the IR, the vibrational transitions have rotational-translational fine structures that give rise to the characteristic appearance of a vibration-rotation band. Hence, absorption lines are not truly discrete and the absorption coefficient from Eq. (4.3) has to be extended by a normalized line shape factor $f(\nu, \nu_{nm})$, which accounts for the line broadening and the fine structure of the absorption bands:

$$\kappa_{nm}(\nu) = \kappa_{nm} f(\nu, \nu_{nm}) \quad (4.2.1)$$

The three sources of line broadening are: (1) natural broadening, (2) collision broadening and (3) Doppler broadening. A fundamental source of line broadening is the natural broadening, which results from the finite radiation lifetime of excited states. In quantum

mechanical terms this is due to the uncertainty principle and depends on the finite duration of each transition. The appropriate line shape function to describe natural broadening is the Lorentz shape:

$$f_n(\nu) = \frac{1}{\sqrt{\pi}} \frac{\Delta\nu_n}{(\nu - \nu_{nm})^2 + \Delta\nu_n^2} \quad (4.2.2)$$

and absorption coefficient is then given by,

$$k_\nu \equiv k(\nu) = \frac{S}{\pi} \times \frac{\Delta\nu_n}{(\nu - \nu_{nm})^2 + \Delta\nu_n^2} \quad (4.2.3)$$

where S is the line strength and $\Delta\nu_n$ is the line half-width and $\Delta\nu_n$ is independent of wavenumber and its value is of the order of 10^{-5} cm^{-1} [10]. Natural line broadening in the IR region is less significant as compared to Doppler and pressure broadening mechanisms in the atmosphere. However, the processes determining natural line widths and pressure broadening of lines are statistically identical, so these two processes have the same analytical form (i.e. Lorentzian shape). At pressures weaker than about 1 mb collisions become infrequent enough that the line shapes become Doppler broadened by making transition from Lorentzian. Doppler broadening is more significant in stratosphere due to the larger mean free path and higher temperature. This results in larger standard deviations for molecular velocity distribution. Molecules in a volume of air possess a Maxwellian velocity distribution, hence the molecular velocity components along any direction of observation produce Doppler broadening of the spectral line, which has the shape of a Gaussian distribution:

$$f_D(\nu) = \frac{1}{\sqrt{\pi}\sigma_D} \exp -\left(\frac{(\nu - \nu_{nm})}{\sigma_D}\right)^2 \quad (4.2.4)$$

where σ_D is given by:

$$\sigma_D = \nu_{nm} \sqrt{\frac{2k_B T}{mc^2}} \quad (4.2.5)$$

and m is the molecule's mass, T the temperature and k_B is used as Boltzmann's constant. The dependence of σ_D on the frequency ν_{nm} of the center of the line provides for a dependence of the half width of the Doppler broadening $\Delta\nu_D$ on frequency:

$$\Delta\nu_D = \sigma_D \sqrt{\ln 2} \quad (4.2.6)$$

Doppler broadening in the dense lower part of the atmosphere is weak. For example, the Doppler half width for CO transition at 2100 cm^{-1} at 270 K is approximately $3 \times 10^{-3} \text{ cm}^{-1}$.

Pressure or collision broadening is the most dominant broadening mechanisms in the lower atmosphere. It is due to the modification of molecular potentials, and hence to the energy levels, which take place during molecular collisions which results in emission or absorption process. The collision between the molecule and the surrounding medium can be elastic or inelastic. The line shape function in this case is also Lorentzian, as for natural broadening, but the half width $\Delta\nu_p$ is several orders of magnitude greater, and is inversely proportional to mean free path between collisions, which indicates that the half width will vary depending on pressure p and temperature T of the gas:

$$f_p(\nu) = \frac{1}{\sqrt{\pi}} \frac{\Delta\nu_p}{(\nu - \nu_{nm})^2 + \Delta\nu_p^2} \quad (4.2.7)$$

The half width due to pressure broadening is related to the mean time between two collisions τ_{coll} by

$$\Delta\nu_p = \frac{1}{2\pi\tau_{coll}} \quad (4.2.8)$$

and since $\tau_{coll} = \frac{\sqrt{mk_BT}}{4\sqrt{\pi}d^2p}$, the half width is proportional to the pressure p and inversely

proportional to the square root of T . In this expression d represents the molecular diameter. A typical value of $\Delta\nu_p$ for CO molecule is $4.22 \times 10^{-2} \text{ nm}$ which is about 8 times larger than Doppler half width [10].

In the transitional (intermediate) regime where neither of the two shapes is satisfactory, since the two process are active at the same time, we use the convolution of Lorentzian and Doppler shape. Therefore, assuming the collisional and Doppler broadening to be independent we can combine the two line shapes (Eq. (4.2.4) and Eq. (4.2.7)) to give Voigt line shape.

4.3 Retrieval Method

The retrieval process in atmospheric measurement is the process of extracting vertical information of atmospheric state parameters from the measurement of spectral radiance at a certain solar zenith angle (SZA)-for ground-based measurements. The measured spectrum is a continuous function of wavelength, while the vertical profile states to be obtained from inversion are a continuous function of altitude. But every measurement takes place in discrete level. As a result of this an inversion problem is generally under-determined. The measured radiance is a function of the volume mixing ratio (VMR) of the individual constituents, temperature, solar zenith angle (SZA), pressure, ILS, altitude, etc. So it is a complex function of different parameters, and the method used to retrieve the state parameters from the measurement is also complex. In order to proceed let's represent the atmospheric measurable quantities by a vector $\mathbf{y}$ and the state parameters by a vector $\mathbf{x}$. Then we can relate the measurement and state vectors by *forward model* which describes the physics of the measurement process [18] as follows:

$$\mathbf{y} = \mathbf{F}(\mathbf{x}) + \epsilon \quad (4.3.1)$$

where $\mathbf{F}(\mathbf{x})$ approximates the detailed physics of the measurement and ϵ is the measurement error. Expanding the forward model function using Taylor's series about x_0 , we get:

$$\mathbf{y} = \mathbf{F}(\mathbf{x}_0) + \mathbf{K}(\mathbf{x} - \mathbf{x}_0) + \dots \quad (4.3.2)$$

where, $\mathbf{K} = \mathbf{K}_{ij} = \frac{d\mathbf{F}(\mathbf{x})_i}{dx_j}$ is the matrix element of Jacobian. Hence the forward model can be rewritten as,

$$\mathbf{y} - \mathbf{F}(\mathbf{x}_0) = \mathbf{K}(\mathbf{x} - \mathbf{x}_0) + \epsilon \quad (4.3.3)$$

All real measurements are subjected to measurement error (random noise) and directly affects the retrieval. The proper analysis of experimental error is the most important considerations in developing the retrieval methods. Thus we need to describe clearly the uncertainty in measurements and uncertainty in retrievals, with which to ensure that the latter should be as small as possible [18]. Experimental error (random error) can be best described using probability density function (pdf). The Gaussian distribution for multivariate vector in measurement space is given by,

$$p(\mathbf{y}) = \frac{1}{\sqrt{(2\pi)^n \mathbf{S}_y}} \exp\left(-\frac{1}{2}(\mathbf{y} - \bar{\mathbf{y}})^T \mathbf{S}_y^{-1} (\mathbf{y} - \bar{\mathbf{y}})\right) \quad (4.3.4)$$

where S_y is the covariance matrix of $\mathbf{y}$. As it is described above, measurements always contain errors which are assumed to be Gaussian distributed with covariance of error S_ϵ . By following the steps mentioned in [18] one can reach a final step which gives the expected value (most probable value), $\hat{x}$. This unknown atmospheric state parameter from the retrieval is given as follows:

$$\hat{\mathbf{x}} = \mathbf{x}_a + (\mathbf{K}^T \mathbf{S}_\epsilon^{-1} \mathbf{K} + \mathbf{S}_a^{-1})^{-1} \mathbf{K}^T \mathbf{S}_\epsilon^{-1} (\mathbf{y} - \mathbf{K} \mathbf{x}_a) \quad (4.3.5)$$

where x_a is the prior expected value and S_a is the a priori covariance.

The very important quantity used as a tool to characterize retrieval is the averaging kernel matrix ($\mathbf{A}$). It gives us information about the sensitivity of the retrieval to atmospheric states as it relates the expected state to the true state. It is given by

$$\mathbf{A} = \frac{\partial \hat{\mathbf{x}}}{\partial \mathbf{x}_t} = \mathbf{G}\mathbf{K} \quad (4.3.6)$$

where x_t is the true profile and $\mathbf{G}$ is called a gain matrix defined by

$$\mathbf{G} = (\mathbf{K}^T \mathbf{S}_\epsilon^{-1} \mathbf{K} + \mathbf{S}_a^{-1})^{-1} \mathbf{K}^T \mathbf{S}_\epsilon^{-1} \quad (4.3.7)$$

The columns of $\mathbf{G}$ are contribution functions for each channel as the product of the contribution function and the measured radiance gives the contribution of the measured radiance to the solution profile [18]. The rows of $\mathbf{A}$ (averaging kernels) indicate the sensitivity of the retrieval to the true profile over a certain height range. The atmospheric level with large peak value of averaging kernel contributes higher to the retrieved profile. The HWHM of the averaging kernel can be used as the vertical resolution of the retrieved profile. Note that the retrieval of atmospheric state vectors is commonly based on the radiance measured from the ground or space based instruments. Therefore the spectrum measured from the ground is the input for our retrieval. Usually it is impossible to determine a non-ambiguous solution from ground based measurements because of little information in the spectrum due to the linear dependence on each other of the expression for radiance presented in radiative transfer equation (RTE) which allows to distinguish between the different layers [6]. In the case of ground-based measurements the ambiguity can only be removed by imposing additional conditions called regularization. Measurements from satellites, airplanes or balloons additionally allow limb scanning of

atmospheric layers which provides for a better information about the height distribution of the trace gases.

The retrieval code we used in this thesis is PROFFIT (stands for PROFileFIT) developed by Hase [20]. The main steps in the retrieval can be divided into two parts generally: first, the forward calculation (PROFFWD) which provides synthetic and measured spectrum and derivatives for error estimation. In this part, the software performs a radiative transfer calculation for a given set of relevant atmospheric (T , p , VMRs) and auxiliary (SZA, ILS) input quantities for the spectral microwindows selected for analysis. The derivative of the spectrum with respect to the target and auxiliary quantities are allowed to vary in the process of searching the best estimate of the atmospheric state; second, the inversion model (PROFFIT), which processes the PROFFWD model output and suggests improved solution, restarts forward model with updated variables, cycles until convergence is reached. In short, PROFFIT determines a best estimate of the observed atmospheric state by improving fit quality to recorded spectrum iteratively. PROFFIT allows to choose between two regularization methods: the Optimal Estimation (OE) and the Tikhonov-Phillips (TP) Methods. We have used the TP method, which additionally enables to impose two kinds of constraints -absolute regularization or slope regularization of a start profile and the retrieved profile. Using the TP approach, PROFFIT allows to perform the whole inversion procedure on a logarithmic scale. This avoids negative VMR values, and we employ it for all results presented here. It is possible to invert various profiles simultaneously by PROFFIT. Additionally, it allows a simple scaling of a given start profile (climatological profile), which is often done for weak interfering gases.

PART II

Stratospheric Aerosols

Chapter 5

Atmospheric Aerosols

5.1 Aerosols Background

In addition to gases such as molecular nitrogen and oxygen, the atmosphere contains particles in the solid and liquid phase. These particles are referred to as *aerosol*. Liquid water and ice particles are generally excluded from this term. The study of aerosols began by John Aitken's experiments with dust in the 1880s. He built apparatus to count particles in suspension by expanding and then cooling samples of air. Water condensed on the particles, allowing the resulting drops to be counted with the aid of a microscope. The size of aerosol particles ranges from tens of a nanometer to hundreds of micrometers. The number density typically ranges from a few hundred to more than 10^6 particles per cm^3 . According to [21], the distribution of the atmospheric aerosols have significant impact on the radiative balance and chemistry of troposphere. This idea will be discussed in detail in latter chapters.

It is usual practice to group aerosols by their origins: those produced as a result of naturally-occurring geological processes; those produced as a result of human activity ('anthropogenic'); and those produced by biological processes ('biogenic'). Distinction is also often made between tropospheric and stratospheric aerosols, as those often share different sources and have different radiative effects [22]. The subdivision of aerosols into

different populations might also reflect a desire to classify things to better understand them. Thus, after introducing the continuous atmospheric aerosol size distribution, Jung (1963) mentioned in [23], also classified them geographically into maritime, continental, and background aerosols and by size into Aitken ($0.001\mu\text{ m}$ - $0.1\mu\text{ m}$), large ($0.1\mu\text{ m}$ - $1\mu\text{ m}$) and giant ($> 1\mu\text{ m}$) radius particles. Whitby (1973) in [23], point out that the plotting of aerosols size distributions on log-log plots, together with the use of an analytical power function, blurred the distinctive pattern of atmospheric aerosol modes. He introduced the terms nucleation mode ($0.001\mu\text{ m}$ - $0.1\mu\text{ m}$), accumulation mode ($0.1\mu\text{ m} - 1\mu\text{ m}$) and coarse particle mode ($> 1\mu\text{ m}$). The nucleation mode was produced by gas-to-particle conversion (GPC), the accumulation mode by coagulation and heterogeneous condensation, and the coarse mode by mechanical processes. For detailed understanding of this section you are referred to [23].

5.2 Sources and Removal of Atmospheric Aerosols

5.2.1 Sources of Atmospheric Aerosols

Aerosols are a very important components of the atmosphere. For instance, the water vapor, in order to condense, has to find a support that may be wettable and on which an initial rain drop can grow. In the absence of such support, condensation is very unlikely to occur. Most of the time the support is provided by a tiny particle that may have a different chemical composition to which we refer condensation nuclei [23]. Besides the strong interaction of aerosols with clouds, they may influence atmospheric chemistry and the amount of radiation absorbed by the atmosphere and reaching the ground [9]. There are two major sources of atmospheric aerosols: widespread surface sources and spatial sources [23]. By widespread surface sources we mean sources at the base of atmospheric volume (i.e, Oceans, biosphere, volcanoes, etc). Additional point sources such as volcanoes, are globally important in their influence on the stratosphere. Table 2.1 shows the

Table 5.1. Global Strength of the Aerosol Particles in the Troposphere [23]

	Sources	Strength($\frac{Tg}{year}$)
1	Surface Sources	
	Oceans and fresh water bodies	1000-2000
	Crust and cryosphere	2000
	Biosphere and biomass burning	450
	Volcanoes	15-90
2	Spatial Sources	
	Gas to particle conversion (GPC)	1300
	Clouds	3000
	Extraterrestrial	10

global strength of the aerosol particles in the troposphere. From the Table 5.1, the main sources of aerosols in the atmosphere can be noticed. The principal mechanism for producing aerosols from the oceans is through sea sprays and consequently these aerosols have a composition that is very similar to the sea salt (which may contain $NaCl$, KCl , $CaSO_4$, and $(NH_4)_2SO_4$). They are hygroscopic aerosols.

Crust and cryosphere production (i.e, ice in the polar region) includes mainly dust from the deserts. Other sources include soils but also snow. These aerosols have a typical mineral composition. Fig 5.1. shows a dust storm in Cairo taken from [4].



Figure 5.1: Severe dust storm near Cairo, 2 May, 1997.

As the contribution of volcanoes has a global effect in stratospheric aerosol distribution,

it gets attention from every part of the world. It is believed that the El Chichon volcanic eruptions in Mexico from March 28 to April 4, 1982 [24] and Pinatubo volcanic eruptions in Philippines in 1991 [25, 26, 27] have persisted in the stratosphere so far and influencing Earth's radiation budget. Different investigations reveal that a year after the El Chichon eruptions, the stratospheric optical thickness were greatly enhanced. Fig.5.2. shows Mount St. Helens volcanic activity in Washington state. It was a major volcanic activity in the USA. This volcanic event had an eruption column of 80,000ft (24.4km) into the atmosphere (which covers a stratospheric region) and deposited ash in eleven U.S. states.



Figure 5.2: Mount St. Helens volcanic eruption in July 22,1980.

Aerosols originating from the biosphere include all the organic and biogenic particles. Biogenic matter is a primary product (i.e, particles injected directly into the atmosphere, either from the biosphere or from other surfaces); organic particles are secondary products (i.e, particles that form in the atmosphere). Aerosols originating from burning biomass are soot and fly-ash particles, their composition being very near to that of elemental carbon. Volcanic eruptions may contribute in different ways to the aerosol population. Solid particles include silicates and metallic oxides, and gases like sulfur dioxide that can be converted to aerosol particles usually to sulfuric acid (mentioned in detail in chapter 11). Sulfur dioxide has a very short life time in the troposphere because of chemical processes

in gaseous and aqueous reactions.

One of the most important spatial source is GPC. As it is already mentioned sulfur dioxide is converted through a series of chemical reactions into sulfuric acid which can be dissolved into water drops, forming important class of aerosols. The direct gaseous precursor for the stratospheric aerosol sulfate is sulfuric acid (H_2SO_4) [27]. With the exception of sporadic direct injections from volcanic eruptions, stratospheric sulfuric acid originates primarily from OCS photolysis and oxidation of SO_2 , OCS , and other reduced sulfur gases reaching the stratosphere including dimethylsulfide (DMS), hydrogen sulfide, carbon disulfide, etc. It is believed that OCS and SO_2 are the main precursor gases for the formation of stratospheric aerosol layer. The detail discussion on OCS conversion to sulfuric acid is presented in chapter 11.

In the precipitation process, the clouds can be both a source and a sink for aerosols [23]. The extraterrestrial source due to the influx of meteorites or dust can easily be neglected. For detailed reading of this section see [9, 22].

As shown in Fig. 5.3 and discussed in [27], the input mechanism of aerosols to stratosphere is through tropical tropopause. The aerosol in tropical regions is rapidly transported zonally with the mean stratospheric winds. The aerosol in the air masses transported into the mid and high latitudes continues to evolve through microphysical processes, such as evaporation at the upper edge of the aerosol layer and nucleation/re-condensation during descent. The air descends diabatically to the lower most stratosphere where it can eventually be removed in the troposphere through quasi-isentropic transport of the air in tropopause folds which is the dominant removal mechanisms for stratospheric aerosol.

5.2.2 Removal of Atmospheric Aerosols

There exists close relationship between atmospheric aerosols and the process of cloud formation and precipitation, implying a water cycle in the atmosphere would not be possible in the absence of aerosols. On the other hand, it is precisely this water cycle, made possible by aerosols that represents the most effective process for their removal from the atmosphere [2]. Let's see some of the processes of removal of aerosol in the following subsections.

Wet removal processes

Aerosol particles may be rained out by collision with falling raindrops (inertial removal). The efficiency of this process (proportion of particles removed by it) is highest for heavy particles. Removal is also possible through diffusion of aerosols into falling drops, which is most efficient for small raindrops and very small particles (less than 10^{-8} m) in size. The raindrop process is composed of the condensation process and subsequent incorporation of aerosol particles by addition to existing water droplets [2, 22]. The strong size dependence of these removal processes means that particles in the region of $10^{-8}m$ to $10^{-7}m$ are generally not efficiently removed. Therefore, for particles of all sizes the total aerosol amount removed through wet processes does, of course, depend on how much moisture is available.

Dry removal processes

The largest difference between wet and dry removal is that while wet removal can occur throughout the atmosphere wherever there is precipitating water, dry removal relies on the particles being transported near to the surface by turbulence or gravity. The movement of small particles will be dominated by Brownian motion, while that of heavy particles will feel the effects of gravitational settling. Diffusive removal is again only important for very small particles, and inertial only for larger particles, with low rates of dry removal

of particles in the range from $0.01\mu\text{m}$ to $1\mu\text{m}$ [22].

Cloud formation and aerosol removal processes

Large aerosol particles are able to act as cloud condensation nuclei (CCN). The formation of clouds themselves, then, provides a method to remove aerosol from the atmosphere. Cloud removal processes tend to be efficient over all aerosol size ranges due to the high surface area of cloud droplets, as well as the rapid condensation of small particles into larger ones which takes place (especially with soluble particles). Clouds are able to form and rain within an hour, which can lead to rapid removal of aerosols [22, 23]. Usually the tropical stratospheric aerosols are transported to the polar regions and serve as sites for polar stratospheric cloud (PSC) particle formation. In this region some PSC particles composed of nitric acid hydrate or ice can grow to several microns in diameter and sediment rapidly to tropopause, taking sulfuric acid particles with them. Observations clearly show the seasonal reduction in polar aerosol mass following periods of PSCs [27]. The overall stratospheric aerosol cycle is shown in Fig. 5.3.

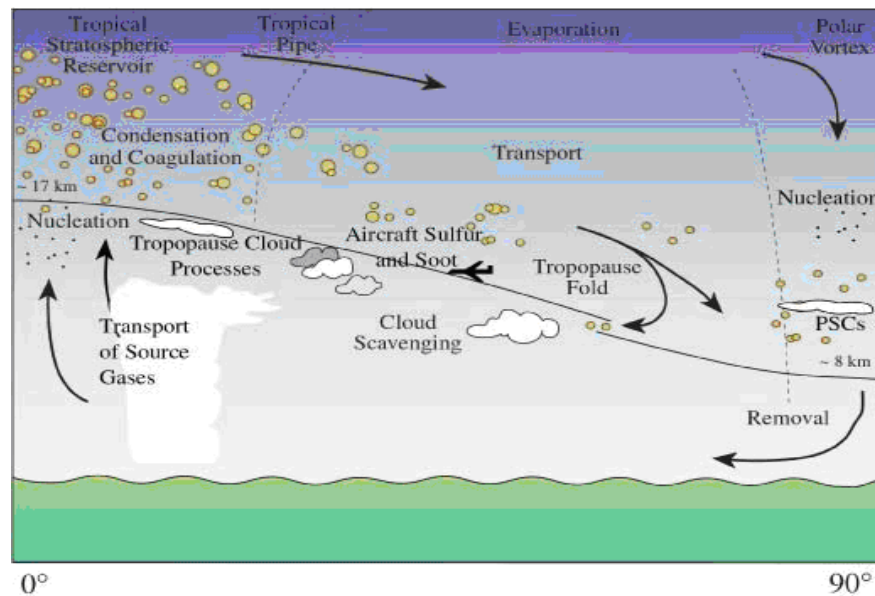


Figure 5.3: Schematic of stratospheric aerosol lifecycle [27]

5.3 Aerosol Size Distribution

The aerosol size distribution is one way of characterizing aerosols. The size distribution also defines the number concentration and dimension of aerosols. In this Section two commonly used aerosol size distributions: the Jung distribution and lognormal distribution are discussed.

5.3.1 The Jung distribution

The original work of Jung in 1955 showed that the size distributions of many natural samples of aerosol could be well modelled by inverse power distributions, also called Jung distribution. Now, if we denote by n_i , the number of particles per unit volume with radius r_i , then the total number of particles will be,

$$N = \sum_i n_i(r_i) \quad (5.3.1)$$

Assuming a continuous distribution we can introduce a density $n(r)$ that represents the number of particles per unit volume with radius between r and $r + dr$, so that

$$n(r) = \frac{dN}{dr} \quad (5.3.2)$$

The function $n(r)$ is called the size distribution and in this case the total density is obtained by integrating Eq.(5.3.2) with respect to the radius. The simplest distribution that relates linearly the logarithms of number concentration and radius is,

$$\log\left[\frac{dN}{d\log r}\right] = C - \beta * \log r \quad (5.3.3)$$

which can be reduced to the form,

$$r^\beta \left(\frac{dN}{d\log r}\right) = C \quad (5.3.4)$$

where β and C are constants.

5.3.2 Lognormal distributions

Another distribution that is often used both for tropospheric and stratospheric aerosols is called Lognormal and is given by

$$\frac{dN}{d\log r} = \frac{N_0}{\sqrt{2\pi\log\sigma}} \exp\left[-\frac{\left(\frac{\log r}{R}\right)^2}{2(\log\sigma)^2}\right] \quad (5.3.5)$$

where N_0 , σ and R are the total number of particles, the semi-dispersion and mean radius characterizing the distribution. According to Davies [1974] and Hesse et.al.[1998] as mentioned in [22] the lognormal distribution is most appropriate for atmospheric aerosols. Once the size distribution is known it is possible to obtain average radius, surface or volume distribution with radius. That is,

$$\bar{r} = \frac{\int_0^\infty r n(r) dr}{\int_0^\infty n(r) dr} = \frac{\int_0^\infty r n(r) dr}{N} \quad (5.3.6)$$

It is known that several aerosol properties depend on the particle surface area and volume distributions with respect to particle size [1]. If we consider particles with radius r , the surface of a number dN is given by

$$dS = 4\pi r^2 dN \quad (5.3.7)$$

so that the surface distribution is

$$\frac{dS}{d(\log r)} = 4\pi r^2 \frac{dN}{d(\log r)} \quad (5.3.8)$$

and in a similar way the volume distribution is obtained from,

$$\frac{dV}{d(\log r)} = \frac{4\pi r^3}{3} \frac{dN}{d(\log r)} \quad (5.3.9)$$

5.4 Optical Properties of Aerosols

The optical property of aerosols cannot be seen independently from aerosol physical properties such as size distribution. The optical property of aerosols may be calculated by means of the Mie theory, once size distribution and complex refractive index are known. The Mie theory is based on the assumption of particles of spherical shape and homogeneous composition, which is not true for the large aerosol types [28]. The aerosols optical properties are determined by their chemical composition besides their size distribution. The complex refractive index reflects the aerosol chemical composition. The real part of refractive index is responsible for reflection, refraction and scattering of light, and the imaginary part is responsible for absorption. In addition, the following parameters are used to quantify optical properties:

The single scattering albedo (ssa)-(ω_0): represents the fraction of extinction due to scattering and is expressed by

$$\omega_0 = \frac{\sigma_s}{\sigma_s + \sigma_a} \quad (5.4.1)$$

where σ_s and σ_a are the scattering and absorption cross sections, respectively. The value of ω_0 is one for purely scattering aerosol. The angular dependence of the scattering is described by the phase function P. The phase function is closely related to the probability that photons incoming from an incident direction will be scattered into and outgoing direction. It is usually assumed that phase function depends only on the scattering angle θ between incident and emergent directions. When θ is close to zero, it is called forward

scattering. When the scattering radiation has been reflected back within an angle θ close to 180° , it is called backward scattered. The phase function $P(\cos\theta)$ is normalized so that the total probability of scattering is unity.

$$\int P(\cos\theta) \frac{d\bar{\omega}}{4\pi} = 1 \quad (5.4.2)$$

where $d\bar{\omega}$ is the differential element of solid angle.

The asymmetry factor g is defined as,

$$g = \frac{1}{2} \int_{-1}^{+1} P(\cos\theta) \cos\theta d(\cos\theta) \quad (5.4.3)$$

and theoretically can vary between -1 and $+1$; $g = 0$, for isotropic scattering, positive for forward scattering and negative for backward scattering. An analytic expression for the phase function in terms of the asymmetry factor g which is adequate for scattering patterns that are not strongly peaked in the forward direction is given as [28]:

$$P(\cos\theta) = \frac{\omega_0(1 - g^2)}{(1 - g^2 - 2g\cos\theta)^{\frac{3}{2}}} \quad (5.4.4)$$

Atmospheric aerosols attenuate solar radiation through absorption and scattering, though their effectiveness depend both on their amount and dimension. The Angstrom formula for the aerosol optical depth (AOD) accounts for both amount and dimension of aerosols in

$$AOD(\lambda) = \beta \lambda^{-\alpha} \quad (5.4.5)$$

where α and β are called Angstrom coefficients. β expresses the amount of aerosols

in the column and α is related to the particles' dimensions (size). Large values of α indicate the major presence of small particles. The upper limit for α is 4 (Rayleigh scattering approximation), while values close to zero (positive or negative) are found for large particles.

Chapter 6

Scattering by Small Spherical Particles

When a particle is illuminated by a beam of light with specified characteristics, the amount and angular distribution of the light scattered by the particle, as well as the amount absorbed, depends in a detailed way on the nature of the particle, that is its shape, size and materials of which it is composed [29].

If we are given a particle of specified size, shape and optical properties that is illuminated by an arbitrarily polarized monochromatic wave we can determine the electromagnetic (EM) field at all points in the particle and at all points of the homogeneous medium in which the particle is embedded. For instance if a plane wave of EM radiation is incident on a homogeneous spherical obstacle, if it is scattered so that far away from the scatterer, the fields are represented by a plane wave plus outgoing spherical wave [29, 30].

Scattering of EM waves by any system is related to the heterogeneity of that system (in molecular scale or aggregate of different molecules). Regardless of the particle type of heterogeneity, the underlying physics of scattering is the same for all systems. Matter is composed of discrete electric charges: electrons and protons. If an obstacle which could be a single electron, an atom or molecule, a solid or liquid particle is illuminated by an

EM wave as shown below, electric charges in the obstacle are set into oscillatory motion by the electric field of the incident wave. These accelerated electric charges radiate electromagnetic energy in all directions; it is this *secondary radiation* that is called the *radiation scattered* [29, 30, 31]. That is, Scattering = Extinction + Reradiation.

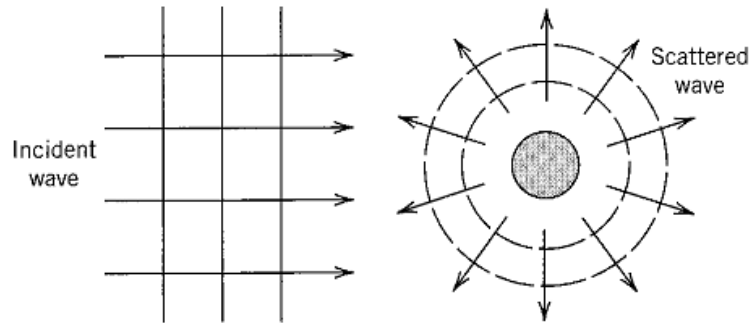


Figure 6.1: Scattering by spherical particle.

The phenomenon of scattering, absorption and emission of light or EM radiation by small particles is very important in many disciplines, such as communication.

6.1 Mie Scattering

Mie scattering is one of the kinds of atmospheric scattering in which the wavelength of the incident radiation is not changed. It applies to isotropic and homogeneous sphere, when the complex index of refraction is known. When the above assumptions are met, equations governing attenuation and scattering of solar radiation are given by the following Fredholm integral equation of the first kind [10],

$$\tau(\lambda) = \int_0^\infty \pi r^2 Q_{ext}(r, \lambda, m) n(r) dr \quad (6.1.1)$$

where, $\tau(\lambda)$ is the aerosol optical depth, $n(r)$ is the aerosol size distribution, m is the

complex refractive index of aerosol, λ is the wavelength of the incident radiation and $Q_{ext}(r, \lambda, m)$ is the Mie extinction efficiency, given by

$$Q_{ext}(r, \lambda, m) = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) \Re(a_n + b_n) \quad (6.1.2)$$

The scattering coefficients a_n and b_n can be given by

$$a_n = \frac{\varphi'_n(y)\varphi_n(x) - m\varphi_n(y)\varphi'_n(x)}{\varphi'_n(y)\xi_n(x) - m\varphi_n(y)\xi'_n(x)} \quad (6.1.3)$$

$$b_n = \frac{m\varphi'_n(y)\varphi_n(x) - \varphi_n(y)\varphi'_n(x)}{m\varphi'_n(y)\xi_n(x) - \varphi_n(y)\xi'_n(x)} \quad (6.1.4)$$

Here $\varphi_n(z)$ and $\xi_n(z)$ are given by

$$\varphi_n(z) = zj_n(z) = \sqrt{\frac{\pi z}{2}} J_{n+\frac{1}{2}}(z) \quad (6.1.5)$$

$$\xi_n(z) = xh_n^{(2)}(z) = H_{n+\frac{1}{2}}^{(2)}(z) \quad (6.1.6)$$

where,

$$y = mx$$

$J_{n+\frac{1}{2}}(z)$ being first kind Bessel function;

$j_n(z)$ being first kind Bessel spherical function;

$H_{n+\frac{1}{2}}^{(2)}(z)$ being third kind Bessel function; and

$h_n^{(2)}(z)$ being Riccatti-Bessel functions, and z is arbitrary variable.

Note that the prime in Eq. (6.1.3) and Eq. (6.1.4) indicate differentiation with respect to the argument in parentheses. Practically, the scattering coefficients a_n and b_n are

calculated as,

$$a_n = \frac{j_n(x)}{h_n^{(2)}(x)} \frac{D_n(y) - mD_n(x)}{D_n(y) - mG_n(x)} \quad (6.1.7)$$

$$b_n = \frac{j_n(x)}{h_n^{(2)}(x)} \frac{mD_n(y) - D_n(x)}{mD_n(y) - G_n(x)} \quad (6.1.8)$$

where,

$$G_n(x) = \frac{d}{dx} \log \xi_n(x) = \frac{d}{dx} \log(xh_n^{(2)}(x)) = \frac{d}{dx} \log(\sqrt{x}H_{n+\frac{1}{2}}^2(x)) \quad (6.1.9)$$

$$D_n(z) = \frac{d}{dz} \log \varphi_n(z) = \frac{d}{dz} \log(zh_n^{(2)}(z)) = \frac{d}{dz} \log(\sqrt{z}J_{n+\frac{1}{2}}^2(z)) \quad (6.1.10)$$

The Mie extinction efficiency, as derived from the preceding equations for different values of the imaginary refractive indices are shown in Fig. 6.2.

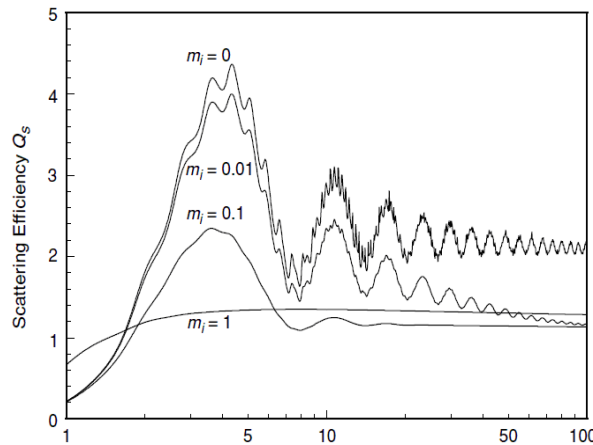


Figure 6.2: Mie extinction efficiency for different values of imaginary refractive indices [13].

The above figure shows the extinction efficiency factor Q_{ext} as a function of size parameter x for real index of refraction 1.33 with several values of the imaginary part. For $m_i = 0$, perfect reflector, there is no absorption so that $Q_{ext} = Q_{scattered}$. Q_{ext} in this case shows a series of major maxima and minima and ripples.

Chapter 7

Aerosol's Role in Atmospheric Energy Balance

The energy that the Earth and the Planets receive from the sun determines the physical characteristics of the planetary atmospheres together with the emitted planetary (infrared) radiation. Sun which is about $1.5 \times 10^8 km$ far from the Earth provides all of the energy that drives the Earth's atmospheric motion [13]. The source of solar energy is believed to be generated from the steady conversion of four hydrogen atoms to one helium atom in fusion reactions, which takes place in the deep interior of the sun with temperature up to 15 million degrees [9, 13]. The amount of energy released in nuclear fusion causes a reduction of the sun's mass. According to Einstein's law relating the mass and energy, $E = mc^2$, many million tons of mass per second is converted into energy and radiated by the sun in the form of electromagnetic radiation.

Radiant energy, arranged in order of its wavelength λ , is called the spectrum of radiation. The sun radiates over the entire EM spectrum, although as we will see, most of the energy is concentrated near the visible portion of the spectrum (i.e, the narrow bands of wavelength from $0.4\mu m - 0.7\mu m$). The power per unit area at the top of the atmosphere of the Earth, that is, the solar constant, has a value around $1380 \frac{W}{m^2}$, which is a widely accepted value. Recently, based on a series of measurements from high altitude platforms, a revised value of $1353(\pm 21) \frac{W}{m^2}$ issued by the National Aeronautics and Space

Administration (NASA) has been accepted as a standard solar constant [1, 9, 13].

The standard solar spectrum in terms of the spectral irradiance is shown below. Also shown in this diagram is the spectral solar irradiance reaching the sea level in a clear atmosphere.

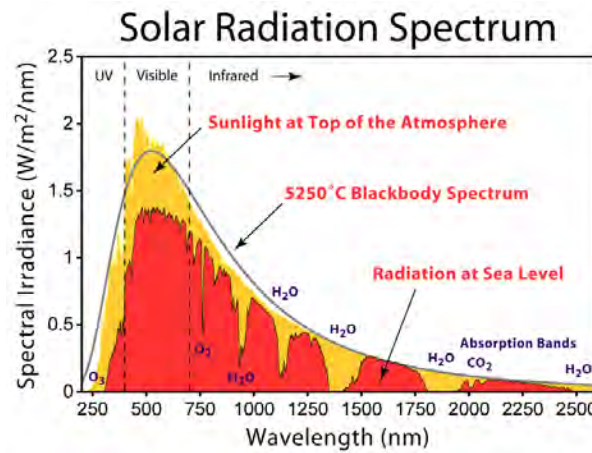


Figure 7.1: The spectrum of the solar radiation outside and below the atmosphere of the Earth. The gases responsible for absorption are indicated. The solid line is a black body emission at 5250°C .

Fig. 7.1 compares the solar spectrum taken outside the atmosphere with a spectrum taken at the surface at solar zenith angle of 60° . Due to the absorption by ozone and other atmospheric gases that are indicated in the figure, the power reaching the surface is reduced. Atmospheric absorption is responsible for the attenuation of about 15% of the power reaching the surface [9].

7.1 Distribution of Insolation Outside the Atmosphere

Insolation is defined as the flux of solar radiation per unit horizontal area. It depends strongly on the solar zenith angle and to some extent on the variable distance of the Earth

from the sun. The flux density at the top of the atmosphere may be expressed by,

$$F = F_0 \cos \theta_0 \quad (7.1.1)$$

where $F_0 = \int_0^\infty F_{\lambda_0} d\lambda$ represents the solar flux density at the top of the atmosphere when the instantaneous (actual) distance between the Earth and sun is d , and θ_0 denotes the solar zenith angle. The solar constant is simply given by

$$S = F_0 \left(\frac{d}{d_m} \right)^2 \quad (7.1.2)$$

where d_m is the mean distance between the sun and Earth. F_{λ_0} is the monochromatic solar irradiance at the top of the atmosphere.

Define the solar heating received at the top of the atmosphere per unit area as Q , then the solar flux density may be written as

$$F = \frac{dQ}{dt} \quad (7.1.3)$$

Thus, the insolation for a given period of time is,

$$Q = \int_t F(t) dt \quad (7.1.4)$$

The total solar energy received per unit area per one day may be evaluated by integrating over the daylight hours. Upon substitution of Eq.(7.1.2) into Eq.(7.1.4) we find the daily insolation as follows:

$$Q = S \left(\frac{d_m}{d} \right)^2 \int_{sunrise}^{sunset} \cos \theta_0 dt \quad (7.1.5)$$

Eq. (7.1.5) is also described as the average value of the flux $\langle F \rangle$ in some region at

ω by $\frac{dh}{dt}(= \frac{2\pi rad}{day})$, we obtain

$$Q = S(\frac{dm}{d})^2 \int_{-H}^H (sin\lambda sin\delta + cos\lambda cos\delta) \frac{dh}{\omega} \quad (7.1.7)$$

where H represents the half-day, e.g, from sunrise or sunset to solar noon. After performing the simple integration we get,

$$Q = \frac{s}{\pi}(\frac{dm}{d})^2 (sin\lambda sin\delta H + cos\lambda cos\delta sinH) \quad (7.1.8)$$

where H , in the first term on the right is expressed in units of radians. Eq. (7.1.7) allows us to calculate the distribution of the daily solar energy per unit area over the top of the global atmosphere as function of latitude and day of the year. The solar inclination is a function of day of year only, and is independent of the location of the observation point. It varies from $23^0 27'$ on June 21 to $-23^0 27'$ on December 22. The hour angle is zero at solar noon, and increases by 15^0 for every hour before or after solar noon.

However, the solar radiation observed at the top of atmosphere (TOA) doesn't appear as it is (unattenuated) at the surface; it is modified by gaseous and particulate matters in the atmosphere. The effect of anthropogenic gases and aerosols over climatological period influence the Earth's climate.

7.2 Climate Impact of Aerosols

Aerosols scatter and absorb shortwave (solar) and long wave (thermal infrared) radiation, thereby perturbing the energy budget of the Earth-atmosphere system and exerting a direct radiative forcing (RF). By RF we mean a change in the radiative energy budget of the Earth's climate system due to an external perturbation, like introduction of an agent, such as aerosols or greenhouse gases [28, 32, 33]. Aerosol radiative forcing (ARF)

is a measure of the net reduction or increase in the amount of surface-reaching or outgoing radiation due to total columnar aerosol burden. Aerosol forcing (AF) is also defined as the difference in quantity such as solar irradiance or flux with and without aerosols present [28, 32]. Atmospheric aerosols are usually considered to be very important because of their contribution to the Earth's climate. Non-absorbing aerosols increase the albedo of the atmosphere and reduce the amount of solar radiation (short wave) reaching the surface, but if it is absorbing aerosols in the shortwave (SW) range of the spectrum, energy is directly transferred to the atmosphere, and the effect is heating of the atmosphere and cooling of the underlying surface [34].

According to (Liu and Lou (1990)) mentioned in [34], enhanced heating due to aerosols absorption of solar radiation occurs particularly in the lower troposphere. This is because large amount of tropospheric aerosols are confined to the planetary boundary layer (closer to the surface). Due to the high spatial and temporal variations of the aerosol concentration and their physical and chemical properties, it is difficult to assess quantitatively the exact impact of aerosols on climate [35, 36].

Chapter 8

Results and Discussion

8.1 Vertical and spectral distribution of stratospheric aerosols

In this thesis we tried to analyze data obtained from Stratospheric Aerosols and Gas Experiment (SAGE)II instrument aboard the Earth Radiation Budget Satellite (ERBS) which was launched in October 5, 1984. This instrument was able to provide high quality measurements of ozone, nitrogen dioxide, water vapor, and profiles of aerosol extinction at wavelengths centered at 386, 452, 525, and 1020 nanometers from the mid-troposphere to as high as the lower mesosphere. All profiles are at 0.5 *km* vertical resolution. These products are nearly global in coverage, with data spanning from 80°*N* to 80°*S*. The temporal coverage of SAGE II is from 5, Oct. 1984 to 8, Sep. 2005.

SAGE II instrument views a small portion of the sun through the Earth's atmosphere during the spacecraft's sunrise and sunset (using limb occultation technique). Data are obtained from the attenuation of the sun light due to scattering and absorption by different atmospheric species. The spacecraft's motion just before entering or just after leaving the Earth's shadow provides vertical scanning through the atmosphere. Measurements taken from a tangent-height of 150 *km*, where there is no attenuation, provides a self

calibration feature for every event [37, 38].

From the global data of SAGE II instrument recorded during the life time of the spacecraft, we filtered out the aerosol extinction data at four channels over Ethiopian region (i.e, $3^0N - 15^0N$ and $33^0E - 48^0E$) for the entire years using matlab code. Then we calculated the monthly mean aerosol optical depth (AOD) from the measured extinction data by multiplying each extinction value by the level height (i.e, 0.5 km) for each channel. This thesis is focussed on stratospheric aerosols as they are very important in influencing the Earth's radiation budget and climate in other sense. To filter out the data over Ethiopian region for stratospheric aerosols, we need to know the average tropopause height over this region. To determine the tropopause height, we filtered the temperature values of SAGE II instrument over our study area and plotted the seasonal variation of temperature profile. The result is shown in Fig. 8.1.

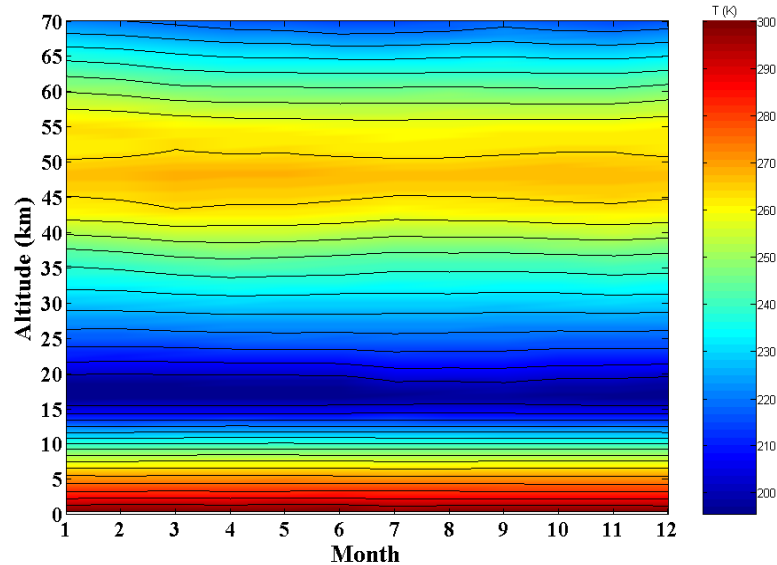


Figure 8.1: Seasonal variation of temperature profile over Ethiopia.

It is not the aim of this thesis to discuss about temperature distribution over the study area, we would like to show the tropopause level over the study area, to support our choice of stratospheric region above 15 km over Ethiopia (Tropics in general). It is common to

define the tropopause level as the coldest point in the atmosphere. Accordingly the mean tropopause level over Ethiopia is located somewhere between 16 to 18 km, as it can be seen from the Fig. 8.1. According to [39] the height of 100 *hpa* level is a good estimate of tropopause height in tropics. Other studies [40] also reveal that the tropopause level of tropics is above 15 km, which is in pretty good agreement with fig.(8.1). Therefore, our choice of stratospheric region (which is above 15 km) is sufficient to study stratospheric aerosols over Ethiopia.

Even if the altitude coverage of the spacecraft is from 1-40 km, the data quality at altitudes closer to the surface is different from one channel to another. For instance, the longer wavelength channel can see deeper through the atmosphere than the shorter wavelength radiation which cannot reach closer to the surface as it is scattered by molecules and smaller particles in the upper atmosphere and also absorbed by ozone layer. Due to such reasons we are supposed to focuss only on stratospheric aerosols. In fact the mission of the SAGE II was also to provide data about stratospheric aerosols and gases. Now we present the vertical and seasonal variation of aerosol optical depth from 1984 to 2005 at different channels. Fig. 8.2 shows the vertical distribution of mean aerosol extinction values for altitude range of 15-40 km at 386 nm wavelength.

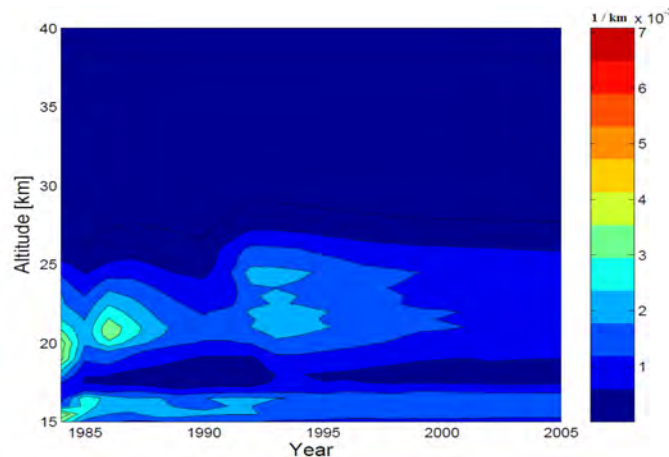


Figure 8.2: Vertical distribution of aerosol extinction value during measurement period at 386 nm.

As it can be seen from Fig. 8.2 the stratospheric aerosols show vertical and seasonal distribution throughout a year in the stratosphere. The reason is that smaller aerosols tend to rise higher in the atmosphere than larger size aerosols (depending on the nature of their source). In fact stratospheric aerosols are smaller in size so that they have longer life time in the atmosphere [2]. The higher the altitude the smaller the aerosol size and the less probable to interact with clouds and to precipitate (in tropics). As the extinction of light depend on the concentration of particles, the higher extinction value in our result corresponds to high concentration of aerosols which is observed about 17 - 25 km. Fig. 8.2 also reveals that the instrument sees aerosols in the stratosphere at 386 nm wavelength, and cannot see deep to the troposphere at this channel. The seasonal variation of columnar extinction value corresponding to the above channel is also shown in Fig. 8.3.

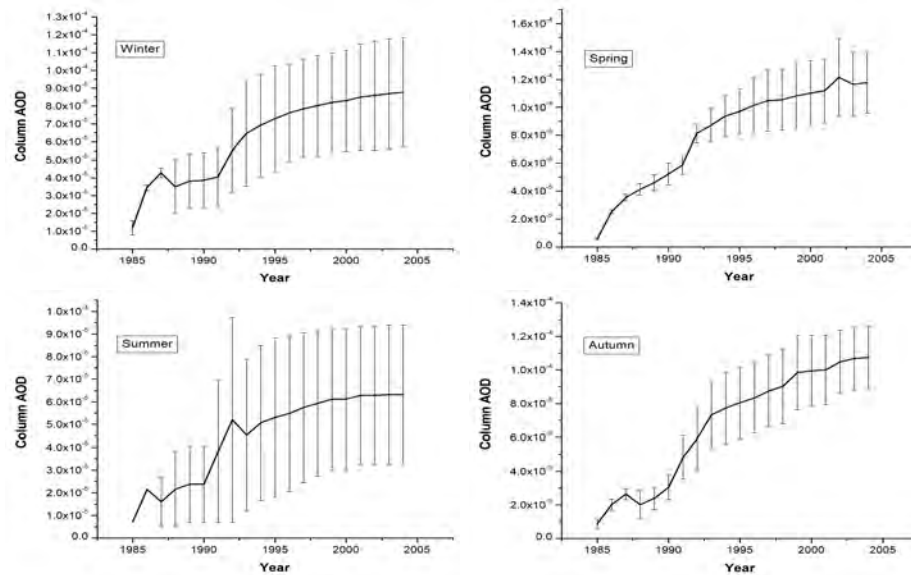


Figure 8.3: Seasonal variation of column AOD values at 386 nm.

From the AOD distribution shown in Fig. 8.3 we can see that during some seasons (particularly Spring and Autumn) the column aerosol amount shows slight enhancements; and relatively lower concentration during Summer.

The vertical distribution of aerosol extinction values at 452 nm reveals almost the same

feature as the 386 nm, except the former can catch aerosols better (can see deeper up to upper troposphere).

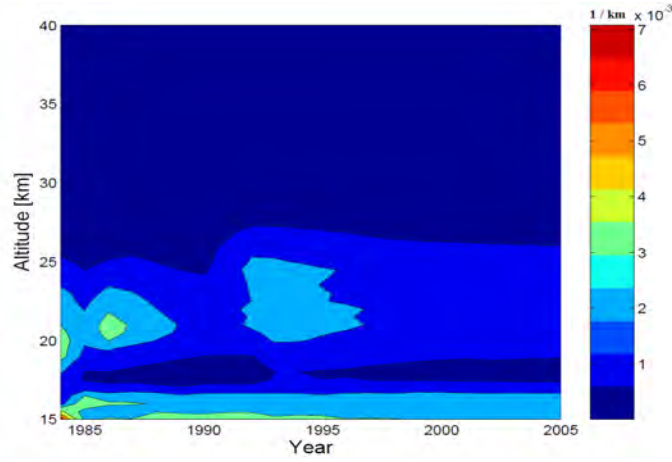


Figure 8.4: Vertical distribution of aerosols extinction value during measurement period at 452 nm.

From Fig. 8.5 we can see that the seasonal variation of mean AOD follows almost the same pattern as in the Fig.8.3 except the slight increment of AOD value during all seasons at this channel.

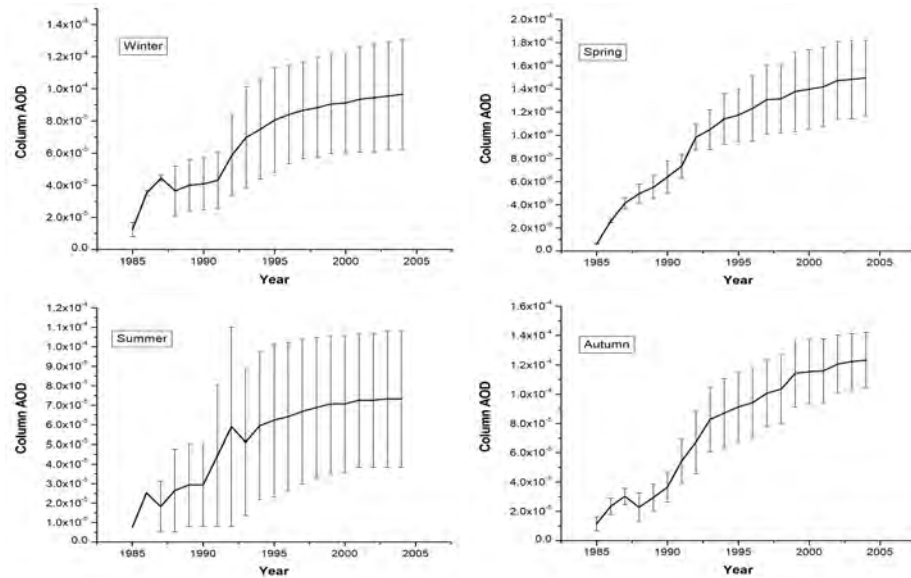


Figure 8.5: Seasonal variation of column AOD values at 452 nm.

Similar results of extinction values at 525 nm are also shown in figs. 8.6 - 8.7. Figs. 8.4

and 8.6 representing vertical distribution of AOD at 452 and 525 nm which exhibit nearly the same feature.

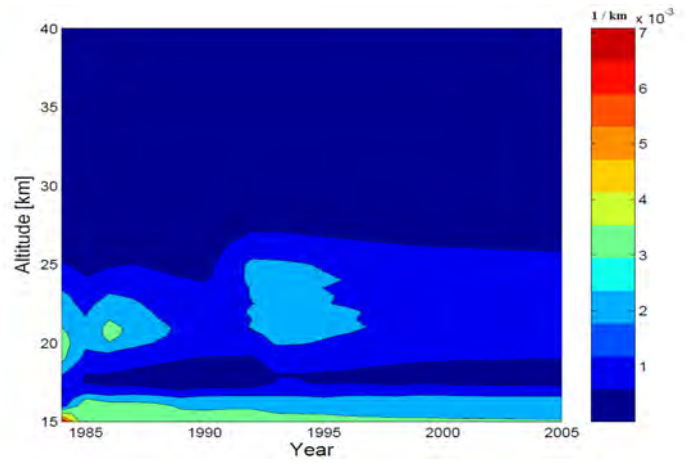


Figure 8.6: Vertical distribution of aerosol extinction value during measurement period at 525 nm.

The seasonal variation of AOD values at 525 nm is also shown in Fig. 8.7. In this figure we can observe maximum value of AOD in the upper troposphere.

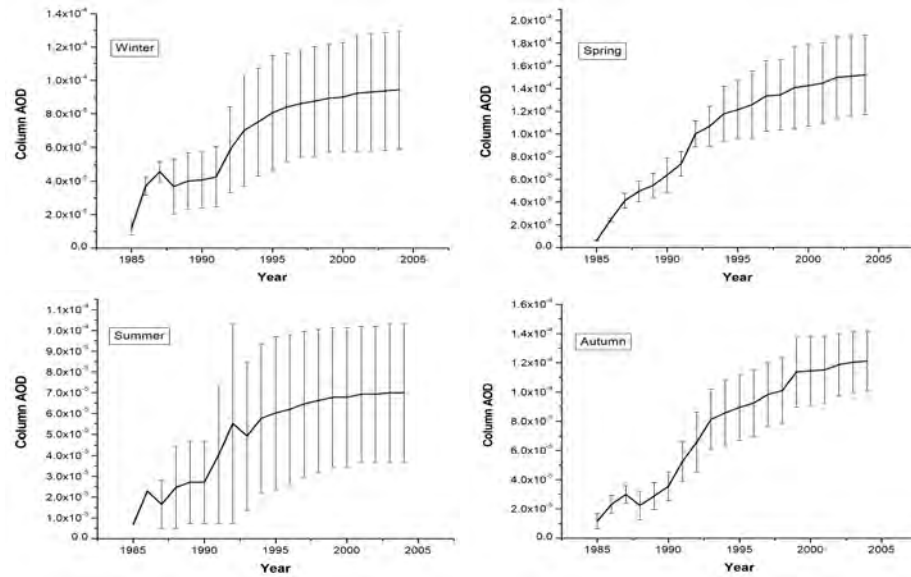


Figure 8.7: Seasonal variation of column AOD values at 525 nm.

The spectral variation of aerosol extinction values can be seen from the above figures.

The 525 nm channel can capture aerosols better than the other two shorter wavelength channels in the upper troposphere because of atmospheric transmittance; that is, the strong lines of water vapor and other trace gases are absent near this (visible) wavelength region (see Fig. 7.1), in which maximum solar radiation can reach the Earth's surface.

The vertical distribution of aerosol extinction values at 1020 nm wavelength is also shown in Fig. 8.8. This channel is not too sensitive to stratospheric aerosols, as it is discussed above.

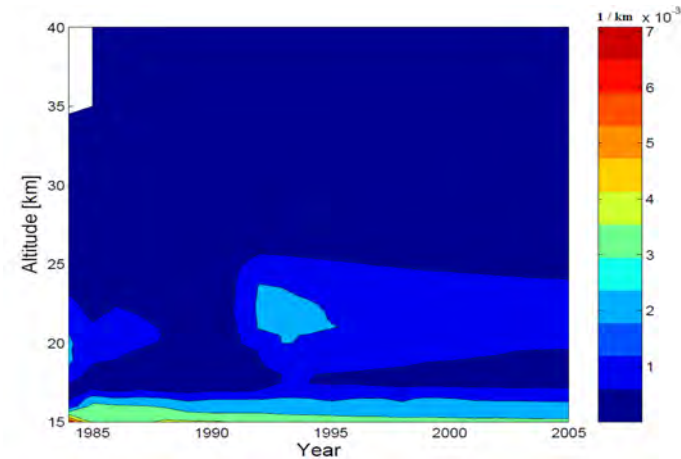


Figure 8.8: Vertical distribution of aerosols extinction values during measurement period at 1020 nm.

The values of the mean columnar AOD of different seasons at 1020 nm is shown in Fig.8.9. As it is discussed at the beginning of this chapter the 1020 nm channel is not good to capture stratospheric aerosols. It is best suited to tropospheric aerosols which are relatively larger in size. From all the figures showing the seasonal variation of aerosols, we can infer that the maximum value of AOD appears in Spring and the minimum appears in Summer.

In all plots of seasonal variation of column AOD values, aerosols show an increasing trend in all seasons during the measurement period. The abrupt increase of the column AOD

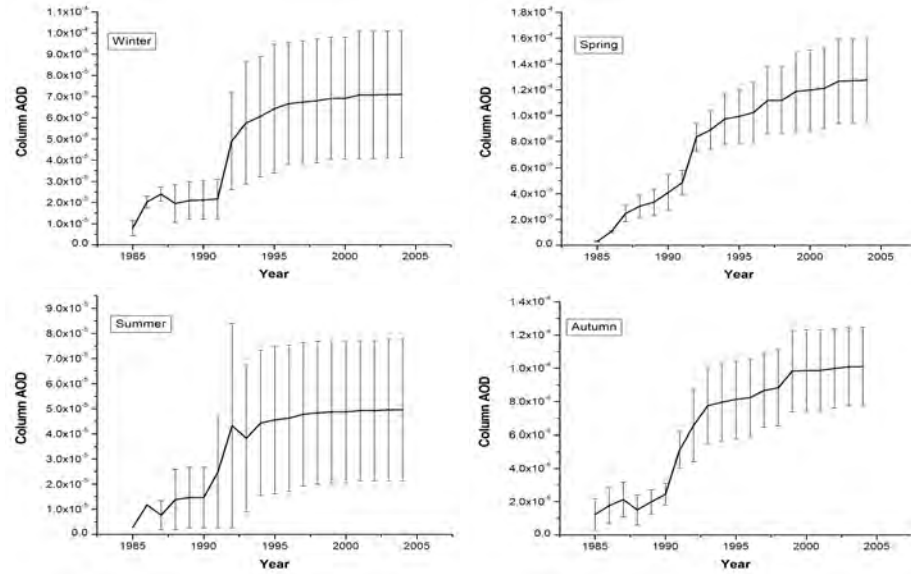


Figure 8.9: Seasonal variation of column AOD values at 1020 nm.

values in 1991 (shown in Figs. 8.3, 8.5, 8.7 and 8.9) is associated with the Mt. Pinatubo eruption discussed in section 8.2. As the dominant sources of stratospheric aerosol is from the troposphere (discussed in detail in part III) the seasonal variation of AOD during the Summer shows slow rate of increment as compared to other seasons. This may be due to the lower temperature of our region during this season, as temperature enhances gas to particle conversion. The 1020 nm wavelength represents coarse mode (larger) aerosol sizes which are found in the lower atmosphere as they are highly affected by gravity. Thus the stratospheric concentration and its trend at this channel changes very slowly as compared to smaller size aerosols. The vertical line shown in all plot of seasonal variation of column AOD represents the error bar. As it is clearly seen from the figures, the uncertainty of the measurement was increasing during the life time of the satellite. This may be due to the reduction of the signal count reaching the instrument after the satellite was launched [38]. Particularly, the uncertainty is very high during the Summer season and lesser during Spring. This may be associated with the weather condition of the region as the satellite had taken no measurements during bad weather. From Figs. 8.6 and 8.8, we can see that the 525 nm and 1020 nm wavelengths can capture upper tropospheric aerosols better than

the 386nm and 452 nm channels. According to these figures, the aerosol optical depth value is high in the troposphere, which shows high concentration of aerosols in the lower troposphere.

The seasonal variation of AOD can be associated with its sensitivity to humidity and dynamics of the atmosphere [41]. According to King et al(1980) [41], dry and hot air inhibits cloud and rainstorm development which results in smaller values of AOD; on the other hand hot and humid air may cause AOD to increase. According to Flower et al. as mentioned in [41], high turbidities (in Angstrom relation) are normally associated with high humidities characteristic of maritime tropical air masses. Low turbidities on the other hand, were found to be associated with continental polar air masses. The climatology of dust sources in North Africa (North of Equator) as studied by J. Barkan et al [42] using TOMS instrument data taken for 14 years (1979 - 1992) shows that the maximum value of dust aerosol index (AI) over Ethiopia is in July and the minimum values of AI is in November and December. The maximum and minimum values of AOD using SAGE II instrument over Ethiopia is also attained during these months but we don't see them in our results as they are averaged in to seasonal values. The recent in situ measurements of AOD in Addis Ababa made by [43, 44] shows that dust is the dominant aerosol type over Ethiopia. Therefore, the major contribution of solar extinction over Ethiopia is due to dust aerosols. If this is so, the study of [42] supports our result, the AOD climatology over Ethiopia. The work of J. Barkan et al. [42] also points out that the major dust source over Ethiopia is found at $14.3^{\circ}N$ and $40.6^{\circ}E$ which is the North-East part of Ethiopia and characterized as dry area; the active volcanic eruptions are also found in this region and it may contribute to the stratospheric AOD over Ethiopia.

8.2 Time series of annual mean column AOD

The annual mean value of AOD as seen by different channels over Ethiopia is shown below. We can see the 'trend' of aerosols during the life time of the SAGE II instrument.

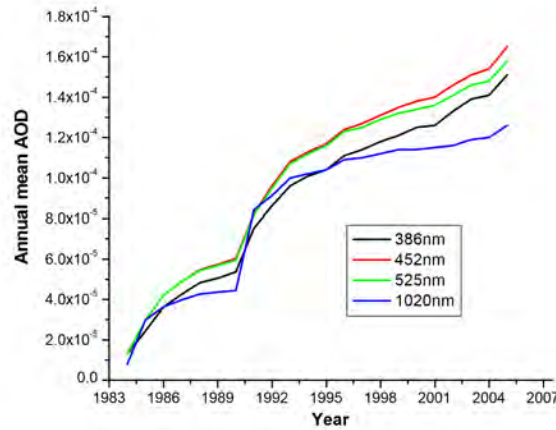


Figure 8.10: Annual mean column AOD at different channels.

Fig. 8.10 shows that the mean AOD value over Ethiopia has been steadily increasing from year to year during the life time of ERBS (1984 to 2005). The increment of AOD values in all channels (386 nm, 452 nm, 525 nm and 1020 nm) indicates that both fine and coarse mode aerosol loading has also been increasing during this period. The reason for increment may be due to industrial development, desertification, biomass burning, different constructions, etc. The transport of aerosols from developed (industrialized) countries and active volcanic eruption areas may also result in accumulation of aerosols over less developed countries. The abrupt increment of annual mean column AOD after 1991 may be associated with the Mt. Pinatubo volcanic eruption in 1991. This eruption is believed to load large aerosol mass to the stratosphere and contributed to climate change. The strong dust storms in north Africa and Asia can also be a reason for aerosol loading in Ethiopia. According to the AI climatology study obtained from TOMS instrument during 1979 - 1992, the dust loading over Ethiopia shows increasing during this period, which is in good agreement with our result as dusts are the major components of aerosols over

Ethiopia.

From Fig.8.10, we observe that the time series of aerosols show trends both before and after the 1991 historical event of Mt. Pinatubo volcanic eruption. The trend before 1991 at 525 nm has a slope of 7.3×10^{-6} and the trend after 1991 has a slope of 2.1×10^{-6} . This can be associated with the reaction rate of aerosols in the stratosphere before and after the event. Thus we understand that the reaction rate is higher before eruption. This also reveals that the period from 1992 to 2005 (after the eruption) is relatively volcanically quiescent period [38] and the higher slope before 1991 indicates there was volcanic eruption, as a result the atmosphere was not stable during that period.

8.3 Size distribution of stratospheric aerosols

Next, we shall retrieve the size distribution of aerosols using Mie retrieval algorithm based on scattering theory. The possible sources of the aerosols can also be suggested by looking for their size distribution. In this thesis we retrieve for the size distribution and study its relation with monthly mean value of aerosols in different years. Aerosol size distribution function for columnar aerosol optical depth is given in Fig. 8.11. As it is mentioned in previous sections the columnar aerosol optical depth is calculated from SAGE II data. The columnar AOD is the mean column optical depth of the measurement taken for about 21 years (from 1984 to 2005) of the Earth's Radiation Budget Satellite (ERBS). The complex refractive index we used for retrieval of size distribution is $m = 1.51 + 0.005i$. This is different from the real refractive index of sulfate aerosol which is about 1.45 due to the presence of different aerosol types. The value of the complex refractive index shows that the contribution of stratospheric aerosols over Ethiopia to climate is scattering, which results in cooling effect. Therefore, the net effect of stratospheric aerosols over Ethiopia is counteracting the effect of green house gases. It is well known that AOD and ASD depend

on complex refractive index. This value of complex refractive index is chosen by retrieving the size distribution for different values of refractive indices by simulating aerosol optical thickness. The value of refractive index for which the square of the difference between the measured and simulated aerosol optical depth (chi-squared error) is minimum provides the best guess of the refractive index. Note that at the minimum chi-squared error, the retrieval converges rapidly.

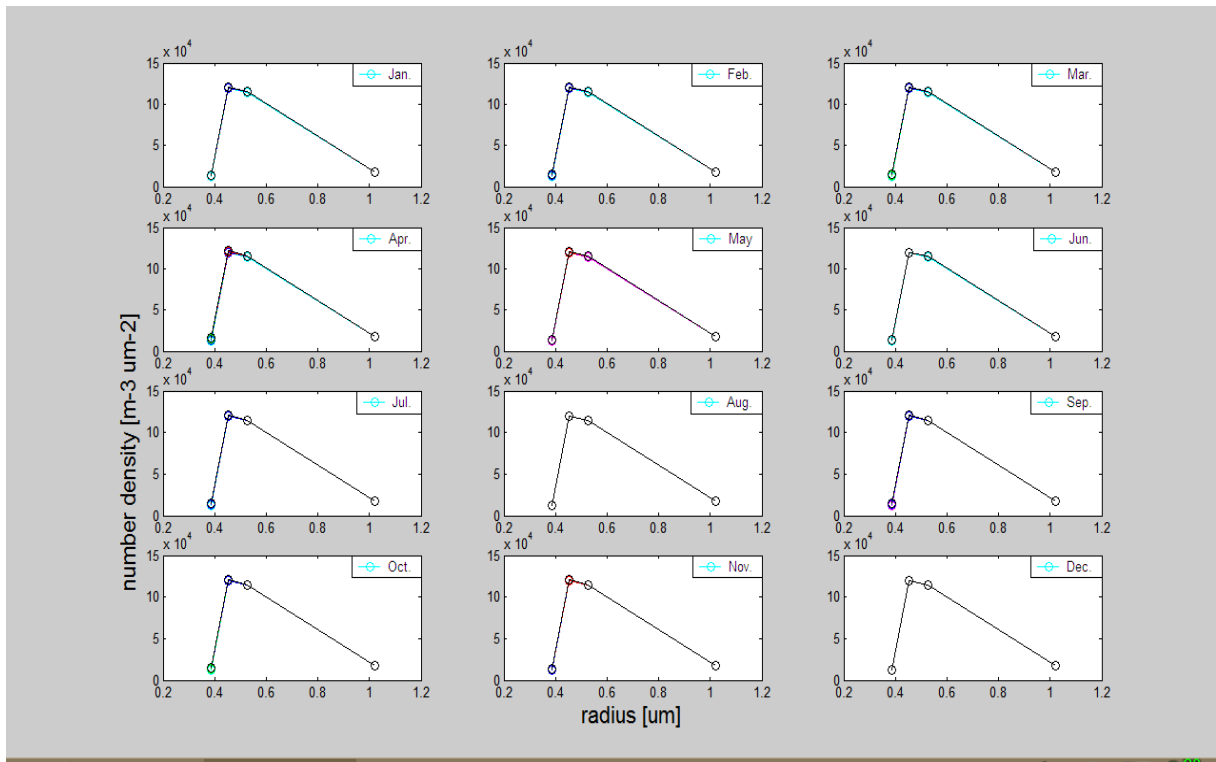


Figure 8.11: Monthly mean aerosol size distribution function for the years 1985, 1989, 1991, 1993, 1997 and 2004.

We used the same value of complex refractive index for retrieval of climatological stratospheric size distribution of all months (January to December) of the selected years (1985, 1989, 1991, 1993, 1997 and 2004) because the stratosphere is more stable and the aerosols are long-lived in the stratosphere relative to troposphere. From the retrieved aerosol size distribution function one can suspect the production mechanisms of atmospheric aerosol. According to [17], those particles with radii $\leq 0.5 \mu m$ are produced by a combination of nucleation from the gas phase and subsequent coagulation. Particles having radii

$\geq 1.0\mu m$ are principally the result of mechanical and wind stresses at the Earth's surface. From the aerosol physics, these production mechanisms are not very effective in the $0.5 - 1.0\mu m$ range [17]. Therefore, the size distribution climatology shown in Fig. 8.11 can be divided into two components according to the above discussion. The smaller particles can be given by the Jung distribution, but the multi-modal nature of size distribution is more appropriate to capture all sizes of aerosol. One can see the relation between the columnar aerosol optical depth and aerosol size distribution by comparing the seasonal mean AOD values (shown in Fig. 8.3 to Fig. 8.9) for different channels with Fig. 8.11. It is known that the maximum AOD shows maximum loading of aerosols or high concentration of aerosols as expected. As a result the ASD function is maximum during April and minimum ASD function is shown during February, June and December (even if the difference is not significant to be shown in Fig. 8.11) and other months are intermediate. This can be associated with the seasonal variation of columnar AOD. Since the ASD doesn't show significant variation for different years, we can infer that the size distribution doesn't show a trend.

PART III

Carbonyl sulfide from FTIR Spectrometer at Addis Ababa

Chapter 9

FTIR Spectrometer set up in Addis Ababa

Introduction

The high-resolution FTIR Spectrometer, IFS120M, manufactured by Bruker Optics Company is installed in Addis Ababa, at Arat Killo Campus of Addis Ababa University(AAU) in May, 2009 in collaboration with the Karlsruhe Institute of Meteorology and Climate Research (IMK), currently called Karlsruhe Institute of Technology (KIT) found in Germany. This instrument is the first of its kind in Africa, so the Addis Ababa sky can be considered as a representative of the region (tropical region), to detect trace gases in the atmosphere from the ground. The location of the observation site is closer to geo-observatory, which is found in science faculty of AAU. The container (housing) of the instrument is first set in a level made of concrete by clearing bushes and trees near by the container in order to prevent shadings. For optimum spectrometer performance and long-term reliability, the instruments operates at stable temperature of $20^{\circ}C$, which is maintained by air conditioner. As the instrument is the first in our country, it is important to report the set up of the instrument and measuring performance of the instrument. Next we introduce some of the main parts of the instrument briefly but we begin by solar tracker.



Figure 9.1: The FTIR measurement site in Addis Ababa.

9.1 FTIR Components

9.1.1 Solar Tracker

The need for solar tracker is to measure direct solar spectra. The solar tracker in use for Addis Ababa station is not interfaced with the instrument and computer. It is a tripod with reflecting mirror facing the sun, moving with the 'speed of the sun'. The tracker has a motor to provide a constant power so that the incoming solar radiation is reflected from the plane mirror of the tracker to another plane mirror inside the container which in turn reflects the beam to interferometer passing through aperture of size of interest.

The stability of the solar radiation (being remain focussed on the aperture) is about an hour, which is sufficient time to take measurements in five filters for ten scan times. Actually, the stability can be improved by aligning the elevation and azimuth of the tripod, directly to polaris (north star) during clear sky night, or by developing a software to automate tracking.

Table 9.1. Spectral Coverage of the IFS120M instrument at Addis Ababa site

Filter	Wavenumber(cm^{-1})	Wavelength(μm)
1	4000-4300	2.3-2.5
2	2900-3500	2.6-3.3
3	2400-3100	3.3-4.1
4	2000-2700	3.9-5.0
5	1500-2200	4.7-6.3
6	750-1350	7.4-14

9.1.2 Optical Devices

The optical components of the FTIR are the most sensitive parts of the instrument. It consists of **paraboloids** (parabolic mirrors) used to focus the beam on to aperture and to transform the beam into parallel rays; **aperture** is used to limit the field of view and to limit the intensity of incoming radiation as per the choice of the operator. Note that the smaller the aperture size, the lesser self apodization (interference of light emerging from the aperture due to finite aperture size); **Filters** are used to limit the wavenumber range as per our interest. Note that filters are responsible for **channelling**, and any leakage of the filter can be seen on baseline of the measured spectrum. Our IFS120M instrument has two sets of filter wheels each has seven separate filters. The spectral coverage of these filters have overlaps in order to guarantee the possibility of retrieval using lines in one extreme of the filter coverage; and the band coverage for each filter is given in Table 9.1. These filter ranges are also used by NDACC (Network for the Detection of Atmospheric Composition and Change). The **beam splitter** is a core of the interferometer and it is very expensive and highly sensitive to the environment. The role of beam splitter is to split the incoming beam into two parts: the one transmitted goes to movable mirror (also called Retroreflector) and the reflected one goes to fixed mirror, as shown in Fig. 9.2. The two beams are then recombined at the beam splitter after moving different path lengths. Then the recombined beam goes to a detector. There are two beam splitters in our FTIR room, CaF_2 and KBr . KBr is highly hygroscopic and it's recommended

not to use during rainy season and put it in a dry, warm places. It is kept in a beam splitter storage box to protect it from exposure to humidity. Fig. 9.2 shows our IFS120M instrument optical setup.

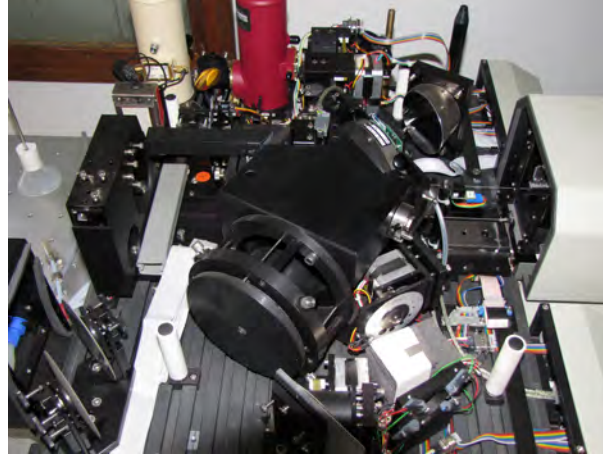


Figure 9.2: The IFS120M instrument optical set up in Addis Ababa.

9.1.3 Detectors

Eventhough detectors are part of the optical devices, we better introduce it independently. Detector is very important component of FTIR. It has analogues function as eyes for human beings. We use two detectors to cover the mid infrared (mid-IR) region . The two detectors are made of mercuric cadmium telluride (HgCdTe or MCT) and indium antimonide (InAs) alloys. The InAs detector covers a spectral range of $(1,850 - 9,600) \text{ cm}^{-1}$ and the MCT covers $(750 - 5,000) \text{ cm}^{-1}$ while both effectively operate at a temperature $\leq 70 \text{ K}$ attained by filling the detector dewar by liquid nitrogen (LN_2). In our IFS120M instrument, we usually use InAs detector to cover spectral range from $4200 - 1800 \text{ cm}^{-1}$ using five filters, and MCT for $780 - 2000 \text{ cm}^{-1}$. Both types of detectors operated in Photo-voltaic principle while the InAs is a linear detector. That is, both the MCT and InAs elements absorb IR photons, and as a result electrons are promoted from the valence band to conduction band, and give rise to an electrical current. The current is then a

direct measure of infrared(IR) intensity which increases with the number of IR photons. The disadvantage of MCT over InAs is its easy saturation, which results in non-linearity of detector response for incoming radiation [45].

9.1.4 Scanner

The moving mirror is the only moving part in FTIR spectrometer. The mirror, driving cables and two driving units constitute the main part of FTIR scanner. The two driving units of the scanner are 1 DC motor and 1 linear drive unit. The two driving units are also called the outer and inner scanners [46]. The outer scanner ensures the gliding movement of scanner, and the main function of the inner scanner is to compensate the fluctuations of the outer scanner, same purpose as fine tuning in radio. The position of the moving mirror is precisely controlled by stabilized HeNe laser signal (631.8 nm), so that the optical path difference can be measured accurately. The laser signal is also used to determine the data sampling positions. In our IFS120M we get more than 2100000 data points from 0 to 4000 wavenumber intervals. If the scanner moves with uniform speed, the sinusoidal signal is generated as a result of modulation of HeNe laser, and this generated signal reaches the detector (either InAs or MCT). The intensity of the interfering beams (after reflection from the fixed and moving retroreflector and recombined at the beam splitter) is measured as a function of optical path difference (OPD), and the result is an interference pattern, called interferogram. Note that, the beam splitter, retroreflectors, and detector constitute the main components of interferometer. The angle of incidence of the beam to the interferometer is 30° [47]. This narrow angle of incidence reduces polarization effects and uses the beam splitter more efficiently [46].

9.1.5 IR Source

The IR source in FTIR is used to provide IR radiation to the spectrometer. Our instruments uses globar (glow bar), which is a piece of ceramic usually made of silicon carbide

rod. When electric current passes through it, the resistance of the device makes it heat up and give off IR radiation. The globar may heat above 1400 K , so that we can get more IR radiation, which in turn results in higher throughput and lower noise in our FTIR spectra. The globar compartment is supplied with a closed-loop cooling system, where the cooling unit accommodate about half-a-litter of water for this purpose. The cooling unit must be filled with distilled or deionized water only; and it is recommended to change the water at least once every three months. The globar is mainly used for the calibration of the FTIR by means of a black body, and also to align optical device to get maximum radiation at the detector. In order to determine the instrumental line shape (ILS), which tells us the status of the instrument, we take black body radiation with globar source and the radiation passes through a low-pressure gas cell filled with HBr, which has sharp absorption lines. We will discuss about ILS in chapter 10 in detail.

9.1.6 Electronics Unit

The electronics unit of an FTIRS is used to convert optical signals into electrical signals. The intensity of IR photons reaching the detector is converted into electrical current by the electronics unit and send to monitor (PC). The electronics unit is also used to calibrate the IR wavenumber with respect to the laser wavenumber [45]. Some of the jobs carried out by electronics units is the analog-to-digital conversion (ADC), phase correction, pre-amplification of the raw data (Interferogram) and automatic component recognition (ACR). The IFS120M instrument is controlled by a PC data system, provided the Microsoft *windows*TM operating system and the optical user software (*OPUS*TM), which is a spectrometer software, installed on PC to take measurement, and further analysis of the spectra. The ethernet connection allows to control statu of the spectrometer components via internet. The interference between the two secondary beams (Interferogram) is digitized and sent to PC where the Fourier transformation (FT) takes place using OPUS software to get the final infrared spectrum for analysis.

Chapter 10

FTIR Spectrometer Principle

10.1 Ideal Fourier Transform Spectrometer

The working principle of FTIR is such that the incoming IR energy splits into two secondary beams and recombined at the beam splitter after reflecting back from a fixed and movable retroreflectors. Then, the two beams interfere to form interferogram.



Figure 10.1: Schematic diagram of IFS120M working principle.

The spectrum is then calculated from the interferogram by Fourier transforming it. Unlike the interferogram a spectrum is a transmittance or absorbance as a function of wavenumber in IR spectroscopy, while the interferogram is a digitized voltage Vs optical path difference. The wavenumber is a reciprocal of wavelength λ (without a factor of 2π). The

mathematical steps toward Fourier transform (FT) are discussed as follows. First assume the movable mirror is displaced by an amount of x parallel to the optical axis, which produces a phase difference (optical retardation of $2x$). Whenever the optical retardation is an integral multiple of the wavelength λ (for monochromatic source), of radiation, the two partial (secondary) waves will interfere constructively:

$$2x = n\lambda \quad n = 0, 1, 2, \dots \quad (10.1.1)$$

and the interference will be destructive if the OPD is an odd integral multiple of half the wavelength:

$$2x = \frac{n}{2}\lambda \quad n = 1, 3, 5, \dots \quad (10.1.2)$$

Let R be the reflectance (coefficient of reflection) and T be the transmittance of the beamsplitter. The amplitude of the EM wave reaching the detector can be described by the superposition of the two secondary beams by the relation,

$$A(x_1, x_2, \nu) = R.T.\hat{A}(\nu).[e^{i(\omega t - 2\pi\nu x_1)} + e^{i(\omega t - 2\pi\nu x_2)}] \quad (10.1.3)$$

In most atmospheric inversion problems, what's really measured is energy (intensity), which is proportional to the square of the amplitude. Therefore, the intensity of the monochromatic source interferogram, $I(x_1, x_2, \nu)$ is a real (not complex) quantity, given by:

$$I(x_1, x_2, \nu) = A(x_1, x_2, \nu).A^*(x_1, x_2, \nu) = 2|R.T|^2\hat{A}^2(\nu)[1 + \cos(2\pi\nu(x_1 - x_2))] \quad (10.1.4)$$

Let us denote the OPD between the two secondary beams by $x = x_1 - x_2$, the spectral intensity by $S(\nu)$, and extend the discussion to non-monochromatic sources. Then, by

superposition principle, the intensity $\tilde{I}(x)$ recorded in the interferogram is then described by the integral of $S(\nu)$ over all wave numbers:

$$\tilde{I}(x) = 2|R.T|^2 \int_0^{+\infty} S(\nu)[1 + \cos(2\pi\nu x)]d\nu \quad (10.1.5)$$

or,

$$\tilde{I}(x) = 2|R.T|^2 \int_0^{+\infty} S(\nu)\cos(0)d\nu + 2|R.T|^2 \int_0^{+\infty} S(\nu)\cos(2\pi\nu x)d\nu \quad (10.1.6)$$

The first integral expression in Eq.(10.1.6) is constant in x and equals the intensity of the interferogram for a path difference of zero, where the maximum of the interferogram is located [48]. The second integral on that line describes the modulation of the signal as a function of the OPD. If we consider a perfect beam splitter that splits up the incident light among the two secondary beams at any wavenumber equally, i.e, $R = T = \frac{1}{\sqrt{2}}$, the interferogram can be written as,

$$[\tilde{I}(x) - \frac{1}{2}\tilde{I}(0)] = 2 \cdot \frac{1}{4} \cdot \int_0^{+\infty} S(\nu)\cos(2\pi\nu x)d\nu \quad (10.1.7)$$

As $\tilde{I}(x)$ is a real quantity, $S(\nu)$ has to be Hermitian, (Bell,1972, as mentioned in [48]), i.e,

$$S^*(\nu) = S(-\nu) \quad (10.1.8)$$

With this relation and Euler's theorem applied to Eq.(10.1.7), the r.h.s of this equation can be transformed into Fourier integral:

$$[\tilde{I}(x) - \frac{1}{2}\tilde{I}(0)] = \frac{1}{2} \int_0^{+\infty} \Re[S(\nu)e^{i(2\pi\nu x)}]d\nu$$

$$[\tilde{I}(x) - \frac{1}{2}\tilde{I}(0)] = \frac{1}{2} \int_0^{+\infty} [(\frac{1}{2}S(\nu)e^{i(2\pi\nu x)})^* + \frac{1}{2}S(\nu)e^{i(2\pi\nu x)}]d\nu$$

$$[\tilde{I}(x) - \frac{1}{2}\tilde{I}(0)] = \frac{1}{4} \int_{-\infty}^0 S(\nu)e^{i(2\pi\nu x)}d\nu + \frac{1}{4} \int_0^{+\infty} S(\nu)e^{i(2\pi\nu x)}d\nu = \frac{1}{4} \int_{-\infty}^{+\infty} S(\nu)e^{i(2\pi\nu x)}d\nu \quad (10.1.9)$$

The limits of the integral are as required for Fourier integral which describes the relation between the recorded interferogram and the desired spectrum:

$$I(x) = \tilde{I}(x) - \frac{1}{2}\tilde{I}(0) = \frac{1}{4} \int_{-\infty}^{+\infty} S(\nu)e^{i(2\pi\nu x)}d\nu \quad (10.1.10)$$

The inverse Fourier transform of Eq.(10.1.10) gives the spectrum $S(\nu)$ from the interferogram $I(x)$ as,

$$S(\nu) = 4 \int_{-\infty}^{+\infty} I(x)e^{-i(2\pi\nu x)}dx \quad (10.1.11)$$

The following figure help us visualize the difference between monochromatic and polychromatic source interferograms.

The interferograms of ideal spectrometer would be symmetrical about the centerburst (ZPD), i.e, the two wings would be identical to each other. In this case only the centerburst and one wing of the interferogram need to be measured to enable a spectrum to be computed, which is known as measuring a single sided interferogram.

In the real world, the spectrometer introduces asymmetries into the interferogram which might necessitate measuring double sided interferograms to obtain an accurate spectrum. The asymmetric single sided interferogram can be made symmetric by a process known as

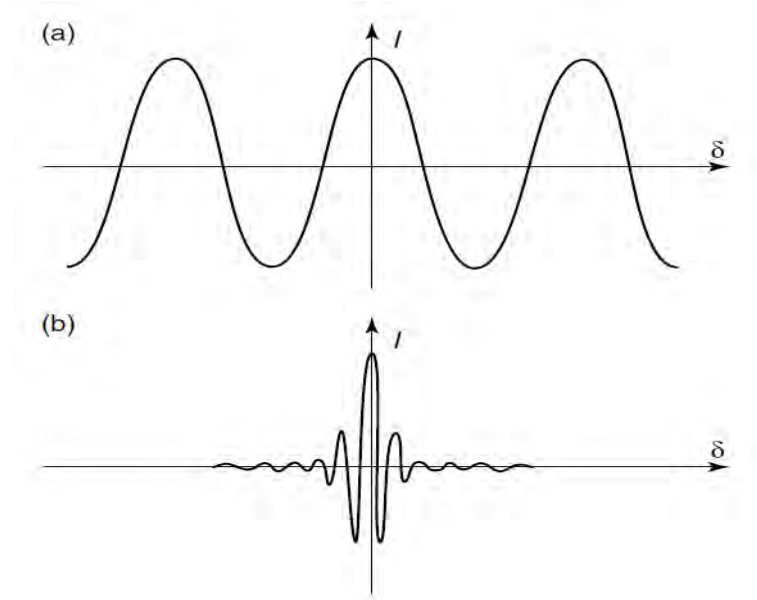


Figure 10.2: Monochromatic (a) and polychromatic (b) source interferograms [49].

phase correction. The phase error can be introduced because of each monochromatic contributions in Eq. (10.1.10) have not the same phase [6, 45]. According to [6], the phase depends on the wavenumber. This is due to the dispersion of the beam splitter, frequency-dependent electronic devices or the exact definition of the point of the movable mirror's zero displacement (ZPD). Therefore, by incorporating the wavenumber dependent phase $\phi(\nu)$ Eq. (10.1.11) becomes,

$$\mathbf{S}(\nu) = S(\nu)e^{i\phi(\nu)} \quad (10.1.12)$$

This can be written in another form as,

$$\mathbf{S}(\nu) = S_{Re}(\nu) + iS_{Im}(\nu)$$

$$\mathbf{S}(\nu) = S(\nu)\cos(\phi(\nu)) + iS(\nu)\sin(\phi(\nu))$$

where $\mathbf{S}(\nu)$, (L.H.S) of Eq. (10.1.12) is a complex spectrum composed of real ($S_{Re}(\nu)$) and imaginary part ($S_{Im}(\nu)$). In general, in IR spectroscopy, the interferogram and spectrum are related by a general Fourier transformation.

10.1.1 Discrete Fourier Transform

The measured interferogram is not continuous as in Eq.(10.1.11), instead it is sampled at discrete equidistant points (position of movable mirror) with finite step size Δx . Therefore, we have to use summation instead of integration in Eq.(10.1.11). In order to relate the continuous interferogram $I_c(x)$ to the sampled interferogram $I_s(x)$, we introduce the Shah function $\gamma(x)$ (Bell, 1972 as mentioned in [48]). That is,

$$I_s(x) = \gamma\left(\frac{x}{\Delta x}\right) I_c(x) \quad (10.1.13)$$

where,

$$\gamma\left(\frac{x}{\Delta x}\right) = \sum_{-\infty}^{+\infty} \delta\left(\frac{x}{\Delta x} - n\right) \quad (10.1.14)$$

where n is an integer, and δ is a delta function. The Shah function has only two possible values, namely zero and infinity. It equals zero anywhere except for those points where $\frac{x}{\Delta x}$ becomes an integer. Other properties of Shah function are periodicity and the FT of a Shah function yields a Shah function again,

$$\gamma(x + m) = \gamma(x) \quad (10.1.15)$$

where, m is an integer

$$F \gamma(ax) = \frac{1}{|a|} \gamma\left(\frac{\nu}{a}\right) \quad (10.1.16)$$

As it is already discussed, the FT of the continuous interferogram $I_c(x)$ is a continuous

spectrum $S_c(\nu)$. Similarly the FT of the sampled interferogram $I_s(x)$ is given by:

$$FI_s(x) = S_s(\nu)$$

$$FI_s(x) = F\gamma\left(\frac{x}{\Delta x}\right).I_c(x) \quad (10.1.17)$$

$$FI_s(x) = F\gamma\left(\frac{x}{\Delta x}\right) \otimes FI_c(x) \quad (10.1.18)$$

$$FI_s(x) = \Delta x.\gamma(\nu.\Delta x) \otimes S_c(\nu) \quad (10.1.19)$$

By expressing Δx in the Shah function by $\frac{1}{\Delta\nu}$ and making use of a principle characteristic of the Dirac delta functional, that is,

$$\delta(ax - n) = \frac{1}{|a|}\delta\left(x - \frac{n}{a}\right) \quad (10.1.20)$$

it follows that,

$$\frac{1}{\Delta\nu}\gamma\left(\frac{\nu}{\Delta\nu}\right) = \frac{1}{\Delta\nu} \sum_{-\infty}^{+\infty} \delta\left(\frac{\nu}{\Delta\nu} - \frac{n\Delta\nu}{\Delta\nu}\right) = \sum_{-\infty}^{+\infty} \delta(\nu - n\Delta\nu) \quad (10.1.21)$$

Inserting this Shah function into Eq. (10.1.19), we get the relation between sampled interferogram and the continuous spectrum:

$$FI_s(x) = \mathbf{S}_s(\nu) = \sum_{-\infty}^{+\infty} \mathbf{S}_c(\nu - n\Delta\nu) \quad (10.1.22)$$

This is an infinite Fourier series, which is the discrete analogue of Eq.(10.1.19). The sampled spectrum $S_s(\nu)$ consists of an infinite series of equidistant Delta functionals. The weights of these equal the value of the continuous spectrum and the whole sampled spectrum repeats itself in intervals of the spectral band width $\Delta\nu$.

10.2 Real FT Spectrometer

The real spectrometer is the one with finite OPD and the interferogram is sampled only with finite step size Δx . Therefore, Eq.(10.1.11) can not be used in real FT spectrometry. Two things which are inseparable and we have to consider in this case are apodization and instrumental line shape (ILS), which determine the resolution of the spectrometer and performance of the instrument. The performance of the FT spectrometer is measured in terms of ILS, modulation efficiency and phase error [50].

10.2.1 Apodization and ILS

The infinite scanner length in Eq. (10.1.11) can be limited to finite scanner length (maximum OPD) of say L by a process known as **apodization**, which can be done by multiplying the ideal interferogram by an apodization function. All apodization functions have a characteristics of being zero out of the interval $[0, L]$ and non-zero within the interval. There are different types of apodization functions: boxcar, triangular, $\cos^2(x)$, Blackman-Harris, etc. However, the boxcar function is the most simple function, and preserves the maximum of information from the interferogram, but introduces side lobes. The Blackman-Harris is better in reducing side lobes, but results in loss of information. Let's consider the boxcar ($B(x)$) apodization function, which has a value of unity in $[0, L]$ interval and zero outside. To get interferogram with finite OPD, multiply the infinite interferogram in Eq. (10.1.11) by the boxcar function $B(x)$, then we get finite interferogram/spectrum ($I_{fin}(x)$) from the ideal infinite interferogram/spectrum ($I_{inf}(x)$) of Eq. (10.1.11) as,

$$\begin{aligned} S_{fin}(\nu) &= \int_{x=-\infty}^{+\infty} I_{inf}(x).B(x)e^{-i2\pi\nu x}dx \\ S_{fin}(\nu) &= S_{inf}(\nu).b(\nu) \end{aligned} \tag{10.2.1}$$

where, $b(\nu)$ is the Fourier transform of boxcar function, also known as the instrumental

line shape (ILS). This name is given because of the broadening effect and introduction of negative intensities on the incoming single spectral component of the beam by FTIR spectrometer according to the function $b(\nu)$. Therefore $b(\nu)$ determines how the spectrometer distorts an incoming sharp spectral line [6, 48]. The analytical form of the ILS corresponding to boxcar truncation can be derived easily from the Fourier integral of a unit operand using a finite integration limit. The result is a sinc function,

$$b(\nu) = \frac{\sin(2\pi\nu L)}{2\pi\nu L} = \text{sinc}(2\pi\nu L) \quad (10.2.2)$$

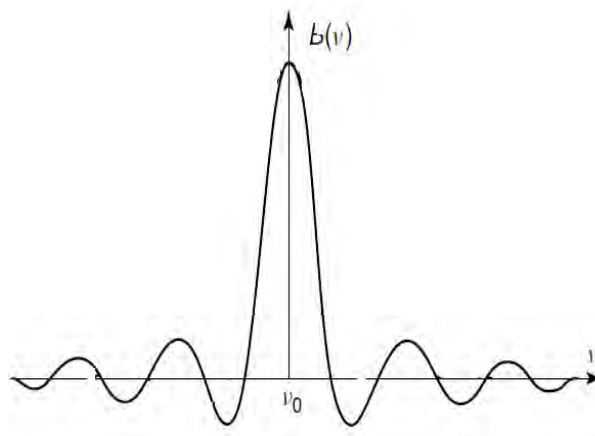


Figure 10.3: Instrumental Line Shape with Boxcar apodization function.

The resolution of the FTIR instrument is limited by the maximum path difference between the two secondary beams. It is proportional to the reciprocal of the maximum OPD. In order to say two lines of equal intensity are resolved, we can employ two rules: one can be a Rayleigh criterion and the other may be characterization by full width at half maximum (FWHM). According to Rayleigh criterion, the spectral resolution is defined as the distance between the maximum and the first minimum of the sinc function, which is given by,

$$\Delta\nu_{\text{Rayleigh}} = \frac{0.71}{L} \quad (10.2.3)$$

and the FWHM yields a resolution of,

$$\Delta\nu_{FWHM} = \frac{0.61}{L} \quad (10.2.4)$$

In our case, the maximum OPD is 250cm, but due to some technical reasons we limited the maximum OPD to 100cm only and it can attain a resolution of 0.009cm^{-1} using boxcar apodization. The spectral half width of an ideal monochromatic line after triangular apodization is used to specify spectral resolution which is a common practice by commercial FTS manufacturers like BRUKER Optics, which is given by,

$$\Delta\nu = \frac{0.9}{OPD_{max}} \quad (10.2.5)$$

We use this criterion conventionally, however the resolution is expected to be higher for usage of boxcar apodization. The other thing which affects ILS is the so called self-apodization, which is discussed in chapter nine. Self-apodization is due to finite field of view of the spectrometer, i.e, finite aperture size [6, 51]. Comparing the true resolution of two spectra calculated from the same interferogram by using either boxcar or triangular apodization, the loss in resolution for triangular apodization is 47% to real ILS [48].

The real ILS of our IFS120M instrument is determined nearly regularly from low pressure gas cell measurement which is filled with HBr. We usually use the wavenumber range of NDACC filter 3 range which covers from 2400 to 2700 cm^{-1} . Our radiation source is a globar of about 1273 K and we used the latest version of LINEFIT [52] (LINEFIT12) software to retrieve ILS.

Fig. 10.4 shows the retrieved ILS of IFS120M for the HBr cell measurement taken on June 01, 2009. As it is seen from Fig. 10.4 the true ILS resembles the ideal ILS shown in Fig. 10.3. The comparison of the true and ideal ILS's will be done using the modulation

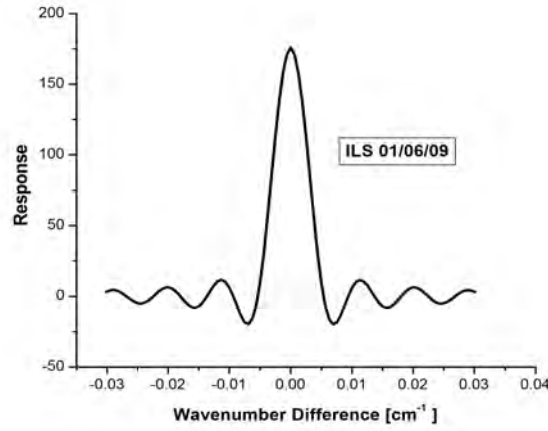


Figure 10.4: Retrieved ILS of the IFS120M in Addis Ababa

efficiency loss and phase error evolution. The real ILS differs from the ideal ILS which is determined by the applied apodization function and the self-apodization due to the non-perfect alignment. As it is mentioned in previous chapter, the observed line shape can be used to retrieve atmospheric trace gas profiles because of the height dependent pressure broadening. The tropospheric trace gas total column retrieval is relatively insensitive ($< 1\%$) to realistic distortions of the ILS from ideal. But for stratospheric gases, realistic distortion of the ILS may modify retrieved total columns by amounts of up to 3% [53].

Next we try to see the evolution of ILS since the first measurement date of our IFS 120M instrument. As we mentioned before the performance of the instrument is measured in terms of the modulation efficiency and phase error of ILS.

The modulation efficiency and phase error are calculated using LINEFIT (version 12) software developed by Hase (1999) [52]. Fig. 10.6 shows the variation of modulation efficiency of our IFS120M instrument since the beginning of measurement. We used different microwindows of the transmission spectra containing HBr features. The modulation efficiency and phase error as a function of OPD are then calculated using the software such that the residual between the retrieved and the measured spectra is minimized. Even if

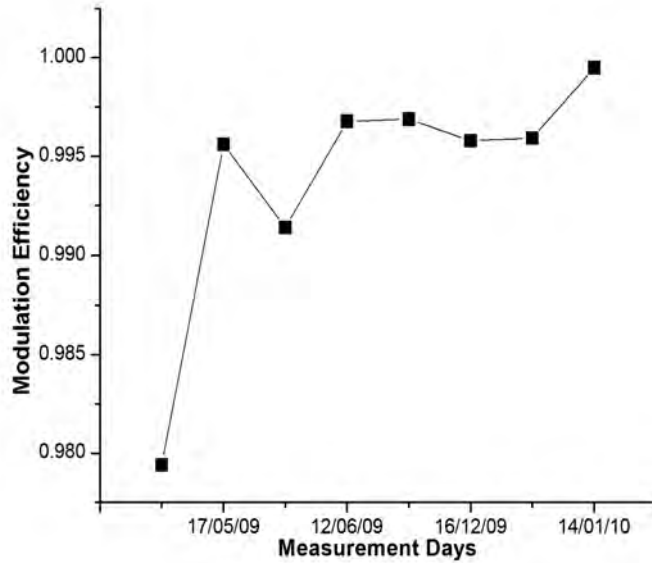


Figure 10.5: Evolution of Modulation efficiency loss

we are not strict to take regular cell measurements, it is recommended to have it periodically. The retrieval of modulation efficiency is done by assuming a linear decline with the optical path difference. The declination of modulation efficiency at maximum OPD on May 8, 2009 is less than 6% and on Jan. 14, 2010 the declination in modulation efficiency at maximum OPD is less than 2%. This shows that the instrument's alignment has been improved since the beginning of the measurement time.

The other parameter which characterizes the instrumental line shape is the phase error. Fig.10.7 shows the variation of phase error with OPD corresponding to the time period considered for modulation efficiency.

Fig. 10.7 shows the evolution of phase error since the first measurement on May 8, 2009. The figure reveals that the phase error is relatively getting improved since May, 2009. The assumed phase error we used in the LINEFIT software is zero, but as it is seen in Fig.10.7 the retrieved result is non-zero as expected because of the finite aperture size, non-perfect alignment, etc. The phase error changes sign between forward and backward scans during the measurement [53]. The effect of phase error as described earlier is that

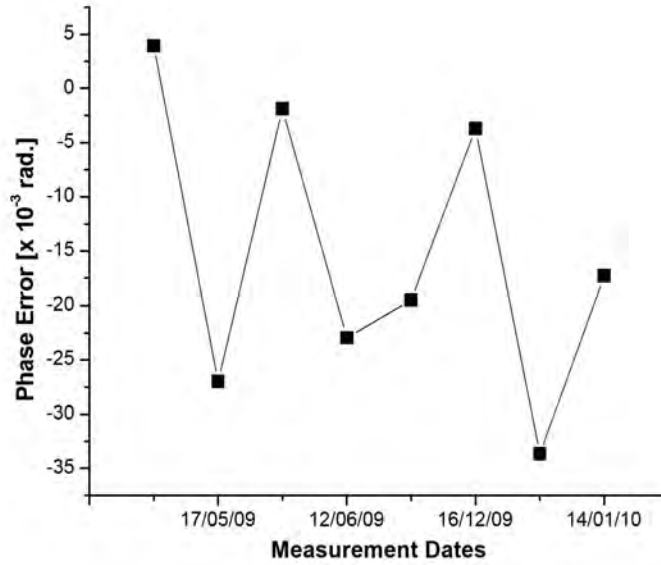


Figure 10.6: Evolution of Phase error

it causes asymmetry in ILS. Taking the phase error into account in the calculated spectra to fit the measured spectra helps to correct the effect of zero off-set. An ideal spectrum should show zero transmission in the center of absorbed spectral line. Uncorrected phase error will cause the center of such a line to show non-zero transmission.

According to [53], phase error affects the retrieved total columns in two separate ways; first, through the change in lineshape of the actual absorption line and second, through a change in the effective continuum level at the center of the absorption line nearby whose wings overlap the narrow line of interest. In the later case the phase error distorts the strong band and affects the local zero and continuum levels in the observed spectrum. In general Figs. 10.5 and 10.6 demonstrate the evolution of ILS since the beginning of the measurement in Addis Ababa using IFS120M instrument.

Finally we would like to discuss the spectral fits of the measurement on 1st June, 2009. Fig. 10.7 shows the HBr spectral fit for the indicated wavenumber region. The upper panel is a plot of the measured and calculated transmission spectra and the lower panel

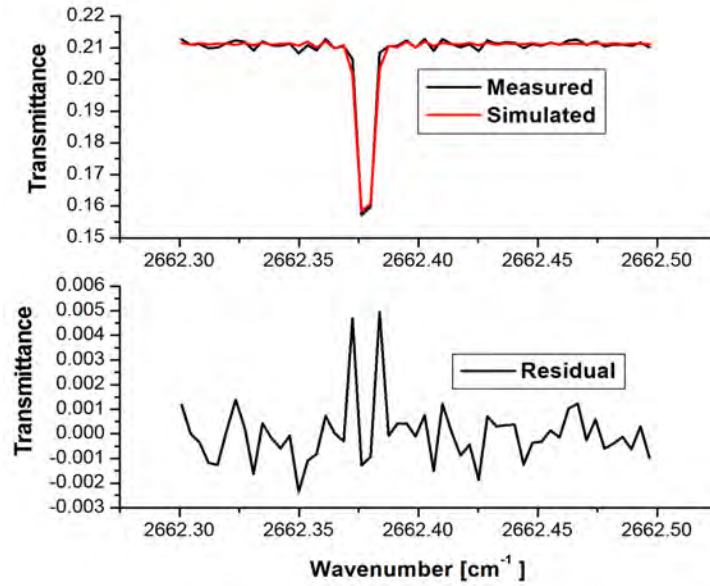


Figure 10.7: The measured and simulated transmittance spectral fit from HBr cell measurement (upper panel) and the corresponding residual spectra between the measured and calculated spectra (lower panel) for the date of 01 June, 2009

is the residual between the two spectra with a resolution of 0.008cm^{-1} . The root-mean-squared (RMS) value of the noise is below 1% and it is comparable to the result reported by Hase et al. (1999) [52]. We can judge from the figure that the residual is a random noise. The ILS, modulation efficiency and phase error corresponding to this spectral fit has been shown in Figs. 10.4-10.6.

Chapter 11

Measurement of Carbonyl Sulfide over Addis Ababa

11.1 Carbonyl Sulfide (OCS): background and chemistry

Carbonyl sulfide (OCS or COS) is one of the sulfur containing inorganic compounds in the Earth's atmosphere. Its main sources are oceans, biomass burning, soils, wet lands, oxidation of carbon disulfide and dimethyl sulfide (DMS), volcanic eruptions, industrial uses, automobiles, etc. [1, 6, 54]. There are different types of OCS (isotopes) $^{16}\text{O}^{12}\text{C}^{32}\text{S}$, $^{16}\text{O}^{13}\text{C}^{32}\text{S}$, $^{16}\text{O}^{12}\text{C}^{34}\text{S}$, $^{16}\text{O}^{12}\text{C}^{33}\text{S}$ and $^{18}\text{O}^{12}\text{C}^{32}\text{S}$. Among these the dominant (most abundant) compound is $^{16}\text{O}^{12}\text{C}^{32}\text{S}$. Carbonyl sulfide is considered as a component of the atmosphere at a tropospheric concentration of approximately 500 parts per trillion (ppt) by volume, corresponding to a global burden of 2.4 million tons; but enhanced *OCS* mixing ratios up to 600 ppt from biomass burning emissions have been found below the tropical tropopause at altitudes between 10 and 18 km [1]. According to [54], the average total worldwide release of *OCS* to the atmosphere has been estimated at about 3 million tons per year. Carbonyl sulfide is the most abundant sulfur gas in the global background atmosphere because of its low reactivity in the lower troposphere and its corresponding long residence time. It is the only sulfur compound that survives

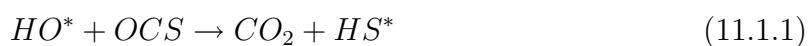
Table 11.1. Global budget of *OCS*.

Type of Sources	Sources, $\times 10^9 \text{ g } S \text{ yr}^{-1}$
Direct OCS flux from oceans	41
Indirect OCS flux as CS_2 from oceans	84
Indirect OCS flux as DMS from oceans	154
Direct anthropogenic OCS flux	64
Indirect OCS flux as anthropogenic CS_2	116
Total sources	459
Type of Sinks	Sinks, $\times 10^9 \text{ g } S \text{ yr}^{-1}$
OCS uptake by soils	130
OCS uptake by plants	238
OCS reaction with OH radical	94
Total sinks	462

This table is taken from [1].

to enter the stratosphere except SO_2 which is directly injected into the stratosphere during volcanic eruptions [1]. The transport of *OCS* into stratosphere is considered to be responsible for the maintenance of normal stratospheric sulfate aerosol layer. The other sulfur compounds, CS_2 and dimethyl sulfide (DMS), have much shorter tropospheric life time than carbonyl sulfide, and thus they do not contribute appreciably to the sulfur budget of the stratosphere during non volcanic periods. According to [1, 55], out of the total estimated *OCS* quantity in the atmosphere (5.2 Tg), of which 4.63 Tg is in the troposphere and 0.57 Tg in the stratosphere. Based on the estimated global source of *OCS* strength of 0.86 Tg per year, the global atmospheric lifetime of *OCS* is estimated to be about 6 years. Table 11.1 shows the estimated global budget of carbonyl sulfide (*OCS*).

In the atmosphere, the hydroxyl radical HO^* initiates the oxidation of *OCS* and carbon disulfide (CS_2) and result in a yield of 8 – 12 million tons as sulfur (*S*) in atmospheric sulfur dioxide per year. The oxidation of carbonyl sulfide and carbon disulfide in the atmosphere initiated by hydroxyl radical is shown below:





These reactions with hydroxyl radical initiate oxidation processes that occur through a series of atmospheric chemical reactions. Oxidation of OCS with hydroxyl radical contributes about 7% of the total stratospheric sink mechanisms. As it is pointed out above, OCS is chemically inert in the troposphere. As a result nearly all of its concentration is transported to stratosphere where it is eventually photodissociated and attacked by oxygen (O) atoms and OH radicals. The gaseous sulfur product of the chemical breakdown of OCS is SO_2 , which is finally converted to H_2SO_4 aerosol, as shown below:

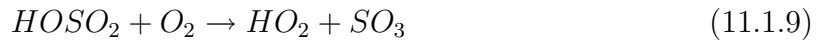
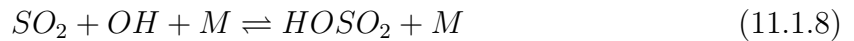


The dominant stratospheric sink of OCS is by photolysis, which weighs about 71% of the total sink mechanisms. The second largest stratospheric sink of OCS is by oxidation with atomic oxygen which contributes about 22%. The wavelength region from 185 to 388 nm is energetic enough to break the $C = S$ double bond in OCS [55] which has a bond length of 1.5601 Å. CO has in its ground state dissociation energy of 11.09 eV, while CS has 7.36 eV. The production of stratospheric sulfur also result in reduction of stratospheric ozone, and production of stratospheric sulfur dioxide SO_2 as shown below:





The gas phase SO_2 compound is then undergo further reaction to form stratospheric sulfuric acid, which forms the background stratospheric sulfate aerosol (SSA) layer:



The composition of stratospheric sulfate background aerosol depends on ambient temperature and relative humidity, with sulfate fraction varying between 40% and 90%. A typical aerosol particle has H_2SO_4 fraction of $\sim 75\%$ with water making up the remainder. Latest models estimate that 43% of SSA particles is originated from OCS photolysis, 30% from upwardly transported sulfate and 27% from SO_2 oxidation [1]. Therefore, carbonyl sulfide indirectly contributes to reduction of stratospheric ozone and increment of stratospheric background aerosol layer.

11.2 OCS Spectral Signature in mid-infrared

11.2.1 Microwindow Selection

In this section, we analyze the ground based-spectra of carbonyl sulfide. For the retrieval of carbonyl sulfide we have used different microwindows in the spectral range of 2038.8 to 2051.5 cm^{-1} . The optimum microwindows are selected by a software called ALFIP (Automatic Line Finding Program) and INTDIF (INTerfering gases based on DIFferences) [57].

Table 11.2 Microwindows and interfering species.

Microwindow (cm^{-1})	Main interfering species
2038.900000 - 2039.080556	H_2O , CO_2 , O_3 , CO
2045.480000 - 2045.660000	H_2O , CO_2 , O_3 , CO
2047.800000 - 2048.700000	H_2O , CO_2 , O_3 , CO
2049.303050 - 2050.115000	H_2O , CO_2 , O_3 , CO
2051.200000 - 2051.500000	H_2O , CO_2 , O_3 , CO

ALFIP calculates the spectra and finds the most suitable lines and optimized microwindow size and INTDIF uses the output of ALFIP and calculates the interfering gases; and the outcome is a number of optimized microwindows. An optimum microwindow is a spectral interval consisting of grid points selected by minimizing the retrieval error of the target quantity. For the retrieval of *OCS* we used 5 microwindows, shown in Table 11.2.

11.2.2 Error Analysis

PROFFIT allows error estimation. The random and systematic errors of the retrieved *OCS* is shown in Fig. 11.1. The percentage of both random and systematic error for selected heights are also shown in Table 11.3 and 11.4. Fig. 11.1 shows that the ILS, LOS and solar line errors are very small as compared to the rest. The error quantities to be handled in this software are: spectral base line (offset, channelling), ILS (linear modulation loss and constant phase error), line of sight (LOS), error in temperature, error in spectroscopic data and spectral noise.

The spectral noise is due to the uncertainty of the depth of the absorption line with respect to its surrounding continuum, which is proportional to the uncertainty of the line strength. The uncertainty in line strength in turn is proportional to the uncertainty of scaling factor, for scaled retrieval of the profile. The spectral noise is estimated by

$$err_{noise} = \frac{\sigma}{S_0\sqrt{N}} \quad (11.2.1)$$

where σ stands for the standard deviation of the spectrum from its mean (the noise on the

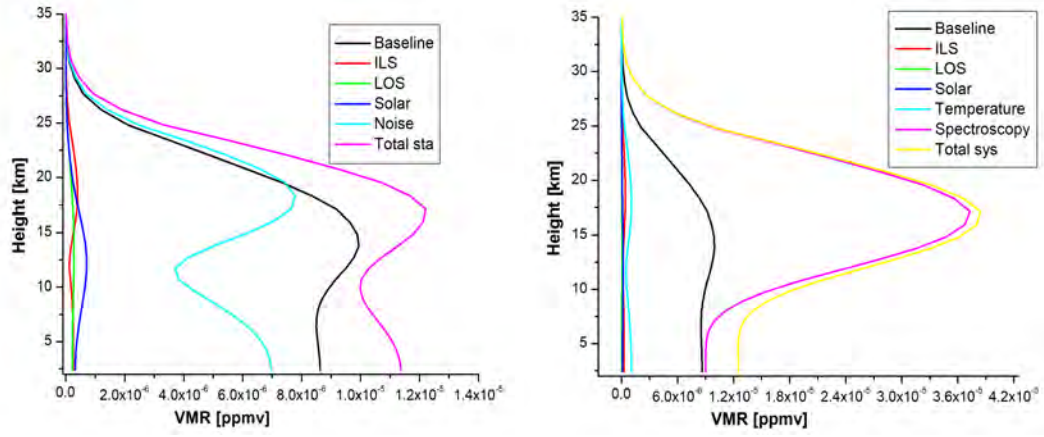


Figure 11.1: Random (left panel) and systematic (right panel) errors of OCS on 27th Jan., 2010.

Table 11.3. Percentage random error of OCS.

Height	Baseline	ILS	LOS	Solar	Noise	Total sta.
2.43	1.983	0.0589655	0.0514713	0.0737471	1.601	2.611
6.38	1.883	0.0551396	0.0514621	0.0972308	1.367	2.377
12.71	1.770	0.0236456	0.0514948	0.129000	0.747	1.939
18.31	1.982	0.0950629	0.0515072	0.0793022	1.846	2.775
36.34	2.086	0.1320000	0.0515187	0.0454829	2.464	3.319

spectrum) and N is the number of independent spectral grid points within the half width of the absorption line. Therefore, $\frac{\sigma}{\sqrt{N}}$ is the error of the spectral continuum value that surrounds the absorption line, which is divided by the depth of the absorption line S_0 . Typical values for strong absorbers (e.g. O_3 , HCl , HF , N_2O , CH_4) are less than 1.5%, whereas this uncertainty can exceed 12% for weak absorbers (e.g. NO_2 , $ClONO_2$) [6]. An offset signal in the spectrum may be mainly due to nonlinearity of the detector. The offset typical value of MCT detector is 1% of the continuum signal which results in an error of approximately 1%. The spectroscopic data error is the error due to spectroscopic parameters such as line intensity and gamma values. The absorption coefficient and its temperature and pressure dependence are usually obtained from laboratory measurements, which are only possible up to a certain accuracy. Spectroscopic errors lead to systematic deviations from a real profile and column amounts. The ILS influences the

Table 11.4. Percentage systematic error of OCS.

Height	Baseline	ILS	LOS	Solar	Temperature	Spectroscopy	Total sys.
2.43	1.983	0.058966	0.0057195	0.018437	0.24	2.071	2.878
6.38	1.883	0.055140	0.0057100	0.024302	0.202	2.085	2.818
12.71	1.770	0.023646	0.0057202	0.03214	0.095	4.954	5.262
18.31	1.982	0.095063	0.0057228	0.019828	0.251	8.452	8.687
36.34	2.086	0.132000	0.0057243	0.011371	0.324	9.704	9.93

result by modifying the shape of the VMR profile, specially at altitudes where the Doppler broadening is significant (above 20 km) [6]. The temperature uncertainty also influences both column amount and shape of the profile. As the change in temperature profile affects the pressure level which in turn alters the number density of air molecules (according to ideal gas law), the retrieved quantities will be affected. Another parameter that influences the simulated spectrum by the radiative transfer code is the solar zenith angle (SZA) or line of sight. The solar zenith angle used for the simulation of the spectrum must correspond to the angle of the sun beam analyzed by the spectrometer. There are two reasons for disagreement between these angles: first, the effect of a poorly pointing sun tracker; second, the sun angle used in the radiative transfer code may be calculated erroneously due to incorrect input parameters, like geographical position or time. For SZA higher than 80° the error in mixing ratio can exceed 8% for tropospheric gases, whereas for stratospheric gases, the resulting error in the mixing ratio is less than 2% at all altitude levels. At low-latitude regions where the solar zenith angle changes rapidly as compared to high-latitude, the error due to change in SZA influences the result. We use the SZA corresponding to the mean time of measurement ($\frac{t_{start}+t_{end}}{2}$) in the radiative transfer code (the detail of error estimation is found in [6, 20]). The line of sight error (LOS), which significantly affects the retrieval in low latitude areas is less than 0.1%. In general, the random and statistical error contributions of both atmospheric and auxiliary parameters is less than 10% of which 9.7% is the spectroscopic error from systematic contribution at 36.34 km while the total random error (without temperature error) is less than 4%

at the same atmospheric level. The percentage errors for both random and systematic contributions confirm the accuracy of our job.

11.2.3 Retrieval of OCS from FTIR Observation

Retrieval of OCS is performed using 5 microwindows following retrieval algorithm described in previous section. Fig.11.1 shows the spectral fit between the measured and calculated spectra for one of the microwindows in Table 11.2. The figure shows the mea-

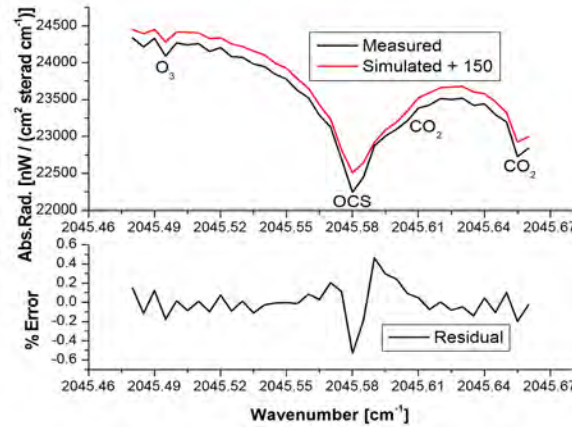


Figure 11.2: The measured and calculated spectra.

sured and calculated spectra. Besides, the target species (OCS) and the interfering species (ozone, and carbon dioxide) identified by INTDIF are shown. The difference between the measured and simulated spectra is shown in the lower panel of the figure. The lower panel of the figure shows the residual (the difference between the measured and calculated) spectra. The maximum percentage error for the spectral fit shown in Fig.11.2 is less than 1%. In all microwindows used for the retrieval of OCS the maximum percentage error is less than 2%, which is less than the 4% error in [58]. As the fit quality is an assurance for good retrieval, we expect a nice retrieval results. The noise in Fig.11.2 is dominantly random except some systematic features near the peak positions of the target and interfering species.

The other parameter worth discussing is the averaging kernel matrix which is the measure of the sensitivity of the retrieved state to the true state given by Eq. (4.3.6). The plot of the rows of the averaging kernel matrix for some selected heights is shown in Fig. 11.3 for a profile retrieval of OCS consisting of 41 layers (height grids). According to [50], the integrated area under each averaging kernel is a simple measure of the amount of non-a priori information that appears in the retrieval at the corresponding height. Since the mean tropopause height over Ethiopia is above 17 km (see Fig. 8.1 and the daily NASA/goddard meteorological data also confirms this) the averaging kernel tells us that the gaseous OCS is dominantly a tropospheric gas. Therefore, the retrieval is more sensitive in the troposphere.

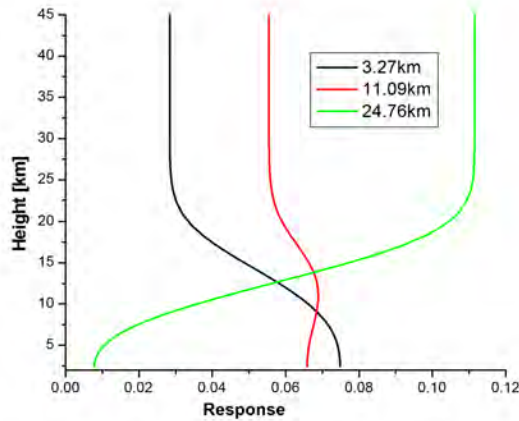


Figure 11.3: Averaging Kernel for selected heights.

One of the main objectives of this thesis is to retrieve vertical profile of carbonyl sulfide (OCS) over Addis Ababa (a representative of tropical region in Africa for FTIR measurement). The vertical profile of OCS for solar attenuated spectra measured by FTIR spectrometer is retrieved in the 5th NDACC filter band, in the microwindows region given in Table 11.2. In these microwindow regions there is additional H_2O , CO_2 , O_3 and CO features. We used slope regularization method for the retrieval of OCS and CO_2 profiles, while the signature of others species is calculated by simple scaling of start profile.

The profile of OCS shown in Fig.11.4 shows a minor slope from 0.55 ppbv at nearly 13 km

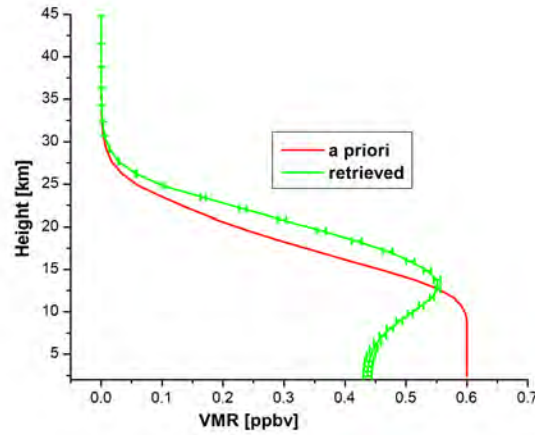


Figure 11.4: Retrieved profile of OCS.

to 0.45 ppbv at the observation site, 2.443 *km*. This slope is due to interferences with CO_2 and unknown lines. The decrease in profile amount mentioned here is also reported by [6]. The profile of OCS shows that the VMR of OCS is rapidly decreasing with altitude above 15 km. It declines from 0.55 ppbv in troposphere to less than 0.25 ppbv at 20 km. The standard deviation of the retrieved profile is shown in the same figure as error bar having a magnitude between 6.964×10^{-6} at the observation site to 4.536×10^{-10} at 85 km. According to [59], the OCS profile at the tropical tropopause can reach levels comparable to the lower tropospheric mixing ratios most likely as a result of convective uplift of biomass burning plumes. This is in good agreement with our retrieved profile shown in Fig. 11.4 except a minor gradient in VMR from 13 km to observational level. The conversion of OCS to background stratospheric aerosol by photochemical reactions in the stratosphere (mentioned in the introductory part of this chapter) could be one reason for a rapid gradient of OCS VMR above free troposphere.

The time variation of OCS VMR for a particular day is shown in Fig. 11.5. The measurement was taken on March 14, 2010 starting from morning 3:03 a.m to 7:35 p.m local time.

It is shown that the VMR of OCS increases with time from morning to just noon and tends

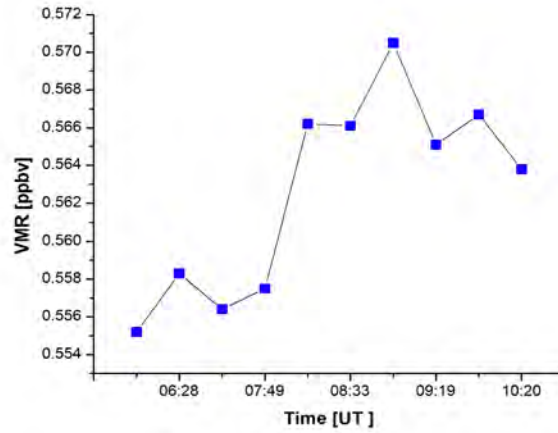


Figure 11.5: Variation of OCS VMR with time at 13 km .

to decrease right after noon. This may be associated with the photochemical production of OCS during noon or less sink of OCS by plants and soil during day time because of the absence of photosynthesis in day time. It is known that OCS reaches its minimum value of mixing ratio at night due to photosynthesis process [60]. It is mentioned before that OCS is consumed by plants almost simultaneously with carbondioxide.

The partial column and the integrated columns of OCS are shown in Fig.11.6. These two graphes (upper and lower panels) tell us the vertical distribution of the gas as well as the level at which the highest concentration is found.

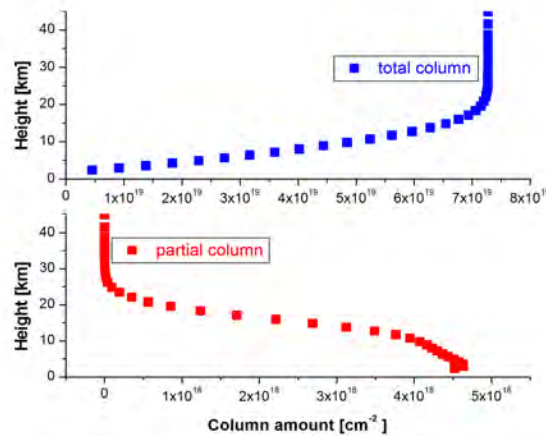


Figure 11.6: Partial and integrated columns of OCS on the 27th of January, 2010.

The minimum concentration of OCS is found in the partial layers of $76.95\text{ km} - 85.00\text{ km}$ which is about 5×10^{10} molecules/ cm^2 . This tells us that OCS exists also in mesosphere and lower thermosphere though in less concentration.

11.2.4 Time series of carbonyl sulfide

The data at hand and considered for this study is limited to short measurement periods, however we tried to see the time series of carbonyl sulfide for 49 measurement days since the first date of continuous operation of our FTIR spectrometer. We presented the time series of the total column amounts and vertical profiles of OCS from May 2009 to April 2010 and the time series of total column OCS for January 2010. The limited number of measurements within this period is due to unaffordable natural phenomena of the rainy season (from middle of June to late September) and unexpected cloud cover over Addis Ababa which severely limited the observing capability of our FTS.

Carbonyl sulfide is the most abundant sulfur-containing gas in the Earth's atmosphere. Owing to its long life time of about (2-6 years) OCS is transported to the stratosphere where it is either photodissociated by UV radiation or reacts with atomic oxygen or OH radical, to ultimately form sulfate aerosol particles (Jung layer) that influence the Earth's radiation budget and stratospheric ozone chemistry (reduction in stratospheric ozone concentration) [61].

Fig. 11.7 shows the time series of the total column OCS (in molecules/ cm^2) observed during the measurement period from May, 2009 to April, 2010. The blank space between 13th June 2009 to 26th November 2009 when no measurement is taken. The total column amount of OCS observed during this period ranges from 5.3×10^{19} to 8.5×10^{19} molecules/ cm^2 . Low OCS total column might be expected in our region because of the distance from industrialized regions (North hemisphere) and the open ocean, however the observed value is much higher than the mid-latitude total column amount observed

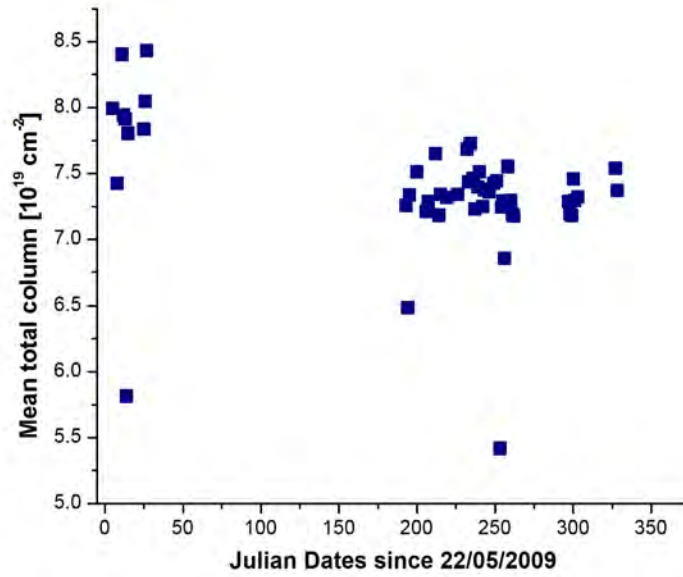


Figure 11.7: Time series of the total column OCS.

at Izana ($28^{\circ}18' N, 16^{\circ}29' W$) on the Canary Island of Tenerife at 2367 m.a.s.l which is in the order of 10^{15} molecules/ cm^2 . This higher value of total column of OCS in our region (Tropics or equatorial Africa) may be due to high tropopause levels. This results in higher life time of OCS in troposphere before undergoing any photochemical reaction to form background sulfate aerosol in the stratosphere (where OCS mixing ratios begin to decrease.) However, the high temperature in tropics may cause OCS to undergo photodissociation and results in reduction.

The time series of the vertical profile OCS for the above mentioned measurement period is shown in Fig.11.8. Like the total column the mixing ratio of OCS also shows a slight enhancement up to 0.6 *ppbv* which is higher than the mean 0.45 *ppbv*-0.5 *ppbv* in the troposphere.

In Fig. 11.8 the light gray color indicates the non-measurement days and/or zero VMR values of OCS. As indicated in this figure the mixing ratio reaches up to 0.6 *ppbv* and steadily decreases in the stratosphere. According to [59] the OCS at the tropical tropopause can reach levels comparable to the tropospheric mixing ratios, as a result of convective uplift

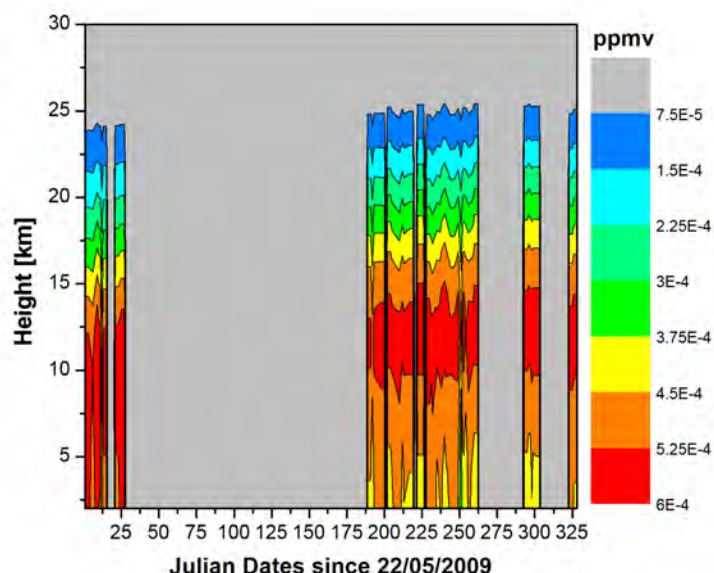


Figure 11.8: Time series of the vertical profile of OCS.

of biomass burning plumes. As we mentioned before the vegetation uptake is the dominant sink of atmospheric OCS. This accounts for 80% of the total atmospheric loss [59], but the stratospheric loss is associated with photodissociation of OCS and oxidation with OH radicals. The conversion of carbonyl sulfide into stratospheric aerosols is one of the sink mechanisms of this compound. The important roles of the stratospheric aerosol in influencing the Earth's radiation budget as well as heterogeneous reactions involved in stratospheric ozone chemistry [56] have drawn attention to the sources and sinks of *COS*.

As it is mentioned above, we were not successful in taking continuous measurements due to unexpected cloud covers over most parts of Ethiopia, but for January month we have a better number of measurements than other months. As a result we presented the time series for total column and vertical profile of this month as shown in Fig. 11.9. and Fig. 11.10.

The left panel of Fig. 11.9 shows the daily mean time series of the total column of OCS (in molecules/ cm^2), and the right panel shows the time series of the vertical profile of OCS for January, 2010. The total column amount is between 6.8×10^{19} and

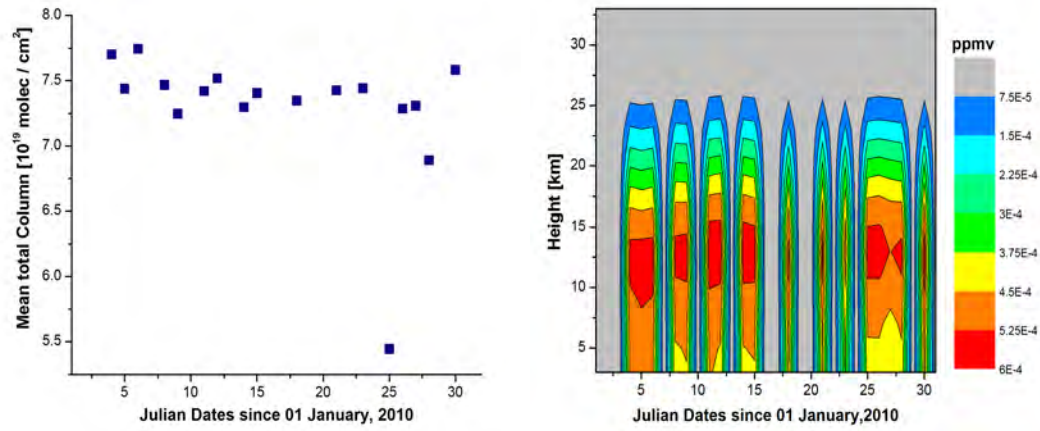


Figure 11.9: Time series of total column and vertical profile of OCS for January, 2010.

7.6×10^{19} molecules/cm² except for the date Jan. 25, 2010 which is about 5.4×10^{19} molecules/cm². The daily variation of OCS can also be seen from the same plot. The lower vmr values closer to the surface (observation site) is due to unknown interfering species. A small decrease below 12 km is also reported by [62]. The OCS vmr observed in the stratosphere is due to the transport of OCS from the lower and free troposphere which occurs mainly through the tropical tropopause. According to [62], OCS is the highest among the background aerosol source gases due to its long atmospheric life time, as ranked by flux transported from the troposphere through tropical tropopause layer.

As shown in Fig. 11.7, the total column OCS shows seasonal variation. The column amount tends to decrease from May to April. This can be shown in Fig. 11.10.

Fig. 11.10 shows the time series of tropospheric (lower most panel) and stratospheric (middle) total column amount of OCS during the measurement period (between May 22, 2009 and Apr 10, 2010). The upper panel is the ratio between tropospheric and stratospheric total column amount. The tropospheric total column amount is seen to be decreasing while the stratospheric column amount is increasing during the measurement period. The ratio between the tropospheric and stratospheric column also confirms this.

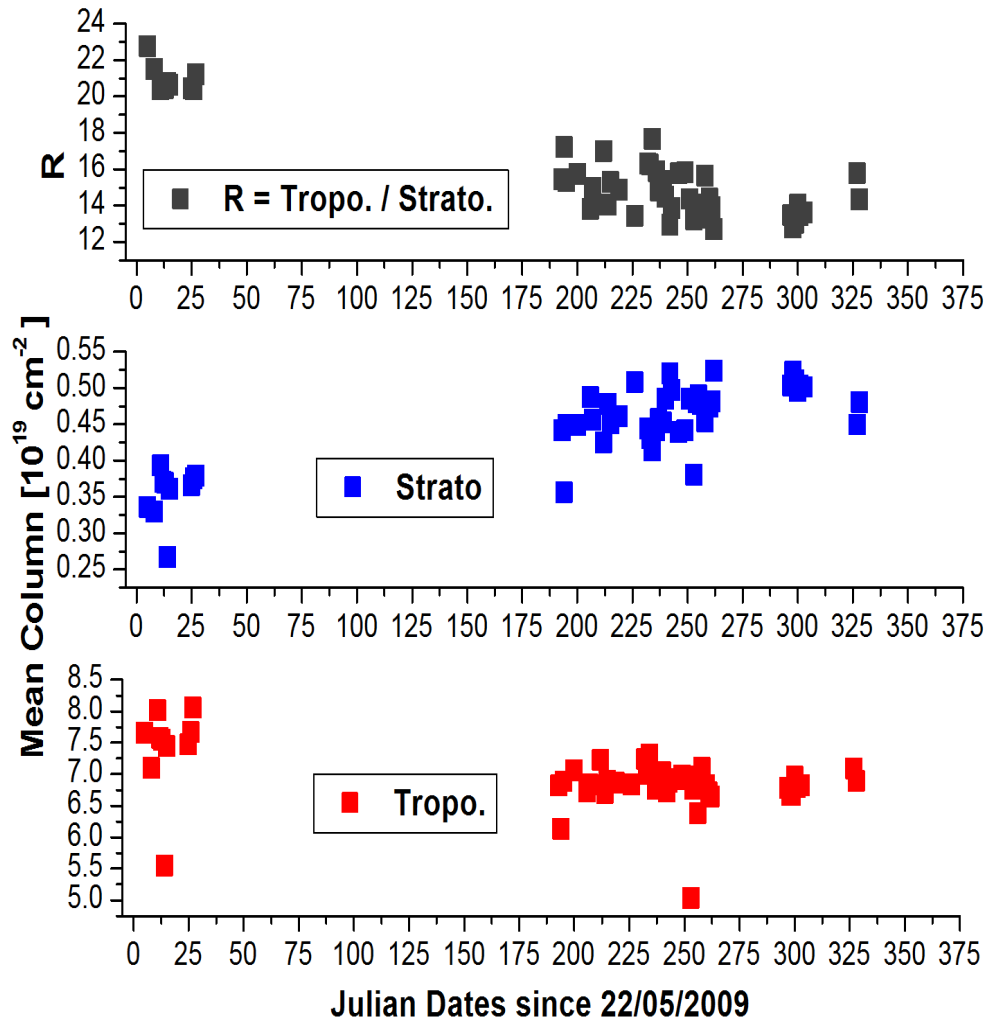


Figure 11.10: Time series of Tropospheric and Stratospheric total column OCS .

11.2.5 Correlation between OCS , CO_2 and O_3

The carbonyl sulfide measurement from ground-based FTS shows strong correlation with the observation of CO_2 in the Northern Hemisphere mid and high latitudes [64], however the climate feed back of the two species is opposite (i.e, OCS undergoes different chemical processes and finally converted to back ground aerosol and result in cooling of the surface while CO_2 is responsible for global warming by heating the atmosphere). According to [59], the tropospheric OCS concentration has risen by approximately 30% since 1600 G.C. from a mean value of 373 ppt over the period 1616-1694 to something to the order

of 485 ppt today. The increment of both atmospheric CO_2 concentration and temperature experienced over this period were the deriving forces for the related increase in OCS concentration.

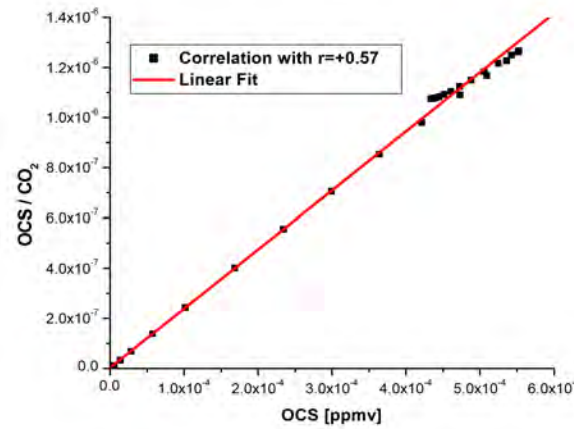


Figure 11.11: Relationship between atmospheric OCS and CO_2 .

The relation between OCS and CO_2 and temperature is associated with the biosphere and this relation is revealed in a laboratory study of samples of the lichen (*Ramalina menziesii*) California, USA by Kuhn and Kesselmeier [64]. They found that when the lichens were optimally hydrated, they absorbed OCS from the air at a rate that gradually doubled as air temperature rose from approximately $3^\circ C$ to $25^\circ C$, whereupon their rate of OCS absorption began a decline that led to zero absorption of OCS at 35° . From this findings they explained that, most terrestrial plant prefer warmer temperature, so that as their environment warm they grow better and extract more OCS from the atmosphere in an attempt to promote even more warming and grow better still. At the point where the warming becomes dangerous to them, however, they reverse this course of action and begin to rapidly reduce their rates of OCS absorption in an attempt to forestall warming-induced death. This results in increasing of OCS. Fig. 11.11 shows the relationship between carbonyl sulfide and carbon dioxide in the atmosphere observed at Addis Ababa ($9.1^\circ N$ and $38.8^\circ E$). The actual strength of the relationship or the Pearson's coefficient (r) is calculated and the value obtained here is $+0.57$ for the entire

profiles; but for tropospheric profiles (not shown here) the value of r is $+9.3$, which shows strong correlation in the troposphere. It is known that mostly both gases belong to tropospheric trace gas categories as they are populated in troposphere. The ratio of OCS/CO_2 reported by [65] is in the order of 10^{-6} which is in good agreement with our result.

On the other hand we calculate the correlation between carbonyl sulfide and ozone and found the Pearson's coefficients of -0.70 for the entire profile and -0.94 for stratospheric profile.

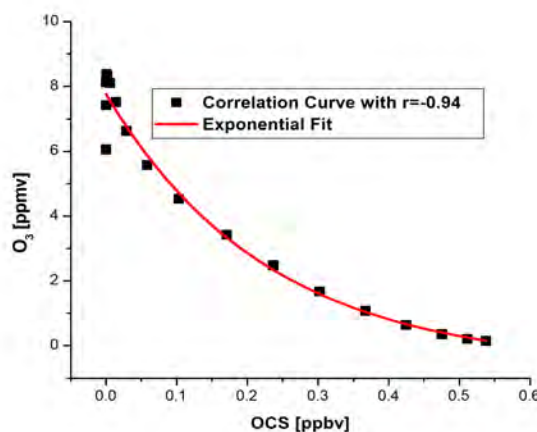


Figure 11.12: Relationship between stratospheric OCS and O_3 .

Fig. 11.12 shows the relationship between OCS and O_3 . As it is expected the two gases anti-correlate in the stratosphere where the OCS undergo different chemical processes and changes to back ground aerosols while the ozone concentration attains its maximum value in this atmospheric layer. As it is described in the introductory part of this chapter, OCS undergoes different chemical reactions and finally converted to sulfate aerosols. The presence of sulfur in the stratosphere in turn results in destruction of ozone. Therefore OCS can indirectly contribute to stratospheric depletion of ozone layer through heterogenous chemical reactions in the stratosphere.

11.2.6 Distribution, Total mass and Life time of OCS in the Atmosphere

The vertical profile of retrieved OCS is shown in Fig.11.5 and discussed in detail. Under this section we present the tropospheric and stratospheric mean vmr value of OCS, its total mass in both atmospheric regions and approximate value of its life time.

To distinguish between tropospheric and stratospheric mean OCS we used simple arithmetic mean suggested by Chin and Davis [55] given below:

$$\chi_{t,s} = \frac{\sum \chi(z)M(z)\Delta z}{\sum M(z)\Delta z} \quad (11.2.2)$$

where $\chi(z)$ is the OCS mixing ratio at altitude z and $M(z)$ is the number density of the air (*molecules/cm³*). The subscripts t and s refer to troposphere and stratosphere respectively. The altitude bin (Δz) used by Chin and Davis [55] is a constant, but in our case it is variable with altitude. This is due to non-uniform spacing of the altitude assignment for the calculation of model atmosphere in PROFFIT software. Therefore the difference between two consecutive altitudes is used as the altitude bin in this work. In order to calculate the mean vmr values in the two regions we need to know the mean tropopause and stratopause levels. The mean tropopause and stratopause levels from May 22, 2009 to Jan. 10, 2010 is determined from the daily profiles of temperature obtained from NASA Goddard Earth Observing System model and we found 17.12 km and 52.85 km respectively. Note that the observation site has an altitude of 2443 m.a.s.l. Then using the above formula we obtained the tropospheric mean OCS vmr value of approximately 488 pptv (parts per trillion by volume). Observed values of OCS by different investigators is slightly different. For instance tropospheric mixing ratio for OCS reported by Leifer [1989] as mentioned in [55] is 410 pptv with 400 pptv at tropopause level. The result mentioned in [61] is that the global tropospheric mean is 433 pptv and Notholt

et al.,[2006] as mentioned in [61] confirms the global mean tropospheric mixing ratio is 480–520 pptv; but most investigators report the tropospheric OCS mixing ratio is nearly constant and it is about 500 pptv with latitudinal gradient [55]. Our result deviates by 2.4% from the global mean value. Therefore the tropospheric mean value of OCS mixing ratio we obtained is in good agreement with different literatures.

Following similar procedure we calculated the stratospheric mean OCS vmr and obtained about 230 pptv. This number is small as compared to the mean value reported by [61] between $20^{\circ}N - 20^{\circ}S$ - 389 ± 19 pptv from ATMOS and 356 ± 27 pptv from ACE satellite measurement. The global stratospheric mean reported in the same journal using ACE data is 330 pptv. The reduction in vmr in stratosphere is due to conversion of OCS into stratospheric aerosol layer and oxidation by hydroxyl radicals and oxygen atoms. Dissociation of OCS into carbon monoxide and carbondioxide is also one mechanism for stratospheric reduction of OCS. The stratospheric OCS vmr is found to decrease rapidly with altitude, decreasing from about 500 pptv in the tropopause to less than 10 pptv at about 30 km.

Next we try to estimate the tropospheric and stratospheric mass of OCS and finally we estimate the atmospheric life time of OCS in our region (tropics). The tropospheric or stratospheric mass of OCS (W_{ocs}) can be estimated using the following formula:

$$W_{ocs}^{t,s} = \left(\frac{W_{air}^{t,s}}{M_{air}} \chi_{t,s} \right) M_{ocs} \quad (11.2.3)$$

where, $W_{ocs}^{t,s}$ is mass of OCS either in troposphere(t) or stratosphere(s); $W_{air}^{t,s}$, mass of air in troposphere or stratosphere= 4.56×10^{21} g or 7.2×10^{20} g respectively; $\chi_{t,s}$, mean tropospheric or stratospheric OCS vmr; M_{air} , molecular weight of air= 28.99 g/mol and M_{OCS} is the molecular weight of OCS= 60 g/mol. Using these given quantities the tropospheric and stratospheric mass of OCS is estimated by 4.6056157×10^{12} g and $0.342738875 \times 10^{12}$ g.

The total mass of OCS in the atmosphere is nearly the sum of tropospheric and stratospheric mass which is given by

$$W_{OCS} = (\frac{W_{air}^t \chi_t + W_{air}^s \chi_s}{M_{air}}) M_{OCS} \quad (11.2.4)$$

Using this formula, the total mass of OCS in tropical atmosphere can be estimated to be about $4.9483546 \times 10^{12} \text{ g}$ or 4.9483546 Tg . We use this value to estimate the life time of OCS in our region. According to Chin and Davis [1993] mentioned in [55] the global source strength of OCS was estimated at 1.2 Tg/yr and no secular evidence has been found for secular trends in recent studies. Therefore, it is reasonable to assume that the global source is nearly balanced by a similar magnitude sink. Under this assumption, the atmospheric life time of OCS can be estimated by dividing the total OCS mass by its source strength. This gives an estimation of OCS atmospheric life time (τ) of 4.1236 years. This is comparable to the estimated global OCS life time of 4.3 years reported by Chin and Davis[1995] [55] however it is slightly lesser. According to [59], the tropospheric lifetime of OCS has recently been revised downward from 4.3 years [55] to about 2.5 years based on an increase in the estimate of the land biosphere sink. As different authors come up with different global OCS source strengths and different global life times, we have got to keep this result for our site until the source strength of our region is specifically determined.

PART IV

Conclusions

Chapter 12

Conclusions

12.1 The climatology, microphysical and optical properties of stratospheric aerosols

The stratospheric aerosols and gas experiment (SAGE)II instrument aboard on Earth's radiation budget satellite (ERBS) is designed to measure solar extinction by aerosols and trace gases. We used this data (recorded during the life time of the satellite) to analyze stratospheric aerosol climatology in four different channels centered at 386 nm, 452 nm, 525 nm and 1020 nm wavelengths from mid-troposphere to stratosphere with a vertical resolution of 0.5 km. The satellite views the atmosphere during the spacecraft's sun rise and sunset using limb occultation technique.

We filtered out the aerosol extinction data over Ethiopia (3N-15N and 33E-48E) above 15km from the global data measured during the life time of the satellite using matlab code as this thesis is focussed on stratospheric aerosol climatology. From the coldest point of the mean temperature profile measured by SAGE II instrument, we determined the tropopause level to be above 17 km which agrees with different literatures. The vertical profile of aerosol optical depth (extinction) observed at different channels show the spectral variation of stratospheric aerosols as well as the vertical distribution of stratospheric aerosol. As the light extinction depends on the particle concentration, the stratospheric aerosol extinction at the first three wavelengths (386 nm, 452 nm, 525 nm) show high

stratospheric extinction between (17-25) km, indicating high concentration of aerosols around this altitude region. The 1020 nm channel is not as good as the rest channels to capture stratospheric aerosol. This channel captures aerosols found between lower stratosphere to lower troposphere.

The AOD at different channels is also calculated in this thesis. The seasonal variation of column AOD is calculated by multiplying the monthly mean extinction data by the level height (0.5 km) for each channel. The plots of seasonal variations of AOD values show an increasing trend during all seasons with slower rate during Summer. In Spring, maximum stratospheric loading is observed during ERBS functional period while Summer is among the minimum loading of stratospheric aerosol in all channels. This reveals the increasing trend of both coarse and fine mode stratospheric aerosols in each season. From the seasonal variation of AOD we clearly observed the effect of the volcanic eruptions of the Mt. Pinatubo (in 1991) and the El Chichon volcanic eruption (1982) on the global atmosphere.

The annual mean column value of AOD as seen by different channels shows the trend of AOD (aerosol loading) over Ethiopia from 1984 to 2005. This trend shows the steadily increasing of AOD distribution from year to year during this period in all channels. This indicates that both fine and coarse mode aerosol loading has also been increasing during this period over Ethiopian stratospheric regime. The aerosol index climatology from TOMS instrument during 1979 - 1992 by J. Barkan also supports this result.

The stratospheric aerosol size distribution is also retrieved from the monthly mean total column optical depth for selected years of 1985, 1989, 1991, 1993, 1997 and 2004. The assumed aerosol size distribution we used is Jung power law. The complex refractive index used for the size retrieval is $m = 1.51 + 0.005i$. The real refractive index of hydrated

sulfate aerosol is about 1.45 but our result is different from this value. This indicates the existence of different components of aerosols in the stratosphere, however sulfate aerosols and dust are expected to be dominant. The maximum ASD function is retrieved during which maximum columnar AOD is observed as expected. However, in our result the ASD doesn't show significant variation with season. For a better handling of stratospheric aerosols size distribution it would have been better to use channels of shorter wavelengths and multi-modal aerosol size distribution (number density) retrieval.

12.2 Observation of carbonyl sulfide over Addis Ababa

A high resolution FTIR spectrometer of Bruker IFS120 is installed in Science faculty of Addis Ababa University in May 2009. This instrument is the first to be continuously operated in Africa. The measurement site is chosen such that no shade during our measurement time fall on the solar tracker. The room temperature of the FTIRs container is adjusted to 20°C . The performance of the instrument is quantified by ILS and phase error. The real ILS of our IFS120M instrument is determined nearly regularly from low pressure HBr cell measurement using a laboratory source (global $\approx 1273\text{ K}$) using the latest version of LINEFIT12 software. The ILS itself is characterized by modulation efficiency loss and phase error. The declination of modulation efficiency at maximum OPD on May 08, 2009 is less than 6% and on Jan. 14, 2010 the declination in modulation efficiency at maximum OPD is less than 2%. Therefore the instrumental performance has been improved. This shows the instrument's alignment has been improved since this date. The magnitude of maximum phase error observed since the first operation of the instrument is less than 0.04 radian. The HBr spectral fit for $(2412.75 - 2413.20)\text{ cm}^{-1}$ wavenumber region shows a nice fit between the measured and calculated transmission spectra. The RMS value of the residual is less than 1% and it is comparable to the result reported by Hase et al. [52].

The retrieval code we used in this thesis is PROFFIT95, and this software allows to choose between different regularization techniques and handling of different error quantities. The spectral fit between the measured and calculated spectra of OCS is also discussed and the maximum error between the measured and calculated spectra for all microwindows of this species is less than 2%, which guarantees our fit quality. The vertical profile and partial columns of OCS from the FTIR spectra measured over Addis Ababa is also presented. The VMR of OCS show some increment as compared to the mean (500 *pptv*) tropospheric value. This may be due to biomass burning in the region. The total column value of OCS also shows increment relative to the Izana observatory result reported by Schneider (2002) [6]. This may be due to the higher tropopause level over tropical region. We also showed the time series of OCS, but due to unexpected cloud cover over Addis Ababa for long time our measurement days were limited. As a result we are not lucky to see the seasonal variation of OCS for longer period of time. However, we showed the time series of the total column and vertical profile of this gas for January 2010. This result shows a slight variation of the OCS amount on a daily basis. Finally we estimated the mean tropospheric and stratospheric vmr of OCS, its total atmospheric load and mean atmospheric lifetime. Accordingly, the tropospheric and stratospheric mean OCS mixing ratios are estimated to be 488 *pptv* and 230 *pptv* respectively. The tropospheric and stratospheric mass of OCS (in gram) is also estimated and we found it to be 4.6056 Tg and 0.3427 Tg respectively. The total mass of OCS in our region is then estimated to be 4.9484 Tg. This suggests that more than 90% of OCS is found in troposphere. Using the total mass of OCS and the global mean source strength of OCS (which is 1.2 Tg/yr) we estimated atmospheric lifetime of OCS by dividing the total mass by the source strength to be 4.1236 yrs in our region with assumption of nearly balanced source and sink strength of the gas. This result is comparable to the global OCS life time of about 4 years. The random and systematic error contributions were analyzed for baseline, ILS, LOS, solar

line, noise, temperature and spectroscopic data and we found a percentage error of less than 0.1% for LOS and 10% for spectroscopic data. The rest are intermediate between these two values.

Bibliography

- [1] Seinfeld, J.H., and Pandis, S.N.(2006). *Atmospheric Chemistry and Physics; From Air pollution to climate change*, A Wiley-Interscience Publication, 2nd Edition.
- [2] Israel, H. and Israel, G.W.(1974). *Trace Elements in the Atmosphere*, Ann Arbor, Michigan.
- [3] IPCC, 2007.
- [4] Slobodan, N.(2006). *The Use of Satellite and other Observations in a WMO Sand and Dust Storm Warning System(SDSWS)*, Atmospheric Research and Environment Program(AREP), WMO.
- [5] Solomon, S., Portman,R.W., Garcia,R.R., Thomason,L.W., Poole,L.R. and McCormick, M.P.(1996). *The role of Aerosol variations in anthropogenic ozone depletion at northern mid latitudes*, J.Geophys. Res., **101**, D3, 6713.
- [6] Schneider, M.(2002). *Continuous Observations of Atmospheric Trace Gases by Ground-based FTIR Spectroscopy at Izana Observatory, Tenerife Island*, Ph.D. Dissertation, Institut fur Meteorologie Und Klimaforschung, Karlsruhe, Germany.
- [7] Etyemezian, V., et al.(2005). *Results from pilot-scale air quality study in Addis Ababa*, Atmospheric Environment, **39**, 7849-7860.

- [8] Prasa, A.K., Singh, R.P., and Singh, A.(2006). *Seasonal climatology of aerosol optical depth over the Indian subcontinent:trend and departures in recent years*, International Journal of Remotes Sensing, Vol.27, No.12, 2323 - 2329.
- [9] Visconti, G.(2001). *Fundamentals of Physics and Chemistry of the Atmosphere*, Springer-Verlag, Berlin.
- [10] Guzzi, R.(1986). *Introduction to the Electromagnetic Processes in the Atmosphere*, Istituto per lo Studio delle Metodologie Geofisico Ambientali IMGA CNR Via Emilia Est 770 Modena Italy.
- [11] Brimblecomb, P.(1996). *Air Composition and Chemistry*, Cambridge Environmental Chemistry Series 16, 2nd Edition.
- [12] Birhanu, A.(2007). *Modeling Interaction of Radiation with Aerosol using Mie Scattering formulation and Retrieval of Aerosol size parameters*, MSc. thesis, Addis Ababa University.
- [13] Liou, K.N.(2002). *An Introduction to Atmospheric Radiation*, 2nd Edition, International Geophysical Series, Vol.84, Academic press, New York.
- [14] Bakker, W.H., et al.(2000). *Principles of Remote Sensing*, ITC Educational Textbook Series;2, The Netherlands.
- [15] Cheng, A.Y.S. and Voelger, P.(2002). *Aerosol Properties Measured from Sky Radiometer*, Laboratory for Atmospheric Research, Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Ave., Kowloon, Hong Kong.
- [16] Pearson, R.,Fitzgerald, R.M. and Polanco, J.(2007). *An Inverse Reconstruction Model to Retrieve Aerosol Size Distribution from Optical Depth Data*, J.Opt.A: Pure Appl. Opt.**9**, 56-59.

- [17] King, M.D., et al.(1978). *Aerosol Size Distributions Obtained by Inversion of Spectral Optical Depth Measurements*, J. Atmos. Sci., **35**,2153-2167.
- [18] Rodgers, C.D.(2004). *Inverse Methods for Atmospheric Sounding theory and practice*, Series on Atmospheric, Oceanic and Planetary physics, Vol.2.
- [19] Dani, K.K., Maheskumar, R.S. and Devara, P.C.S.(2003). *Study of total Column Atmospheric Aerosol Optical Depth, Ozone and Precipitable water content over Bay of Bengal during BOBMEX-99*, proc. Indian Acad.Sci.(Earth Planet. Sci.), **112**, No.2, PP. 205-221.
- [20] Hase, F., (2000). *Inversion von spurengasprofilen FTIR-Messungen in Absorption*, Dissertation, genehmigt von der Facultat fur physik der Universitat Karlsruhe(TH).
- [21] Chowdhary, J. and Cairns, B.(2002). *Case Studies of Aerosol Retrievals over the Ocean from Multiangle, Multispectral Photometric Remote Sensing Data*.
- [22] Sayer, A.M.(2006). *Aerosol Remote Sensing using AATSR*, Atmospheric, Oceanic and Planetary Physics, Department of Physics, University of Oxford.
- [23] Hobbs, P.V.(1993). *Aerosol-Cloud-Climate Interactions*,University of Washington, Seattel, Washington, Academic Press Inc., Harcourt Brace and Company.
- [24] James, D.S., and King, M.D.(1985). *Latitudinal Variation of Spectral Optical Thickness and Columnar Size Distribution of the El Chichon Statospheric Aerosol Layer*, Journal of Geophysical Research, Vol.90, No.D6, Pages 10,607-10,619.
- [25] Wondimu, A.(2009). *Methane VMR and Climatology of Aerosols over Tropical Latitudes from Remote Sounders*, MSc. thesis, Physics Department, Addis Ababa university.

- [26] Thomason, L.W., Burton,S.P., Luo,B.-P., and Peter, T. (2007). *SAGE II Measurements of Stratospheric Aerosol Properties at non-volcanic Levels*, Atmos.Chem.Phys.Discussion **7**,6959 - 6997.
- [27] Thomason, L.W. and Peter,T. *Report on the Assessment of Stratospheric Aerosol Properties: New Data Record, but no Trend*.
- [28] Meloni, D.(2000). *Optical Properties and Radiative Effects of Tropospheric Aerosols and Ozone in the Central Mediterranean*, Ph.D. Dissertation, University Degli Studi di Roma.
- [29] Jackson, D.J.(1999). *Classical Electrodynamics*,2rd Edition, printed in the United State of America, Wiley.
- [30] Craig, F.B., Donald, R.H.(1983). *Absorption and Scattering of light by Small Particles*, John Wiley and Sons, Inc., New York.
- [31] Mishchenko, M.I., Travis, L.D.,and Lacis, A.A.(2005). *Scattering, Absorption and Emission of light by Small Particles*, Cambridge University Press, New York.
- [32] CCSP, Aerosol Properties and their Impacts on Climate: U.S. Climate Change Science Program, 5-year Assessment Review, Synthesis and Assessment Product 2.3 .
- [33] Fu, Q., et al,(1999). *Aerosol Direct Radiative Forcing: A Five year Climatology at the ARM SGP CART site*, Ninth ARM Science Team Meeting Proceedings, San Antonio, Texas.
- [34] Tzanis, C., and Varotsos, C.A.(2008). *Tropospheric Aerosol Forcing of Climate: a case study for the greater area of Greece*, International Journal of Remote Sensing, Vol.29, No.9, 2507-2517.

- [35] Gadhavi, H. and Jayaraman, A.(2004). *Aerosol Characteristics and Aerosol Radiative Forcing over Maitri, Antarctica*, Physical Research Laboratory, Ahmedabad 380,009, India, Current Science, Vol.86, No.2.
- [36] Yu, H., et al.(2006). *A Review of Measurement-based Assessments of the Aerosols Direct Radiative Effect and Forcing*, Atmos.Chem.Phys., **6**, 613-666 .
- [37] SAGE II Readme file.
- [38] Thomason, L.W., Burton, S.P., Luo, B.-P. and Peter, T.(2007). *SAGE II Measurements of Stratospheric Aerosol Properties at Non-Volcanic Levels*, Atmos. Chem. Phys. Discuss., **7**, 6959-6997.
- [39] Varotsos,C., Efstathiou,M., and Tzanis,C.(2009). *Scaling Behaviour of the global Tropopause*, Atmos.Chem.Phys. **9**, 677-683.
- [40] Seok-Woo Son and Sukyoung Lee(2006). *Intraseasonal Variability of the Zonal-Mean Tropical Tropopause Height*, American Meterological Society, **64**,2695-2706.
- [41] King, M.D., et al.(1080). *Spectral Variation of Optical Depth at Tucson, Arizona between August 1975 and December 1977*, Journal of Applied Meteorology, **19**, 723-732.
- [42] Barkan, J., Kutiel, H. and Apert, P.(2004). *Climatology of Dust Sources in North Africa and the Arabian Peninsula, Based on TOMS data*, Indoor Built Environ., **13**, 407-419.
- [43] Melaku, T.(2009). *Retrieval of Atmospheric Aerosol Optical and Microphysical Parameters from Ground Based Passive and Active Remote Sensing Measurements*, MSc. thesis, Physics Department, Addis Ababa university.

- [44] Anteneh, G.(2009). *The Study of Aerosol Microphysical and Optical Parameters, Total Columnar Ozone and Water Vapor Content using MICROTOPS II*, MSc. thesis, Physics Department, Addis Ababa university.
- [45] Brain,C.S.,(1996). *Fourier Transform Infrared Spectroscopy*, CRC press.
- [46] User Manual of IFS125HR FTIR spectrometer.
- [47] Personal communication with Gregor Surawicz, service Engineer of Bruker Optics GmbH.
- [48] Meier, A.(1997).*Determination of atmospheric trace gas amounts and corresponding natural isotopic ratios by means of ground-based FTIR spectroscopy in the high Arctic.*, a PhD Dissertation, Alfred-Wegener-Institut für Polar-Und Meeresforschung, Forschungsstelle Potsdam, Potsdam.
- [49] Barbar Stuart (2004). *Infrared Spectroscopy: Fundamentals and Applications*, John Wiley and Sons, Ltd.
- [50] Wiacek,A., et al,(2007). *Ground-Based Solar Absorption FTIR Spectroscopy: Characterization of Retrievals and First Results from a Novel Optical Design Instrument at a new NDACC Complementary Station*, Journal of Atmospheric and Oceanic Technology, **24**,432-448.
- [51] Personal communication with Dr. Thomas Blumenstock.
- [52] Hase, F., T.Blumenstock, and C.Paton-Walsh(1991). *Analysis of the instrumental line shape of high-resolution Fourier Transform IR spectrometers with gas cell measurements and new retrieval software*, Appl. Opt., **38**, 3417-3422.
- [53] Griffith, et al, (2003). *Intercomparison of NDSC Ground-based Solar FTIR Measurements of Atmospheric Gases at Lauder, New Zealand*, Journal of Atmospheric and Oceanic Technology, **20**, 1138-1153.

- [54] "Chemical Summary for Carbonyl Sulfide" prepared by Office of Pollution prevention and Toxics U.S. Environmental Protection Agency, August 1994.
- [55] Mian Chin and D.D.Davis, (1995). *A reanalysis of carbonyl sulfide as a source of stratospheric background sulfur aerosol*, Journal of Geophysical Research, **100**, 8993-9005.
- [56] Gunther Uher and Meinrat O.Andreae (1997). *Photochemical Production of Carbonyl Sulfide in North Sea Water: A Process Study*, the American Society of Limnology and Oceanography, Inc.
- [57] J. Notholt et al, (2006). *Spectral line finding program for atmospheric remote sensing using full radiation transfer*, Journal of Quantitative Spectroscopy and Radiative Transfer **97**, 112-125.
- [58] K. Sung et al, (2007). *N₂O and O₃ arctic column amounts from PARIS-IR observations: Retrievals, characterization and error analysis*, Journal of Quantitative Spectroscopy and Radiative Transfer **107**, 385-406.
- [59] M.Ayidin, et al, (2008). *Carbonyl sulfide in air extracted from a South Pole ice core: a 2000 year record*, Atmospheric Chemistry and Physics Discussion, 7533-7542.
- [60] M. L. White et al, (2010). *Carbonyl sulfide exchange in a temperate loblolly pine forest grown under ambient and elevated CO₂*, Atmospheric Chemistry and Physics Discussion, **10**, 547-561.
- [61] Barkley, et al, (2008). *Global distributions of carbonyl sulfide in the upper troposphere and stratosphere*, Geophysical Research Letters, **35**, 1-7.
- [62] C.P.Rinsland, et al, (2008). *Measurements of long-term changes in atmospheric OCS(carbonyl sulfide) from infrared solar observations*, Journal of Quantitative Spectroscopy and Radiative Transfer, **109**, 2679-2686.

- [63] S. A. Montzka. *On the Relation Between Atmospheric Carbonyl Sulfide and Carbon Dioxide.*
- [64] Kuhn, U. and Kesselmeier, (2000). *Environmental variables controlling the uptake of carbonyl sulfide by lichens*, Journal of Geophysical Research, **105**, 26, 783-26, 792.
- [65] Nicola J. Blake et al, *Carbonyl sulfide (OCS): Large scale distributions over North America during INTEx-NA and relationship to CO₂*, 1-30.

Declaration

This thesis is my original work, has not been presented for a degree in any other University and that all the sources of material used for the thesis have been dully acknowledged.

Name: Milkessa Gebeyehu Homa

Signature:

Place and time of submission: Addis Ababa University, July 2010

This thesis has been submitted for examination with my approval as University advisor.

Name: Dr.Gizaw Mengistu

Signature: