

TROPOSPHERIC OZONE OVER TROPICAL
LATITUDES: MEASUREMENTS AND 1-D STEADY
STATE CHEMISTRY MODEL

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By

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To Enani and Muzie

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Abstract

Atmospheric ozone is of interest not just because of the danger of ozone depletion in stratosphere but also because of its basic role in tropospheric chemistry and oxidation reactions, in controlling the temperature structure of atmosphere through absorption in the solar and terrestrial infrared radiation and air pollution along with various gases. The distribution of ozone in troposphere is resulted mainly from the interaction of various atmospheric gases, transport and chemistry and radiation processes. A full description of photochemistry ozone would be very complicated since hundreds of chemical species and reactions, many of which are interlinked, have to be included. In view of these facts, tropospheric ozone over tropics is retrieved from solar spectral radiance measurements by Fourier Transform Infrared Spectrometer (FTIR) onboard German Polar and Marine Research Vessel (Polarstern) during the 1996 expedition. 1-D steady state chemistry model is also used to determine tropospheric ozone over tropics. The retrieved tropospheric ozone distribution agrees with existing understanding that ozone is produced over tropics and transported to higher latitudes by general atmospheric circulation. The 1-D steady state chemistry model prediction is able to capture the main features of the retrieved ozone profile at altitude below 6 km. However, discrepancy between 1-D model and measurement above this altitude might be an indication of inadequacy of 1-D chemistry model.

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Introduction

The rapidly changing concentration and distribution of trace gas composition in the earth's atmosphere in the recent decades leads to an increase in atmospheric researches. In particular, a great effort have been directed toward the measurement of trace gases. Trace gases played a great role in atmospheric composition, chemical reaction, radiative interaction, climate change and pollution even if their abundance is very low. Knowledge of these trace gases is important to understand and quantify the atmospheric changes, such as global warming, atmospheric pollution and change in the chemical composition of the troposphere. The atmospheric compositions have rapidly increased due to an increase of fossil fuel combustion and biomass burning emissions of trace gases such as carbon dioxide (CO_2), carbon monoxide (CO), Nitrogen oxides($\text{NO}_x=\text{NO}+\text{NO}_2$), methane (CH_4), sulphur dioxide (SO_2) and non-methane hydrocarbon compounds (NMHCs). The emission of hydrocarbon compounds into the atmosphere contributes to the chemical production of ozone (O_3) in troposphere which can cause atmospheric pollution and green house effect.

Ozone in tropical region in fact plays various important roles in atmospheric photochemical and radiative processes. Ozone is a toxic gas, and is an absorber of radiation at ultra violet, visible, and infrared wavelengths. Ozone in the upper troposphere and lower stratosphere acts as a green house gas. Because of these characteristics ozone

sometimes referred to as 'good' ozone while tropospheric ozone is referred to as 'bad' ozone. It is primarily a source of hydroxyl free radical (OH), which acts as a detergent in the atmosphere, initiating almost all oxidation reaction processes in the removal of atmospheric pollutants and toxic gases in tropical region [2]. Ozone strongly absorbs UV-radiation in the wavelength bands from 0.20 to 0.32 μm and in the visible region between 0.45 and 0.70 μm wavelengths [3,4,5]. Absorption of UV by ozone shields the earth's system from harmful UV-radiation and acts as a source of heating up in the air in stratosphere. Because OH-radical is formed from troposphere ozone, and both are sensitive to UV-radiation and, therefore, to the overhead abundance of ozone. Thus, one consequence of stratospheric ozone depletion is increase in UV-radiation and the change of tropospheric chemistry. Finally, the photochemical processes in troposphere and stratosphere must be viewed as fully coupled, because the troposphere is also the chemical filter for surface emitted species in their way to stratosphere.

However, near the ground level excess amount of ozone concentration can cause toxicity and atmospheric pollution to the earth's ecosystems and life. In the upper free troposphere, it absorbs the terrestrial infrared radiation at wavelengths around 9.6 μm . Thus ozone is an effective green house gas as important as the green house gases like methane. Essentially no ozone emitting sources of natural or anthropogenic directly into the troposphere, rather than it is formed in the troposphere through a complex chain of reaction initiated by UV-radiation with the involvement of NO_x , and volatile organic compounds (VOCs). This series of complex reaction is known as 'photochemical smog' reaction. The photochemical smog is primarily determined by an abundance of nitrogen oxides and volatile organic compounds in the atmosphere and the presence of particular environmental conditions. The processes of smog occur

in the simultaneous presence of Sun light, production of oxides of nitrogen (NO_x), production of volatile organic compounds and temperature exceeding 18°C (room temperature). If these criteria are met, several photochemical reactions will occur and produce toxic chemical constituents of smog products. The most dominant smog product constituents are ozone and peroxy-acetyl nitrate (PAN).

Despite complex tropospheric chemistry and atmospheric dynamics, a lot of effort have been done to understand processes regulating tropospheric ozone over tropics. As part of this continued effort we will try to study tropospheric ozone distribution both from measurement and 1-D steady state chemistry model.

Review of tropospheric ozone is given in chapter one. Chapter two discusses the radiative transfer process in the atmosphere and model to be used in conjunction with the measurement. Chapter three covers general retrieval theory and its variant used in this thesis; and results and discussion are given in chapter four. Finally, we give summary and conclusion of our study in chapter five.

Chapter 1

Tropospheric Chemistry

In this chapter, a brief introduction to atmospheric composition, layers and distribution are given followed by detailed discussion on tropospheric chemistry.

Atmosphere is thin layer of gaseous envelop surrounding the earth's surface. It is composed of a myriad of gaseous constituents. Some of the gaseous constituents in the atmosphere are listed in Table 1.

From Table 1, it is possible to observe that the major gases are nitrogen, oxygen, and argon which account for about 99.966% of the total volume of atmospheric gases. Because of their high abundance, the major gases are permanent in the atmosphere. The minor gases exhibit spatial and time dependent variation. Because of their small contribution to the total volume of atmosphere, they are called trace gases. The earth's atmosphere is divided into four regions, very different in their structures, thermodynamics, photochemistry and dynamics. The partition is best related to atmospheric vertical temperature profile, whose points of inflection are used to distinguish the four regions starting from the ground.

Troposphere is the lower part of the atmosphere. Its thickness is about 9 km over the

Chemical species	Formula mass(g/mole)	Percentage by volume
N_2	28	78
O_2	32	21
Ar	30.9	0.934
H_2O (vapor)	18	0.5
CO_2	44	360ppm
CH_4	16	1.7ppm
O_3	48	0.5ppm
N_2O	44	0.31ppm
CO	28	0.12ppm
NO_2	46	0.001ppm
SO_2	64	0.2ppm

Table 1.1: The most important atmospheric constituents.

polar region and about 20 km over the equator. Temperature decreases with altitude (0.6-0.9°C/100 m). Almost all of the weather activities occur in troposphere. High convective and turbulent processes also characterize troposphere. Because the pressure decreases exponentially with altitude, $P(z) = P(0)\exp(-\frac{z}{H})$, where z is altitude in km, H is the scale height given by $\frac{RT}{mg}$, it contains about 80% of the total mass of the atmosphere. This region is rich in myriad of major and minor constituent gases. Most of the photochemical and physical changes of the atmosphere are taking place in this region. As a result, troposphere is also called the chemical reservoir of the atmosphere. In troposphere there are large number of trace gases in addition to the permanent nitrogen and oxygen gases. These trace gases such as carbon dioxide, nitrogen oxides, ozone, methane, etc. have great influence on climate of the earth, photochemical and dynamical processes. In particular the way these trace gases interact with each other and with the earth's surface including human activities characterize the chemical and physical properties of the troposphere. Some of the most important trace gases in

troposphere which determine the chemical processes are ozone, hydroxyl radical, water vapor, atomic oxygen, oxides of nitrogen etc. Knowing the physical and chemical properties of these active gases is important to understand atmospheric phenomena.

Stratosphere is the second layer of the atmosphere. Its thickness rise up to 50 km altitude with increasing temperature. The increase in temperature is due to the existence of natural ozone layer in which high absorption of UV-radiation from the sun takes place. Because of small variation in temperature vertical circulation of air is prevented. Mesosphere is the third region above an altitude of 50 km, in which temperature increases with altitude. A minimum of temperature of the atmosphere occurs at about 80 to 90 km in this region. Thermosphere is the fourth layer in which temperature increases with altitude. The maximum temperature of the atmosphere occurs at about 500 km in this region.

1.1 Source of Tropospheric Ozone

Knowing the origin and fate of tropospheric ozone (O_3) is critically important to understand the climatic and photochemical processes in troposphere and the fate of pollution in it. The production of ozone in the troposphere depends on the presence of CO, hydrocarbons, NO_x and light. hence tropospheric ozone can serve as a tracer of tropospheric pollution. Therefore, the sources of ozone in troposphere are twofold. The first is the downward transport from stratosphere where ozone is formed naturally. The second source is in situ chemical production through the process of photochemical smog.

Before we discussed the in situ chemical production of ozone in detail, it is important to review a few points about the physical and chemical properties and its formation in stratosphere.

1.1.1 Distribution and absorption bands of Ozone

Ozone in the atmosphere is very important for different reasons. Ozone absorbs UV-radiation very strongly, large amount of solar radiation from sun is absorbed by stratospheric ozone. The absorbed UV heats the air in the region and causes the warm temperature around 50 km altitude. Ozone in the atmosphere has also strong absorption band in the infrared region around $9.6 \mu\text{m}$ due to its vibrational and rotational transitions. In this case ozone has a great contribution to green house effect in upper troposphere at high concentration. When it is at elevated concentration in troposphere it causes pollution and has harmful effect to life on the earth. Besides ozone is a key component in troposphere in relation to atmospheric chemistry, because it initiates chemical reaction and is a cause for the formation of the most important free radical called hydroxyl-ion (OH).

The amount of ozone in the atmosphere at any place is found to vary considerably from day to day. Even-though most of it is found above tropopause, yet, these variation is found to be closely related with variation in the weather condition. In addition to the day-to-day variations, ozone has unexpected type of annual variation and its distribution over the world is equally unexpected. From these variations with seasons and latitude, it has been possible to deduce the general world wide circulation of the air between the troposphere and the stratosphere [6].

While ozone is a form of oxygen, its properties are very different from those of normal oxygen. Ozone is very unstable molecule and easily oxidized. A large amount of heat is required to form ozone from the reaction of atomic oxygen and normal oxygen molecule. This energy is given up again when ozone returns to the normal oxygen. Pure ozone is actually explosive and will detonate under suitable condition. Generally ozone is very reactive, strong oxidizing agent and unstable molecule.

The most important physical properties of ozone in the atmosphere is absorption of solar radiation in different parts of the spectrum. It absorbs solar radiation very strongly in the ultraviolet (UV) region between 220 nm and 330 nm. The peak absorption, in this region, occurs at wavelengths of about 250 nm. The small amount of ozone in the atmosphere effectively cut-off the UV-radiation of the sun whose wavelength is less than 300 nm. It is this absorption of the solar radiation that is the cause of the formation of the warm region in the stratosphere at about 50 km altitude. If it were not for this absorption the ecosystems on the earth's surface would be exposed to excessive sunburn. Ozone absorbs radiation in the yellow-green region of the visible parts of the spectrum [6]. Because, the absorption in this spectrum is rather weak, yet, it occurs in part the spectrum where the amount of incoming radiation has maximum intensity. Thus, the absorption provides appreciable warming in the troposphere where relatively high concentration of ozone is found. The most important region of absorption band of ozone is in the infrared part of the spectrum, chiefly at wavelengths around $9.6 \mu\text{m}$. The absorption in this band occur in the incoming solar radiation partly and in the out-going terrestrial radiation in the lower atmosphere.

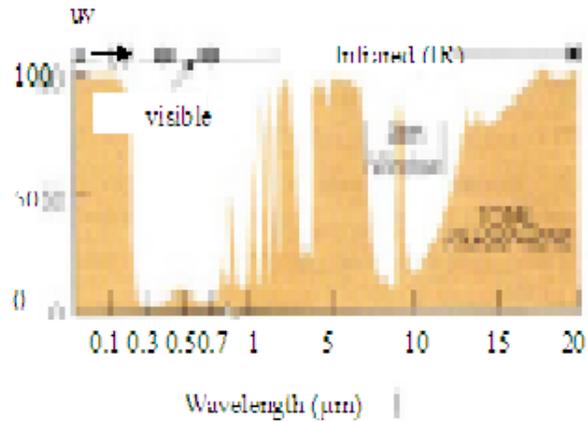
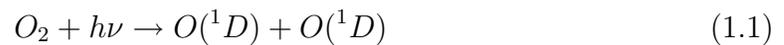


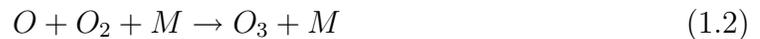
Figure 1.1: Absorption region of solar radiation

1.1.2 Formation of Ozone

Ozone occur naturally in the stratosphere above 30 km altitude where UV-radiation of wavelengths less than 240 nm slowly dissociates molecular oxygen into atomic oxygen [7,8].



The oxygen atom (O) in turn reacts rapidly with the molecular oxygen (O_2) in the presence of intermediate molecule (mainly O_2 or N_2) to conserve energy (momentum) to form ozone.



This reaction is, for all practical purpose, the only reaction which produce ozone in the atmosphere either in the stratosphere or troposphere. The ozone molecule produced in (1.2) strongly absorbs radiation in the wavelength range between 240 nm

and 320 nm to decompose back to O and O₂ rapidly as in:



Finally ozone can recombine with oxygen atom to regenerate two oxygen molecules, (O₂), but the reaction is very slow



This reaction is the main sink for ozone in the upper atmosphere (stratosphere). The reaction cycles for the production of ozone in stratosphere was first proposed by an English physicist Chapman in 1930. This reaction cycle is nowadays known as Chapman cycle.

From the analysis of kinetic reaction, reaction (1.1) is the source of oxygen atom with reaction rate, $j_{O_2}[O_2]$. Once the oxygen atom is formed reaction (1.2) proceeds with rate of reaction $K_{1.2}[O][O_2][M]$ to form the ozone molecule. The ozone molecule in turn photolyzed (1.3) with rate of reaction j_{O_3} or reacts with oxygen atom in (1.4) with reaction rate $K_{1.4}$.

The net formation of ozone is, then

$$\frac{d[O_3]}{dt} = K_{1.2}[O][O_2][M] - j_{O_3}[O_3] - K_{1.4}[O][O_3] \quad (1.5)$$

and the balance of oxygen atom is given by

$$\frac{d[O]}{dt} = 2j_{O_2}[O_2] - K_{1.2}[O][O_2][M] + j_{O_3}[O_3] - K_{1.4}[O][O_3] \quad (1.6)$$

Many chemical reactions involve very reactive intermediate species such as free radicals, which, as result of their high reactivity, are consumed virtually as rapidly as they

are formed and consequently exist at very low concentrations. Under this condition the pseudo-steady-state approximation (PSSA) is a fundamental way of dealing with such reactive intermediates when deriving the overall rate of reaction mechanisms [7].

Thus, once oxygen atoms are produced in (1.1), reactions in (1.2) and in (1.3) proceed relatively very rapid, and the characteristic time for these reactions also relatively very short [5]. Because of the rapidity of reactions in (1.2) and in (1.3) the conversion between O and O₃ is very fast. These oxygen atom species which interconvert to each other are called Odd-Oxygen Species and denoted by O_X(O + O₃). Odd oxygen species are produced in (1.1) and are destroyed in (1.4), since the reaction cycles in (1.2) and (1.3) occur many times before reaction (1.4) takes place. For such reasons the equilibrium conditions for rate of reactions are determined by reactions (1.2) and (1.3) approximately. Such equilibrium condition is said to be pseudo (quasi) steady-state approximation (SSA). The pseudo steady state concentration for oxygen atom from (1.2) and (1.3) is given by

$$\frac{[O]}{[O_3]} = \frac{j_{O_3}}{K_{1.2}[O_2][M]} \quad (1.7)$$

The rate of production of ozone is approximated by the rate of odd-oxygen production and destruction reactions (1.1) and (1.4) respectively, because odd-oxygen is produced by reaction (1.1) and destroyed in (1.4). Thus steady state approximation for ozone is given by

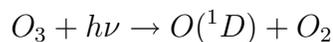
$$[O_3]_{ss} = [O_2] \sqrt{\frac{K_{1.2}[M]j_{O_2}}{K_{1.4}j_{O_3}}} \quad (1.8)$$

Then the Chapman mechanism for stratospheric ozone approximation is proportional to the square root of oxygen photolysis rate constant j_{O_2} . The rate of ozone formation is a function of altitude, latitude, solar intensity and solar zenith angle.

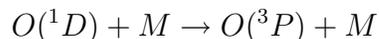
1.2 Formation of Ozone in Troposphere

The troposphere behaves as a chemical reservoir of the atmosphere. The transport of species from troposphere into stratosphere is much slower than the mixing of species within the Troposphere itself. A myriad of species are emitted into it from the earth surface naturally and anthropogenically. Unlike stratosphere, removal and formation of ozone is central to the chemical interaction of troposphere [7,8].

The oxidizing capacity of the atmosphere is determined by the concentration of the reactive oxidants of hydroxyl (OH), ozone (O_3), nitrate radical (NO_3), excited oxygen atom ($O(^1D)$) and organic peroxide (ROOH) [7]. The main oxidizing agent in the gas phase reaction is OH-radical. Other species such as $O(^1D)$, NO_3 -radical and O_3 also contributes but they are less important. For troposphere species dissolved in aqueous form, the most important oxidizing gases (OH, O_3 , and H_2O_2 -radical) are produced in gaseous phase reaction when ozone is photolyzed in the presence of water vapor (H_2O):



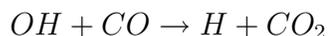
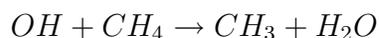
Large amount of $O(^1D)$ produced is stabilized by air molecule and finally react with O_2 to produce O_3 as in the following reaction:



A few amount of $O(^1D)$ reacts with $H_2O(g)$ to yield two OH-radicals :



The OH-radical is very reactive and is responsible for the transformation and initiation of the removals of many important atmospheric trace gases. For example the main sinks for CH_4 and CO are the reaction with OH-radical. CO and CH_4 undergoes a low temperature oxidation reaction as follows.



The reaction path way between OH and CO, CH_4 and NMHC at optimal conditions initiates production of tropospheric ozone, since HO_2 and RO_2 radicals are resulted in chain reaction.

In troposphere, the dominating oxidizing reaction of NO to NO_2 is through the reaction with O_3 :



In the presence of UV-B light with wavelength less than 400 nm, NO_2 is photolyzed into NO and atomic oxygen:



The atomic oxygen may recombine with abundant oxygen molecule to produce ozone [7] as in:



The kinetic rate of reaction for NO_2 in (1.10) and (1.11) gives

$$\frac{d[NO_2]}{dt} = -j_{NO_2}[NO_2] + K_{1.10}[NO][O_3] \quad (1.12)$$

where j_{NO_2} is NO_2 photolysis rate constant and $K_{1.10}$ is the reaction rate constant of the reaction between NO and O_3 . In photochemical reactions among NO, NO_2 , O_3 and solar radiation, the reaction in (1.11) is very rapid. So, applying steady state approximation for rapid reaction is fundamental to calculate the steady state ozone concentration $[O_3]_{SS}$ as

$$[O_3]_{SS} = \frac{j_{NO_2}[NO_2]}{K_{1.10}[NO]} \quad (1.13)$$

This equation accounts for lower $\frac{[NO_2]}{[NO]}$ ratio during the day time and higher $\frac{[NO_2]}{[NO]}$ ratio at night time. This confirms that without NO_2 and its photolysis there is no formation of ozone in troposphere.

The quasi-steady state equation can be further simplified by applying the conservation of mass action and stoichiometric reaction as follows. From the conservation of mass action for nitrogen oxides, we get

$$[NO]_0 + [NO_2]_0 = [NO] + [NO_2] \quad (1.14)$$

Solving for $[NO]$ and substituting into the steady-state solution in (1.13) yields

$$[O_3]_{SS} = \frac{j_{NO_2}[NO_2]}{K_{1.10}\{[NO]_0 + [NO_2]_0 - [NO_2]\}} \quad (1.15)$$

From stoichiometric reaction of O_3 with NO , we obtain

$$[O_3]_0 - [O_3] = [NO]_0 - [NO] \quad (1.16)$$

Now solving (1.14) and (1.16) simultaneously and substituting for NO_2 in (1.15) and finally solving a resulting quadratic equation, we get

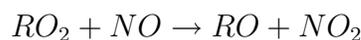
$$[O_3]_{SS} = \frac{j}{2K} \sqrt{\left(\frac{K}{j}([NO]_o - [O_3]_o) + 1\right)^2 + \frac{4K}{j}([O_3]_o + [NO_2]_o) + \frac{K}{j}([O_3]_o - [NO]_o) - 1} \quad (1.17)$$

We used $j_{NO_2} = j$ and $K_{1.10} = K$ for convenience of writing. If we assume that initially $[NO]_o = [O_3]_o = 0$ then (1.17) become

$$[O_3]_{SS} = \frac{j}{2K} \left[\sqrt{1 + \frac{4K}{j}[NO_2]_o} - 1 \right] \quad (1.18)$$

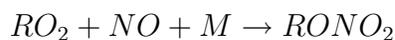
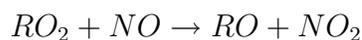
In the lower region of troposphere the only exclusive source of NO_2 is the reaction in (1.10) and NO that feeds this reaction originates from the emission that resulted from natural and human activities such as combustion of fossil oils/fuels and biomass burning. Virtually there are no sources that emit NO_2 directly into the atmosphere. Therefore, nitric oxides (NO) from anthropogenic sources are essential sources of

regional formation because it produces NO_2 which photolyzed to produce O_3 . Moreover, NO is an essential sinks for ozone because its reaction with tropospheric ozone regenerates NO_2 . So the reaction processes in (1.2) and (1.10) do not lead to a net accumulation of ozone unless another mechanisms exist that oxidize NO into NO_2 with out consumption of ozone. However, there is a chemical reaction path way that leads to a chemical oxidation of anthropogenic ally emitted compounds of CO, CH_4 , VOCs and other hydrocarbon compounds with OH-radical which resulted in H-atoms and alkyl radicals. These radicals readily react with oxygen molecules to form alkyl proxy radicals. The peroxy radicals oxidize NO into NO_2 in general form [7,8]:



where R = H , CH_3 , CH_2CH , etc.

Under tropospheric conditions, alkyl proxy radicals (RO_2) readily undergo a chemical reaction with NO through two chemical path ways shown below.



1.3 Photolysis Reaction

Solar radiation derives the chemistry of the atmosphere. These reaction that involves the breaking down of a chemical bond by an incident photons are called photolysis reaction.



where X is the chemical specie photolyzed by absorbing a photons of radiation $h\nu$ and Y and Z are the products of photo-dissociation of specie x.

The rate of reaction is:

$$-\frac{d[X]}{dt} = \frac{d[Y]}{dt} = \frac{d[Z]}{dt} = j_x[X] \quad (1.20)$$

where j_x is the photolysis rate constant for the reaction of specie x photolyzed in units s^{-1} .

In order to calculate the rate of photochemical reaction we need to know the number of photons absorbed per unit volume of air containing the given specie of concentration [X] (molecule cm^{-3}) an absorbing molecule, the absorption cross section area of the specie σ_x , which is defined as absorption coefficient divided by the number density of the specie, (in $cm^2 molecule^{-1}$), the quantum yield $\Phi_x(\lambda)$, which is defined as the ratio of number of molecules undergoing the process of dissociation to the number of photons absorbed (molecules $photon^{-1}$) and the spectral actinic flux, $I(\lambda)$, the number of photons crossing a unit surface area per unit time from any direction (photons $cm^{-2}s^{-1}nm^{-1}$).

Thus the rate of photolysis in the wavelength region λ to $\lambda + d\lambda$ is

$$\Phi_x(\lambda)\sigma_x(\lambda)I(\lambda)d\lambda[X] \quad (1.21)$$

The total photolysis rate of the specie x is expressed over all possible wave lengths

$$\left(\int_{\lambda_1}^{\lambda_2} \Phi_x(\lambda)\sigma_x(\lambda)I(\lambda)d\lambda \right)[X] \quad (1.22)$$

where λ_1 and λ_2 are, respectively, the shortest and the longest wavelengths at which absorption occurs. For troposphere, for example $\lambda_1 = 290$ nm.

The quantity in (1.22) under brackets is identified as the first order photolysis rate constant, j_x

$$j_x = \int_{\lambda_1=290nm}^{\lambda_2} \Phi_x(\lambda)\sigma_x(\lambda)I(\lambda)d\lambda \quad (1.23)$$

The calculated values of $j_{NO_2} = 8 \times 10^{-3}s^{-1}$ if $\lambda > 310$ nm while at 298 K, and the values of the reaction rate coefficient in (1.10) is approximated, $K_{1.10} = 1.8 \times 10^{-14}cm^3molecule^{-1}s^{-1}$ [7]. We will use these constants in the final estimation of the tropospheric ozone profile in (1.13) of 1-D steady state chemistry model.

In this chapter, we have given detail account of tropospheric ozone chemistry from which 1-D steady state chemistry model involving ozone is systematically deduced. This 1-D steady state chemistry will be used together with measurements to estimate tropospheric ozone. The next chapter will discuss the general radiative transfer equation of the atmosphere and spectrally how the physical model is adapted to the measurement system (FTIR) to reproduce the observed solar spectral radiances.

Chapter 2

Atmospheric Radiative Transfer Theory

Atmospheric radiative theory concerns about the interaction of EM-radiation energy with the material medium through which it propagates. The interaction processes can result in absorption, emission or scattering of radiation in the form of photon energy [9]. The knowledge of radiation interaction processes with atmospheric constituents helps to study the chemical compositions, physical structure of the gaseous medium through which it travels. In particular the atmospheric compositions and climate changes are illustrated by the interaction of solar and terrestrial radiation with atmospheric constituents. A molecule that absorbs a quantum of radiation becomes excited in the absorption process. Absorption in short wavelength region lead to electronic transition (excitation) and at a longer wavelengths initiates vibration or rotational excitation of molecules from their ground states.

In the next sections the theory of radiative transfer in the atmosphere will be introduced in great depth. At the end of this chapter basic radiative transfer equation used for our observation geometry will be presented.

2.1 Radiative Transfer Equations

Radiative transfer equations (RTEs) are the mathematical description for the processes of transfer of EM-radiation through the gaseous atmosphere and its interaction with the atmosphere. In quantum mechanics atoms/molecules thought to have an infinite number of energy levels. The particles/electrons in an atom/molecule may exist in any one of infinite number of quantized energy levels (states) ranging from ground state to the continuum of the atom. A complete understanding of the interaction of radiation with matter (i.e. molecules, atoms, etc.) would therefore require including all these states.

2.1.1 Two level atom

Basically interaction of radiation with matter and radiative transfer processes occur due to absorption or emission of photons energy. Here we attempted to derive a simple RTE for atmospheric process by considering a spectral radiation of frequency, ν , being absorbed or emitted by atmospheric gas which is assumed to consists of a 2-level model of atoms/molecules having energy difference, $h\nu_0$, between upper and lower states [10]. For the sake of simplicity let's constrain ourselves to the model of an atmosphere which have no mass motion i.e. the volume element of the atmosphere is fixed in space and only radiation goes in and out.

Let's proceed the derivation of RTE by assuming that the number of photons of frequency, ν , at a time, t , entered one end of the cylindrical volume element of

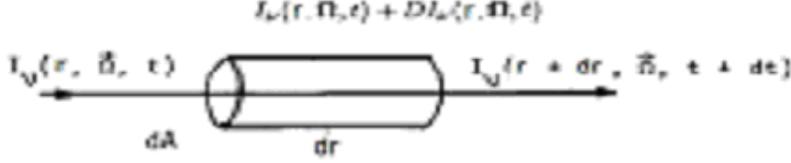


Figure 2.1: Emission and Absorption of Photons

atmospheric gas across cross sectional area, δA , is $\rho(\vec{r}, \nu, \Omega, t)\delta A$. The corresponding number of photons leaving the volume element at the other end is then, $\rho(\vec{r} + \delta\vec{r}, \nu, \Omega, t + \delta t)\delta A$; where t is the time interval for photons to traverse a distance, r , from one end to the other, $\delta\vec{r} = c\delta t$, c is the speed of photons in the atmospheric medium and $\rho(\vec{r}, \nu, \Omega, t)$ is the photons of frequency, ν at a point in a time, t .

An equation involving the change in number of photons across the cylindrical volume from \vec{r} to $\vec{r} + \delta\vec{r}$ is

$$\rho(\vec{r} + \delta\vec{r}, \nu, \Omega, t + \delta t)\delta A - \rho(\vec{r}, \nu, \Omega, t)\delta A \quad (2.1)$$

Quantum mechanical theory reveals that the radiative interaction processes in atoms or gases involve absorption of photons, stimulated and spontaneous emissions of photons as electrons/particles transfer from one energy levels to another [10,11]. This shows that photons can be added or withdrawn from the beam of radiation as it traverses through the volume element of the gas in consideration. Hence the number of photons added into the beam of radiation per unit time due to stimulated and spontaneous emission at frequency, ν , in the direction of, $\hat{\Omega}$, is

$$(\beta_1 N_u A_{ul} j(\nu, \omega) + \beta_2 N_u \rho(\vec{r}, \nu, \Omega, t) \psi(\nu, \Omega)) \cdot \delta r \delta A \quad (2.2)$$

where $N_u \delta r \delta A$ total number of atoms/molecules in the cylindrical volume element capable to emit photons due to stimulation or spontaneously and A_{ul} is coefficient for spontaneous emission. $j(\nu, \Omega)$ and $\psi(\nu, \Omega)$ are probabilities of photons emission at frequency, ν in the direction, $\hat{\Omega}$, of respectively, N_u , number of atoms in the upper state, and β_1 and β_2 are constants. Similarly the total number of photons withdrawn from the beam during the interaction process due to absorption is

$$\beta_3 N_l \rho(\vec{r}, \nu, \Omega, t) \phi(\nu, \Omega) \delta r \delta A \quad (2.3)$$

$\phi(\nu, \Omega)$ is the probability of photons at frequency, ν , traveling in the direction of, $\hat{\Omega}$, being absorbed, and N_l number of atoms in the lower state β_3 is also another constant.

The net change of photons due to emission and absorption as the beam traverses across the cylinder is

$$\beta_1 N_u A_{ul} j \delta r \delta A + (\beta_2 N_u \psi - \beta_3 N_l \phi) \rho \delta r \delta A \quad (2.4)$$

where $\beta_1, \beta_2, \beta_3$ are constants as described earlier.

Now let's define the intensity, I , of an EM-radiation such that $I(r, \nu, \Omega, t)$ is the energy flux of frequency, ν , along the direction of, $\hat{\Omega}$, traveling across the elemental area, δA , per unit time. We know that any radiation field can be expressed as a superposition of monochromatic field with different polarization of the electromagnetic fields that interact with the quantum system [10,11,12]. It is clear that the photon density is related to the energy density of the field in such way that each photons at frequency, ν , carries a quantum energy of magnitude $h\nu = \hbar\omega$. The energy density of the radiation field is

$$|\vec{S}| = \frac{c}{4\pi} |\vec{E} \times \vec{B}| \quad (2.5)$$

where \vec{E} and \vec{B} are electric and magnetic field respectively.

$$\vec{E}(r, t) = E_0(\omega)\hat{\epsilon}\sin(\hat{k}.r - \omega t)$$

and

$$\vec{B}(r, t) = \frac{E_0(\omega)}{\omega}(\hat{k} \times \hat{\epsilon})\sin(\hat{k}.r - \omega t)$$

where ω is frequency of radiation, \hat{k} is unit wave vector, $\hat{\epsilon}$, direction of polarization and E_0 is amplitude of electric field. Then, the energy density is

$$|\vec{S}| = \frac{1}{2}\left\{\epsilon_o|E^2| + \frac{|B^2|}{\mu_o}\right\} = \epsilon_o E_o^2(\omega)\sin^2(\hat{k}.r - \omega t) \quad (2.6)$$

from which the average energy density, $\rho(\omega)$, is determined to be

$$\rho(\omega) = \frac{1}{2}\epsilon_o E_o^2(\omega) \quad (2.7)$$

If the number of photons of frequency, ν , with in the volume δV is $N(\nu)$ then the energy density is

$$h\nu\frac{N(\nu)}{\delta V}.$$

which implies

$$|E_o|^2 = \frac{4\pi\rho(\nu)}{\epsilon_o} \quad (2.8)$$

This indicates that the intensity of radiation is proportional to the square of the magnitude of the radiation field, i.e.

$$I \propto |E|^2$$

Using the proportionality constant α and (2.7) the intensity becomes

$$I = \alpha\rho(\vec{r}, \nu, \hat{\Omega}, t) \quad (2.9)$$

From (2.1) and (2.2) we can get the change in number of photons in the volume element δV to be given by

$$[\rho(\vec{r}, \nu, \hat{\Omega}, t) - \rho(\vec{r} + \delta\vec{r}, \nu, \hat{\Omega}, t + \delta t)]\delta A = [\beta_1 N_u A_{ul} j + \beta_2 N_u \rho \psi - \beta_3 N_l \rho \phi] \delta r \delta A \quad (2.10)$$

using (2.9), (2.10) becomes

$$I(r, \nu, \Omega, t) - I(r + \delta r, \nu, \Omega, t + \delta t) = (\alpha\beta_1 N_u A_{ul} j + \gamma N_u B_{ul} I \psi - \gamma N_l B_{lu} I \phi) \delta r \quad (2.11)$$

where we defined a new constant γ such that

$$\beta_2 = \gamma B_{ul}$$

$$\beta_3 = \gamma B_{lu}$$

Now we can rewrite (2.11) as

$$I(r, \nu, \Omega, t) - I(r + \delta r, \nu, \Omega, t + \delta t) = \gamma(N_u A_{ul} j + N_u B_{ul} I \psi - N_l B_{lu} I \phi) \delta r \quad (2.12)$$

Applying Taylor expansion to the right side of (2.12), we obtain

$$I(r, \nu, \Omega, t) - I(r + \delta r, \nu, \Omega, t + \delta t) = -\frac{\partial I}{\partial r} dr - \frac{\partial I}{\partial t} dt \quad (2.13)$$

Substituting from (2.13) into (2.12) we get

$$-\frac{\partial I}{\partial r} dr - \frac{\partial I}{\partial t} dt = \gamma(N_u A_{ul} j + N_u B_{ul} I \psi - N_l B_{lu} I \phi) dr \quad (2.14)$$

where $dr = c dt$.

Finally (2.14) becomes

$$-\frac{\partial I}{\partial r} - \frac{\partial I}{c \partial t} = \gamma(N_u A_{ul} j + N_u B_{ul} I \psi - N_l B_{lu} I \phi) \quad (2.15)$$

This is the differential form of Radiative Transfer Equation (RTE). Since excitation or de-excitation process undergoes through absorption or emission of photons of energy,

$h\nu$, throughout an angle of 4π -radians (a total solid angle, the constant γ -should be $\gamma = \frac{h\nu}{4\pi}$ for a particular direction of angle $\hat{\Omega}$ [9,10], so that (2.15) becomes

$$\frac{\partial I}{\partial r} + \frac{\partial I}{c\partial t} = \frac{h\nu}{4\pi}(N_l B_{lu}\phi - N_u B_{ul}\psi)\left[I - \frac{N_u A_{ul}j}{N_l B_{lu}\phi - N_u A_{ul}\psi}\right] \quad (2.16)$$

where A_{ul} , B_{ul} and B_{lu} are Einstein coefficients for spontaneous emission, stimulated emission and absorption respectively. For transition of two level states [10,11]

$$g_l B_{lu} = g_u B_{ul} \quad (2.17)$$

where g_i is weight function of the i^{th} state. Substituting (2.15) into (2.14) we can get

$$\frac{\partial I}{\partial r} + \frac{\partial I}{c\partial t} = \frac{h\nu}{4\pi}N_l B_{lu}\left(\phi - \frac{g_l N_u}{g_u N_l}\psi\right)\left[I - \frac{N_u A_{ul}j}{N_l B_{lu}\left(\phi - \frac{g_l N_u}{g_u N_l}\psi\right)}\right] \quad (2.18)$$

we know that $\frac{\partial}{\partial r}$, is the directional derivative it can be written as

$$\frac{\partial}{\partial r} = \hat{\Omega} \cdot \nabla$$

And now we are a position to define new quantities

$$K_\nu = \frac{h\nu}{4\pi}N_l B_{lu}\left(\phi - \frac{g_l N_u}{g_u N_l}\psi\right)$$

where K_ν is the opacity of the medium and

$$S_\nu = \frac{N_u A_{ul}j}{N_l B_{lu}\left(\phi - \frac{g_l N_u}{g_u N_l}\psi\right)}$$

is the source function of the medium through which the radiation traveled. Now the RTE can be rewritten as

$$\hat{\Omega} \cdot \nabla I + \frac{\partial I}{c\partial t} = K_\nu(I - S_\nu) \quad (2.19)$$

For time independent radiation traveling through the cylindrical element $\frac{\partial I}{\partial t} = 0$ the differential form of RTE becomes

$$\hat{\Omega} \cdot \nabla I = K_\nu (I - S_\nu) \quad (2.20)$$

2.1.2 Radiative Transfer Equation using an Extended light Source

The model of two level atom can serve to understand the basic processes in radiation-matter interaction. However, atmospheric radiative transfer processes involve radiation processes such as scattering at large scale size. In the next sections, we extend the concept of two level atomic model to derive radiative transfer equation applicable to the atmosphere. The radiative transfer equation can also be derived by considering the radiated from an extended surface into a hemisphere whose equatorial plane is along the radiating surface of elemental are dA , [9,13,14,15,16]. The radiance, L_ν , is defined as the energy (E) radiated per unit area (A) normal to the direction specified per unit time (t) per unit frequency (ν) per unit solid angle ($\hat{\Omega}$) as

$$\begin{aligned} dE(\nu, \Omega, t) &= L_\nu dA d\hat{\Omega} dt d\nu \\ dE(\nu, \Omega, t) &= L_\nu \cos \theta dA dt d\nu d\Omega \end{aligned} \quad (2.21)$$

In atmospheric radiative transfer problem the earth's surface, the cloud and in general the atmosphere is considered as a black body for the sake of calculation of the radiance of a given air mass using Kirchhoff's law. However, Kirchhoff's law is applicable under the circumstance of local thermodynamic equilibrium (LTE) [9,12,14,15,16]. Under

LTE conditions the radiation transfer through atmospheric constituents which can either absorb or emit radiation expressed in terms of specific intensity which defined as

$$dE_\nu = I_\nu \cos \theta dA dt d\nu d\Omega \quad (2.22)$$

Note that $I_\nu = I(x, y, z, \theta, \phi) = I(r, \theta, \phi) = I(r, \Omega)$ and $d\Omega = \sin \theta d\theta d\phi$

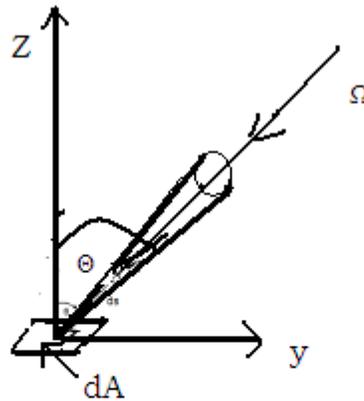


Figure 2.2: illuminated surface

Now let's assume that a pencil of radiation as in Fig 2.2 traveling through an atmosphere is attenuated (changed) due to the interaction with the constituent matter. If the specific intensity, I_ν , changes from its value at top surface of the atmospheric layer to $I_\nu + dI_\nu$ after it travels a distance of ds in the direction of propagation the change in intensity is

$$dI_\nu = -K_\nu \rho I_\nu ds \quad (2.23)$$

where ρ is mass density and K_ν is the extinction coefficient. Extinction ($K_\nu = \kappa_\nu^s + k_\nu^a$) is resulted from absorption and scattering of radiation by molecules, gases and particles. The atomic scale extinction K_ν derived on the previous section has similar meaning as the current K_ν . This means that the radiation lost may reappear in other direction with the same frequency (Rayleigh scattering) or it may be transformed into other form of energy (radiation) at other frequency (absorption). The radiation in the pencil may also be added by emission. This includes the radiation emitted from the matter and the radiation of the same frequency scattered from all other directions into the pencil. By defining emission coefficient, j_ν , the change in I_ν due to emission is written as

$$dI_\nu = j_\nu \rho ds \quad (2.24)$$

By combining (2.24) and (2.25) we can get the general specific radiative transfer equation as

$$dI_\nu = -K_\nu \rho I_\nu ds + j_\nu \rho ds \quad (2.25)$$

$$-\frac{dI_\nu}{K_\nu \rho ds} = I_\nu - \frac{j_\nu}{K_\nu} \quad (2.26)$$

By defining the source function again as

$$S_\nu = \frac{j_\nu}{K_\nu} \quad (2.27)$$

Equation (2.26) can be rewrite in simplified form as:

$$-\frac{dI_\nu}{K_\nu \rho ds} = I_\nu - S_\nu \quad (2.28)$$

The above detailed derivation of the radiative transfer equation has been treated in many text books and literature [9,10,13,14,15,16]. For a simple case of RTE when both scattering and emission are considered negligible, for e.g. in the case of upper atmosphere, where UV- radiation absorption occur stratospheric ozone (2.28) becomes after integration, the intensity after attenuation by the medium of thickness s is

$$dI_\nu = -\kappa_\nu \rho I_\nu ds$$

So that

$$I_\nu(s) = I_\nu(0) \exp \int_0^s \kappa_\nu \rho ds \quad (2.29)$$

where $I_\nu(0)$ is the value of specific intensity at the point where $s = 0$. This equation is known as Beer-Lambert law for transmission of radiation[11,12,14]. It is applicable for determination of vertical distribution of atmospheric constituents. The quantity in $\exp(-\int_0^s \kappa_\nu \rho ds)$ of the fractional transmission, τ , of the atmospheric path which represent $\int_0^s \kappa_\nu \rho ds$ is known as the optical thickness and denoted by, u . If the absorption coefficient is independent of the path length, s , through which the radiation traverses, the optical path, u , becomes

$$u = \kappa_\nu \int_0^s \rho ds \quad (2.30)$$

where $\int_0^s \rho ds$ is an integrated mass or optical length (ι). Then, the optical depth u can be written as

$$u = \kappa \iota$$

u is a dimensionless quantity called optical depth.

The quantity which plays an important role in the theory of infrared transfer in the atmosphere is transmissivity, τ_ν . It is defined as the ratio of the transmitted radiation to the incoming radiation, provided that the emission radiation being considered negligible.

$$\tau_\nu = \frac{I_\nu(s)}{I_\nu(0)} = \exp \int_0^s \kappa_\nu \rho ds \quad (2.31)$$

If the atmospheric layer is in LTE condition [9,11,12,14,15,16], then we can apply Kirchhoff's law to represent the source function, S_ν by the Planck's function.

$$S_\nu = \frac{j_\nu}{K_\nu} \equiv L_{\nu B}(T) \quad (2.32)$$

where $L_{\nu B}(T)$ is spectral intensity of Black-Body radiation as already given by Planck's law [10,13,14,16].

The earth's atmosphere is not precisely in thermodynamic equilibrium [14]; however, in the lower atmosphere LTE holds true so that the black body emission is applicable for radiation of emission from atmospheric layer. Hence the RTE for an atmospheric layer which includes both absorption and emission becomes

$$dI_\nu = -K_\nu \rho I_\nu ds + \kappa_\nu \rho L_{\nu B}(T) ds \quad (2.33)$$

$$dI_\nu = I_\nu du - L_{\nu B}(T) du \quad (2.34)$$

where $du = \kappa_\nu \rho ds$

This equation some times called Schwarzschild's equation [12,14]. If the temperature T (and hence $L_{\nu B}(T)$) assumed to be constant for thin layer of atmospheric height,

Schwarzschild equation can be integrated as

$$\int_{I_\nu(0)}^{I_\nu(s)} \frac{dI_\nu}{I_\nu - L_{\nu B}(T)} = - \int_0^u du \quad (2.35)$$

where $u = \int \kappa_\nu \rho ds$ and $I_\nu(0)$ is the spectral intensity at the top of the atmosphere.

Finally the incident intensity attenuated by atmospheric layer of thickness s becomes

$$I_\nu(s) = I_\nu(0) \exp\left(- \int_0^s du(s) + L_{\nu B}(T)(1 - \exp(- \int_0^s du(s)))\right) \quad (2.36)$$

since, $\exp(- \int_0^s du) = \tau_\nu(s)$, transmittance then (36) becomes

$$I_\nu(s) = I_\nu(0)\tau_\nu(s) + L_{\nu B}(T)(1 - \tau_\nu(s)) \quad (2.37)$$

differentiating (2.37) with respect to (wrt), s , we can get

$$dI_\nu(s) = I_\nu(0)d\tau(s) - L_{\nu B}(T)d\tau(s) \quad (2.38)$$

For plane parallel atmospheric layer $s = z$ integrating (2.38) wrt ν we obtain.

$$I_\nu(z) = I_\nu(0)\tau_\nu(z) + \int_0^\infty L_{\nu B}(T)d\tau_\nu(z) \quad (2.39)$$

If we multiply both sides of (2.34) by an integrating factor $\exp(-u(s))$, it becomes

$$d(I_\nu(s) \exp -u(s)) = L_{\nu B}(T) \exp -u(s) du(s) \quad (2.40)$$

Integrating from $s_1 = 0$ to $s_2 = s$, Since temperature of atmospheric medium depends on altitude (z), (2.40) becomes

$$I_\nu(s) = I_\nu(0) \exp(-u(0, s)) - \int_{s=0}^s L_{\nu B}(T(s')) \exp(-u(s', s)) du(s') \quad (2.41)$$

2.2 Radiative Transfer Equation For Plane Parallel Atmosphere

In general the intensity of radiation depends on the zenith angle (θ) and the azimuthal angle (ϕ) [12,13,14]. The radiative transfer equation for stratified parallel plane atmosphere of density ρ and vertical layer thickness dz in the z -direction is given by

$$dI_\nu(r, \theta, \phi)k_\nu\rho ds - S(r, \theta, \phi)k_\nu\rho ds \quad (2.42)$$

where ds is the slant distance through which the radiation beam of intensity I_ν travels in a plane parallel stratified atmospheric layer as in Fig 2.3. The slant path is related to the vertical distance dz by

$$\begin{aligned} \frac{dz}{ds} &= \cos \theta \\ ds &= \sec \theta dz \end{aligned}$$

where θ is solar zenith angle.

If we represent $\cos \theta = \mu$ and $ds = \frac{dz}{\mu}$ then (2.42) become

$$-\mu \frac{dI_\nu(z, \mu, \phi)}{k_\nu\rho dz} = I_\nu(z, \mu, \phi) - S_\nu(z, \mu, \phi) \quad (2.43)$$

Since the optical thickness of the atmospheric layer increases with decrease in altitude, z , i.e. $du = -k_\nu\rho dz$ can be rewritten as

$$\mu \frac{dI_\nu(z, \mu, \phi)}{du} = I_\nu(z, \mu, \phi) - S_\nu(z, \mu, \phi) \quad (2.44)$$

Using integrating factor $\exp(-\frac{u}{\mu})$, (2.43) becomes

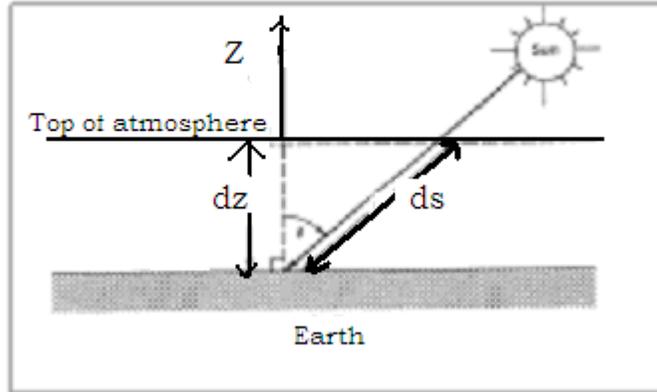


Figure 2.3: parallel plane Atmospheric layer

$$d(I_\nu(z, \mu, \phi) \exp(-\frac{u}{\mu})) = -S_\nu(z, \mu, \phi) \exp(-\frac{u}{\mu}) \quad (2.45)$$

After integrating from u_0 to u we get

$$I_\nu(u, \mu, \phi) = I_\nu(u_0, \mu, \phi) \exp(-(\frac{u_0 - u}{\mu})) + \int_{u_0}^u S_\nu(u', \mu, \phi) \exp(-(\frac{u' - u}{\mu})) \frac{du'}{\mu} \quad (2.46)$$

Eqn (2.46) is a common form of radiative transfer equation used in modeling radiative transfer in the atmosphere. We considering plane parallel atmosphere is a good approximation for real atmosphere, refraction is not as dominant as in condensed media, we have used (2.46) to simulate the measured spectral radiance. In the next chapter, we consider inverse theory for atmospheric applications. An effort will be made on how to use the RTE and inverse method to infer atmospheric parameters from direct measured spectral radiance.

Chapter 3

Inverse Theory and Retrievals

We have seen in the preceding chapters, how the spectral radiance arriving at a sensor is physically described. This chapter will discuss inverse methods useful for deriving atmospheric rate from joint use of direct measurement of spectral radiance and physics or radiative transfer in the atmosphere. Remote sensor senses the atmosphere, and allow to determine the global composition of the atmosphere, the temperature changes and other atmospheric states. To investigate the atmosphere of the earth and to detect changes in our environment, in recent decades, different satellites pay-loaded with valuable measuring devices such as Mechelson Interferometer for Passive atmospheric sounding (MIPAS) and has been launched. Most of these satellites were designed to measure vertical profile of pressure temperature and mixing ratio of the most active trace gases like O_3 , H_2O , CH_4 , NO , NO_2 , CO , N_2O , SO_2 , etc. [17]. For instance the Tropospheric Emission Spectroscopy (TES) is, one of the spetroradiometer in Fourier Transform infrared spectroscopy (FTIS) used to measure three dimensional distribution of ozone and other gases [18]. In nadir mode, TES record the spectral radiance from the Earth's atmosphere in the form of line integrals with respect to altitude z .

However, remote sensing of the atmosphere is in a sense harder problem than sensing of the surface because the atmosphere is 3-D. Many of atmospheric quantities are functions of altitude. Typical examples are Temperature, wind velocity, volume mixing ratio of ozone and other active gases. We call the curve of any such atmospheric quantities as function of height or altitude a Profile. The bulk of atmospheric work and research devotes to estimating the profile of atmospheric quantities from remotely sensed data. There are different methods of measuring the atmospheric state and collecting data from space. All of them use the range of wavelengths from ultraviolet to the microwaves. The waves of radiation detected may be thermal emission from the air constituents or it may be radiation from the sun which is being absorbed or scattered by the constituents. Details of these measurement methods are taught to be the Fundamentals of Remote sensing and Radiative Transfer model. The methods of obtaining profile for atmospheric quantities (states) from these measurements is termed Inverse Method.

There are various methods for solving the inverse problems. For instance, the measurement recorded by the TES need to be inverted in order to obtain the vertical profile concentration of atmospheric gases. The measurement in fact recorded in discrete value whereas the profile function is continuous. Therefore, different methods ought to be used for inverting the measurement values.

3.1 Description of Retrieval Process

The retrieval process in atmospheric measurement is the process of extracting vertical information of atmospheric state parameters from sequential spectra measurement of

different altitudes in the case of space born sensors. In the case of ground base sensors, the process involves the use of spectral radiance measured at a certain zenith angle. An exact physical description of the retrieval problem requires continuous functions. The spectrum to be measured is a continuous function with frequency, while the vertical profile states to be obtained from inversion or retrieval processes are continuous functions of altitude. Measurements are always discrete nature. In this sense most of the retrieval problems are formally ill-posed.

The continuous function of the vertical profiles are discretely defined and arranged in n-number of state-vectors, \mathbf{x} , of unknown quantities. These vectors contain a finite number of unknown quantities which will determine the retrieval. The m-dimensional measurement vectors, \mathbf{y} , to be defined also contain all measured radiances of atmospheric measurement for inversion [18,19].

For solar radiances we can assume spectral intensity at the top of the atmosphere where the absorptions for general case is negligible at frequency, ν , to be zero so that the measured intensity is modeled as

$$I_\nu = \int_0^\infty L_{\nu B}(T) \frac{d\tau_\nu}{dz} dz \quad (3.1)$$

The vertical coordinate may be considered geometric height or a coordinate related to pressure. Here we can consider a set of frequencies $\nu_i, i = 1, 2, \dots, m$ for which the transmittance varies greatly.

Now we can consider an instrument that makes measurements of radiation emitted by the atmosphere at these m-frequencies. Now (3.1) can be rewritten for a chosen frequencies by replacing $K_i(z)$ for $\frac{d\tau_\nu}{dz}$ at the i^{th} frequencies.

$$Y_i = \int_0^{\infty} L_{\nu B}(T)K_i(z)dz \quad (3.2)$$

where $K_i(z)$ is a function of only z and i . The radiance as a continuous function of frequency, L_{ν} , has been replaced by the measured radiance, y_i , at i^{th} frequency. A function y_i which represents measurable quantities based on the state of the atmosphere is called a Forward Function and the computer code that implements such function is called Forward Model.

Because the frequencies have been chosen at closely spaced interval, $L_{\nu B}(T)$ is necessarily assumed to be the same and linear for all our measurements and the result would be a profile of $L_{\nu B}(T)$. This is because for instance the Planck function is invertible if we know T , we know $L_{\nu B}(T)$ and vice-versa. The radiance is thus a weighted mean of the Planck function profile with $K_i(z)$ as a weight function.

The problem at this point to be raised is how the continuous function converted into a discrete one. We can change the forward function by representing the state function $X(z)$ as

$$Y_i = \int_0^{\infty} X(z)K_i(z)dz \quad (3.3)$$

and replacing the integral is replaced by summation using $X_j, j = 1, 2, \dots, n$ state vectors as

$$Y_i = \sum_{j=1}^n K_{ij}X_j \quad (3.4)$$

This equation relates two lists of numbers. By considering these numbers as a vector, we can rewrite (3.4) as

$$y = Kx \quad (3.5)$$

where \mathbf{y} is the measurement vector and \mathbf{x} the state vector. This equation represents a set of linear simultaneous equations. The forward function can be write as a general form of function \mathbf{x} :

$$y = F(x) \quad (3.6)$$

Expanding (3.6) in Taylor series

$$Y \simeq F(x_0) + K(x - x_0) + \dots \quad (3.7)$$

where K_{ij} given by

$$K_{ij} = \frac{d(F(x))_i}{dx_j} = K \quad (3.8)$$

K_{ij} is the matrix element of Jacobian. Hence (3.7) can be rewritten as

$$y - F(x_0) = \frac{\partial F(x)}{\partial x}(x - x_0) + \epsilon = \mathbf{K}(x - x_0) + \epsilon \quad (3.9)$$

$$y = \frac{\partial F(x)}{\partial x}(x) + \epsilon = \mathbf{K}x + \epsilon$$

$$y = \mathbf{K}x + \epsilon$$

after including the measurement error term. \mathbf{K} is defined as $m \times n$ weight function, not necessarily a square, since it is partial derivative of the forward model with respect to the state. If $m < n$ the equations are described as under-constrained (under determined) because there are fewer measurements than unknowns (states). If $m > n$ the equations are often described as over constrained.

3.2 Retrieval Techniques

All real measurements are subjected to some measurement error or noise, so that any real retrieval process is also affected. The proper analysis of experimental error is the

most important considerations in developing the retrieval methods. Thus we need to describe vividly uncertainty in measurements and uncertainties in retrievals, and with which to ensure that the latter should be as small as possible [19]. Experimental (random errors) can best be described using the probability density function (PDF). For example, if a measurement has a value, \mathbf{x} , and an estimated error, σ , then 'true' value of the measured parameter is a PDF of $\mathbf{p}(\mathbf{x})$ with mean of \bar{x} and variance, σ^2 :

$$\begin{aligned}\bar{x} &= \int xp(x)dx \\ \sigma^2 &= \int (x - \bar{x})^2 p(x)dx\end{aligned}$$

These equations gives information about the knowledge of measurement \mathbf{x} rather than the distribution function. It is clear that the form of $\mathbf{p}(\mathbf{x})$ in the PDF is a Gaussian or normal. Hence, $\mathbf{p}(\mathbf{x})$ can be written as

$$p(x) = N(x - \bar{x}, \sigma) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{1}{2} \frac{(x - \bar{x})^2}{\sigma^2}\right) \quad (3.10)$$

Such function is best to approximate the random error and is very convenient for mathematical manipulation. We know that all measurements have some degree of accuracy because of random error that can be quantified as a PDF over the measurement space. Now the question to be raised is how the measurement of PDF maps into the state space and combines with the prior knowledge of it.

The essence of priori knowledge (information) can be described on the basis of Baye's Theorem, that is, the posterior probability density function (PDF) of $p(x/y)$ via a likelihood function $p(y/x)$ and a priori PDF of $\mathbf{p}(\mathbf{x})$ [19,20,21,22,23,24], i.e..

$$p(x/y) \propto p(y/x)p_{prior}(x) \quad (3.11)$$

provided that the prior PDF is known and assuming that it is Gaussian.

The Gaussian distribution for multivariate vector space value \mathbf{y} expressed as

$$p(y) = \frac{1}{\sqrt{(2\pi)^n S_y}} \exp\left(-\frac{1}{2}(y - \bar{y})^T S_y^{-1}(y - \bar{y})\right) \quad (3.12)$$

where S_y is the covariance of \mathbf{y} .

The covariance of vector S is given by

$$S_{ij} = \varepsilon(y_i - \bar{y}_i)(y_j - \bar{y}_j) \neq 0 \quad (3.13)$$

For linear model the forward function for the measurement \mathbf{y} is given by:

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

as described by (3.20) measurement always contain errors that shall be assumed to be Gaussian distribution with covariance of error S_ϵ , and the error in real measurement of $\mathbf{p}(\mathbf{y}/\mathbf{x})$, which is the probability of making measurement \mathbf{y} when the atmospheric state is \mathbf{x} , given by

$$p(y/x) \propto \exp\left(-\frac{1}{2}(y - kx)^T S_\epsilon^{-1}(y - kx)\right)$$

taking both the logarithms, we get

$$-2 \ln p(y/x) = (y - kx)^T S_\epsilon^{-1}(y - kx) + C_1 \quad (3.14)$$

where C_1 is a constant.

According to the probability measurements $\mathbf{p}(\mathbf{x})$ is our information (knowledge) on state \mathbf{x} prior to making any measurement, so that the Gaussian distribution of the priori probability of the profile having a value, \mathbf{x} , is given by

$$p(x) \propto \exp\left(-\frac{1}{2}(x - x_a)^T S_a^{-1}(x - x_a)\right)$$

$$-2 \ln p(x) = (x - x_a)^T S_a^{-1} (x - x_a) + C_2 \quad (3.15)$$

where x_a is the prior value of \mathbf{x} and S_a^{-1} is the corresponding covariance matrix. To obtain the posterior PDF of \mathbf{x} , we use Baye's Theorem.

$$p(x/y) \propto p(y/x)p(x)$$

combining (3.) and (3.) we get

$$-2 \ln p(x/y) = (y - kx)^T S_\epsilon^{-1} (y - kx) + (x - x_a)^T S_a^{-1} (x - x_a) + C_3 \quad (3.16)$$

It is obvious that the posterior PDF is also Gaussian with expected value \hat{x} and associated covariance \hat{S} :

$$p(x/y) \propto \exp\left(-\frac{1}{2}(x - \hat{x})^T \hat{S}^{-1} (x - \hat{x})\right) \quad (3.17)$$

This is the expected value that we seek after retrieved. Taking the natural logarithm both sides, we obtain

$$-2 \ln p(x/y) = (x - \hat{x})^T \hat{S}^{-1} (x - \hat{x}) \quad (3.18)$$

Now equating like terms in (3.17)and (3.19), we get

$$\begin{aligned} x^T \hat{S}^{-1} x &= x^T (K^T S_\epsilon^{-1} K + S_a^{-1}) x \\ x^T \hat{S}^{-1} \hat{x} &= x^T (K^T S_\epsilon^{-1} y + S_a^{-1} x_a) \\ \hat{x}^T \hat{S}^{-1} \hat{x} + C_4 &= y^T S_\epsilon^{-1} y + x_a^T S_a^{-1} x_a + C_3 \equiv C \end{aligned}$$

From the solution of these equations we obtain

$$\hat{S}^{-1} = K^T S_\epsilon^{-1} K + S_a^{-1}$$

and

$$\hat{S}^{-1} \hat{x} = K^T S_\epsilon^{-1} y + S_a^{-1} x_a \quad (3.19)$$

Substituting for \hat{S}^{-1} in (3.20) and solving for \hat{x} we arrive at

$$\hat{x} = (K^T S_\epsilon^{-1} K + S_a^{-1})^{-1} (K^T S_\epsilon^{-1} y + S_a^{-1} x_a) \quad (3.20)$$

Again if we substitute y from the forward model into (3.21) we arrive at

$$\hat{x} = (K^T S_\epsilon^{-1} K + S_a^{-1})^{-1} (K^T S_\epsilon^{-1} K x + S_a^{-1} x_a + K^T S_\epsilon^{-1} \epsilon) \quad (3.21)$$

This equation relates the expected value obtained from Bayesian solution to the state, \mathbf{x} , the prior state, \mathbf{x}_a , and the measurement error, ϵ . It shows that $\hat{\mathbf{x}}$ is the weighted mean of the true state and the prior state with relative weights $K^T S_\epsilon^{-1} K$ and S_a^{-1} , respectively, in addition to the term due to the measurement error. The matrix

$$A = (K^T S_\epsilon^{-1} K + S_a^{-1})^{-1} K^T S_\epsilon^{-1} K \quad (3.22)$$

is the absolute weight of the true state and is known as Averaging Kernel or Model Resolution Matrix [19,20,24,25]. The weight of the prior state is $\mathbf{I} - \mathbf{A}$, where \mathbf{I} is a unitary matrix. Hence

$$S_a^{-1} = \mathbf{I} - \mathbf{A} \quad (3.23)$$

If we use this in eq(3.21), then it becomes

$$\hat{x} = x_a + (K^T S_\epsilon^{-1} K + S_a^{-1})^{-1} K^T S_\epsilon^{-1} (y - K x_a) \quad (3.24)$$

We note that the constant terms in (3.21) are not included because they added no further information rather than increased the value of the system. Equation (3.24) indicates that $\hat{\mathbf{x}}$, which is the expected value, is a linear functions of the prior expected value $\hat{\mathbf{x}}_{\mathbf{a}}$.

In this chapter, we have given detail description of the inverse model. It will be used with the physical forward radiation transfer model and measurement to retrieve atmospheric state, in the case of this thesis: retrieval tropospheric ozone profile over tropics. In the next chapter, the derived tropospheric ozone will be analyzed for its consistency with existing evidence from literature. Furthermore, the results of 1-D steady state model will be compared with the derived ozone profile within tropospheric altitude range.

Chapter 4

Analysis of Result and Discussion

In this work tropospheric ozone has been determined from indirect measurement of spectral radiance at infrared wavelengths using FTIR. The radiative transfer and inverse models are employed to retrieve ozone profile over tropics from data onboard German Polar and Marine Research Vessel (Polarstern) during 1996 expedition. More over an effort has also been made to estimate the volume mixing ratio of ozone originating from in situ chemical reaction from 1-D steady state chemistry model.

The determination of ozone profile from solar absorption spectral radiance is accomplished by minimizing the difference between simulated and measured transmittance. The most commonly adopted way to accomplish this is to minimize the number of functional sets (in our case the square of difference between simulated and measured transmittance) with respect to atmospheric state. This criterion is known as the least square fit (LSF). When the forward model does not depend linearly on the unknown state of the atmosphere, the problem of retrieval procedure is best handled by non-linear least square fit (NLSF) which cannot be solved directly using a formula, so that an iteration procedure will be used [26].

An iterative retrieval procedure can be performed by fitting the measurement to the model such that the solution will be unique regardless of the initial guesses employed. The most important thing here is to go beyond the outcome of the fit parameters. It is natural that data obtained from measurements are not generally exact because they are always constrained with some errors or measurement noise. In other words the data never always fit exactly to the model used even if the model is correct. What is important is to understand the degree of accuracy with which the retrieved parameters have been determined by the measurement. In this case the source of errors have to be analyzed and taken in to account since the radiative transfer model used involve many observable parameters. Therefore the model in our study is a multivariate one that requires a multivariate error analysis. Another means of controlling error is the χ^2 for radiance measurements. The retrieval may fail or converge to an appropriate parameter values when a high or low values of χ^2 is obtained at the end of iterative procedure.

Based on this goodness of fit approach and the absorption properties of ozone in the infrared radiation, a great effort has been made to retrieve the ozone profile from spectral data from FTIR Spectroscopy measurement made in 1996 over tropical latitude. A best retrieval result is obtained in wave number range between 1124 to 1128 cm^{-1} .

4.1 Spectral Regions for Ozone Retrieval

The spectral region used for ozone retrieval consist of three spectral range. The selection procedure looks for strong ozone absorption lines which are highly sensitive

Microwindow	Target gas	Major Interfering gases
1124.190 1124.390	O_3	N_2O, CH_3D
1125.405 1126.235	O_3	N_2O, HDO
1127.455 1128.050	O_3	H_2O, CH_3D

Table 4.1: Microwindows used for retrieval

to the troposphere [27]. However, the three microwindows are not used in the form determined by the technique. The spectral ranges are modified in ad hoc manner such that the effect of interference is minimum. The spectral ranges (commonly referred to as spectral microwindow) used in this work is listed in Table 4.1 along with major interfering gases.

Fig.4.1 (on page 51) shows that the major interfering gases over spectral region containing the three spectral window used for O_3 retrieval. The ozone contribution, shown by green line in Fig 4.1, is shifted by a factor of 0.02 from the total signal shown by black line for the sake of clarity. Similarly the signals of CH_3D (an isotope of methane), H_2O , HDO (an isotope of water) and N_2O are shifted by 0.10, 0.15, 0.20 and 0.25 from the total signal respectively.

The signal of O_3 contributes close to 100% over all the spectral microwindows (see green line Fig. 4.1). In the same figure, it is possible to see the contribution of the major interfering gases to the total transmittance. CH_3D , as an isotope of CH_4 , has small contribution near 1124.25 cm^{-1} , 1126.5 cm^{-1} and 1127.3 cm^{-1} , however, these contributions lie outside O_3 spectral microwindows used except at 1124.25 cm^{-1} . But the concentration of CH_3D is nearly negligible. HDO, an isotope H_2O , has absorption in the spectral microwindow range ($1125.405 - 1126.235\text{ cm}^{-1}$) at about 1125.75 cm^{-1} but its concentration in the atmosphere is quite negligible. N_2O has contribution around at 1124.25 , 1125 , 1125.75 , 1126.5 and 1127.5 cm^{-1} . But its contribution at

these points is quite small. The contribution of H_2O , in these spectral microwindows used for O_3 retrieval, is also quite negligible.

4.2 Retrieved VMR of Ozone

The retrieved ozone profile is sensitive to the accuracy of the retrieval process, the atmospheric condition and the instrument used. In a general case the retrieved ozone is based on the comparison of the priori information, measured radiance data, the radiative transfer model, and the conditions of the instrument. The quality of retrieved VMR of ozone is evaluated on the basis of independent pieces of information contained in retrieved VMR, absolute root mean square error of difference of simulated and measured radiances and the quality of the fit. The independent pieces of information derived from the ozone signal can be determined from the trace of averaging kernel matrix (see chapter 3, eq.(3.22) for detail). Using evaluation parameters as diagnostic factors, we report the results of the inversion procedure for tropospheric ozone profile over tropical latitudes.

The best result obtained from spectral microwindows shown in Table 4.1 has a degree of freedom of 3.579 and a percentage RMS error of 2.38. The corresponding ozone VMR is shown in Fig 4.2 (on page 52). The apriori ozone VMR is indicated by a line with circles and the retrieved ozone VMR is indicated by a line with stars. The apriori and the retrieved profiles exhibit the same shape except altitude range near 20 km. However, the apriori and the retrieved profile show some minor differences over all altitude range.

The measured and best fit simulated spectra for the three microwindows are shown

in Fig 4.3 (on page 53). The simulated and measured spectra over all the three O_3 microwindows fit very nicely. This shows that the interferences from other trace gases and water vapor are very small. The only exception is the small difference between the two spectra in the a second window (1125.405-1126.235). This is due to HDO signal which is not included in retrieval procedure.

The distribution of ozone over tropical latitudes from 26°S to 26°N is displayed in figure 4.4 (on page 54). The latitudinal distribution of ozone number density shows that it is relatively higher around the equator (0°) latitude and gradually decreases to wards higher latitudes as far as 5°S/N . Above 5°S/N , it again begins to rise as far as pole. This observation is similar to observation for water vapor in the troposphere over tropical region.

During the 1996 expedition, the measured spectra are mostly contaminated by clouds and as a result large number of spectra were excluded from our calculation. Moreover, due to bad convergence which again might be related to the noisy measured spectra, we are able to retrieve at very few latitude points, in the given latitude band of $26^{\circ}\text{S} - 26^{\circ}\text{N}$. So, our retrieval has yield a few sparse ozone distribution.

4.3 1-D Steady-State-Approximation Chemistry Model

The reaction pathway for ozone production in troposphere from anthropogenic sources are briefly discussed and the kinetic reactions of 1-D steady state chemistry model appropriately formulated in chapter 1 eq.(1.13). For any reaction with non-zero activation energy, the rate constant is dependent mainly on temperature. The temperature dependence often modeled by a general Arrhenius equation, $K = A \exp(-\frac{E_a}{RT})$,

where E_a is activation energy for the reaction and A is known as the pre-exponential factor. We used the value of $2 \times 10^{-12} \exp(-\frac{1400}{T})$ [28]. The concentrations of NO_2 and NO are retrieved from the same measured spectra.

The steady-state approximate value of ozone in 1-D model is calculated according to eq(1.13) in chapter 1, where [NO] and [NO_2] are retrieved VMR values. The steady state model estimate for ozone is shown in Fig 4.5 (on page 55).

There are two curves which represent steady state model estimate for two consecutive measurement times. Since the measurement is taken onboard research vessel, the location of measurement is also different latitudewise. The steady state model is used valid for tropospheric altitude range. As a result, the values above troposphere is not reasonable.

4.4 Comparison between Model and Retrieved Profile

The retrieved ozone profile from measurement and calculated values from steady state chemistry model are plotted in Fig 4.6 (on page 56).

From Fig 4.6 we observe that the ozone obtained from measurement and SSA model have a good agreement with small deviation from the surface to about 4 km altitude. The differences in magnitude between the measurement and the calculated values are significant from about 4 km to 15 km altitudes. The maximum difference between first measurement and its steady state approximation is about 0.26 ppmv, while the

maximum difference for the second set is 0.16 ppmv, which are located between 7 km and to 9 km altitudes.

The possible explanation for the difference is related to the existing limitations of 1-D steady state chemistry model. The photolysis rate coefficient depend on the solar zenith angle, altitude, radiation flux, the column number density of the species above the considered location and the surface albedo, all of which are not incorporated in the model. In addition, the amount of aerosols have great impact on the photolysis rate because aerosols increase the scattering of radiation flux. Apart from radiative factor, the dynamics of the atmosphere affects the distribution of vmr, cloud cover, aerosols concentration etc by transporting from one region to the other. Therefore, 1-D steady state chemistry model is a simple model which may not fully explain atmospheric processes.

The chemical processes included in the SSA-model are of course very simplified compared to the real tropospheric chemistry where hundreds of reactions occurred. Another limitation of 1-D SSA model is omission of the gaseous and aqueous phase reactions, which resulted in destruction and removal of ozone. In short tropospheric ozone budget is the result of the balance between the source and sinks. The main sinks of ozone in troposphere are local photochemical destruction and wet or dry deposition (removal), which are not fully included.

In summary, the present out come shows that the simplified theoretical steady state approximation model does not describe the complex and interlinked tropospheric chemistry. But it provides a clue about the tropospheric ozone chemistry.

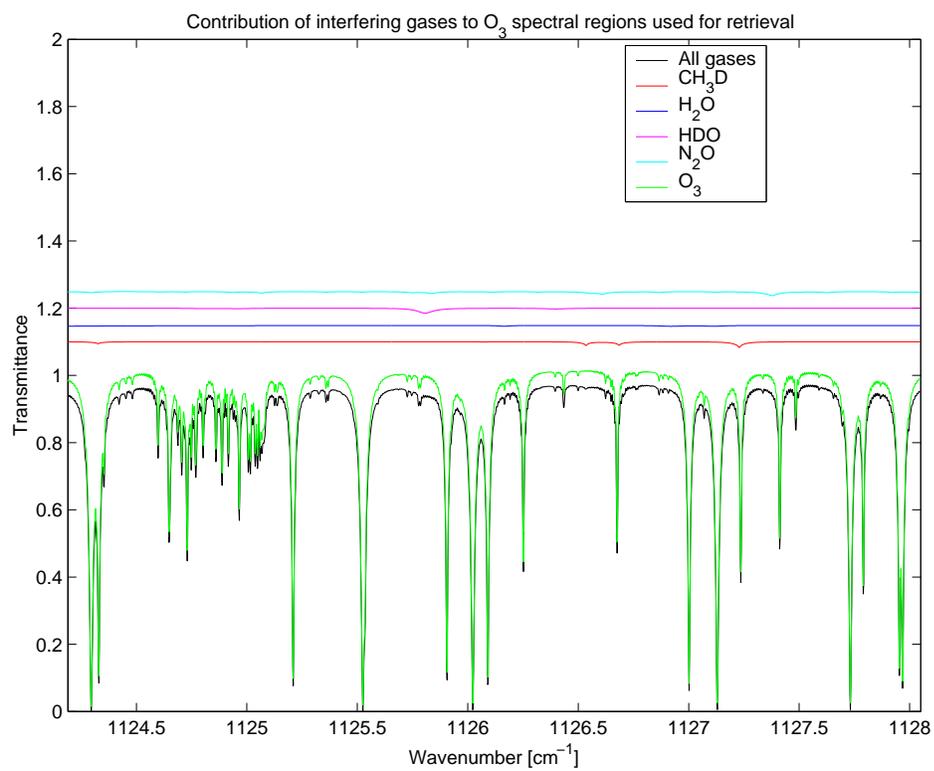


Figure 4.1: Transmittance of target gas and contribution

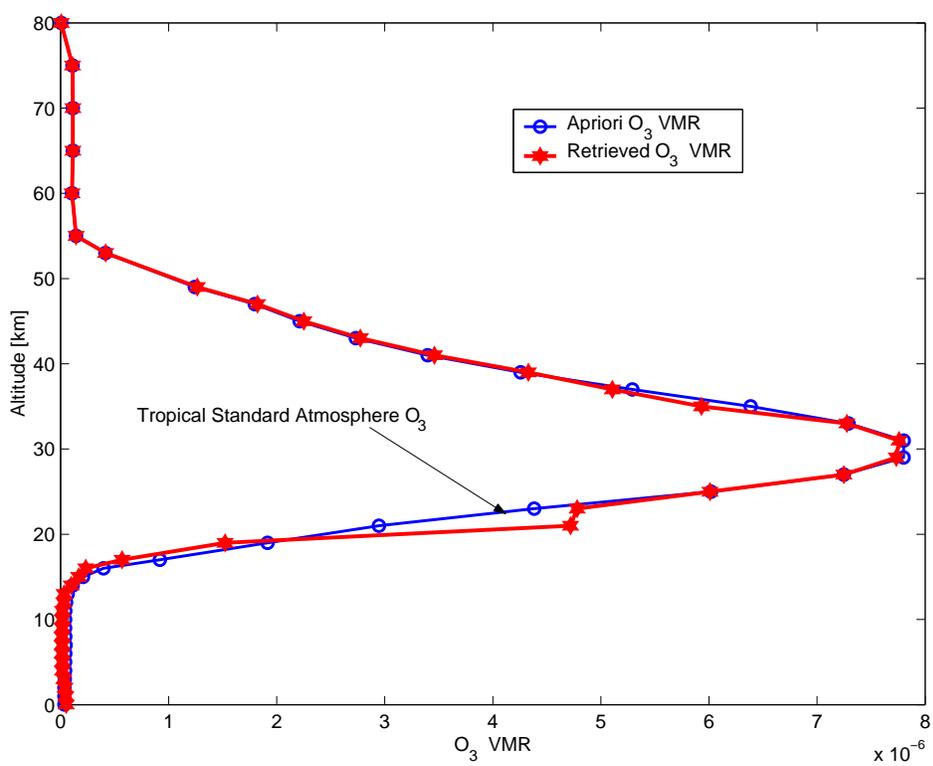


Figure 4.2: Ozone profile

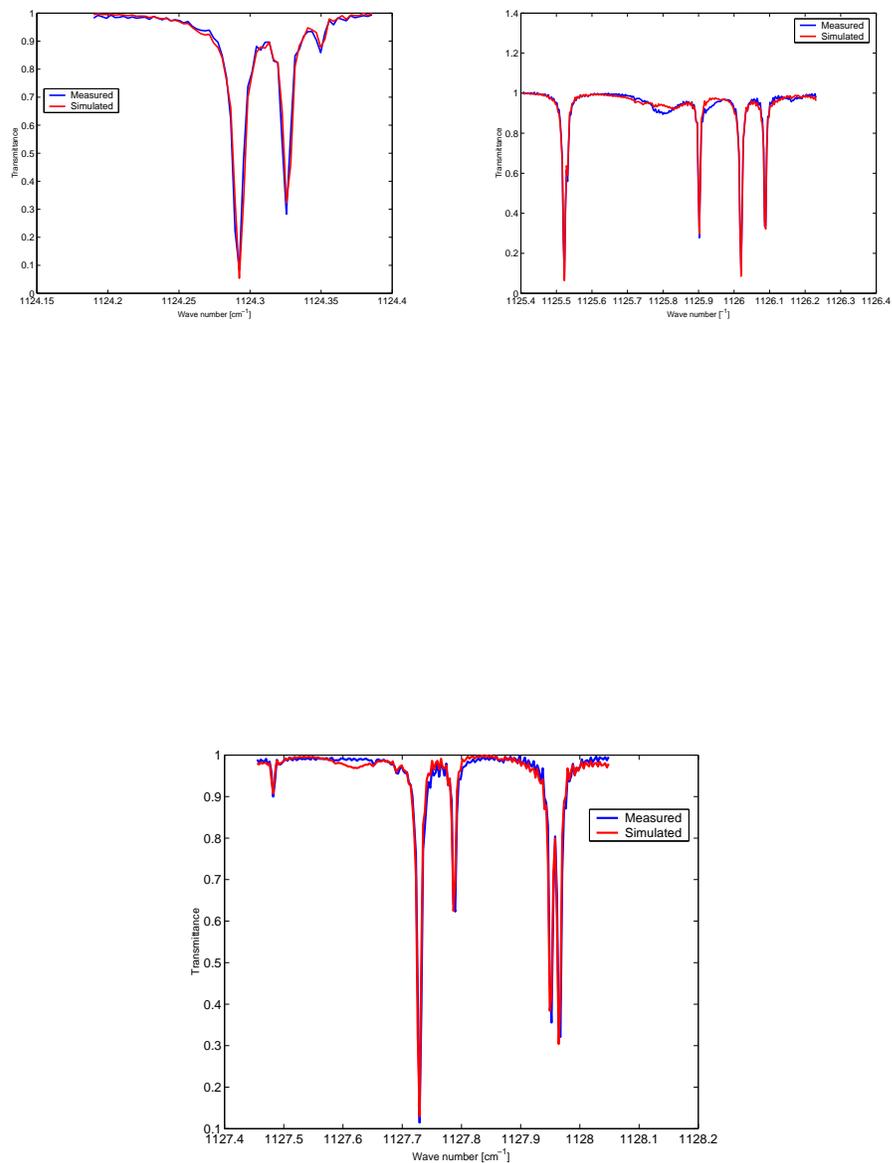


Figure 4.3: Transmittance of spectral microwindow used for O_3 Retrieval

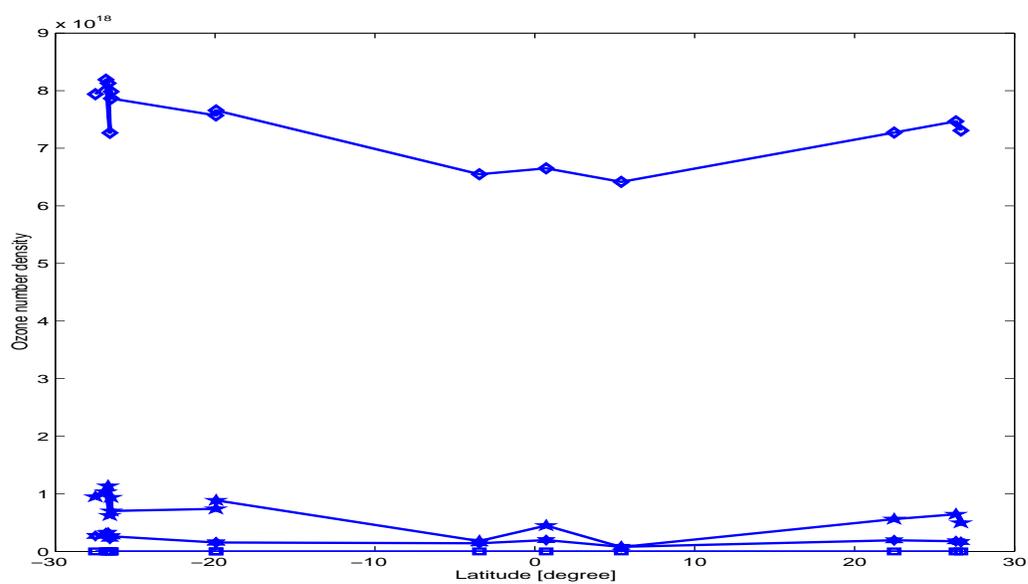
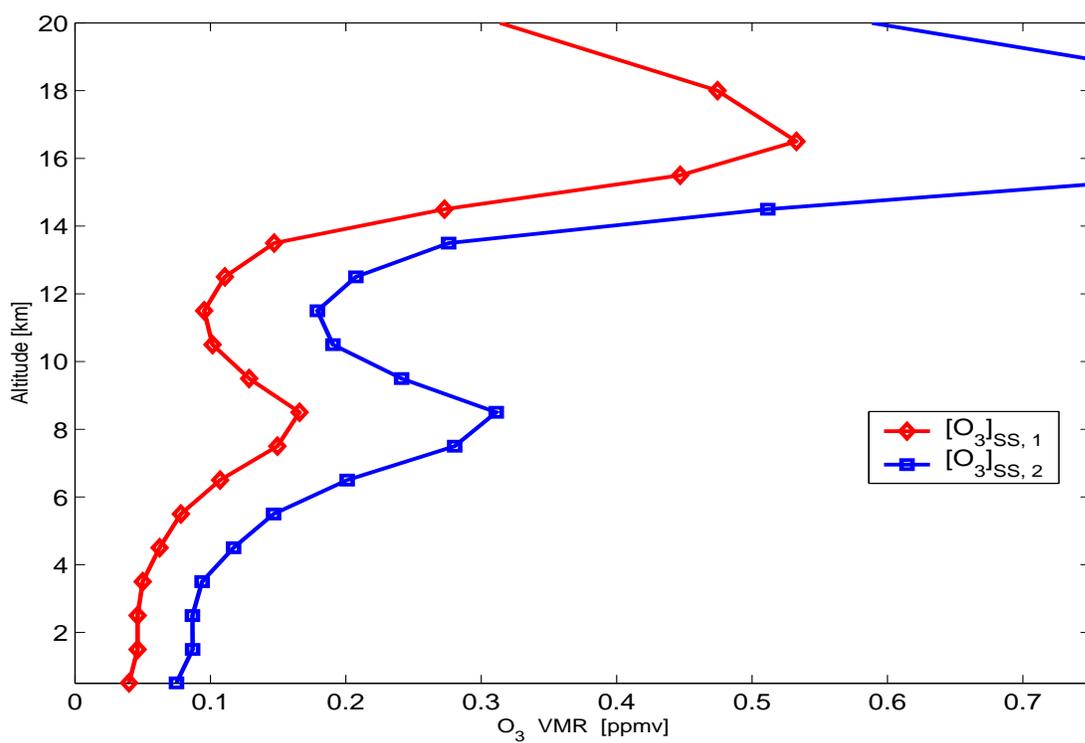


Figure 4.4: Ozone density versus latitude over tropics

Figure 4.5: Altitude versus $[O_3]_{SS}$ graph

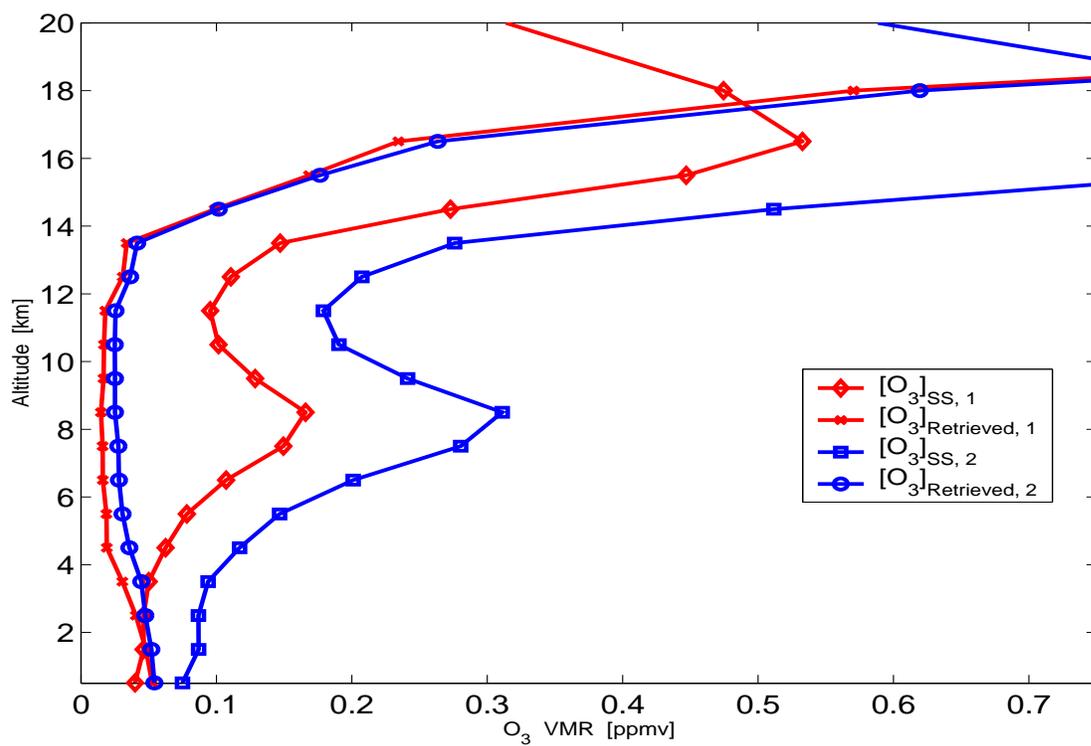


Figure 4.6: Altitude verses $[O_3]$ vmr of measurement and calculated

Chapter 5

Summary and Conclusion

Knowledge of the tropospheric ozone about its origin, its chemistry as whole and its role in controlling air pollution, climate change as well as the green house effect and cause is important. Because it affect either directly or indirectly the oxidizing capacity of the atmosphere which is very necessary for removal of gaseous composition in order to prevent accumulation. Change in oxidation capacity of atmosphere affect the level of climate gases and distribution of temperature. Because of the reactivity, it easily photolyzed to form free radicals that promotes oxidation chemistry and so to catalysis its own formation (it is an autocatalyses). At high concentration, ozone affects the lung, the respiratory tract and the eyes. It has also seen found that it increases the susceptibility inhaled allergens and asthma.

Considering these and other facts tacitly, the general objectives of this thesis have been to obtain quantitative information on tropospheric ozone level over tropics, from measurement and to estimate its concentrations and distribution with altitude using 1-D Steady State Approximation (SSA) of the kinetic reactions of tropospheric reaction mechanisms.

The retrieval of ozone from the selected three microwindows have yields ozone profile consistent with other measurement. The quality of the fit is extremely remarkable with minor exceptions.

On the other hand, our study revealed that estimated from 1-D SSA exceeds the true measurement of tropospheric ozone profile in magnitude. This shows that

- The simplified 1-D SSA of Tropospheric ozone kinetic reaction mechanism is insufficient to describe the complex and interlinked ozone chemistry in the troposphere.
- It is difficult to find a kinetic reaction mechanism that is constant with over all reaction and rate law to determine over all kinetic reaction and rate law.
- The steady state approximations are useful to have clues about the complex atmospheric reactions but could not be a generalization.

In conclusion, the selection of the optimum spectral region for ozone retrieval is successful in that the retrieved ozone and its latitudinal distribution exhibit a pattern consistent with past measurement and model studies. The steady state approximation in one dimension is not generally good, for reaction involved interlinked chain reaction, like ozone chemistry, particularly tropospheric chemistry involving complex and branched chain reaction. Final we recommend that a further and comprehensive study that includes dynamics and complete chemistry to obtain reliable and better result.

Bibliography

- [1] Geer,A.J., etal., (2007) Evvaluation of Linear Ozone Photochemistry Parametrization in a Stratosphere-Troposphere Data Assimilation System. *Atmos.Chem. Phys.*, 7.939-959, 2007
- [2] Pietewr,V., (2003) Retrievals of Total Tropospheric Ozone from observation. Global Ozone Monitoring Experiment, PhD. Thesis. Nederlands Meteorological Institute, Eindhover.
- [3] Hayman, G.D., etal., (2002) Modeling of Tropospheric Ozone Formation. AEA Tecnology Report AEAT/ENV/R-1029,Issue-2, AEA Technology p/c. A Final Project Report produced for the Department for Environment, Food and Rural Affairs on Contract EPG 1/3/143
- [4] Fuglestedt, J.S. (1995) Model studies of indirect effects on climate through changes in the chemistry of the troposphere. Thesis submitted to Department of Chemistry. CICERO Center for International Climate and Environmental Research - Oslo University of Oslo P.O. Box 1129 Blindern N-0317 Oslo Norway
- [5] Meszaros, E., (1993) Global and Regional Changes in Atmosphere. Lewis Publisher.

- [6] Dobson, G.M.B. (1963) Exploring the Atmosphere. Oxford University Press (1963).
- [7] Seinfeld, J.H. and Pandis, S.N. (2000) Atmospheric Chemistry from Air Pollution to Climate Change. A Wiley-Interscience Publication, John Wiley and Sons inc.
- [8] Visconti, G. (2001) Fundamentals of Physics and Chemistry of the Atmosphere.
- [9] Buglia, J.J. (1986) Introduction to the Theory of Atmospheric Radiative Transfer. NASA Reference Publication 1156 1986. Langley Research Center Hampton, Virginia.
- [10] Cannon, C.J. (1985) The Transfer of Spectral Line Radiation. Cambridge University Press (1985), Cambridge.
- [11] Thorne, A.P. (1988) Spectroscopic Physics, 2nd Ed. Chapman and Hall Ltd.
- [12] Liu, N.K. (1983) An Introduction to Atmospheric physics. Academic Press Inc. (London) Ltd.
- [13] Craig, R.A. (1965) The Upper Atmosphere: Meteorology and Physics. Academic Press, 1965, New York and London.
- [14] Houghton, J. (2001) The Physics of Atmospheres, 3rd Ed. Cambridge University Press (2001).
- [15] Rutten, R.J. (2003) Radiative Transfer in Stellar Atmospheres, Utrecht University lecture notes, 8th edition. [R.J.Rutten @ astro.uu.nl].
- [16] Aller, L.H. (1963) Astrophysics: The Atmosphere of the Sun and Stars, 2nd ed. The Roland Press Company, New York.

- [17] Stack, T. and Clarmann, Th. V. Constrained Profile Retrieval Applied to MIPAS Observation Mode. [tilman steck@jpl.nasa.gov].
- [18] Bal, G. and Ren, K. (2004) Atmospheric concentration Profile Reconstructions from Radiation Measurement. *Inverse Problems* 21(2005), Institute of Physics Publishing.
- [19] Rodgers, C.D. (April 3, 1996) *Inverse Methods for Atmospheric Sounding: Theory and Practise* [Compiled text] [<http://www.atm.ox.ac.uk/>].
- [20] Eyer, J.R. (April 1991) Inversion methods for satellite sounding data. Meteorological Training Course Lecture Series (Printed 9 January 2001).
- [21] Lohnert, U., Crewell,S. and Simmmer, C. (2003) An Integrated Approach toward Retrieving Physically Consistent Profiles of Temperature, Humidity, and Cloud Liquid Water. *Journal of Applied meteorology*, v-43,1295-1306, 2004.
- [22] Sofieva, V. F., etal. (2004) Ozone profile smoothness as a priori information in the inversion of limb measurements. *Annales Geophysicae* (2004) 22: 34113420 SRef-ID: 1432-0576/ag/2004-22-3411 European Geosciences Union 2004.
- [23] Tsidu, G. M. (2004) On the accuracy of covariance matrix: Hessian versus Gauss-Newton methods in atmospheric remote sensing with infrared spectroscopy. *Journal of Quantitative Spectroscopy and Radiative Transfer* 96 (2005) 103121.
- [24] Livesey, et al.: Retrieval Algorith for the EOS Microwave Limb sounder (MLS). *Journal of Geoscience and Remote Sensing*. [<http://mls.jpl.nasa.gov/>].

- [25] Glatthor, N., et al. (2005) Retrieval of stratospheric ozone profiles from MIPAS/ENVISAT limb emission spectra: a sensitivity study. *Atmos. Chem. Phys. Discuss.*, 5, 1203112066, 2005 [www.atmos-chem-phys.org/acpd/5/12031/]
- [26] Mengistu, G. (1998) Determination of Optimized Microwindow for Analysis of Absorption Spectra from ground based FTIR Spectrometer. Msc. Thesis.
- [27] Notholt, J., et al., (2004) Spectral Line finding program for atmospheric remote sensing using the line radiation transfer, absorption plus emission. *Journal of Quantitative Spectroscopy & Radiative Transfer*, JQSRT:2359, pp. 1-13.

Declaration

I hereby declare that this thesis is my original work and has not been presented for a degree in any other university. All sources of material used for the thesis have been duly acknowledged.

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