NEW NON-LTE MODEL OF OH AND CO₂ EMISSION IN THE MESOSPHERE-LOWER THERMOSPHERE AND ITS APPLICATION TO RETRIEVING NIGHTTIME PARAMETERS

by

Peter A. Panka A Dissertation Submitted to the Graduate Faculty of George Mason University In Partial fulfillment of The Requirements for the Degree of Doctor of Philosophy Physics

Committee:

	Dr. Erdal Yiğit, Dissertation Director
	Dr. Michael Summers, Committee Member
	Dr. Jie Zhang, Committee Member
	Dr. Alexander Kutepov, Committee Member
	Dr. Paul So, Department Chair
	Dr. Donna M. Fox, Associate Dean, Office of Student Affairs & Special Programs, College of Science
	Dr. Peggy Agouris, Dean, College of Science
Date:	Fall Semester 2017 George Mason University Fairfax, VA

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at George Mason University

By

Peter A. Panka Master of Science George Mason University, 2014 Bachelor of Science University of Massachusetts - Amherst, 2011

Director: Dr. Erdal Yiğit, Professor Department of Physics and Astronomy

> Fall Semester 2017 George Mason University Fairfax, VA

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Dedication

I dedicate this dissertation to my parents. Without your love and support I would not have made it this far. Thank you for everything.

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Abstract

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Peter A. Panka, PhD

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Dissertation Director: Dr. Erdal Yiğit

The hydroxyl, OH, and carbon dioxide, CO_2 , molecules and oxygen atoms, $O(^{3}P)$, are important parameters that characterize the chemistry, energetics and dynamics of the nighttime mesosphere and lower thermosphere (MLT) region. Hence, there is much interest in obtaining high quality observations of these parameters in order to study the short term variability as well as the long term trends in characteristics of the MLT region. The Sounding of the Atmosphere using Broadband Emission Radiometry (SABER) instrument on board the Thermosphere, Ionosphere, Mesosphere, Energetics, and Dynamics (TIMED) satellite has been taking global, simultaneous measurements of limb infrared radiance in 10 spectral channels, including the OH 2.0 and 1.6 μ m and CO₂ 4.3 μ m emissions channels, continuously since late January 2002. These measurements can be interpreted using sophisticated non-Local Thermodynamic Equilibrium (non-LTE) models of OH and CO₂ infrared emissions which can then be applied to obtain densities of these parameters (2.0 and 1.6 μ m channel for O(³P)/OH and 4.3 μ m channel for CO₂). The latest non-LTE models of these molecules, however, do not fully represent all the dominant energy transfer mechanisms which influence their vibrational level distributions and infrared emissions. In particular, non-LTE models of CO₂ 4.3 μ m emissions currently under-predict SABER measurements by up to 80%, and its application for the retrieval of CO₂ will result in unrealistic densities. Additionally, current O(³P) retrievals from SABER OH emissions have been reported to be at least 30% higher compared to studies using other instruments. Methods to obtain OH total densities from SABER measurements have yet to be developed. Recent studies, however, have discovered a new energy transfer mechanism which influences both OH and CO₂ infrared emissions, OH(v) \Rightarrow O(¹D) \Rightarrow N₂(v) \Rightarrow CO₂(v_3). This study focuses on the impact of this new mechanism on OH and CO₂ infrared emissions as well as model applications for the retrieval of nighttime O(³P), OH, and CO₂ densities.

We first study in detail the impact of the new mechanism on OH(v) vibrational level populations and emissions. We compared our calculations with the SABER/TIMED OH 1.6 and 2.0 μ m limb radiances of the MLT and with ground and space observations of OH(v)densities in the nighttime mesosphere. We find that the new mechanism produces OH(v)density distributions which are in good agreement with both SABER limb OH emission observations and ground and space measurements.

We then couple our OH non-LTE model with CO_2 to study the impact of the new mechanism on $CO_2(\nu_3)$ vibrational level populations and emissions. We compare our calculations with the SABER/TIMED 4.3 μ m CO₂ limb radiances and find that the new mechanism provides a strong enhancement of the 4.3 μ m CO₂ emissions, agreeing to within a 10-30% range.

Further, a two-channel retrieval algorithm is developed to self-consistently invert the SABER measured radiances in the OH 2.0 and 1.6 μ m channel to obtain vertical profiles of OH and O(³P) Volume Mixing Ratio (VMR). Studies of the inversion algorithm made with synthetic radiances indicate that a stable solution of the inverse problem can be obtained that is nearly independent of the starting conditions.

The results presented from the two-channel algorithm to the SABER v2.0 data include comparisons of retrieved $O(^{3}P)$ with current SABER $O(^{3}P)$, in addition to $O(^{3}P)$ retrievals measured by the SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY) instrument, as well as those calculated by the WACCM (Whole Atmosphere Community Climate Model) model for four different days. The $O(^{3}P)$ density retrieved between 90-95 km are, on average, lower than current SABER $O(^{3}P)$ by 10-50%. OH retrievals are performed over the same days and are compared with OH WACCM calculations as well as other studies.

Finally, a similar self-consistent algorithm used for the retrieval of daytime CO_2 densities is adopted for nighttime. The situation, however, is more complex for nighttime CO_2 , where lack of solar irradiation excitation greatly reduce 4.3 μ m emission sensitivity to CO_2 density and, therefore, produces unrealistic retrievals. Alternative retrieval methods will be required to overcome these obstacles. For daytime, retrieval of temperature and CO_2 are performed simultaneously due to strong coupling between these two parameters. Consideration of this effect will be crucial to obtain accurate nighttime CO_2 densities.

Chapter 1: Introduction

Observations of the atmosphere test our understanding of its chemistry, physics and evolution. The Mesosphere-Lower Thermosphere (MLT) covers the altitude range between 60-120 km where neutral particles become weakly ionized due to the solar radiation and eventually forms the ionosphere at higher altitudes. Metallic layers, which weakly contribute to airglow, also reside here as a result of meteor ablation adding to the complexity of this region. Numerous dynamical features are also present such as strong zonal winds, atmospheric tides, gravity waves, and planetary waves. Gravity wave breaking and tidal wave propagation significantly perturb the temperature structure and chemistry of the MLT and provide a coupling mechanism of this region with processes in the lower atmosphere. As a result, this region is difficult to study, experimentally and theoretically.

Advancements in satellite instrumentation have allowed us to probe the middle and upper atmosphere over continuous periods of time with high quality measurements. Over the last decade, new information of the major driving forces governing the thermal structure, energy budget, and chemistry of the MLT region has been gained. The dominant mechanisms influencing certain nighttime radiance measurements, however, are still not well understood. As a result, characterization and model validation of key nighttime atmospheric parameters such as atomic oxygen (O(³P)), hydroxyl (OH), and carbon dioxide (CO₂) concentrations are not accurate enough.

1.1 Non Local Thermodynamic Equilibrium in the MLT

Studying physical process involving energy transport in the MLT poses major difficulties because molecular vibrational levels begin to depart in this region from Local Thermodynamic Equilibrium (LTE). This directly effects the analysis of infrared space based measurements of the MLT and becomes problematic for numerical models which aim to understand the atmospheric energetics and dynamics from the troposphere up through the thermosphere. Radiative cooling (i.e. when a radiating species absorbs translation energy via collisional excitation and then emits it as a photon) and radiative heating (i.e. conversion of solar energy into translational energy of molecules) are important for calculating the kinetic temperature profiles in Global Circulation Models (GCMs) of the middle and upper atmosphere (Fomichev et al. [1996], Kutepov et al. [2007]). Both processes, however, are affected by non-LTE, and the radiative transfer calculation schemes of GCMs must include these effects to accurately derive the temperature distribution and pressure gradients in this region.

In the lower atmosphere, the state of the gas is in LTE where the velocity distribution of molecules is Maxwellian, populations follow the Boltzmann distribution, but the radiation intensity is not, in general, given by Planck function. Such a state can exist when radiative absorption and emission processes and external sources (chemistry, solar radiation, etc.) are weak in comparison to collisional excitation. In the middle and upper atmosphere, where the density is much lower, the gas is said to be in a non-LTE state when the level populations deviate from the Boltzmann law, but the molecular velocity distribution remains Maxwellian. Processes such as absorption and emission of radiation in molecular bands, inelastic collisions which result in vibrational-translational (V-T) and vibrational-vibrational (V-V) energy exchanges (redistribution of excitation between colliding molecules), and chemical production and loss of excited molecules must be taken into account. The analysis of infrared emissions in the MLT requires accounting for non-LTE for molecular vibrational, and in some cases also rotational, populations. These populations must be found by self-consistently solving a system of statistical equilibrium equations (SEE), which express the balance of all processes that populate and depopulate vibrational levels, and the radiative transfer equation (RTE).

A more detailed formulation of the non-LTE problem and its method of solution will be described in Chapter 2.

1.2 Infrared Observations of the MLT

In general, direct in-situ, LIDAR (LIght Detection And Ranging), and satellite remote sensing are the main methods of observing middle-upper atmospheric structure and dynamics. Direct in-situ measurements of the MLT are performed by instruments on board rockets but they are limited by time and space. LIDARs can observe the upper atmosphere from the ground over continuous periods of time but are limited to fixed locations. Therefore, to obtain long term global information on atmospheric composition, satellite remote sensing is warranted. Among these satellite observations of various emissions, infrared observations have an advantage because they are directly linked with temperature and concentration of trace gases. With advances in instrument technology, limb satellite remote sensing is capable of probing the MLT with reasonable Signal-to-Noise (SNR) for certain atmospheric infrared bands up to the tangent altitudes of the lower thermosphere. The limb geometry observations are particularly advantageous for observing the MLT since the signal from the atmosphere benefits from the cold space as a background. Radiation emerging from this region, however, is influenced by non-LTE effects for many infrared molecular bands and, therefore, careful accounting for non-LTE is crucial for the interpretation of satellite data.

Several experiments that have studied atmospheric infrared emissions influenced by non-LTE include the Cryogenic Limb Array Etalon Spectrometer (CLAES) [Roche et al., 1993], Improved Stratosphere and Mesosphere Sounder (ISAMS) [Taylor et al., 1993], Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) [Endemann et al., 1993], and more recent instruments such as, the Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere (CRISTA) [Offermann et al., 1999], ACE-FTS (Atmospheric Chemistry Experiment Fourier Transform Spectrometer) [Bernath, 2001], and SABER (Sounding of the Atmosphere using Broadband Emission Radiometry) [Russell III et al., 1999]. For this study, the data collected by the SABER instrument on board the TIMED (Thermosphere, Ionosphere, Mesosphere Energetics and Dynamics) satellite will be used for the analysis of observational nighttime infrared (IR) measurements. The main science objective of the SABER experiment is to explore the MLT region on a global scale and to improvement our understanding of the fundamental processes governing the structure, energetics, chemistry, dynamics, and transport of this atmospheric region [Russell III et al., 1999].

The SABER instrument was launched on board the TIMED satellite on December 7, 2001. The satellite orbits the Earth at 625 km, inclined at 74° with an orbital period of 97 minutes. SABER makes simultaneous measurements of infrared radiances in 10 broadband channels by scanning the limb of Earth's atmosphere. The scanning procedure begins at the surface going to 350 km and then back down to the surface in about 110 seconds, taking a sample every 0.4 km and 2 km FOV.



Figure 1.1: SABER latitude vs time coverage. The color bar indicates the average value of the solar zenith angle for a particular latitude bin (in degrees).

SABER measures radiances in both day and night with latitudinal coverage alternating between 83°N-52°S and 83°S-52°N every 60 days (see Figure 1.1) as a result of a yaw

maneuver which is performed in order to keep the SABER side of the TIMED spacecraft away from direct sunlight. Each day, SABER measures about 1400 radiance profiles per channel. For a complete description of the SABER instrument see Russell III et al. [1999]. Table 1.1 summarizes the science motivation and pass bands for each SABER channel.

Channel	Gas	Wavelength	Start	Stop	Science
Number		(μm)	(cm^{-1})	$({\rm cm}^{-1})$	Measurement
1	$CO_2 N$	15.2	606	714	T(p), cooling rates
2	$\rm CO_2 W$	14.9	568	811	T(p), cooling rates
3	$\rm CO_2 W$	14.9	567	807	T(p), cooling rates
4	O_3	9.6	981	1184	Ozone, cooling rates
5	H_2O	6.3	1306	1628	Water Vapor, cooling rates
6	NO	5.3	1837	1988	Thermospheric cooling
7	CO_2	4.3	2284	2409	Carbon Dioxide, cooling rates
8	OH	2.0	4435	5847	Chem. Heating, photochemistry
9	OH	1.6	5676	6476	Chem. Heating, photochemistry
10	$O_2(^1\Delta)$	1.27	7599	8071	Daytime O_3 , solar heating

Table 1.1: SABER pass bands and science motivation for the measurement

1.3 Non-LTE Retrieval Schemes

There have been a number of studies (s.f. López-Valverde et al. [1991], Mertens et al. [2001], López-Puertas and Taylor [2001], Kaufmann et al. [2002], Funke et al. [2005], Grossmann et al. [2006], Gusev et al. [2006], Mlynczak et al. [2007], Feofilov et al. [2009], Feofilov et al. [2012], Kaufmann et al. [2014]) that have developed retrieval algorithms under non-LTE conditions for temperature and various atmospheric constituents such as CO_2 , O_3 , H_2O , CO, and NO_x in MLT regions. The retrieval approaches for the above mentioned studies, however, do not reflect the full nature of non-LTE. These algorithms retrieve a single parameter from a single emission feature, relying on inputs of all other required atmospheric parameters previously retrieved or taken from models. This approach significantly degrades

the accuracy of the retrieved product. This becomes problematic under non-LTE conditions because populations of vibrational states of different molecules are coupled and can influence their respective observed emissions. Different molecular levels of different species are strongly linked in this region by V-T and, particularly, V-V exchanges coupling these levels and, therefore their emissions will be coupled. Additionally, for retrieving parameters such as temperature, hydrostatic adjustments can also influence the populations of molecular species and their emissions. It is typical that the CO_2 15 μ m emission band is used to retrieve kinetic temperature and the CO_2 4.3 μm emission band is used for CO_2 densities. Perturbations in the kinetic temperature influence the populations of CO_2 and 4.3 μm emissions. Rezac et al. [2015] were the first to develop a self-consistent two channel retrieval algorithm for temperature and CO_2 densities to avoid these errors and non-negligible biases in the retrieved atmospheric parameters. The algorithm switches between the SABER retrieval channels sensitive to temperature and CO_2 densities to allow for adjustments. This study is a good example of when the non-LTE nature of two emission bands as well as significant coupling between these two emissions channels caused by hydrostatics was managed. Following this general idea, we will develop a two-channel retrieval algorithm for OH emissions and subsequently perform tests incorporating a third channel including CO_2 emissions.

1.4 Overview of OH, $O(^{3}P)$, and CO_{2} in the MLT

1.4.1 Hydroxyl

The hydroxyl radical (OH) plays a fundamental role in the middle atmosphere. OH is a main chemical quencher of ozone [Brasseur and Solomon, 2006] and also a component in several reactions between stable and active forms of other ozone quenching partners. OH can also be used as a proxy for mesospheric water vapor [Summers et al., 2001], which is considered to be an element of global climate change. Additionally, OH ro-vibrational line intensities, where distributions of low rotational levels are assumed to be in LTE, are used to derive kinetic temperature and observe dynamical processes such as tides, planetary waves, and gravity waves (Grygalashvyly et al. [2014] and references therein). Therefore, detailed knowledge of OH densities and variabilities is crucially important in understanding mesospheric chemistry and dynamics and, as I will show in my studies, in understanding the nighttime 4.3 μ m emission.

At night, OH is formed in the chemical reaction between hydrogen and ozone forming a narrow layer residing around 82 km. In the stratosphere and lower mesopshere, hydrogen, H, mostly combines with O_2 to form HO_2 rather than react with O_3 . In MLT regions, specifically between 80-85 km, HO_2 formation decreases with pressure and therefore, subsequently increasing the H density and also the importance of the H + O_3 reaction, producing OH. The main chemical quencher of OH in the MLT is the reaction with $O(^{3}P)$. At slightly higher altitudes above 82 km, $O(^{3}P)$ densities increase rapidly with altitude as a result of the decreased rate of formation of O_3 from $O(^{3}P)$, which also depends on the pressure. The chemical balance between production by H and O_3 and destruction by $O(^{3}P)$ form the vertical structure of OH in the MLT [Brasseur and Solomon, 2006]. The chemical lifetime of OH increases with altitude from hours at 80 km to months around 100 km [Pickett et al., 2006].

There are no observations of total OH densities in the MLT, however, there are several approaches to determining OH(v) population densities. Pickett et al. [2006] used the Microwave Limb Sounder (MLS) instrument on the Aura satellite to directly measure the thermal emission from 2.5 THz rotational lines and retrieved the ground vibrational state of OH. Cosby and Slanger [2007] used the echelle spectrograph and imager (ESI) on the Keck II telescope at Mauna Kea to measure emission intensities of 16 OH Meinel bands which were converted into the $OH(\nu)$ column densities from v=4-9. Migliorini et al. [2015] analyzed VIRTIS (Visible and Infrared Thermal Imaging Spectrometer) measurements on board the Rosetta mission. VIRTIS performed limb scans of the OH Meinel bands from 87-105 km covering the latitude range from 38-47°N. Only the relative $OH(\nu)$ population distribution was derived in this study as well as corresponding uncertainties. SABER observations include radiances of two OH spectral regions, however, the applied non-LTE models of these emissions have yet to develop the algorithms which retrieve OH total densities. Overall, with the exception of a few studies which derive specific OH populations densities, there have been no reported studies which retrieve total nighttime OH densities in the MLT region.

1.4.2 Atomic Oxygen

Atomic oxygen, $O(^{3}P)$, is generated during the day through photolysis of molecular oxygen, O₂, and ozone, O₃, by solar UV radiation. Formed mostly in the thermosphere, $O(^{3}P)$ is transported downward through both diffusion and advection, reaching peak concentrations at altitudes of around 96 km. It is the most abundant reactive trace species in this region of the atmosphere with a chemical lifetime varying from seconds at 50 km to months at 100 km [Smith et al., 2010]. $O(^{3}P)$ plays a critical role in the photochemistry and energy balance in the upper MLT [Brasseur and Offermann, 1986]. During the day and night, $O(^{3}P)$ fuels exothermic chemical reactions involving O₃, OH, and NO_x [Mlynczak and Solomon, 1993]. The dominant radiant cooling process in this region of the atmosphere comes from collisions between $O(^{3}P)$ and CO₂, exciting vibrational states of CO₂ which are subsequently radiated to space in the infrared, cooling the MLT. Additionally, several methods for deriving temperature (López-Valverde et al. [1991], Gusev et al. [2006]), ozone (López-Valverde et al. [1991]), and other constituents depend on the knowledge of this species. It is therefore crucial in obtaining the most accurate atomic oxygen densities to understand the photochemistry and energy budget of the MLT.

A fundamental problem in the chemical aeronomy of Earth's MLT region is the determination of the atomic oxygen density. $O(^{3}P)$ has no vibration-rotation spectra, but two fine structure lines centered at 63 μ m and 145 μ m. The former is optically thick and not observable in the MLT from space [Grossmann et al., 2000] but by rocket-borne instruments [Grossmann et al., 1997] and high-altitude balloons [Mlynczak et al., 2004]. The latter is optically thin, however, technology is currently limited to observe this emission from a satellite. Therefore there are no global observations of atomic oxygen densities from direct $O(^{3}P)$ emissions in the MLT.

The general approach to determining $O(^{3}P)$ densities in the MLT is to infer it from satellite measurements of airglow observations of $O(^{1}S)$, O_{2} A-Band, and the Meinel bands of the OH molecule. Photochemical models are developed to provide the basis for the derivation of atomic oxygen from satellite remote sensing measurements. There have been several satellites since the 1970s which measured airglow emissions used to derive atomic oxygen. Most recent satellites include WINDII (WIND Imaging Interferometer) [Russell et al., 2005] on the Upper Atmosphere Research Satellite, OSIRIS (Optical Spectrograph and Infrared Imager System) [Sheese et al., 2011] on the Odin satellite, SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric Chartography) instrument on Envisat [Kaufmann et al., 2014], and the SABER instrument on board the TIMED satellite (Mlynczak et al. [2014], Smith et al. [2010]). The WINDII atomic oxygen densities were derived from O(^{1}S) green line emissions data at high altitudes and from OH(v) emission below. OSIRIS data were derived from O₂ A-band emission data [Sheese et al., 2011], SCIAMACHY data from O(^{1}S) green lines emission, and SABER atomic oxygen was derived from OH(v) emissions.

Good [1976] developed a technique utilizing the OH Meinel 2.0 μ m band emissions which assumes that the production of ozone (O₃) by recombination of O(³P) and O₂ is balanced by reaction of O₃ with hydrogen, where the latter reaction generates the OH Meinel band emission. The derived O(³P) using this technique relies on the assumption of ozone photochemical equilibrium and the physical quenching rates and spectroscopic parameters for highly vibrationally excited states of the OH molecule. Several studies have been conducted describing the observed properties of O(³P) from SABER measurements (Marsh et al. [2006], Smith et al. [2010], Xu et al. [2012], and Mlynczak et al. [2014]). Current SABER atomic oxygen densities, however, are considered to be at least 30% higher



Figure 1.2: Derived atomic oxygen densities using various space-based satellites. SABER, SCIAMACHY, OSIRIS, and MSIS (model) data are for winter 2005/2006 at 0°-20°N. WINDII data are for 1993/1994. Taken from Figure 4 of Kaufmann et al. [2014].

in comparison with atomic oxygen densities derived using other satellites [Kaufmann et al., 2014].

Figure 1.2 displays derived atomic densities in the MLT using the different emissions features and techniques for each satellite. WINDII, OSIRIS, and SCIAMACHY all retrieved similar atomic oxygen density profiles while SABER is consistently higher. The figure was taken from Figure 4 of Kaufmann et al. [2014].

1.4.3 Carbon Dioxide

Above the tropopause, carbon dioxide, CO_2 , becomes a dominant greenhouse gas due to the diminishing water vapor opacity [Lindzen, 2007]. CO_2 plays an important role in the energy budget of Earth's stratosphere, mesosphere, and lower thermosphere. Its dominant role is due to infrared radiative cooling from emissions in the 15 μ m band [Roble and Dickinson, 1989]. CO_2 also has a relatively long chemical lifetime and can act as a tracer for dynamical

transport processes, such as molecular and eddy diffusion, transport by atmospheric tides and also for determining the residual mean circulation. In the lower atmosphere, CO_2 concentrations are increasing by ~5% per decade as a result of anthropogenic activity. CO_2 is believed to propagate upward to the MLT where recent studies have shown increases in concentrations by ~5-6% per decade (priv. comm. Ladislav Rezac). In the MLT, the CO_2 15 μ m emission feature is the dominant cooling mechanism. Due to the low optical depth, vibrationally excited CO_2 molecules will emit most of its radiation to space, making the corresponding increased cooling of these low density layers as indicators for global climate change [Yue et al., 2015].

The vertical structure of CO_2 Volume Mixing Ratio (VMR) is determined by only a few processes. In the lower troposphere, biological processes cause CO_2 to exhibit a weak seasonal cycle [Brasseur and Solomon, 2006]. In the lower and middle atmosphere (10-70 km), the CO_2 VMR is almost constant with altitude due to eddy mixing and lack of significant sources or sinks. In the upper mesosphere (above 70 km), observations have shown that CO_2 VMR decreases with height due to molecular diffusion and shortwave ultraviolet radiation [López-Puertas et al., 2000].

Rocket-borne experiments, using a mass spectrometer, can measure CO_2 VMR for both day and nighttime conditions. Satellite instruments, however, relying on sophisticated retrieval algorithms to interpret the limb radiance measurements of CO_2 emissions, could only measure CO_2 vertical structure during the daytime. There are numerous rocket-borne and satellite instruments aimed at measuring the vertical structure of CO_2 VMR in the MLT. Rocket-borne experiments suggested a uniformly mixed CO_2 VMR up to 90-100 km for observations taken during the day- and nighttime (Offermann and Grossmann [1973]; Trinks and Fricke [1978]; Offermann et al. [1981]). At the time, derived theoretical profiles supported these observations [Wintersteiner et al., 1992] as well as early model simulations [Rodrigo et al., 1986]. A few rocket-borne emission experiments (Spectral Infrared Rocket Experiment (SPIRE) [Nebel et al., 1994] and Spectroscopic Infrared Structure Inverstigation (SISI) [Vollmann and Grossmann, 1997]) provided information on non-LTE processes affecting the daytime 4.3 μ m band, which is typically used to retreived CO₂ VMR. This information helped develop non-LTE kinetic models which were applied to limb radiances measured by SAMS on NIMBUS 7 [López-Puertas and Taylor, 1989]. The experiment showed that CO₂ VMR starts to decrease around 80 km. In a later experiment, ISAMS on board the Upper Atmospheric Research Satellite (UARS) confirmed the finding of SAMS [Zaragoza et al., 2000]. Additional experiments such as CRISTA on the space shuttle [Kaufmann et al., 2002] and ACE-FTS on SCIentifit SATellite (SCISAT) have also observed daytime CO₂ vertical structures start decreasing between 70-80 km.

The SABER instrument is designed to measure 4.3 μ m emissions and retrieval algorithms can be applied to obtain global day and nighttime CO₂ VMR using this emission channel. Recently, daytime temperature/pressure and CO₂ densities have been obtained from the SABER 15 μ m and 4.3 μ m emission observations [Rezac et al., 2015] using a self-consistent two-channel retrieval approach which accounts for strong coupling between both emissions. However, no observations of CO₂ at nighttime are currently available. Little is known about CO₂ distribution and variability, particularly about its diurnal variation and its distribution in polar night. The extensive SABER nighttime 4.3 μ m radiance observations, which are supposed to fill this knowledge gap, still remain unprocessed due to a lack of understanding of physical mechanisms generating this emission.

A detailed study of nighttime 4.3 μ m emissions was conducted by López-Puertas et al. [2004] aimed at determining the dominant mechanisms of exciting CO₂(ν_3), where ν_3 is the asymmetric stretch mode that emits 4.3 μ m radiation. The authors studied the transfer of vibrational energy from chemically produced OH(ν) in the nighttime mesosphere to the CO₂(ν_3) vibration via a mechanism first proposed by Kumer et al. [1978], OH(ν) \Rightarrow N₂(ν) \Rightarrow CO₂(ν_3). López-Puertas et al. [2004] showed that calculations based on the Kumer et al. [1978] model do not reproduce the 4.3 μ m radiances observed by SABER. Although accounting for energy transfer from OH(ν) did provide a substantial enhancement to 4.3 μ m emission, up to 80% difference between simulated and observed radiance remained. As a result, realistic nighttime CO_2 densities could not be retrieved and because of this, nighttime temperatures are currently retrieved independently from the SABER 15 μ m channel radiances using day-night mean CO_2 densities from the WACCM (Whole Atmosphere Community Climate Model) model [Garcia et al., 2007].

Recently, Sharma et al. [2015] suggested a new mechanism of the OH vibrational energy transfer to $\text{CO}_2(\nu_3)$, i.e. $\text{OH}(\nu) \Rightarrow \text{O}(^1\text{D}) \Rightarrow \text{N}_2(\nu) \Rightarrow \text{CO}_2(\nu_3) \Rightarrow 4.3 \ \mu\text{m}$. Accounting for this mechanism, but only considering $\text{OH}(\nu=9)$, these authors performed simple model calculations to validate its potential for enhancing mesospheric nighttime 4.3 μm emission from CO₂. They reported a simulated radiance enhancement between 18-55% throughout the MLT, which brought it closer to observed measurements. In a recent study, Kalogerakis et al. [2016] provided a definitive laboratory confirmation for the validity of this new mechanism. In my study presented here, I will demonstrate that OH and $O(^3\text{P})$ are integral parts of $\text{CO}_2(\nu_3)$ excitation, via this new reaction, allowing non-LTE models to accurately simulate 4.3 μ m emissions and retrieve nighttime CO₂ VMR. It is therefore crucial to have reliable densities of atomic oxygen and OH when modeling 4.3 μ m emissions.

1.5 Research Statement

In this study a new OH non-LTE model will be presented. We will investigate the effects of the new mechanism of OH(v) quenching suggested by Sharma et al. [2015] and compare vibrational temperatures and relative population distributions with other OH models. Additionally, comparison of SABER measurements, as well as other ground and space based instruments, with our simulated radiances and populations will be performed. We will then turn to modeling nighttime 4.3 μ m emissions by coupling our new OH non-LTE model with CO_2 . The OH quenching mechanism suggested by Sharma et al. [2015] triggers well-known daytime pumping mechanisms for $CO_2(v_3)$ that will be utilized in our CO_2 nighttime model. We will study in detail the impact of the new mechanisms on $CO_2(v_3)$ vibrational level populations and emissions and compare our calculations with the SABER/TIMED nighttime 4.3 μ m CO₂ limb radiances of the MLT in the nighttime mesosphere.

Following these studies, the new OH and CO_2 non-LTE models will be applied for the retrieval of OH, $O(^{3}P)$, and CO_2 VMR in the MLT. A detailed analysis will be presented of a self-consistent simultaneous retrieval algorithm for $O(^{3}P)$ and OH VMR using broadband limb infrared OH radiance measurements of the non-LTE atmosphere. This study will focus on investigating the sensitivity, stability and convergence of the algorithm and potential limitations. This technique will be applied to infer the vertical structure of $O(^{3}P)$ and OH VMR in the MLT region from observed limb infrared radiance obtained by the SABER instrument on board the TIMED satellite. Finally, the retrieved $O(^{3}P)$ and OH VMR will be used as inputs for the CO_2 non-LTE model. First retrievals of nighttime CO_2 VMR will be presented using a single-channel retrieval algorithm.

In this study, the 4.3 μ m channel (2284-2409 cm⁻¹, CH7) is used for retrieval of CO₂ VMR from 65-100 km and the 2.0 and 1.6 μ m channels (4435-5847 cm⁻¹, CH8 and 5675-6476 cm⁻¹, CH9, respectively) will be used for O(³P) and OH VMR retrievals from 80-100 km. The focus will be only on nighttime retrievals, at solar zenith angles greater than 105°, in addition to, quiet (non-auroral) conditions to avoid interactions between charged particles and molecules. Mechanisms of these interactions are still not well studied.

In chapter 2, a formulation of the multilevel vibrational-rotational non-LTE problem for a mixture of gases is provided along with a method of solution that is used in the Accelerated Lambda Iteration for Atmospheric Radiation and Molecular Spectra (ALI-ARMS) radiative transfer code. Chapter 3 and 4 describes our OH and CO₂ non-LTE model, respectively. Chapter 5 provides details of the development of a self-consistent retrieval method for simultaneous atomic oxygen and OH VMR retrieved from the measured limb radiances. Chapter 6 includes $O(^{3}P)/OH$ retrieval results using measured signals for nighttime conditions. Chapter 7 contains first retrievals of nighttime CO₂ VMR using retrieved $O(^{3}P)$ and OH VMR as inputs and then a discussion of the future direction in this research. Chapter 8 provides a summary of the important conclusions.

Chapter 2: The Non-LTE Problem

2.1 Overview of non-LTE

This chapter presents a general formulation of the non-LTE problem, i.e. determining the populations of ro-vibrational levels for a mixture of molecules relevant to Earth's atmosphere. A method of solution for the coupled equations (statistical equilibrium and radiative transfer) will also be discussed in this chapter. The mathematical formulation describing the non-LTE problem and the method of solution represent the theoretical basis implemented in ALI-ARMS (Accelerated Lambda Iterations for Atmospheric Radiation and Molecular Spectra) and utilized in our forward model of SABER limb radiances.

This chapter begins with a discussion for when LTE conditions are valid and when it breaks down. The distribution of internal energy across the various ro-vibrational modes for a given molecule is influenced by numerous processes at any time. The most important to consider in Earth's atmosphere are: 1) thermal collisions, 2) spontaneous emissions, 3) absorption of external radiation (either solar radiation or upwelling earth and lower atmosphere radiation), 4) chemical or photochemical reactions, and 5) vibration-to-vibration (V-V) energy transfer as well as electronic-to-vibrational (E-V). The conditions of LTE exist when the frequency of collisions strongly couple the molecular energy levels to the molecular kinetic energy reservoir. The distribution of excited states for a particular molecule, thus, is a function of a single parameter, the kinetic temperature, and is described by the Boltzmann distribution. When thermal collisions are not frequent enough to dominate external excitation mechanism influencing the level populations, the condition is referred to as non-LTE.

In Earth's atmosphere, as pressure decreases with altitude, the collisional frequency decreases as well and non-LTE effects are expected to be more influential at higher altitudes.

The altitude at which non-LTE effects become significant, however, depends on the internal energy gap between levels of a particular molecule. For example, a transition with a large energy gap generally requires a larger number of collisions to keep the level populations in thermal equilibrium. Additionally, the influence of the above mentioned processes which may cause level populations to depart from LTE vary for each molecule. However, for situations in planetary atmospheres, complete non-LTE for all energy states of a molecule can hardly exist. It is somewhat of a general rule that internal energy states of a particular molecule depart from LTE while others remain in LTE [Kutepov et al., 1998].

The general multilevel non-LTE problem for infrared ro-vibrational molecular bands is described below following the formalism of (Kutepov et al. [1998], Gusev and Kutepov [2003], Rezac [2011]).

2.2 General Formulation

The multi-level non-LTE radiative transfer problem for molecular lines has two main components: 1) The Statistical Equilibrium Equation (SEE) which describes all of the population and depopulation processes for molecular levels and 2) the Radiative Transfer Equation (RTE), which describes the propagation of radiation through matter and gives the solution to the radiation field along the Line of Sight (LOS). The radiative transfer equation can be solved if the populations for all the excited molecular levels are known.

Let us consider a molecular gas, which could be a component of a complex gas mixture. Its molecules are assumed to have a large number of levels, each characterized by its statistical weight g_i , energy E_i and population n_i .

We consider only the steady state of this molecular gas, in which its kinetic temperature and the degree of excitation do not change with time. The statistical equilibrium equation (SEE) which expresses the balance between various elementary processes can be written in
standard notation as

$$n_i \left(\sum_j R_{ij} + C_i^{\rightarrow}\right) = \sum_j n_j R_{ji} + C_j^{\leftarrow} + Y_i.$$
(2.1)

Here n_i is the population of vibrational level *i*, R_{ij} and C_{ij} are the radiative and collisional rate coefficients for transitions from energy level *i* to *j*. Y_i is a source term for level *i* which considers excitation processes other than collision excitation and absorption of radiation emitted within the atmosphere, such as the absorption of "solar" or "ground" radiation, production of excited molecules in various chemical reactions, etc.

As the SEE are linearly dependent, one of its equations must be replaced by the particle conservation equation

$$\sum_{i} n_i = n, \tag{2.2}$$

where n is the total number of molecules per unit volume of the particular molecule.

The collisional rate coefficient, C_{ij} , is the total loss for level, i, through various types of collisional processes as shown below

$$C_{i}^{\to} = \sum_{j} C_{ij}^{V-T} + \sum_{jkl} n_{k} C_{ij,kl}^{V-V}$$
(2.3)

The first term is defined as the rate for ro-vibrational energy transfer to translational energy, (V-T). This rate is written as

$$C_{ij}^{V-T} = \sum_{\beta} n^{\beta} k_{ij}^{\beta}, \qquad (2.4)$$

where k_{ij}^{β} are the rate constants for the V-T transition i to j by collisions with atoms and molecules, each labeled as a β -constituent, with density n^{β} . The second term describes the collisional loss rate of level i through vibration-vibration (V-V) energy exchange processes. The V-V collisional process influences the vibrational energy levels of both colliding partners. Thus, the rate coefficient, $C_{ij,kl}$, in Eq. (2.3) defines the transition i to j for one and the transition k to l in the other of the two colliding molecules and/or atoms.

The C_{ji} term on the right hand side of Eq. (2.1) is the reverse process of Eq. (2.3) and can be written as

$$C_{j}^{\leftarrow} = \sum_{j} n_{j} C_{ji}^{V-T} + \sum_{jkl} n_{j} n_{l} C_{ji,lk}^{V-V}.$$
(2.5)

The collisional rate coefficients are related by the detailed balance relations

$$n_i^* C_{ij} = n_j^* C_{ji}$$
 and $n_i^* n_k^* C_{ij,kl} = n_j^* n_l^* C_{ji,lk}$ (2.6)

where n^{*} are populations in LTE.

The radiative rate coefficients in the SEE are given by

$$R_{ij} = \begin{cases} A_{ij} + B_{ij}\bar{J}_{ij} & \text{if } i > j \\ B_{ij}\bar{J}_{ij} & \text{if } i < j \end{cases}$$
(2.7)

where $\bar{J}_{ij} = \bar{J}_{ji}$ is the integrated mean intensity, defined as

$$\bar{J}_{ij} = \frac{1}{4\pi} \int d\Omega \int I_{\mu\nu} \varphi_{ij}(\nu) d\nu.$$
(2.8)

Here $\phi_{ij}(\nu)$ is the line profile function normalized such that $\int d\nu \varphi_{ij}(\nu) = 1$ and $I_{\mu\nu}$ is determined by solving the radiative transfer equation (RTE). It is clear that based on Eq. (2.7) and (2.8), in order to solve the SEE equation, the radiation field must be known at each altitude grid point. For simplicity, we confine ourselves to the case of a plane-parallel atmosphere and the differential equation of radiative transfer describing the emission, absorption, and propagation of photons along some line of sight can be written as

$$\mu \frac{\partial I_{\mu\nu}}{\partial z} = -\chi_{\mu}(\nu)I_{\mu\nu} + \eta_{\mu}(\nu), \qquad (2.9)$$

where $I_{\mu\nu}$ is the specific intensity of atmospheric radiation and $\chi_{\mu}(\nu)$ and $\eta_{\mu}(\nu)$ are the total opacity and emissivity, respectively, at frequency ν and direction cosine μ . The radiative properties of the gas being considered are characterized by the emissivity η_{ij} and the opacity χ_{ij} for each pair of levels associated with a line transition. For i > j,

$$\eta_{ij}(\nu) = \frac{h\nu_{ij}}{4\pi} n_{ij} A_{ij} \vartheta_{ij}(\nu)$$
(2.10)

$$\chi_{ij}(\nu) = \frac{h\nu_{ij}}{4\pi} (n_j B_{ji} - n_i B_{ij}) \varphi_{ij}(\nu)$$
(2.11)

where ν_{ij} is the line center frequency, A_{ij} , B_{ij} , and B_{ji} are the Einstein coefficients, $\varphi_{ij}(\nu)$ and $\vartheta_{ij}(\nu)$ are the line profile functions normalized such that $\int \varphi_{ij}(\nu) d\nu = 1$.

The profile functions $\varphi_{ij}(\nu)$ and $\vartheta_{ij}(\nu)$ are equivalent under the assumption of complete frequency redistribution. Therefore, the source function for any transition is independent of frequency and angle and is given by,

$$S_{ij} = \frac{\eta_{ij}(\nu)}{\chi_{ij}(\nu)} = \frac{n_i A_{ij}}{(n_j B_{ji} - n_i B_{ij})}.$$
 (2.12)

One may account for angle and frequency dependence, however, this is not required in the solution and will not be considered here.

For certain conditions, overlapping lines within a band (or even between lines of different bands) need to be considered. In this case, the total emissivity and opacity coefficients are summed over all transitions of all molecules at frequency, ν

$$\eta(\nu) = \sum_{ij} \eta_{ij}(\nu) + \eta_{cont.}(\nu)$$
(2.13)

$$\chi(\nu) = \sum_{ij} \chi_{ij}(\nu) + \chi_{cont.}(\nu)$$
(2.14)

where the background continuum contributions $\eta_{cont.}(\nu)$ and $\chi_{cont.}(\nu)$ have been included and are assumed to be known a-priori and constant throughout the iteration process. It should be noted here that because our study deals only with infrared limb emissions, the effect of Rayleigh and Mie scattering are not relevant and, therefore, not included. Accounting for equations (2.13) and (2.14), the total source function is just

$$S(\nu) = \frac{\eta(\nu)}{\chi(\nu)}.$$
(2.15)

The SEE is a linear system and can be solved for the populations if all rate coefficients are prescribed, which in the case of R_{ij} means that the radiation field is known. On the other hand, the RTE is also linear and can be solved for the radiation field if the populations are known. The non-LTE problem requires the joint solution of the SEE and RTE. Figure 2.1 shows show these quantities couple to one another.



Figure 2.1: Flow diagram of the coupled SEE and RTE equations of non-LTE radiative transfer. See text for a description of symbols and detailed explanation.

The mean intensity, \bar{J} , is found by integrating the specific intensity, $I_{\mu\nu}$, using Eq.

(2.8), where one needs to first solve the RTE. The RTE is comprised of the source function, extinction and emission coefficients which, in turn, depend on the level populations (2.10) and (2.11). The level populations, however, are dependent on the intensities (2.1) and (2.8). To solve this set of coupled equations, the radiative field and level populations must be determined simultaneously. The RTE, Eq. (2.9), couples the level populations at different altitudes to one another, making the level populations in the SEE, (2.1), non-local (and non-linear). The densities terms, n^{β} , in both collisional processes, V-T and V-V, are considered to be known, however, only the latter process (V-V) creates additional (local) non-linearity in the SEE.

The following section, more detail regarding several unique steady states of the molecular gas will be considered, including Complete Thermodynamic Equilibrium (CTE) (when mechanical, chemical, and thermal equilibrium are all satisfied without any tendency for change of the state), LTE and partial LTE (when complete thermal equilibrium breaks down but rotational sub-levels for each vibrational transition remain in LTE). The discussion will follow similar situations presented in Mihalas [1978] and Ivanov and Avrett [1975] for an atomic gas in the astrophysical context.

In the following discussion, the index i corresponds to the pair of indices vj, which specify the ro-vibrational states of a molecule, where v and j represent the vibrational level and rotation sub-level, respectively. For a triatomic molecule, such as CO₂, v represents the combination of three vibrational quantum numbers in addition to the associated angular momentum quantum number.

2.2.1 Complete Thermodynamic Equilibrium (CTE)

In CTE, the velocity distribution of molecules is Maxwellian and the level populations obey the Boltzmann law

$$\frac{n_{v'j'}}{n_{vj}} = \frac{g_{v'j'}}{g_{vj}} \exp\left(-\frac{E_{v'j'} - E_{vj}}{kT}\right),$$
(2.16)

where the temperature T is the only parameter that completely determines this state. The primed quantities represent the upper level for the transition, k is the Boltzman constant, and $g_{v'j'}$ and g_{vj} are the degeneracy of the ro-vibrational state. Additionally, in CTE, the radiation intensity is isotropic, unpolarised, homogenous and is given by the Planck function, where the line center frequency is expressed as

$$\nu_{\upsilon'j'} = \frac{1}{h} (E_{\upsilon'j'} - E_{\upsilon j}) \tag{2.17}$$

$$\bar{J}_{\upsilon'j',\upsilon j} = \mathcal{B}(\nu_{\upsilon'j',\upsilon j}, T) = \frac{2h\nu_{\upsilon'j',\upsilon j}^3}{c^2} \left[\exp\left(\frac{h\nu_{\upsilon'j',\upsilon j}}{kT}\right) - 1 \right]^{-1}.$$
 (2.18)

Here $\bar{J}_{\nu\nu'}$ is the radiative mean intensity which is also the Planck function. Moreover, in CTE all processes obey the principle of detailed balance: each process is exactly compensated by its inverse. In particular, the number of radiative transitions from $v'j' \rightarrow vj$ then is equal to the number of radiative excitations $vj \rightarrow v'j'$

$$n_{\upsilon'j'}(A_{\upsilon'j',\upsilon j} + B_{\upsilon'j',\upsilon j}\bar{J}_{\upsilon'j',\upsilon j}) = n_{\upsilon j}B_{\upsilon j,\upsilon'j'}\bar{J}_{\upsilon j,\upsilon'j'}$$
(2.19)

For collisional transitions the detailed balance relation has the form

$$n_{v'j'}C_{v'j',vj} = n_{vj}C_{vj,v'j'}$$
(2.20)

or with accounting for equation (2.16)

$$C_{vj,v'j'} = C_{v'j',vj} \frac{g_{v'j'}}{g_{vj}} \exp\left(-\frac{E_{v'j'} - E_{vj}}{kT}\right).$$
 (2.21)

2.2.2 Local Thermodynamic Equilibrium (LTE)

LTE is the state of the gas in which the velocity distribution of molecules is Maxwellian, populations follow the Boltzmann distribution (2.16), while the radiation intensity is not, in general, given by Planck function. Such a state can exist when both radiative and external source terms in the SEE are small in comparison to the collisional terms. If the velocity distribution of all molecules is Maxwellian then the detailed balance relations in equation (2.6) are still valid. If one now neglects all radiative terms as well as the source terms in the SEE, these equations reduce to the Boltzmann law. Since these equations are linear in the quantities n_{ν} , the equilibrium populations are in fact the only solution. The temperature in the Boltzmann relation may now change from point to point. A Maxwellian gas is also in LTE in those layers where the external source terms in the SEE are small compared to collisional terms and the radiative terms dominate the collisional terms but cancel each other according to the relations in equation (2.19). This occurs, for instance, for optically thick transitions in deep atmospheric layers. LTE is valid in the lower atmosphere where thermal collisions are frequent enough to maintain the Boltzmann statistics of the internal energy levels of a particular molecule.

The population probability W_{vj} of a specific molecular species α to be in ro-vibrational level vj can be written as

$$W_{\upsilon j} = \frac{n_{\upsilon j}}{n^{\alpha}} \tag{2.22}$$

where n^{α} is the total number density of molecular species α . Accounting for the Boltzmann relation, the expression can be written as

$$W_{vj}^{*} = \frac{g_{vj}}{Q^{*}(T)} \exp(-\frac{E_{vj}}{kT})$$
(2.23)

where the star symbol (*) denotes LTE values and

$$Q^*(T) = \sum_{\upsilon j} g_{\upsilon j} \exp(-\frac{E_{\upsilon j}}{kT})$$
(2.24)

is the sum of all internal ro-vibrational probability sates, such that

$$\sum_{vj} W_{vj}^* = 1.$$
 (2.25)

The vibrational probability, \mathbf{W}_{v}^{*} , that a molecule in the vibrational state, v, is

$$n_{\upsilon} = \sum_{j} n^{\alpha} W_{\upsilon}^* \tag{2.26}$$

where n_v is the population of vibrational level v. It should be noted that the energy of a given ro-vibrational level is equal to the sum of the vibrational energy E_v of state v and the rotational energy $E_{j,v}$ relative to j=0 of sub-level j of state v

$$E_{vj} = E_v + E_{j,v}.$$
 (2.27)

Additionally, the statistical weight of a given ro-vibrational level is given by

$$g_{\upsilon j} = g_{\upsilon} g_{\upsilon}(j) \tag{2.28}$$

which is the product of statistical weight g_v of level v and degeneracy $g_v(j)$ of its rotational sub-level, j.

Based on Eq. (2.22) and accounting for (2.27) and (2.28), it can be shown that

$$W_{\upsilon}^{*} = g_{\upsilon} \frac{Q_{\upsilon}^{*}(T)}{Q^{*}(T)} \exp(-\frac{E_{\upsilon}}{kT})$$
(2.29)

where $Q_{v}^{*}(T)$ is the rotation partition function for level v

$$Q_{v}^{*}(T) = \sum_{j} g_{v}(j) \exp(-\frac{E_{j,v}}{kT})$$
(2.30)

Finally, the population probability for the rotational sub-level, j, of vibrational level v can be expressed as

$$W_{v}^{*}(j) = \frac{g_{v}(j)}{Q_{v}^{*}} \exp(-\frac{E_{j,v}}{kT}).$$
(2.31)

Based on the derivations above, Eq. (2.22) can be rewritten as

$$W_{vj}^* = W_v^* W_v^*(j). (2.32)$$

From (2.26), the LTE ratio of two vibrational populations can be expressed as

$$\frac{n_{v'}}{n_v} = \frac{W_{v'}^*}{W_v^*} = \frac{g_{v'}}{g_v} \exp(-\frac{E_{v'} - E_v}{kT}) \frac{Q_{v'}^*(T)}{Q_v^*(T)}.$$
(2.33)

2.2.3 Partial LTE

In planetary atmospheres, complete LTE or non-LTE conditions never exist. At low altitudes where the density is relatively high, collisional processes dominate the excitation and de-excitation mechanisms governing the population of molecular levels which leads to LTE. In the middle and upper atmosphere, where the density is much lower, the higest vibrational levels start to depart from the Boltzmann distribution. Processes such as absorption and emission of radiation in molecular bands, inelastic collisions which result in vibrational-translational (VT) and vibrational-vibrational (VV) energy exchanges (redistribution of excitation between colliding molecules), and chemical production and loss of excited molecules must be taken into account. As the density decreases further, lower vibrational levels start to depart from LTE, however, the rotational distribution of all vibrational levels still remain thermalized, where their distribution follows the Boltzmann law. Rotational structure departs from LTE only in the highest layers of the atmosphere. In our case, solving the non-LTE problem in the middle atmosphere requires detailed knowledge of vibrational non-LTE and assuming all rotational levels are in LTE.

The gas is said to be in a vibrational non-LTE state when the level populations do deviate from the Boltzmann law while the molecular velocity distribution remains Maxwellian. One may describe this state with the same probability formalism as was used above for the case of LTE. By assuming rotational LTE, the number of unknown variables in the SEE are greatly reduced since the rotational probability $W_v^*(j)$ is known for each vibrational level, v, and only the vibrational populations, n_v , need to be found. The probability of a molecule in vibrational level v and rotational sub-level j can be expressed as

$$W_{vj} = W_v W_v^*(j)$$
 (2.34)

where $W_v^*(j)$, which is in LTE, is still given by (2.31) but W_v , which is now in non-LTE, is

$$W_{\upsilon} = g_{\upsilon} \frac{Q_{\upsilon}^*(T)}{Q} \exp\left(-\frac{E_{\upsilon}}{kT_{\upsilon}}\right)$$
(2.35)

with excitation temperatures $T_v = T$ for levels that are still in LTE and $T_v \neq T$ for those in non-LTE. The total partition function Q, which is no longer only a function of T, is

$$Q = \sum_{\upsilon} g_{\upsilon} \exp\left(-\frac{E_{\upsilon}}{kT_{\upsilon}}\right) Q_{\upsilon}^{*}(T).$$
(2.36)

The SEE has the same form of Eq. (2.1) but it is summed over the rotational sub-levels, j. Because transitions between rotational sub-levels within vibrational level v cannot change its total population, n_v , these rotational terms cancel, which results in

$$n_{\upsilon'} \left(\sum_{\upsilon} R_{\upsilon'\upsilon} + C_{\upsilon'}^{\to} \right) = \sum_{\upsilon} n_{\upsilon} R_{\upsilon\upsilon'} + C_{\upsilon}^{\leftarrow} + Y_{\upsilon'}.$$
(2.37)

where the radiative coefficients are

$$R_{v'v} = \sum_{j'j} W_v^*(j) R_{v'j',vj} = A_{v'v}(T) + B_{v'v}(T) \bar{J}_{v'v}$$
(2.38)

and

$$A_{v'v}(T) = \sum_{j'j} W_v^*(j) A_{v'j',vj}$$
(2.39)

which is the spontaneous de-excitation rate per molecule for the entire ro-vibrational band $v' \rightarrow v$. For v' < v, $A_{v'v} = 0$. From Eq. (2.38), $B_{v'v} \bar{J}_{v'v}$ is the stimulated emission or absorption rate for a ro-vibrational band per molecule in state v'. These radiative coefficients, also known as Einstein coefficients, are related as follows

$$A_{v'v} = \frac{2h\nu_{v'v}^3}{c^2} B_{v'v} \qquad , \qquad g_{v'} B_{v'v} = g_v B_{vv'} \qquad (2.40)$$

where the vibrational transition frequency $\nu_{\upsilon'\upsilon}$ is

$$\nu_{\upsilon'\upsilon} = \frac{1}{h} \left(E_{\upsilon'} - E_{\upsilon} \right). \tag{2.41}$$

From Eq. (2.38), the Einstein coefficients are dependent on the kinetic temperature, which is a result of summing rotational partition function in Eq. (2.31). However, in planetary atmospheres this dependence can be ignored due to the generally small temperature range. The $\bar{J}_{v'v}$ in Eq. (2.38) can be expressed as

$$\bar{J}_{\upsilon'\upsilon} = \frac{1}{B_{\upsilon'\upsilon}} \sum_{j'j} W_{\upsilon}^*(j) B_{\upsilon'j',\upsilon j} \bar{J}_{\upsilon'j',\upsilon j}$$
(2.42)

which represents the integrated mean intensity in the ro-vibrational band.

The collisional coefficients, $C_{v'}^{\rightarrow}$ and C_{v}^{\leftarrow} , are still very similar to Eq. (2.1) but involve only vibrational populations. The (V-T) collisional coefficients between vibrational levels

$$C_{v'v} = \sum_{j'j} W_v^*(j) C_{v'j',vj}$$
(2.43)

are related thought the detailed balance relation

$$W_{v'}^* C_{v'v} = W_v^* C_{vv'} \quad \text{or} \quad C_{vv'} = C_{v'v} \frac{g_{v'}}{g_v} \exp\left(-\frac{E_{v'} - E_v}{kT}\right) \frac{Q_{v'}^*}{Q_v^*} \tag{2.44}$$

which can be derived by summing the detailed balance equation (2.20) over rotational sublevels j for ro-vibrational transition while accounting for Eq. (2.23).

2.3 Accelerated Lambda Iteration Method of Solution

The majority of studies in planetary atmospheres use the matrix method (see López-Puertas and Taylor [2001] for detailed description) to solve the non-LTE problem, which use very large matrices $(L \times D) \times (L \times D)$, where D is the number of altitude points and L is the number of molecular levels. The matrix method significantly decelerates the calculations for the non-LTE solution. In this section, a brief overview will be given to another approach to the solution of the non-LTE problem implemented in the ALI-ARMS code [Gusev and Kutepov, 2003] called the Accelerated Lambda Iteration (ALI) method.

Discussed in the previous section, the radiative coefficients in the SEE make the non-LTE problem non-liner and non-local, and the $\bar{J}_{v'v}$ depends on the level populations at all altitudes in the atmosphere. Additional non-linearity is introduced by molecular collisions (V-V processes) because their rates depend on the level populations of both colliding molecules. A straightforward solution is to iterate between all equations by following the arrows illustrated in Figure 2.1. This method is called the lambda iteration (LI) [Rybicki and Hummer, 1991]. LI iteratively solves the RTE and SEE until the system converges. Its name comes from the fact that the process of iteration can be mathematically expressed in the form of a "Lambda" operator (i.e. the entire procedure of computing mean intensities \bar{J}_{ij} from the source function). Compared to standard matrix methods, LI uses significantly smaller matrices which are no larger than $L \times L$, where L is the total number of molecular levels. For some transitions, however, the atmosphere is optically thick and the photons can be effectively trapped in cores of optically think lines. An immediate consequence is that a large number of iterations is required before the final state which may result in a slow convergence rate where false solutions appear to be stable or the accumulation of numerical errors will cause the process to diverge. This difficulty is overcome in the accelerated lambda iteration technique.

Astrophysicists developed this technique which is similar to LI but the equations are pre-conditioned to speed up the convergence. The ALI scheme utilizes iteration with an approximate (or accelerated) lambda operator. This method is based on operator splitting where the diagonal part of the matrix, which represents trapped photons in the cores of optically thick lines, is separated from the rest. ALI combines the quick solution to the non-LTE problem using small matrices and significantly accelerates the convergence procedure. Another advantage of the diagonal approximation is that the SEE remain completely local and the linearity is easily restored by preconditioning. Rybicki and Hummer [1991] described several strategies for this procedure. The ALI method is a standard technique in some different versions which is applied in stellar astrophysics for spectral modeling and non-LTE modeling of stellar atmospheres. For an in depth comparison of additional techniques,



Figure 2.2: Convergence plot for the CO_2 problem in Earth's atmosphere from Gusev and Kutepov [2003]. The labels on the profiles describe various iteration schemes applied in combination with the method of solution of the radiative transfer equation. (DFE) Discontinuous Finite Element, (MF) Modified Feutrier method, (Short-0) Short characteristic of zeroth order, (Short-1) Short characteristic of first order. NG indicates that Ng-acceleration was applied and LI stands for Lambda iteration.

see Gusev and Kutepov [2003] and Kutepov et al. [1998].

For solving the non-LTE problem, in addition to the operator splitting technique discussed above, the ALI-ARMS code uses another option for iteration improvement called Ng-accelerations [Ng, 1974]. The Ng-acceleration method uses previous results for molecular level populations to estimate the new "accelerated" set of populations according to some minimization criteria. Figure 2.2 illustrates the efficiency of solving the non-LTE problem using various methods.

2.4 ALI-ARMS current status

The current version of the ALI-ARMS code is based on the adaptionation of Rybicki and Hummer [1991] and is completely generalized, where an arbitrary number of molecules composed of an arbitrary number of excited levels can be treated in a given planetary atmosphere by a-priori information such as (a) planetary atmospheric properties (pressure, temperature, VMR of molecules), (b) solar spectra (for daytime conditions), (c) molecular and atomic vibrational and ro-vibrational energies, (d) spectroscopic information (Einstein coefficients for ro-vibrational or rotational transition, line half-widths), and (e) collisional rate coefficients for V-T, V-V, and V-E transitions.

The ALI-ARMS code provides several options to solve the radiative transfer equation for a plane-parallel atmosphere [Gusev and Kutepov, 2003]. Among them are the long and short characteristics of zeroth and first order, the modified Feautrier algorithm, and the discontinuous finite element algorithm.

Chapter 3: OH Non-LTE Model

3.1 Applied OH non-LTE Model

A detailed description of the components of our OH non-LTE model will be presented. Such components include the molecular (vibrational and rotational) energy levels, spectroscopic parameters, chemical reactions, and main collisional V-T, V-V, and V-E processes.

3.1.1 Molecular Energy Levels

A molecular gas can store energy either as potential or kinetic in a number of different ways including: 1) electronic energy, which is stored as potential in excited electronic quantized configurations. Transitions occurring between these levels emit photons in the ultra-violet (UV) or optical wavelengths; 2) vibrational energy, which is stored in quantized configurations in sub-levels of an electronic energy state. Vibrational energy produces the oscillatory motion of atoms within a molecule by converting potential energy to kinetic energy, and vice versa. Transitions occurring between different vibrational levels of the same electronic state emit infrared radiation; 3) rotational energy, which is stored in quantized configurations in sub-levels of a vibrational energy state. Rotational energy stores kinetic energy associated with the tumbling of molecules. Transitions occurring between rotational levels of the same vibrational state emit radiaton in the microwave. The most commonly observed atmospheric emissions involve these electronic, vibrational, or rotational transitions. In some cases, however, a combination of these types of transitions occur. In this study, a majority transitions involve both a transition to a new vibrational and rotational level, which, for short, are called ro-vibrational transitions.

The hydroxyl (OH) molecule emits infrared radiation from ro-vibrational transitions of the electronic ground state $X^2\Pi$. Produced in the chemical reaction between hydrogen (H) and ozone (O₃), OH is populated up to vibrational level OH(v = 9) (Ohoyama et al. [1985], Charters et al. [1971]). We consider 9 vibrationally excited levels in addition to the ground state of OH. The energies of the vibrational levels, G(v), are determined by the following formula

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 - \omega_e z_e(v + \frac{1}{2})^4 + \dots$$
(3.1)

where v is the vibrational level and ω_e , x_e , y_e , and z_e are well-known constants taken from Bernath and Colin [2009]. Each vibrational level includes two sets of spin-orbit coupling states, $X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$. It should be noted that for calculations using our OH model, the two spin-orbit states within each vibrational level are in LTE with one another, as their energy level differences are very small. Additionally, each spin-orbit state is comprised of its own rotational substructure. The rotational energy levels are represented by unit increments starting from 3/2, for spin state, $X^2\Pi_{3/2}$, and 1/2, for spin state $X^2\Pi_{1/2}$. The energy for the rotational levels in each spin-orbit state relative to the vibrational level can be expressed using the following formulas

$$X^{2}\Pi_{3/2}: F_{1}(J) = B_{v}\left[\left(J + \frac{1}{2}\right)^{2} - 1 - \frac{1}{2}\sqrt{4\left(J + \frac{1}{2}\right)^{2} + Y_{v}(Y_{v} - 4)}\right] - D_{v}J^{4}$$
(3.2)

$$X^{2}\Pi_{1/2}: F_{1}(J) = B_{v}\left[\left(J + \frac{1}{2}\right)^{2} - 1 + \frac{1}{2}\sqrt{4\left(J + \frac{1}{2}\right)^{2} + Y_{v}(Y_{v} - 4)}\right] - D_{v}J^{4}$$
(3.3)

where J represents the rotational level and the constants B_v , Y_v , and D_v for each vibrational level, v, are taken from [Bernath and Colin, 2009].

Vibrational and rotational energy levels implemented into ALI-ARMS were calculated using Eqs. (3.1)-(3.3). Vibrational energy levels of lowest rotational state are displayed in Table 3.1.

The number of rotational energy levels considered are different for each vibrational level.

Spin-State	Level	Vibrational Energy ¹ (cm ^{-1})		
3/2	1	3568.509		
1/2	1	3695.381		
3/2	2	6971.370		
1/2	2	7098.865		
3/2	3	10210.565		
1/3	3	10338.665		
3/2	4	13287.185		
1/2	4	13415.861		
3/2	5	16201.321		
1/2	5	16330.567		
3/2	6	18951.863		
1/2	6	19081.633		
3/2	7	21536.211		
1/2	7	21666.424		
3/2	8	23949.824		
1/2	8	24080.387		
3/2	9	26185.789		
1/2	9	26316.518		

Table 3.1: OH vibrational energy levels included in the model

¹Energy of the lowest rotational level

The low vibrational states are comprised of 40 rotational energy levels and decrease down to 20 levels for high vibrational states. For each rotational structure, the rotational partition function, $Q_v^*(T)$, for each vibrational level v, Eq. (2.30), reaches a maximum value, where additional rotational levels do not change the total rotational partition function, $Q_v^*(T)$.

Figure 3.1 displays the energy level diagram of our OH model where the black horizontal levels represent the vibrational structure at their respective energy levels calculated in Table 3.1. The identification number for each vibrational level is displayed adjacent to their respective level, where the first two digits represent the spin orbit state (32 for $X^2\Pi_{3/2}$ and 12 for $X^2\Pi_{1/2}$) while the last two digits designate the vibrational level number. Rotation substructure for each spin-orbit state is not shown.



Figure 3.1: OH energy level diagram. Arrows show the main radiative transitions and collisional energy exchanges. See text for discussion.

Figure 3.1 also displays ro-vibrational transitions (dashed arrows) and chemical (orange/green) and collisional (red/blue) processes. These depicted processes are specific components associated with the SEE for OH,

$$n_{i}^{OH} \sum_{j} \left(A_{ij} + B_{ij} \bar{J}_{ij} + C_{ij}^{V-T} + \sum_{kl} n_{k} C_{ij,kl}^{V-V} \right) =$$

$$\sum_{j} n_{j}^{OH} \left(A_{j>i} + B_{ji} \bar{J}_{ji} + C_{ji}^{V-T} + \sum_{kl} n_{l} C_{ji,lk}^{V-V} \right) + Y_{i},$$
(3.4)

where Eqs. (2.3), (2.5), and (2.7) have been substituted into Eq. (2.1). Eq. (3.4) represents the SEE for each vibrational level, i, of OH. The following sections will describe each component of Eq. (3.4) as it relates to our OH non-LTE model.

3.1.2 Einstein Coefficients

Spontaneous emission is the process by which a molecule "spontaneously" (without any external influence) decays from a higher energy level to a lower one. The process is defined by the Einstein coefficient $A_{v'j'\to vj}$ (s⁻¹), where the index, i, from Eq. (3.4) now corresponds to the pair of indices vj, which specify the ro-vibrational states of a molecule. The Einstein coefficient gives the probability per unit time that a molecule in ro-vibrational state v'j' with Energy $E_{v'j'}$ will decay spontaneously to ro-vibrational state vj with Energy E_{vj} , emitting a photon with energy $E_{vj'} - E_{vj} = h\nu_{v'j'vj}$, where $\nu_{v'j'vj}$ is the line center frequency.

v'v	0	1	2	3	4	5	6	7	8	$\sum A(s^{-1})$
1	17.26									17.26
2	10.30	23.44								33.74
3	1.121	27.51	22.04							50.67
4	0.1342	4.111	48.53	16.32						69.10
5	0.0194	0.6237	9.396	70.51	9.320					89.87
6	0.0034	0.1096	1.740	17.12	90.81	3.864				113.65
7		0.0226	0.3627	3.773	27.15	106.7	2.537			140.55
8			0.0871	0.9193	6.972	39.31	115.0	7.346		169.63
9				0.2508	1.995	11.33	54.03	110.9	18.79	197.30

Table 3.2: Einstein Coefficients $A_{\nu' \to \nu}$ for the OH $X^2 \Pi_{3/2} \to X^2 \Pi_{3/2}$ state band transitions

The Einstein coefficients, $A_{v'j' \rightarrow vj}$, for ro-vibrational transitions were taken from the HITRAN (HIgh-resolution TRANsmission molecular absorption) 2012 database [Rothman et al., 2013]. This database is a long-running project started by the Air Force Cambridge Research Laboratories (AFCRL) in the late 1960s in response to the need for detailed knowledge of the infrared properties of the atmosphere. For our OH model, we included transition

lines up to $\Delta v=6$ for all vibrational levels (i.e. for v=9, we considered transitions from vibrational levels $9\rightarrow 8$, $9\rightarrow 7$... $9\rightarrow 3$). Each transition takes into account all combinations of spin-orbit states from $X^2\Pi_{3/2} \rightarrow X^2\Pi_{3/2}$ states, $X^2\Pi_{3/2} \rightarrow X^2\Pi_{1/2}$ states, $X^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2} \rightarrow X^2\Pi_{3/2}$ states, and $X^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$ states. Rotational transition selection rules are also allowed: the P-branch, when $\Delta J = -1$, the Q-branch when $\Delta J = 0$, and the R-branch when $\Delta J = +1$. Overall 39 ro-vibrational band transitions for each spin-orbit state combination are considered which make up a total of 11,680 OH ro-vibrational transitions lines.

Table 3.2 displays a set of Einstein coefficients, $A_{\nu' \to \nu}$, for the 39 OH $X^2 \Pi_{3/2} \to X^2 \Pi_{3/2}$ state band transitions calculated using Eq. (2.39), assuming rotational LTE and T = 220 K. The three other spin-orbit state combinations are displayed in Appendix B.

The Einstein coefficient of stimulated emission $B_{v'v}$ and absorption $B_{vv'}$ can be obtained from $A_{v'v}$ using Eq. (2.40), where $\nu_{v'v}$, $g_{v'v}$, and $g_{vv'}$ are given in HITRAN 2012 [Rothman et al., 2013].

Table 3.3 displays main chemical and collisional processes included in the OH model. In the following section, a description of these reactions will be presented, as well as a brief overview of each reaction including their various and state-to-state treatments which previous studies have used.

3.1.3 Chemical Formation of OH(v)

Chemical reactions are considered an external pumping source for OH and are denoted by Y_i in the OH SEE (Eq. 3.4). This component is the product of the chemical rate coefficient and its associated branching ratio for each vibrational level. A description of both terms is presented below.

In the mesosphere and lower thermosphere, OH is produced in the chemical reaction between hydrogen (H) and ozone (O₃), Reaction R1 in Table 3.3. The reaction, which is exothermic, excites OH up to vibrational level v = 9 (Charters et al. [1971], Ohoyama et al. [1985], and Klenerman and Smith [1987]). Laboratory studies by Lee et al. [1978] and

	Reaction	Reaction Rate $(cm^3 sec^{-1})$	Reference				
(R1)	$\mathrm{H} + \mathrm{O}_3 \rightarrow \mathrm{OH}(\nu \leq 9) + \mathrm{O}_2$	$k_1 = f_{\nu}^a \times 1.4 \times 10^{-10} exp(-470/T)$	Sander et al. [2011] &				
			Adler-Golden [1997]				
(R2)	$OH(\nu \leq 9) + N_2(0) \leftrightarrow OH(\nu - 1) + N_2(1)$	$\mathbf{k}_2 = \mathbf{f}_{\nu}^b \times 1.4 \times 10^{-13}$	Adler-Golden [1997] &				
			Lacoursière et al. [2003]				
(R3)	$OH(\nu \leq 9) + O_2(0) \leftrightarrow OH(\nu') + O_2(1)$	$k_6 = f_{\nu}^c \times 10^{-13}$	Adler-Golden [1997]				
	$\nu' \!=\! 0,\!1,\!2,\ldots \nu \!-\! 1$						
(R4)	$\mathrm{OH}(\nu \geq 5) + \mathrm{O}(^3\mathrm{P}) \leftrightarrow \mathrm{OH}(0 \leq \nu' \leq \nu\text{-}5) + \mathrm{O}(^1\mathrm{D})$	$k_4 = f_{\nu}^d \times (2.3 \pm 1) \times 10^{-10}$	Kalogerakis et al. [2016] &				
			Sharma et al. [2015]				
(R5)	$OH(\nu) + O(^{3}P) \rightarrow H + O_{2}$	$k_4 = 1.18 \times 10^{-11} exp(180/T)$	Sander et al. [2011]				
$^{a}\mathrm{f}_{\nu}(\nu$	=5-9) = (0.01, 0.03, 0.15, 0.34, 0.47)						
${}^{b}f_{\nu}(\nu=1-9) = (0.06, 0.10, 0.17, 0.30, 0.52, 0.91, 1.6, 7, 4.8)$							
${}^{c}f_{\nu}(\nu=1-9) = (1.9, 4, 7.7, 13, 25, 43, 102, 119, 309)$							
$^{d}\mathbf{f}_{\nu}(\nu =$	$f_{\nu}(\nu=5-9) = (0.91, 0.61, 0.74, 0.87, 1.0)$						

Table 3.3: Chemical and Collisional Processes Included in the OH model

Keyser [1979] measured the rate coefficient for Reaction R1 over the 200-400 K range. Upon formation, OH is vibrationally excited over a distribution of levels. This distribution, also known as the branching ratios, is defined as the population probability for an OH vibrational level to be excited upon OH formation. Three laboratory studies (Charters et al. [1971], Ohoyama et al. [1985], and Klenerman and Smith [1987]) measured the associated branching ratios for this reaction and their results are displayed below in Table 3.4, where v is the vibrational level and f(v) are the associated normalized branching ratios. Charters et al. [1971] and Klenerman and Smith [1987] showed that the chemical reaction will only excite the upper vibrational levels (v = 6-9) of OH, and no levels below OH(v=6) are excited. Ohoyama et al. [1985], however, measured a lower overall probability for the upper levels to be excited, as well as, moderate probability down to v = 4. The branching ratio displayed from Ohoyama et al. [1985] were adjusted using the relative transition probabilities of Murphy [1971]. Results of two theoretical studies (Steinfeld et al. [1987] and Adler-Golden [1997]) are also displayed in Table 3.4. Steinfeld et al. [1987] extrapolated Charters et al. [1971] branching ratios to lower v using information theory and Adler-Golden [1997] further

Branching Ratio		Reference		
v	f(v)			
9-6	0.39, 0.31, 0.15, 0.15	Charters et al. [1971]		
9-4	0.32, 0.29, 0.19, 0.06, 0.06, 0.06	Ohoyama et al. [1985]		
9-6	0.48, 0.27, 0.17, 0.08	Klenerman and Smith [1987]		
9-5	0.43, 0.35, 0.17, 0.04, 0.01	Steinfeld et al. [1987]		
9-5	0.47, 0.34, 0.15, 0.03, 0.01	Adler-Golden [1997]		

Table 3.4: $H+O_3$ Branching Ratios

renormalized them to the Einstein coefficients of Nelson Jr et al. [1990]. The branching ratios in both studies closely resemble that of Klenerman and Smith [1987].

All sets of branching ratios have been used in OH modeling over the years. Studies performed by McDade et al. [1987] and McDade and Llewellyn [1987] use branching ratios measured by Ohoyama et al. [1985], Makhlouf et al. [1995] and Dodd et al. [1994] used measurements of Klenerman and Smith [1987], while Funke et al. [2012], Xu et al. [2012], López-Puertas et al. [2004], Mlynczak et al. [2013] and Smith et al. [2010] used branching ratios calculated by Adler-Golden [1997] (originally measured by Charters et al. [1971]). In this study, the total chemical production rate of OH(v), Reaction R1 in Table 3.3, is taken from Sander et al. [2011] and the associated branching ratios for v were taken from Adler-Golden [1997]. These values are the most widely accepted and have been used in the most recent OH modeling studies.

3.1.4 Collisional Reactions

The main collisional partners of OH are the atmospheric constituents which comprise the overwhelming majority of the total density in the MLT: molecular nitrogen, N_2 , (~70-78%) per unit volume), molecular oxygen, O_2 , (~8-21%), and atomic oxygen, $O(^{3}P)$, (~1-17%). These constituents are responsible for the dominant relaxation mechanisms due to their high densities, as well as act as intermediate energy pathways between trace gases. After a rigorous check, our OH model only needs to consider relaxation mechanisms with the above collisional partners. All other OH collisional partners, especially with trace gases, can be ignored. It is important to note here that the N₂, O₂, and O(³P) reactions with OH(v) can be treated in several different ways: 1) Single-Quantum relaxation (SQ), where OH in state v quenches to state v-1 upon collision with its partner, 2) Multi-Quantum relaxation (MQ), where OH in state v quenches to v' which can be any state lower that v, and 3) Sudden-Death quenching (SD), where OH in state v quenches to its ground state v=0 (also simulates chemical quenching). Additionally, the state-to-state quenching reactions can either be a thermal (V-T), C_{ij}^{V-T} or C_{ji}^{V-T} in Eq. (3.4), or non-thermal (V-V, V-E, etc.) collision, $C_{ij,kl}^{V-V(E)}$ or $C_{ji,lk}^{V-V(E)}$ in Eq. (3.4), where the latter influences the population (k,l indices) of the collisional partner. A description of quenching treatments used in our model. in addition to its justification will be discussed below.

3.1.5 $OH(v)+N_2$ reaction

The widely accepted treatment of the $OH(v)+N_2$ reaction has been single-quantum V-V quenching. Kumer et al. [1978] showed that there is a strong resonance between OH(v=9,8)and $N_2(0,1)$ vibrational levels if one assumes a single-quantum process. Burtt and Sharma [2008] also showed that this reaction strongly favors a single-quantum process based on

their second-order theoretical calculations. Rate coefficients for a small set of OH vibrational levels, OH(v=7-9) have been measured (Knutsen et al. [1996] and Dyer et al. [1997]) for N₂, which is found to be an inefficient ("slow") quencher of OH(v), except near OH(v=8)were an OH-N₂ resonance occurs. In general, very slow quenching tends to occur in singlequantum steps, as predicted by Schwartz-Slawsky-Hirschfeld theory [Adler-Golden, 1997]. Additionally, a majority of OH modeling studies (sf. Adler-Golden [1997], Xu et al. [2012], Funke et al. [2012], Mlynczak et al. [2013], Makhlouf et al. [1995]) have used this singlequantum treatment for this reaction for all OH(v) levels. López-Puertas et al. [2004], however, which attempted to model nighttime CO_2 4.3 μ m emissions, concluded that in order to fit measurements the $OH(v)+N_2$ reaction (which Kumer et al. [1978] showed contributed a significant amount of energy of $CO_2(v_3)$, needed to be treated as a multi-quantum V-V process (MQ, v'=2 or 3). This lone but controversial result will be considered in our CO₂ modeling studies in next chapter. In the OH model, the OH+N₂ collision, Reaction R2 in Tabel 3.3, is treated as a single-quantum V-V process, as a vast majority of experimental and theoretical studies support this treatment. Rate coefficients and branching ratios were taken from Adler-Golden [1997], which were originally interpolated by Makhlouf et al. [1995] from measurements by Rensberger et al. [1989] and Sappey and Copeland [1990]. We multiplied Reaction R2 by a low temperature factor of 1.4 for MLT regions [Lacoursière et al., 2003].

3.1.6 $OH(v)+O_2$ reaction

There have been numerous laboratory studies which have measured the rate coefficient in the $OH(v)+O_2$ reaction (s.f. Rensberger et al. [1989], Dodd et al. [1991], Chalamala and Copeland [1993], Knutsen et al. [1996], Dyer et al. [1997], and Lacoursière et al. [2003]). Laboratory measurements in addition to modeling studies [Adler-Golden, 1997] have shown that O_2 is at least a factor of ten times more efficient than N_2 at deactivating OH(v). The rate coefficients calculated by Adler-Golden [1997] are higher, by about 38%, than those measured in a laboratory, however, laboratory measurements were performed at room temperature (300 K). Lacoursière et al. [2003] showed that the rate coefficient of the OH- O_2 reaction at room temperature increases by 35% as temperature decreases to 223 K, which is comparable to the mesophere. As a result, calculated rate coefficients in Adler-Golden [1997] match quite well with laboratory measurements when scaled to mesopheric temperatures.

There has been debate as to the treatment of the $OH(v)+O_2$ reaction. The lack of any laboratory studies regarding specific state to state quenching processes for this reaction has led to much speculation for its proper treatment. Studies such as Makhlouf et al. [1995] and Funke et al. [2012] have assumed a single-quantum quenching for their OH modeling studies, whereas Russell and Lowe [2003] and Kaufmann et al. [2008] concluded that total sudden death and a mix of sudden death and single-quantum was the proper treatment. Adler-Golden [1997], using a semi-empirical parameterization of the state-to-state rate constants for OH(v) quenching by O_2 , found that a multi-quantum relaxation at high v but singlequantum at low v best fit their modeling of absolute OH(v) nightglow radiances. Several OH modeling studies (Smith et al. [2010], Savigny et al. [2012], Xu et al. [2012], Mlynczak et al. [2013], Kowalewski et al. [2014], and Grygalashvyly et al. [2014]) have adopted this treatment presented by Adler-Golden [1997]. For the $OH(v \leq 9) + O_2(0)$ collision, Reaction R3 in Table 3.3, we use single and multi-quantum $(v \rightarrow v-(1, \ldots, v))$ quenching, following the treatment described by Adler-Golden [1997]. Rate coefficients with associated branching ratios are taken from Table 1 and Table 3 of [Adler-Golden, 1997], respectively.

3.1.7 $OH(v)+O(^{3}P)$ reaction

Among all the OH collisional partners, the reaction involving $O(^{3}P)$ had created the largest uncertainty regarding the magnitude of its rate coefficients and state to state treatment. The range of published values for the rate coefficient of the OH(v) + O reaction is large. Xu et al. [2012] summarize a handful of the reaction rates determined by laboratory measurements, theoretical calculations, or ones estimated from modeling of observed OH nightglow, as displayed in Table 3.5.

		I I I
Rate Coefficient (× $10^{-11} \text{ cm}^3 \text{s}^{-1}$)	Vibrational Level Dependence	Reference
25.0; 10.5; 3.9	v=2-9; v=0; v=1	Makhlouf et al. [1995]
20.0	v independent	Adler-Golden [1997]
25.0	for $v=9,8$	Russell and Lowe [2003]
5.07, 4.52, 3.87, 3.22, 3.68, 3.05, 3.19, 3.42, 2.89	for $v = 9, 8, 7, 6, \dots, 0$	Varandas [2004]
10.0	for $v=9,8$	Copeland et al. [2006]
5.0	for $v=9,8$	Smith et al. $[2010]$
20.0 - 30.0	for $v=7$	Thiebaud et al. [2010]
$1.8 \times 10^{-11} \exp(180/T)$	v independent	Sander et al. [2011]
23.0 ± 10	for $v = 9$	Kalogerakis et al. [2016]

Table 3.5: Reaction Rate of $OH(v)+O(^{3}P)$ from Published Reports

The rate coefficients for the reactions in Table 3.5 range by more than a order of magnitude from 2.89×10^{-11} cm³s⁻¹ to 30×10^{-11} cm³s⁻¹. Some reports assume that the rate coefficients are dependent on vibrational level while others are vibrationally independent. Additionally, many published reports have assumed different state to state treatment of the OH(v)+O(³P) reaction. In many chemical models of OH nightglow (s.f. Makhlouf et al. [1995], Adler-Golden [1997], Russell and Lowe [2003], Smith et al. [2010]) a chemical reaction, OH(v)+O→O₂+H, is assumed. Theoretical studies by Varandas [2004] and Caridade et al. [2013] also support this by demonstrating that the chemical reaction OH(v)+O→O₂+H is faster than V-T quenching OH(v)+O→OH(v')+O. However, a recent theoretical study by Sharma et al. [2015] suggested a new multi-quantum quenching mechanism of this reaction and discussed in detail its available experimental and theoretical evidence. According to this mechanism, highly vibrationally excited OH(v), produced by Reaction R1, rapidly loses several vibrational quanta in collisions with O(³P) through a fast, spin-allowed, vibration-to-electronic energy transfer process that produces O(¹D),

Reaction R4 in Table 3.3. Recently, Kalogerakis et al. [2016] have presented the first laboratory demonstration of this new $OH(v) + O(^{3}P)$ relaxation pathway and measured its rate coefficient for v = 9. In this study, both multi-quantum and chemical quenching treatments are considered. For vibrational levels $OH(v \ge 5)$, multi-quantum and chemical quenching processes (Reactions R4 & R5, respectively) are active. The rate coefficient for Reaction R4 is taken from Sharma et al. [2015] with corresponding branching ratios while Reaction R5 is taken from Sander et al. [2011]. For vibrational levels OH(v < 5), only chemical quenching, Reaction R5, is active. Rate coefficients are displayed in Table 3.3.

3.2 Treatment of chemical and collisional reactions between spin-orbit states

For inter-vibrational collisions, (i.e ${}^{3/2}OH(v)$ is excited to ${}^{1/2}OH(v)$ after a collision with a main atmospheric constituent, or vice versa) we ensure that these level remain in LTE. For intra-vibrational collisions, (i.e in the case of a collisional reactions, OH in initial state ${}^{3/2}OH(v=9)$ collides with N₂, the final OH state can either quench to ${}^{3/2}OH(v=8)$ or ${}^{1/2}OH(v=8)$, if one assumes single-quantum quenching) the methodology described by Funke and López-Puertas [2000] for NO modeling will be implemented into the OH model. For these reactions, a weighting function is introduced which is derived from energy partition functions and is dependent on the final energy levels of the OH states,

$$W_{\upsilon',J',S'\to\nu'',J'',S''} = k_{\upsilon'\to\upsilon''}Q(T)^{-1} \times g(J'')\exp\bigg(-\frac{E_{J'',S''}^{s} + E_{J'',S''}^{\text{rot}}}{kT}\bigg), \qquad (3.5)$$

$$Q(T) = \sum_{J,S} g(J'') \exp\left(-\frac{E_{J'',S''}^{s} + E_{J'',S''}^{\text{rot}}}{kT}\right),$$
(3.6)

where v, J, and S represent the vibrational, rotational, and spin states of the molecule, respectively. Variable $k_{v' \to v''}$ is the total excitation rate coefficient into the vibrational state v'', g(J) is the statistical weight of J rotational level and E^s and E^{rot} are the spinorbit and rotational energy levels, respectively. Additionally, the chemical production can be described similarly to Eq. (3.5),

$$W_{x \to \nu, J, S} = f_{x \to \nu} k_x Q(T)^{-1} \times g(J'') \exp\left(-\frac{E_{J'', S''}^s + E_{J'', S''}^{\text{rot}}}{kT}\right),$$
(3.7)

$$Q(T) = \sum_{J,S} g(J'') \exp\left(-\frac{E_{J'',S''}^{s} + E_{J'',S''}^{\text{rot}}}{kT}\right),$$
(3.8)

with an additional term $f_{x\to\nu}$ which describes the vibrational nascent distribution and the production rate coefficient k_x .

3.3 Radiative Transfer Calculation

Solving the non-LTE problem for a molecular gas requires knowledge of \bar{J} terms in Eq. (3.4). The \bar{J} component is calculated after solving the radiative transfer equation along a given LOS (see Eq. 2.8). Under optically thick conditions ($\tau > 1$, see discussion in Chapter 5), when a photon is emitted from a given molecule, it gets absorbed and re-emitted along the LOS path at least once. In such cases, solving for \bar{J} is essential because stimulated absorption and emission (B-Einstein coefficients) are significant components in the SEE. For optically thin conditions, however, a photon from an emitting molecule does not get absorbed along the LOS path before escaping to space. Figure 3.2 displays the OH VMR (left-panel) and optical depths of OH (right-panel) as a function of its A-Einstein coefficients for 39 OH band transitions under nadir geometry. The calculated optical depths of OH are $\tau \ll 1$, never exceeding 1e-4, demonstrating that OH is optically thin. We performed rigorous calculations where we estimated \bar{J} and concluded that \bar{J} terms were not necessary for solving hte OH non-LTE problem due to the optically thin situation. Additionally, we

reported checking, and also found that it had very little influence on the calculated OH vibrational populations (<1%). As a result, the radiative transfer equation does not need to be solved and stimulated absorption or emission by OH in the atmosphere can be ignored in Eq. (3.4). Therefore, radiative processes for OH vibrational levels can be described by only considering A-Einstein coefficients. Eq. (3.4) can now be further reduced,

$$n_{i}^{OH} \sum_{j} \left(A_{ij} + C_{ij}^{V-T} + \sum_{kl} n_{k} C_{ij,kl}^{V-V} \right) =$$

$$\sum_{j} n_{j}^{OH} \left(A_{j>i} + C_{ji}^{V-T} + \sum_{kl} n_{l} C_{ji,lk}^{V-V} \right) + Y_{i},$$
(3.9)

where $B_{ij}\bar{J}_{ij}$ and $B_{ji}\bar{J}_{ji}$ components are omitted for optically thin molecules. This greatly reduces computational time for solving the non-LTE problem for OH(v) molecules.

After the non-LTE problem has converged, vibrational populations are used to solve the radiaitve transfer equation along the LOS path and calculate limb radiance. For a description of modeling non-LTE limb radiances, see Appendix A. The radiative transfer calculation for OH limb radiances is a simple and a computationally inexpensive procedure. Due to optically thin conditions, the radiative transfer equation is completely localized and follows Eqns. A.2 and A.3 only now without the need of the exponential terms and B-coefficients. With this considered, Eq. A.2 is not necessary anymore for solving the radiative transfer problem as it is a function of B-Einstein coefficients and may cause the denominator in the Source function (Eq. 2.15) to approach zero. This may cause instabilities and produce unrealistic limb radiances. Eq. A.3, however, is expressed in terms of only the emissivity coefficient (A-Einstein) and presents a stable solution for calculating limb radiance for all ro-vibrational transitions,

$$I(\nu, h) = \int_{x}^{x_{obs}} \eta(\nu, x) dx.$$
 (3.10)



Figure 3.2: Left-panel: Nighttime OH VMR for three WACCM scans taken on 06 May 2000 at Lat+075, 22 November 2000 at Lat+050, and 27 June 2010 at Lat+045. Right-panel: Optical depths for 39 OH band transitions under nadir geometry. The y-axis are the associated A-Einstein coefficients for each band transition.

Eq. 3.10 can be rewritten in matrix form, also known as the Abel Matrix,

$$\mathbf{L}(h) = \mathbf{A}(z, h)\mathbf{b}(h), \tag{3.11}$$

where z and h are altitude and tangent heights, respectively, vector $\mathbf{b}(\mathbf{h})$ represents the emissivity coefficient, $\eta(\nu, x)$, from Eq. (3.10), also known as the volume emission rate (VER) and A(z,h) is a matrix of z×h dimensions and contain the geometrical lengths at each altitude point (dx from Eq. 3.10) along the LOS for each tangent height. Finally, L(h) is a vector of length h and represents the calculated limb radiance, I(ν ,h) from Eq. (3.10). Calculating limb radiance using this matrix form is only valid for optically thin molecules, such as OH, because the stimulated emission and absorption coefficient can be ignored. Further, if limb radiance and geometrical lengths are known, which is true for SABER observations, an Abel Inversion procedure can be performed to calculate VERs.

3.4 Validation of OH Non-LTE Model

The validation the OH model was performed by reproducing vibrational temperatures (populations) simulated by the GRANADA (A Generic RAdiative traNsfer AnD non-LTE population Algorithm) model [Funke et al., 2012] using identical inputs and rate coefficients. Funke et al. [2012] supplied atmospheric inputs for various latitudes (-75, -45, -10, +10, +45, +75) and seasons (January, April, July, October) in their supplementary dataset, while OH reactions and associated rate coefficients were given in Table 13 of this paper.



Figure 3.3: Comparison of nighttime vibrational temperatures of $^{3/2}OH(\nu)$ for 10 April 2009, Latitude = 45°S. Left: dashed lines - ALI-ARMS; solid lines - GRANADA. Right: vibrational temperature differences.

Figure 3.3 (left-panel) displays nighttime vibrational temperatures (T_{vibs} , see Eq. 2.35) of $^{3/2}$ OH on 10 April 2009 at latitude 45°S. Dashed lines represent T_{vibs} from our ALI-ARMS model and solid lines represent the GRANADA model taken from the supplementary

dataset to Funke et al. [2012]. Only half of the OH vibrational levels were plotted to keep temperature profiles easily readable. Figure 3.3 (right-panel) displays their temperature differences.

The ALI-ARMS T_{vibs} are in good agreement with GRANADA T_{vibs} . For selected OH levels, vibrational temperatures differences (right-panel) agree to within 100 K for upper levels, 75 K for middle levels, and 25 K for lower levels. Vibrational temperatures for ^{1/2}OH spin also show similar agreement with GRANADA ^{1/2}OH T_{vibs} . Minor vibrational temperature differences between ALI-ARMS and GRANADA could be a result of methodologies regarding the solution to the non-LTE problem or how spin-orbit states are treated during chemical reactions or V-T, and/or V-V collisions. Additionally, vibrational populations, which are used to calculate limb radiances, agree for all OH(v) to within <1%.

For the remainder of this study, spin-orbit coupling between OH vibrational levels is not considered. This simplified approach has little effect on the OH emissions. The OH model will treat each vibrational level as a single state. The associated spectroscopic parameters will follow the formalism derived in Chapter 2 and the rate coefficients of chemical and collisional processes have not been weighted for spin-orbit dependencies, but are taken as total vibrational pumping/quenching rates.

3.5 Comparison of vibrational temperatures and ground states populations with OH Models

In the following sections, we present OH(v) vibrational temperatures and ground state populations calculated using our OH non-LTE model. These calculations are compared to three other OH models (Adler-Golden [1997], Funke et al. [2012], and Xu et al. [2012]). It should be noted that for this study our references to the various OH models represent the use of their OH relaxation mechanisms in the ALI-ARMS code and not the actual model itself. The differences between the OH models are displayed in Table 3.6 where various treatments to Reactions R3, R4, and R5 (see Table 3.3) are explained. Reaction R3 in Table 3.3, which involves collisions between OH and O_2 , is treated as multi-quantum (MQ) relaxation in this study, Adler-Golden [1997], and Xu et al. [2012] while a single-quantum (SQ) treatment was used in Funke et al. [2012]. Reactions R4 and R5 involve multi-quantum and "sudden death" relaxation between OH and O(³P), respectively. Adler-Golden [1997], Funke et al. [2012], and Xu et al. [2012] treat this reaction as a "sudden death" collision (Reaction R5) for all OH(v), where OH(v) is completely quenched to OH(v=0) per collision with O(³P). Differences between these models lie in the chosen rate coefficients displayed in Table 3.6. In this study, however, as described previously, both a multi-quantum (R4) and "sudden death" (R5) treatment is used for OH($v \ge 5$) and only "sudden death" for OH(v < 5). Reactions R1 and R2 from Table 3.3 are treated similarly for all OH models considered. For the following discussion, Adler-Golden [1997] will be abbreviated to AG, Xu et al. [2012] to XU, and Funke et al. [2012] to FUN. The calculations presented below are modeled using WACCM inputs taken on 6 May 2000 at latitude 45°N at local midnight.

Table 3.6: OH Model Comparisons

Reactions from Table 3.3	This Study	Adler-Golden [1997]	Funke et al. [2012]	Xu et al. [2012]
R3(MQ/SQ)	MQ	MQ	\mathbf{SQ}	MQ
R4/R5	v=5-9: R4 + R5	v=1-9: R5	v=1-9: R5	v = 1-9: R5
	$k^* = (1.7-2.6) \times 10^{-10}$ at 200 K	$\mathbf{k}^{*} = 2.0 \times 10^{-10}$	$k^* = 2.2 \times 10^{-10}$	$k^* = 5.0 \times 10^{-11}$
	v = 1-4: R5			
	$k^* = 2.9 \times 10^{-11}$ at 200 K			

* in units of cm³sec⁻¹

In the MLT, OH(v) is in extreme non-LTE where vibrational temperatures are far greater than the kinetic temperature, in some case by more than 10,000 K. Eq. (2.35) can be rewritten to directly calculate vibrational temperature after the non-LTE problem is solved,

$$T_{\upsilon} = -\frac{E_{\upsilon}}{\mathrm{kln}\left(\frac{n_{\upsilon}g_{0}}{n_{0}g_{\upsilon}} \cdot \frac{Q_{0}^{*}(T)}{Q_{\upsilon}^{*}(T)}\right)}.$$
(3.12)

Figure 3.4 displays vibrational temperatures for four vibrational levels: OH(v=1) (topleft), OH(v=3) (top-right), OH(v=5) (bottom-left), and OH(v=9) (bottom-right). For the bottom panels, vibrational temperatures calculated based on our study, AG, and FUN are all very similar due to the comparable rate coefficients used for $OH+O(^{3}P)$ quenching. The FUN Model, however, shows slightly higher vibrational temperatures from 80-90 km. This effect is a result of the SQ treatment for the $OH-O_2$ reaction which allows for more excited OH molecules in the upper vibrational levels relative to a MQ process. Above 90 km, the effect of the high quenching rate coefficient of Reaction R5 for the upper vibrational levels makes this reaction dominate over the SQ O₂ quenching. This results in a lower vibrational temperature relative to our model and AG.

The top panels in Figure 3.4 show vibrational temperatures for the lower levels of OH(v). Clear discrepancies are present between our OH model and AG/FUN. The significantly lower vibrational temperatures calculated with the FUN and AG models can be explained by the lack of efficient mechanisms redistributing the OH(v) energy from higher vibrational levels to lower ones. The higher vibrational temperatures in our model are from Reaction R4 which allows for additional pumping of lower vibrational levels from higher ones. Additionally, for the lower vibrational levels in our model, Reaction R4 is turned off and only Reaction R5 is active, which uses an inefficient rate coefficient (4-5 times lower than AG/FUN). This allows for higher vibrational temperatures in the lower levels, compared to AG and FUN. Finally, in all four panels, the XU model produces much higher vibrational temperatures due to the low quenching rate of Reaction R5. All vibrational levels are quenched at a slower rate and remain more significantly more populated.

Additional insight can be gain from Figure 3.5, which displays normalized ground state populations of four OH models described in Table 3.6. The AG and FUN models produce the two highest ground state populations. This behavior can be attributed to the "sudden death" treatment of Reaction R5 in addition to an efficient rate coefficient used for this reaction. Therefore, OH(v) is significantly de-populated for all vibrational levels and $O(^{3}P)$



Figure 3.4: OH vibratioanl temperature of four vibrational levels: top-left-OH(v=1); top-right-OH(v=3); bottom-left-OH(v=5); bottom-right-OH(v=1). Four OH models are compared: this study (black), Xu et al. [2012] (red), Adler-Golden [1997] (blue), and López-Puertas et al. [2004] (green)).

becomes a dominant quencher, transferring OH(v) to its ground state with every interaction. Our model, however, produces less OH(v) in its ground as a result of our treatment for Reactions R4 and R5. Reaction R4 is multi-quantum, where collisions of $O(^{3}P)$ with $OH(v \ge 5)$ leave OH(v) vibrationally excited in the lower states and transfers little to its ground state. Additionally, Reaction R5 for OH(v < 5) is inefficient and keep lower vibrational state more excited compared to AG and FUN. Finally, the XU model, which uses an inefficient rate coefficient for Reaction R5 and a MQ treatment for Reaction R3, transfer very little to its ground state after OH is chemically pumped.


Figure 3.5: Relative ground state populations for OH(v) for four different models: this study (black), Xu et al. [2012] (red), Adler-Golden [1997] (blue), and López-Puertas et al. [2004] (green)).

3.6 Comparison of OH Vibrational Populations with ground and space-based observations

In Figure 3.6 we present relative OH(v) populations calculated using four different OH models discussed in the previous section. These calculations are compared with the vibrational populations derived from ground (top panel) and space-based (bottom panel) observations of OH emissions.

Measured populations (black) displayed in the top panel were recorded by Cosby and Slanger [2007] on 03 March 2000 using the echelle spectrograph and imager (ESI) on the Keck II telescope at Mauna Kea (19.8206° N, 155.4681° W). The authors measured emission intensities of the 16 OH Meinel bands which were converted into the OH(v) column densities and normalized to column density of OH(v=9). Several observations of OH emissions were recorded throughout the night. We display the average column densities as well as their variation ranges for each vibrational level. The four simulated distributions (black, red, blue, and green) in this panel are modeled using WACCM inputs taken on 03 March 2000 at latitude 20°N at local midnight.



Figure 3.6: Relative OH(v) populations, normalized to OH(v=9), for measurements taken: (top) on 3 March 2000 at 20°N and (bottom) in November 2009 between 38-47°N. Measured populations (orange with diamonds); Simulations: this study (black); Xu et al. [2012] (red); Adler-Golden [1997] (blue); Funke et al. [2012] (green). See Section 3.5 for a description of calculation scenarios.

Measured densities displayed in the bottom panel of Figure 3.6 were taken from Migliorini et al. [2015] who analyzed VIRTIS (for Visible and Infrared Thermal Imaging Spectrometer) measurements on board the Rosetta mission. VIRTIS performed two limb scans of the OH Meinel bands from 87-105 km covering the latitude range from 38-47°N between 1:30 2:00 am, solar local time, in November 2009. To achieve high signal-to-noise, 300 radiance spectra (OH $\Delta v = 1$ and 2) were collected and averaged. We show in the right panel of Figure 3.6 the OH(v) population distribution normalized to OH(v=9) derived in this study as well as corresponding uncertainties. The four simulated distributions (black, red, blue, and green) in this panel are modeled using WACCM inputs taken on 22 November 2000 at latitude 45°N at local midnight.

To simulate the ground-based observations of Cosby and Slanger [2007] (top panel) the calculated relative populations were integrated over the entire altitude range of our model (30-135 km). For for the bottom panel, we have integrated calculated OH(v) densities from 87-105 km as observed by VIRTIS from Migliorini et al. [2015] to simulate mean population distribution obtained in this study.

The green profiles in both panels of Figure 3.6 represent results obtained with the set of rate coefficients similar to the one used in FUN, see Table 3.6. In the top panel, the green profile shows higher relative populations compared to measurements for upper vibrational levels v > 4, whereas in the bottom panel this model shows populations within the uncertainty range of measurements for v > 4. For lower vibrational levels v < 4, the populations calculated with this model are, however, significantly lower than measured ones: by 30% for v=3 in the top panel and by up to 85% for v=1 in the bottom panel. The FUN model has a significantly slower increase of populations compared to measurements. A description of this behavior was given in detail in section 3.5.

For the XU model (red profiles), relative OH population distribution in both panels show very good agreement with the results from Cosby and Slanger [2007] and Migliorini et al. [2015]. Although the XU model predicts higher populations between vibrational levels v=4-6 in both panels, it reproduces the upward trend in populations from upper to lower vibrational levels.

For the AG model (blue profiles), the relative OH population distribution in the top panel is in very good agreement with the results from Cosby and Slanger [2007]. Although slightly under-predicting the measured results, the populations falls completely within the variation range of these measurements. In the bottom panel, the situation is quite similar to that of the FUN model, showing populations within measurement the uncertainty range for the upper vibrational levels and, for the lower levels, significantly lower than the measured ones.

The situation is different when our model is applied (black curves). Relative OH population distribution in the top panel shows our standard model in very good agreement with the results from Cosby and Slanger [2007], falling completely within the variation range of these measurements. The bottom panel also shows excellent agreement between calculations and measurements, where former lie nearly completely within the measurement error bars for the majority of vibrational levels. In both panels our results reproduce well the steady upward trend in populations from upper to lower vibrational levels. Significantly higher populations of lower OH levels in this model are the result of redistribution of higher vibrational level energy to lower levels due to two dominant multi-quantum quenching mechanisms, namely the new Reaction R4 and the multi-quantum version of reaction R3. A description of the energy distribution of our model was given in section 3.5.

Measured OH(v=3) (bottom panel) was the only population which showed disagreement with our model. Various reasons of increased measured population at v=3 are discussed by Migliorini et al. [2015], however, no definitive conclusions were given.

Above 90 km atomic oxygen density increases rapidly with the altitude. As a result the role of reaction R4 in quenching higher OH vibrational and pumping lower levels increases. This effect is easily seen in the bottom panel of Figure 3.6, where mean OH(v) densities for higher altitude region 87-105 km are compared. The red, black, and green curves (no R4 reaction) in this panel shows lower populations compared to those calculated with with R4 included.

3.6.1 OH 1.6 and 2.0 μ m emissions

The SABER instrument observes OH emissions in two infrared channels: Channel 8 and 9, which are sensitive to photons at 2.0 (5000 cm⁻¹) and 1.6 (6250 cm⁻¹) μ ms, respectively. The left panel of figure 3.7 displays the radiances for the most important vibrational bands contributing to the 2.0 μ m channel, while the right panel shows their associated fractional contribution. Two band transitions, $v=9\rightarrow7$ and $v=8\rightarrow6$, dominate the 2.0 μ m channel. These $\Delta v=2$ transitions are known as Meinel bands, and were first discovered in the 1950s by A. B. Meinel at Yerkes Observatory [Meinel, 1950]. The $8\rightarrow6$ transition dominates the



Figure 3.7: Fractional LOS contribution of various bands into Ch8. Left-panel: Simulated limb radiances for bands which contribution the most to 2.0 μ m emissions. Right-panel: Fractional contribution of the OH bands to the total LOS radiances. Calculations are performed for a mid-latitude nighttime atmosphere.

2.0 μ m emission at all altitudes, while the 9 \rightarrow 7 band contributes roughly a third of the

intensity as seen in the right panel of figure 3.7. OH, which is excited mostly to levels v = 8and 9 upon formation [Adler-Golden, 1997], is quickly quenched via radiative and collisional processes. OH molecules in vibrational state v = 9 experience single quantum quenching with N₂ and a small fraction of single-quantum with O₂ (see footnote in Table 4.1). Both of these processes act as an additional pumping source for OH(v = 8). Additionally, this vibrational level lower total quenching rate coefficients with main atmospheric constituents, allowing for less quenching and higher populations. As a result, the 8 \rightarrow 6 band contributes more radiance to Ch8.



Figure 3.8: Fractional LOS contribution of various bands into Ch9. Left-panel: Simulated limb radiances for bands which contribution the most to 1.6 μ m emissions. Right-panel: Fractional contribution of the OH bands to the total LOS radiances. Calculations are performed for a mid-latitude nighttime atmosphere.

Figure 3.8 displays the radiances of the dominant vibrational bands contributing to the 1.6 μ m channel. Like Ch8, Ch9 is dominated by Meinel bands, specifically the 5 \rightarrow 3 and

 $4\rightarrow 2$ transitions. The right panel of figure 3.8 shows almost identical intensity contributions from both bands. The $5\rightarrow 3$ transition contributes slightly more above 82 km, where the chemical production of OH becomes the dominant pumping mechanism. The branching ratio suggested by Adler-Golden [1997] (see footnote of Table 3.3) treats OH(v=5) as weakly pumped upon formation, which causes a slightly higher emitted radiance.

We simulated channel 8 and 9 radiances for four atmospheric models from Table 3.7. Results are shown in Figure 4.5 as ratios of volume emission rates for channel 8 and 9.

		0			
	Atmosphere	Latitude	Day	Orbit	Scan
(a)	Mid-Latitude Summer (MLS)	$37^{\circ}\mathrm{S}$	26 Jan 2004	11556	62
(b)	Tropical (TROP)	$6^{\circ}N$	20 Jan 2008	33130	48
(c)	Mid-Latitude Winter (MLW)	$34^{\circ}S$	15 Jul 2010	46594	90
(d)	Sub-Arctic Winter (SAW)	$72^{\circ}S$	15 Jul 2010	46585	78

Table 3.7: Selected nighttime SABER scans

Volume emission rate (VER) is defined as the sum

$$R_{\mathcal{U}} = \sum A_{\nu,\nu'}[OH(\nu)] = [OH] \sum A_{\nu,\nu'} p_{\nu}$$
(3.13)

over all transitions contributing to the channel, where $p_v = [OH(v)]/[OH]$ is the probability of the OH molecule to be in the vibrational state v. It follows from this expression that the VER ratio does not depend on the total OH density and is, therefore, convenient for analyzing impacts of various populating/quenching mechanisms on OH(v) distribution. The calculations with our model are shown in Figure 3.9 in black, XU model in red, AG model in blue, and FUN model in green. Orange curves in this plot display SABER measured VER ratios, for which VERs were obtained with the Abel inversion procedure, Eq. (3.11), from the SABER channel 8 and 9 limb radiances for scans listed in Table 3.7.

Comparing black, blue, and green profiles in Figure 3.9, one may see that our model (black) shows significantly lower VER ratios for altitudes 85-100 km than the model of AG



Figure 3.9: Measured and simulated SABER Volume Emissions Rate Ratios (CH8/CH9). Four standard atmospheres are displayed: a) Mid-Latitude Summer (MLS), b) Tropical (TROP), c) Mid-Latitude Winter (MLW), and d) Sub-Arctic Winter (SAW) for selected SABER scans described in Table 3.7. SABER measured with NER (orange); Simulations: this study (black); Xu et al. [2012] (red); Adler-Golden [1997] (blue); Funke et al. [2012] (green). See Section 3.5 for a description of calculation scenarios

(blue) and FUN (green). These differences between ratios are a result of very different OH(v) population distributions (Figure 3.6) for each model, which were discussed in the previous section. The (Channel 8)/(Channel 9) VER ratios reflect these distributions very well since Channel 8 is sensitive to the OH(v) emissions from higher levels 8 and 9, whereas Channel 9 records emissions from lower levels 3-5. Significantly higher population of lower vibrational levels in our model (black curves in Figure 3.6) explain low VER ratios. In

contrast, the AG and FUN models, which under-predicts lower level populations, provides VER ratios which significantly exceed both our model results and measurements for altitudes above 90 km, where [O] density rapidly increases with altitude. This comparison demonstrates the strong impact of Reaction R4, which provides efficient quenching of higher OH vibrational levels in collisions with $O(^{3}P)$ atoms in this altitude region. Finally, the XU model significantly under-predicts SABER VER ratios. Despite very good agreement with measurements presented in Figure 3.6 for upper and lower vibrational levels, the middle levels, OH(v=4-6), were higher than measured values. Such an effect produces higher Channel 9 emissions and, therefore, low VER Ratios.

3.7 Final Remarks

We included the new energy transfer channel (Reaction R4 in Table 3.3) into our non-LTE model of the nighttime MLT emissions of OH molecules and studied in detail the impact of this mechanism on simulated vibrational level populations and OH emissions. The calculations were compared with the ground and space observations of the OH(v) densities in the nighttime mesosphere. Our model produces $OH(\nu)$ density distributions which are in good agreement with both SABER limb OH emission measurements and the ground and space observations in the mesosphere. Other models (Adler-Golden [1997], Xu et al. [2012], and Funke et al. [2012]) do not, however, reproduce both the SABER measured VER ratios of the OH 1.6 and 2.0 m channels and the ground and space measurements of the OH(v)densities. These models lack an efficient redistribution of the OH(v) energy from the higher vibrational levels emitting at 2.0 μ m to lower levels emitting at 1.6 μ m. In contrast, our model, which includes this new mechanism (Reaction R4 in Table 3.3), efficiently removes at least 5 quanta in each $OH(v)+O(^{3}P)$ collision from high OH vibrational levels. Supported also by the multi-quantum $OH(v)+O_2$ quenching (Reaction R3 of Table 3.3), the new mechanism provides OH(v) distributions which are in agreement with both measured VER ratios and observed OH(v) populations.

Chapter 4: CO₂ Non-LTE Model

4.1 Nighttime CO₂ 4.3 μ m Emissions

Knowledge of the mechanisms generating the CO₂ 4.3 μ m radiance in the nighttime mesopshere is important to allow for accurate CO₂ volume mixing ratio retrievals at night. For daytime conditions, the important processes responsible for non-LTE emissions of CO₂ at 4.3 μ m are well-known, however, generation of nighttime emissions are still not well understand. A detailed study of nighttime 4.3 μ m emissions was conducted by López-Puertas et al. [2004] aimed at determining the dominant mechanisms of exciting CO₂(v_3), where v_3 is the asymmetric stretch mode that emits 4.3 μ m radiation. The nighttime measurements of SABER channels 7 (4.3 μ m), 8 (2.0 μ m), and 9 (1.6 μ m) for geomagnetically quiet conditions were analyzed, where channels 8 and 9 are sensitive to the OH ($v \leq 9$) overtone radiation from levels v = 8-9 and v = 3-5, respectively. López-Puertas et al. [2004] showed a positive correlation between 4.3 μ m and both OH channel radiances at a tangent height of 85 km. This correlation was associated with the transfer [Kumer et al., 1978] of energy of the vibrationally excited OH(v) first to N₂(1),

$$OH(v \le 9) + N_2(0) \leftrightarrow OH(v-1) + N_2(1),$$
 (4.1)

and then further to $CO_2(v_3)$ vibrations

$$N_2(1) + CO_2(0) \leftrightarrow N_2(0) + CO_2(v_3)$$
 (4.2)

(hereafter "direct" mechanism). However, López-Puertas et al. [2004] showed that calculations based on the Kumer et al. [1978] model do not reproduce the 4.3 μ m radiances observed by SABER. Although accounting for energy transfer from OH(v) did provide a substantial enhancement to 4.3 μ m emission, up to 80% difference between simulated and observed radiance remained (for the SABER scan 22, orbit 01264, 77°N, 03 Mar 2002, which was studied in detail) for altitudes above 70 km. In order to reproduce measurements these authors found that, on average, 2.8-3 N₂(1) molecules (instead of Kumer's suggested value of 1) are needed to be produced after each quenching of OH(v) molecule in Reaction R2 in Table 3.3. Alternative excitation mechanisms that were theorized to enhance the 4.3 μ m radiance (i.e. via O₂ and direct energy transfer from OH to CO₂) were tested but found to be insignificant.

Recently, Sharma et al. [2015] suggested a new OH multi-quantum quenching mechanism (Reaction R4 in Table 3.3) of the OH vibrational energy. The production at nighttime of electronically excited $O(^{1}D)$ atoms in Reaction R4 triggers well known pumping mechanism of the 4.3 μ m emission, which was studied in detail for daytime (Nebel et al. [1994], Edwards et al. [1996]). Here $O(^{1}D)$ atoms are first quenched by collisions with N₂ in a fast spinforbidden energy transfer process

$$O(^{1}D) + N_{2}(0) \leftrightarrow O(^{3}P) + N_{2}(v \le 7),$$
(4.3)

exciting $N_2(v)$ up to $N_2(v=7)$, then $N_2(v)$ transfers its energy to ground state N_2 via a very fast single quantum VV process

$$N_2(v \le 7) + N_2(0) \leftrightarrow N_2(v-1) + N_2(1),$$
(4.4)

leaving N₂ molecules with an average of 2.2 vibrational quanta, which is then followed by reaction (4.2). Accounting for this mechanism, hereafter "indirect" mechanism, but only considering OH(v=9), these authors performed simple model calculations to validate its potential for enhancing mesospheric nighttime 4.3 μ m emission from CO₂. They reported a simulated radiance enhancement between 18-55% throughout the MLT. In a latest study, Kalogerakis et al. [2016] provided a definitive laboratory confirmation for the validity of this new mechanism and measured its rates for OH(v=9)+O.

By linking the CO₂ with our OH model, we studied in detail the impact of "direct" and "indirect" mechanisms on the CO₂(v_3) emissions and compared our calculations with the SABER/TIMED nighttime 4.3 μ m CO₂ limb radiances of the MLT.

The study was performed for quiet (non-auroral) nighttime conditions to avoid accounting for interactions between charged particles and molecules, whose mechanisms still remain poorly understood.

4.2 Applied CO₂ Non-LTE Model

 CO_2 is a linear, tri-atomic molecule which, depending on the oxygen atoms, can either be symmetric or asymmetric. There are a total of four different isotopes of CO_2 that need to be considered to model SABER emissions, (626 [0.984], 636 [1.1e-2], 628 [3.9e-3], and 627 [7.3e-4]), where the number in the square brackets denote the respective isotope abundance. The abbreviated nomenclature is in reference to the second digit of the mass number for carbon and atomic oxygen. For example the main isotope, ¹⁶O¹²C¹⁶O, can also be referred to as CO_2 (626) isotope or just (626). The CO_2 molecule has three vibrational modes, but only two are experimentally active in the infrared: the bending mode, v_2 , which radiates at 15 μ m, 2) the vibratioanl asymmetric stretch mode, v_3 , which radiates at 4.3 μ m. The third vibrational mode, known as the symmetric stretch mode, or v_1 , which is theoretically inactive in the infrared because the dipole moment is unchanged in the molecule. The $2v_2$ level, however, is in a strong Fermi resonance with the v_1 first excited levels. As a result their quantum mechanical wave functions are mixed, making levels $2v_2$ and v_1 indistinguishable, appearing as three levels which are all active in the infrared. The asymmetric stretch mode, v_3 will be the focus of this study. The SABER instrument, which observes this CO₂ emission feature (see Table 1.1), may be referred to, hereafter, as Ch7.

The current version of the ALI-ARMS non-LTE CO₂ 4.3 μ m model was built for simulating daytime conditions. There are a total of 56 vibrational levels and 120 bands considered to model SABER non-LTE CO_2 radiances. The same CO_2 non-LTE model will be used to simulate nighttime conditions. Although it seems excessive, we kept the same number of levels and bands to avoid any possible loss of information, such as minor contributions from first or second hot bands. Collisional rates between CO_2 and main atmospheric constituents $(O_2, N_2, \text{ and } O({}^{3}P))$ for daytime conditions are used for nighttime [Shved et al., 1998]. Major differences between day- and nighttime modeling are the contributions from vibrationally excited OH and the exclusion of solar irradiation absorption. We coupled CO_2 with our OH model (described in Chapter 3) to account for the "direct" mechanism, reactions (4.1)-(4.2), in a way consistent with that of López-Puertas et al. [2004] and added the "indirect" mechanism of Sharma et al. [2015] and Kalogerakis et al. [2016] as described above. Figure 4.1 displays a simplified energy level diagram of the coupling between the OH and CO_2 nighttime models. For OH, the Meinel bands transitions (dashed arrows), chemical pumping (orange arrows), main collisional V-V (red arrows) and V-T (green arrows) processes, as well as the "indirect" mechanism (blue arrows) are included. For $CO_2(v_3)$, only its contribution from OH(v) is displayed, however, there are numerous V-T and V-V energy exchange processes that influence the vibrational population of $CO_2(\nu_3)$ which are not shown. The efficient exchange of ν_3 quanta through V-V processes between N₂ and $CO_2(\nu_3)$, Eq. 4.2, is shown.

4.3 Collisional Rate Coefficients

Table 4.1 displays main collisional processes used in our CO₂ non-LTE model. For the sake of convenience, we have provided reactions from Table 3.3 in Table 4.1, as the following discussion frequently refers to them. Reaction R1-R5 are all identical to Table 3.3 with the exception of Reaction R2, which we treat as both a single (1Q, v'=1) and multiquantum (MQ, v'=2 or 3) quenching process for this study. For Reaction R6, we use the





	Reaction	Reaction Rate $(cm^3 sec^{-1})$	Reference			
(R1)	$\mathrm{H} + \mathrm{O}_3 \to \mathrm{OH}(\nu \leq 9) + \mathrm{O}_2$	$k_1 = f_{\nu}^a \times 1.4 \times 10^{-10} exp(-470/T)$	Sander et al. $[2011]\ \&$			
			Adler-Golden [1997]			
(R2)	$OH(\nu \leq 9) + N_2(0) \leftrightarrow OH(\nu - \nu') + N_2(\nu')$	$k_2 = f_{\nu}^b \times 1.4 \times 10^{-13}$	Adler-Golden [1997] &			
	$\nu' = 1,2,3$		Lacoursière et al. [2003]			
(R3)	$OH(\nu \leq 9) + O_2(0) \leftrightarrow OH(\nu') + O_2(1)$	$k_6 = f_{\nu}^c \times 10^{-13}$	Adler-Golden [1997]			
	$\nu' = 0, 1, 2, \dots \nu$ -1					
(R4)	$\mathrm{OH}(\nu \geq 5) + \mathrm{O}(^{3}\mathrm{P}) \leftrightarrow \mathrm{OH}(0 \leq \nu' \leq \nu \text{-}5) + \mathrm{O}(^{1}\mathrm{D})$	$k_4 = f_{\nu}^d \times (2.3 \pm 1) \times 10^{-10}$	Kalogerakis et al. [2016] &			
			Sharma et al. [2015]			
(R5)	$OH(\nu) + O(^{3}P) \rightarrow H + O_{2}$	$k_4 = 1.18 \times 10^{-11} exp(180/T)$	Sander et al. $[2011]$			
$(\mathbf{R6})$	$O(^1D) + N_2(0) \leftrightarrow O(^3P) + N_2(\upsilon \leq 7)$	$k_5 = f_v^e \times 2.15 \times 10^{-11} exp(110/T)$	Sander et al. [2011] &			
			Slanger and Black [1974]			
(R8)	$N_2(1) + CO_2(0) \leftrightarrow N_2(0) + CO_2(v_3)$	$k_3 = 8.91\times10^{-12}\timesT^{-1}$	Shved et al. [1998]			
(R8)	$OH(v \le 9) + O(^{3}P) \leftrightarrow OH(0) + O(^{3}P)$	$k_7 = 2.0\times10^{-10}$	Adler-Golden [1997]			
${}^{a}f_{\nu}(\nu=5-9) = (0.01, 0.03, 0.15, 0.34, 0.47)$						
${}^{b}f_{\nu}(\nu=1-9) = (0.06, 0.10, 0.17, 0.30, 0.52, 0.91, 1.6, 7, 4.8)$						
${}^{c}f_{\nu}(\nu=1-9) = (1.9, 4, 7.7, 13, 25, 43, 102, 119, 309)$						
df(u=5.0) = (0.01, 0.61, 0.74, 0.87, 1.0)						

Table 4.1: Significant collisional processes used in OH/CO_2 model

 ${}^{a}f_{\nu}(\nu=5-9) = (0.91, 0.61, 0.74, 0.87, 1.0)$ ${}^{e}f_{\upsilon}(\upsilon=1-7) = (0.244, 0.268, 0.197, 0.108, 0.048, 0.017, 0.005)$

rate coefficient taken from Sander et al. [2011]. The studies by Slanger and Black [1974] and Sharma et al. [2015] suggested that for each $O({}^{1}D)+N_{2}$ Electronic-Vibrational (E-V) collision, on average 2.2 vibrational quanta of energy are transferred to $N_{2}(v=1)$. To properly account for this reaction, we consider seven $N_{2}(v)$ excited levels [Harris and Adams, 1983] and calculated associated branching ratios for Reaction of each $N_{2}(v)$ level assuming a Poisson distribution with a mean value of 2.2 (see footnote, ${}^{d}f_{v}$, in Table 4.1 for branching ratios). The fast and efficient $N_{2}+N_{2}$ reaction, Eq. (4.4), transfers all vibrationally excited $N_{2}(v)$ to $N_{2}(v=1)$, leaving 2.2 $N_{2}(v=1)$ molecules. Rigorous calculations were performed to ensure that 2.2 $N_{2}(1)$ molecules are produced per $O({}^{1}D)+N_{2}(0)$ collision. Reaction R8 is an alternative "sudden death" OH-O(${}^{3}P$) quenching mechanism which previous studies (López-Puertas et al. [2004], Adler-Golden [1997]) applied in their OH models, where atomic oxygen completely quenches $(v \rightarrow v=0)$ OH(v) upon collision. For this reaction, we took the vibrationally independent rate coefficient of 2.0×10^{-10} cm³s⁻¹ from Adler-Golden [1997].

4.4 Model Inputs and Calculation Scenarios

The nighttime atmospheric pressure, temperature, and densities of trace gases and main atmospheric constituents for calculations presented below were taken from the WACCM model [Marsh et al., 2013].

The following sets of processes and rate coefficients were used in our calculations:

- (OH-N2 1Q) & (OH-O2 1Q) & R8: this model accounts for reactions R1, R2, R3, R7 and R8 from Table 4.1. R2 is treated as single-quantum (v'=1) process, R3 is also treated as single-quantum (v' = v − 1). This model reproduces the initial model described by López-Puertas et al. [2004]
- 2. (OH-N2 3Q) & (OH-O2 1Q) & R8: same as model 1, however, R2 is treated as the three-quantum (v'=3) process and R3 is single-quantum (v' = v − 1). As it is shown below, this version matches best with the final model of López-Puertas et al. [2004] where the efficiency of R2 was increased by a factor of 3.
- 3. (OH-N2 3Q) & (OH-O2 MQ) & R8: same as model 2, however, R3 is treated as multi-quantum (any $v' \le v 1$) process.
- 4. (OH-N2 1Q) & (OH-O2 MQ) & R4,R5: reactions R1 through R7 from Table 4.1 are included. This is our basic model version with both "direct", Reaction (R2), and "indirect", Reactions (R4 + R6) mechanisms working together when R2 is treated as the single-quantum process (v'=1) as was suggested by [Kumer et al., 1978], however, R3 is treated as multi-quantum process (any v' ≤ v − 1). New mechanism, Reactions (R4) and (R6), replaces here Reaction (R8) which is used in other models described above.

- 5. (OH-N2 3Q) & (OH-O2 MQ) & R4,R5: same as model 4, but "direct" process (R2) is treated as the three-quantum process corresponding to its 3 times higher efficiency suggested by López-Puertas et al. [2004].
- (OH-N2 2Q) & (OH-O2 MQ) & R4,R5: same as model 5, however R2 is treated as the two-quantum process
- 7. (OH-N2 1,2Q) & (OH-O2 MQ) & R4,R5: same as model 5, however R2 is treated as two-quantum process for highly resonant transitions OH(9)+N₂(0)→ OH(7)+N₂(2) and OH(2)+N₂(0)→ OH(0)+N₂(2), and as single-quantum for all others.

4.5 Vibrational Temperatures of the $CO_2(v_3)$ levels

Figure 4.2 shows the vibrational temperatures of the CO₂ levels of four isotopes, giving origin to 4.3 μ m bands, which dominate the SABER nighttime signal [López-Puertas et al., 2004]. These results were obtained for SABER scan 22, orbit 01264, 77°N, 03 March 2002. The same scan was used for the detailed analysis presented in the work by López-Puertas et al. [2004]. The kinetic temperature retrieved for this scan from the SABER 15 μ m radiances (SABER data version 2.0) and vibrational temperature of N₂(1) are also shown. Solid lines in Fig. 4.2 represent simulations with our basic model [(OH-N2 1Q) & (OH-O2 MQ) & R4,R6], when both the "direct" process R2 (in its single-quantum version, as was suggested by Kumer et al. [1978]), and the new "indirect" process, reactions R4 + R6, are included. For comparison we also show vibrational temperatures (dashed lines) for the model [(OH-N2 3Q) & (OH-O2 1Q) & R8] where the "indirect" mechanism is off and the "direct" process is treated as a three quantum one, which is equivalent to the 3 times higher efficiency suggested by López-Puertas et al. [2004].

Vibrational temperatures of CO₂ levels and N₂(1) depart from LTE around 65 km. For both models vibrational temperatures nearly coincide up to 85-87 km, however, above this altitude, where the O(³P) density is high, vibrational temperatures for [(OH-N2 3Q) & (



Figure 4.2: Nighttime vibrational temperatures of $CO_2(00011)$ of four CO_2 isotopes, $CO_2(01111)$ of main CO_2 isotope, and of $N_2(1)$ for SABER scan 22, orbit 01264, 77°N, 03 March 2002. Solid lines: [(OH-N2 1Q) & (OH-O2 MQ) & R4,R6]; dashed lines: [(OH-N2 3Q) & (OH-O2 1Q) & R8], see Section 2.3 for a description of calculation scenarios

OH-O2 1Q)] & R8] are a few Kelvin lower compared to those for [(OH-N2 1Q)& (OH-O2 MQ) & R4,R6]. These vibrational temperature differences explain differences of simulated $CO_2(v_3)$ emission for both models shown in Figure 4.4.

In both simulations, $CO_2(00011)$ of main isotope 626 and $N_2(1)$ have almost identical vibrational temperatures up to ~87 km which is caused by an efficient VV exchange (reaction (R7)).

4.6 The CO₂ 4.3 μ m emission

The spectral response function of nighttime Ch7 has a non-zero response over the range 2284-2409 cm⁻¹ and covers emissions from 23 bands of the $CO_2(v_3)$ vibrations and 9 $\Delta v=1$

bands of the OH(v) vibrations. The primary pumping mechanisms for the $CO_2(v_3)$ levels is absorption of radiation from lower in the atmosphere and resonant V-V energy exchanges with N₂. The N₂ molecule channels its energy from OH(v) and $O(^1D)$. In addition, the atmosphere is optically thick at 4.3 μ m and energy entering into the system may be scattered multiple times coupling altitudes together.



Figure 4.3: Fractional LOS contribution of different bands into Ch7. The left panel shows the simulated limb radiance for the most important bands and the right panel shows the fractional contribution for the CO_2 bands to the total LOS radiance. Calculations are performed for a mid-latitude nighttime atmosphere.

Figure 4.3 displays the fractional LOS contribution of different 4.3 μ m bands to Ch7 radiance. Three CO₂ isotopes are displayed (626, 628, 627) in additional to an OH band. FB and FH denote the fundamental and first hot bands, respectively. At all altitudes the 626 FB is the dominant contributor to the Ch7 radiance, which supplies 30-60% of the total radiance. During the day, the excitation from solar pumping adds significantly more contribution for the isotopes and first hot bands, however, at night, collisional energy transfer and upwelling radiation are the main sources which favor the fundamental band of main CO₂ isotope, 626. The minor isotopes, 628 and 627, as well as the 626 FH still are able to contribute roughly 50% of the total radiance below 80 km and about 35% above 80 km, due to fast V-V energy transfer between isotopes. This decreasing contribution with altitude is mainly due to the decreasing pressure which decreases the collisional interactions between isotopes. Additionally, the increasing OH(v) relative contribution which mainly pumps 626 FB via the "direct" and "indirect" mechanisms.

Figure 4.4 displays our simulations of SABER channel 7 (4.3 μ m) radiances for inputs which correspond to the measurement conditions of the SABER scan described in section 4.5. The calculations also account for the minor contribution in channel 7 radiation emitted by the OH($v \leq 9$) vibrational levels.

Our simulation for this scan with the [(OH-N2 1Q) & (OH-O2 1Q) & R8] set of rate coefficients is shown as the violet curve. The turquoise curve displays our results for the rate coefficient set [(OH-N2 3Q) & (OH-O2 1Q) & R8], which simulates the model suggested by López-Puertas et al. [2004] with the factor of 3 increased efficiency of reaction R2. One may see that treating R2 as a three-quantum VV process strongly enhances the pumping of the $CO_2(v_3)$ vibrations and the 4.3 μ m radiance is in agreement with López-Puertas et al. [2004] results.

The blue curve in Figure 4.4 displays our run with the model [(OH-N2 3Q) & (OH-O2 MQ) & R8]. In this model R6 is treated, following Adler-Golden [1997], as a multi-quantum VV process. Compared to previous model this run shows a significantly lower channel 7 signal. This is obviously caused by a much more efficient removal of the OH(v) vibrational energy in the multi-quantum quenching by collisions with O₂. As a result, a significantly smaller part of this energy is collected by N₂(1) and delivered to the $CO_2(v_3)$ vibrations with the "direct" mechanism R2. To compensate this OH(v) decay and keep the transfer of energy to $CO_2(v_3)$ unchanged, López-Puertas et al. [2004] adjusted new, presumably higher OH(v) to the SABER 1.6 and 2.0 μ m radiances. In our study the higher channel 7 emission is, however, restored when we include the reactions R4 and R6 ("indirect" mechanism of energy transfer from OH(v) to $CO_2(v_3)$) into the model, but return R2 to its single-quantum mode.



Figure 4.4: Left: measured and simulated SABER nighttime radiances in channel 7 (4.3 μ m) for SABER scan 22, orbit 01264, 77°N, 03 March 2002. SABER measured (black); See Section 2.3 for a description of calculation scenarios displayed in the legend. Right: radiance relative difference (simulated-measured)/measured in percent.

The red curve in Figure 4.4, which corresponds to our [(OH-N2 1Q) & (OH-O2 MQ) & R4,R6] model is nearly overlapped with the turquoise curve for the [(OH-N2 3Q) & (OH-O2 1Q) & R8] model. This demonstrates a very high efficiency of the "indirect" channel, compared to the "direct" one since it provides the same pumping of $CO_2(v_3)$ even when OH(v) energy is efficiently removed in the multi-quantum version of R3.

We show in Figure 4.4 (black curve with diamonds), the channel 7 radiance profile for the SABER scan specified in section 4.5. Comparing turquoise and red curves with this measurement, one may see that both the "direct" mechanism alone in its three-quantum version and the combination of "indirect" and single-quantum "direct" mechanisms are close to the SABER radiance for this scan. However, to provide this pumping level, the multiquantum "direct" mechanism needs to be supported by the inefficient single-quantum OH(v)quenching in reaction R3 by collisions with O₂, which helps keeping higher population of OH(v). We also note here that both our violet [(OH-N2 1Q) & (OH-O2 1Q) & R8] and turquoise [(OH-N2 3Q) & (OH-O2 1Q) & R8] curves reproduce the corresponding results in Figure 10 of López-Puertas et al. [2004] (short-dash and solid lines, respectively) very well.

We also show in Figure 4.4 our study of how both the "direct" and "indirect" mechanisms work together when the "direct" process R2 is treated as multi-quantum. The magenta curve in this plot is the result obtained with the model [(OH-N2 3Q) & (OH-O2 MQ) & R4,R6] when R2 is treated as three-quantum process. This combination of both mechanism provides high $CO_2(v_3)$ pumping and subsequently strong Channel 7 emission. The latter exceeds the turquoise and red curves by 20-45% in the altitude range considered and strongly deviates from the measured radiance profile.

Two other result of this study are shown only in the right panel of this plot for the signal differences. The light blue curve corresponds to simulations with the [(OH-N2 2Q) & (OH-O2 MQ) & R4,R6] model when the quantum transfer in R2 is reduced from 3 to 2. The dark green curve is obtained for the case when R2 is treated as two-quantum process for highly resonant transitions $OH(9)+N_2(0) \rightarrow OH(7)+N_2(2)$ and $OH(2)+N_2(0) \rightarrow OH(0)+N_2(2)$, and as single-quantum for all other vibrational levels. It is seen that both of these input versions bring the calculated radiance closer to our result for a single-quantum "direct" process R2 (red curve) and to our simulation [(OH-N2 3Q) & (OH-O2 1Q) & R8] of results obtained based on López-Puertas et al. [2004] (turquoise).

In Figure 4.5 (upper and middle rows) we compare our simulation results for two sets of rate coefficients: [(OH-N2 1Q) & (OH-O2 MQ) & R4,R6] (red) and [(OH-N2 3Q) & (OH-O2 1Q) & R8] (turquoise). The WACCM model nighttime inputs representing four different atmospheric situations described in Table 3.7 were used for these simulations. These inputs also match the measurement conditions of the four SABER nighttime scans (solar zenith angle > 105°) listed in the Table 3.7. The corresponding SABER measured channel 7 4.3 μ m radiances are shown in black as reference data.

One may see that in Figure 4.5 the "direct" mechanism alone with three-quantum efficiency for reaction R2, as well as both the "direct" (as single-quantum) and "indirect"



Figure 4.5: Top: measured and simulated nighttime radiances for SABER channel 7 (4.3 μ m). Bottom: Channel 7 radiance relative differences (simulated-measured)/measured in percent. Four standard atmospheres are displayed: a) Mid-Latitude Summer (MLS), b) Tropical (TROP), c) Mid-Latitude Winter (MLW), and d) Sub-Arctic Winter (SAW) for selected SABER scans described in Table 3.7. SABER measured with Noise Equivalent Radiance (NER) (black); [(OH-N2 1Q) & (OH-O2 MQ) & R4,R6] (red); [(OH-N2 3Q) & (OH-O2 1Q) & R8] (turquoise); See section 4.4 for a description of calculation scenarios

mechanisms together provide similar results for all four atmospheric models, within a 10 to 30% difference range. By comparing these models to measured radiances, both calculations are close to the observed signal down to 68 km for MLW and down to 75 km for SAW. For MLS and TROP, the two-mechanism calculations are somewhat closer to measurements than those for "direct" mechanism alone in altitude interval 75-90 km.

4.7 Final Remarks

The results of our study suggest that the missing nighttime mechanism of $\text{CO}_2(v_3)$ pumping has finally been identified. This confidence is based on the fact that the new mechanism accounts for most of the discrepancies between measured and calculated 4.3 μ m emission for various atmospheric situations, leaving relatively little room for other processes, among them the multi-quantum "direct" mechanism. Further improvements for the new "indirect" mechanism will require optimizing the set of rate coefficients used for OH(v) relaxation by $O(^{3}P)$ and O_{2} at mesospheric temperatures and, in particular, understanding the dependence of the "indirect" mechanism on the OH vibrational level. Relevant laboratory measurements and theoretical calculations are sorely needed to understand these relaxation rates and the quantitative details of the applicable mechanistic pathways. Nevertheless, the results presented here clearly demonstrate significant progress in understanding the mechanisms of the nighttime OH and CO₂ emission generation in MLT.

Chapter 5: Application of OH Non-LTE Model for the Retrieval of O(³P) and OH Densities using SABER Radiances

5.1 Inverse theory and definitions

The atmospheric parameters that will need to be determined (in our case $O(^{3}P)$ and OH densities) as a function of discrete altitudes will be denoted as,

$$\mathbf{x} = (x_1, x_2, \dots, x_n)^T, \tag{5.1}$$

where each n elements of \mathbf{x} represents a value of a specific parameters at a specific altitude. The superscript T denotes the transpose operation. The measured signals will be represented by a measurement y vector of m discrete points,

$$\mathbf{y} = (y_1, y_2, \dots, y_m)^T.$$
(5.2)

The limb radiance measurement can be presented in the following form

$$\mathbf{y} = \mathbf{F}(\mathbf{x}, \mathbf{b}) + \xi, \tag{5.3}$$

where $\mathbf{F}(\mathbf{x}, \mathbf{b})$ is the non-linear function describing the forward radiance calculations, \mathbf{x} is the parameter vector, and \mathbf{b} represents a-priori information needed to calculate forward radiances (such as collisional rates, line parameters, assumed background atmosphere, etc.). The noise parameter is represented as, ξ , which includes all random and/or systematic errors due to the measurement and the forward modeling.

The Jacobian or kernel matrix, K, is an important mathematical object required for many linear and non-linear retrieval techniques and contains the derivatives of the forward model with respect to the state vector. The matrix is defined as

$$K = \begin{pmatrix} \frac{\partial F_1}{\partial x_1} & \cdots & \frac{\partial F_1}{\partial x_n} \\ \vdots & \ddots & \vdots \\ \frac{\partial F_m}{\partial x_1} & \cdots & \frac{\partial F_m}{\partial x_n} \end{pmatrix}$$
(5.4)

5.2 General inversion approaches

There are, in general, three approaches for the solution of a non-linear inversion. The first approach is to assume an a-priori profile, which one supposes to be close to the true solution, and then iteratively solve the linearized version of the problem. These linear iterative methods find a solution by starting with profile, $\mathbf{x}_{initial}$, and through successive corrections through addition obtain a solution of type $\mathbf{x}_{solution} = \mathbf{x}_{initial} + \Delta \mathbf{x}_1 + \Delta \mathbf{x}_2$ +..., where $\Delta \mathbf{x}$ is the correcting term [Twomey, 2002]. The algorithm has advantages in which the problem retains well defined statistical properties in addition to calculating the averaging kernel [Rodgers, 2000]. Linearization of the non-linear problem, however, may not converge to the true solution at all if the initial guess is not in the vicinity of the true parameters (Rodgers [2000], Twomey [2002]).

The other way to solve a non-linear problem is a more direct approach using a relaxation type algorithm where the initial guess is modified by correactions through multiplication, so that the final solution is of type $\mathbf{x}_{\text{solution}} = \mathbf{x}_{\text{initial}} \Delta x_1 \Delta x_2 \dots$ [Twomey, 2002]. This type of algorithm has been shown to provide stable, reliable convergence and no dependence of the solution on the initial profile (Chahine [1972], Twomey [1977]). The disadvantage of these methods is that there is no way to easily propagate statistical properties of the solution though the iterations. One of the solutions to this problem is to do a linear statistical analysis about the solution determined though the relaxation inversion. Another approach is to perform an independent sensitivity analysis of the retrieval by varying different forward model parameters.

Third, a very general class of solutions designed to handle non-linear inverse problems to "learn" the relationship between the data and state parameters from a training set. These methods often utilize the probabilistic approach of the Bayesian method and the Monte Carlo integration approach, however, it has not been widely used in atmospheric remote sensing application due to the prohibitive computational cost.

For the application to the SABER two-channel inverse problem, focus is placed on relaxation methods.

5.3 Relaxation Methods

The majority of retrieval techniques applied for limb observations are based on the "onion peeling" approach. This approach assumes certain limb geometrical features, namely that atmospheric layers lying below the tangent height do not contribute to the measured signal. In this case, in order to get corrections to the chosen set of parameters, one only needs to solve a set of triangular matrices. In many cases, however, the tangents points are not observable, especially for optically thick molecules, and, because the rows of these matrices are linearly dependent, the entire process collapses. To avoid these situations, various regularizations as well as a priori information are required to search for the so-called "physical solution", which is one of pre-calculated solutions predicting the outgoing radiation within the accuracy of measurements. The solution is usually found through an iterative process. If the problem is nonlinear, then it is linearized, and the iterative search for the solution includes a latent iterative solution of the nonlinear problem, which often leads to time-consuming calculations and instabilities. The iteration equation at tangent layer, i, is given as,

$$x_i^{n+1} = x_i^n + [y_i - F_i(x^n, b)](K_{ii})^{-1},$$
(5.5)

where the partial derivative of the forward model is calculated by letting, x_i change by a small amount. This form of the equation emphasize that one only need to calculate the local (diagonal) of the Jacobian matrix, K_{ii} , and avoids computing the fuller kernel matrix, K.

The forward-fit algorithm is a more stable and reliable approach, in which the retrieval is performed iteratively [Chahine, 1968]. This approach does not involve matrix inversion and relies on the stable and fast forward radiation calculations. The algorithm also allows straightforward accounting for the non-LTE conditions. The computational cost of this method is higher than that of a standard inversion procedure, however, the forward fitting algorithms demonstrate stable convergence and are less prone to false solutions [Rezac et al., 2015].

Chahine [1968] developed a simple feedback formula for non-linear relaxation. This technique modifies the atmospheric parameter at each iteration using the following form,

$$x_i^{n+1} = x_i^n [\frac{y_i}{F_j(x^n, b)}],$$
(5.6)

where i represents each altitude layer and j represents the tangent height altitude. The ratio of measured, y_i , to calculated, $F_j(x^n, b)$, limb radiance is taken at altitude i = j, which is used to update each elements of a current state vector, x, for each iteration, n. More simply, we use the atmospheric constituent, x, as a fitting parameter for any differences between the measured and simulated limb radiances. The iteration proceeds until the residual, r, satisfies some prescribed convergence criteria, ζ ,

$$r = \sum_{i} (y_i - F_i(\mathbf{x}^n, \mathbf{b}))^2 < \zeta.$$
(5.7)

This method works well for the limb viewing geometry where weighting functions are sharply peaked such that the sensitivity of a measurement, y_j , to changes in x_i is largest when i = j. Rezac et al. [2015] demonstrated that this technique produced effective, self-consistent, and accurate retrievals of CO_2 and temperature.

This method has been successfully applied by Gusev et al. [2006] to the non-LTE temperature retrievals in the Earths MLT from the CRISTA 15 μ m spectral limb radiances, by Feofilov et al. [2009] to the H₂O retrievals and Rezac et al. [2015] to the CO₂ retrievals from the SABER radiation measurements, as well as to the temperature retrievals in the Martian atmosphere from the MGS-TES observations (see Feofilov et al. [2012]).

5.4 Previous O and OH Retrieval Studies for SABER

Retrieving atomic oxygen using SABER OH observations has previously been performed by Smith et al. [2010] and Mlynczak et al. [2013]. The retrieval methods only utilize volume emission rates derived from the SABER OH 2.0 μ m channel limb radiance using an Abel Inversion procedure, see Eq. 3.11. These studies developed a model for this 2.0 μ m emission feature which included chemical production of OH in the v=8 and 9 states, spontaneous emission of radiation, and physical quenching by N₂, O₂, and O(³P). To retrieve atomic oxygen, it was assumed that ozone was in chemical equilibrium,

$$k_P[O][O_2][M] = k_L[H][O_3]$$
(5.8)

where the left side of Eq. (5.8) is ozone production, with rate coefficient k_P , and the right side is ozone loss (i.e. OH production), with rate coefficient k_L . Because the OH emission intensity observed by SABER at 2.0 μ m is directly proportional to the product of k_L [H][O₃], by substituting the left-side of Eq. (5.8) in as OH pumping in the SEE, Eq. 2.1, the emission intensity is now directly proportional to the atomic oxygen density. For quenching processes, the OH-N₂ and OH-O₂ treatment and rate coefficients were similar to Adler-Golden [1997]. However, for the OH-O(³P) quenching process, Mlynczak et al. [2013] and Smith et al. [2010] used a rate coefficient of 5.0×10^{-11} cm³/s, about 4-5 times lower than the rate coefficient suggested by Sharma et al. [2015], 2.3×10^{-10} cm³/s. After building

the SEE, atomic oxygen can be solved as a function of the measured volume emission rate and the kinetic and spectroscopic parameters. With the new chemical pumping treatment in addition to collisional and radiative terms, the solution for atomic oxygen was in the form of a quadratic equation and could be directly solved. Kaufmann et al. [2014], however, reported that SABERs atomic oxygen densities retrieved by Mlynczak et al. [2014] and Smith et al. [2010] using this method are still at least 30% higher in comparison with other MLT instruments (WINDII, OSIRIS, MSIS, and SCIAMACHY). Additionally, Mlynczak et al. [2013] and Smith et al. [2010] stated that using a higher rate coefficient for the OH- $O(^{3}P)$ reaction, similar to the one suggested by Sharma et al. [2015], gave unphysical atomic oxygen density values due to significant quenching of vibrationally excited OH(v).

There have been no reported studies of retrieving total OH densities using SABER data, however, Mast et al. [2013] derived OH(v=8+9) densities from OH volume emission rates (VER) using SABER over several seasons and years. Mast et al. [2013] recognized that the A-Einstein coefficient for the $9\rightarrow7$ (110.9) and $8\rightarrow6$ (115.0) are very similar and if treated as equal can reduce the VER equation for OH 2.0 μ m emissions as follows,

$$VER^{Ch8} = \sum A_{9,7}[OH(9)] + \sum A_{8,6}[OH(8)] = A_{avg}([OH(9)] + [OH(8)]).$$
(5.9)

Because VER^{Ch8} and A-Einstein coefficients are measured quantities, the absolute density of OH(v=9+8) can be determined.

5.5 The Retrieval Algorithm

In this section, I will go into detail of the combined $O(^{3}P)/OH$ retrieval algorithm, starting with atomic oxygen. Previous discussion of general methods for solving the inverse problem is not applicable to our development of the atomic oxygen module with the exception of the applied feedback formula which is similar to Chahine's ideas.

5.5.1 Atomic Oxygen Module

For retrieving atomic oxygen, $[O(^{3}P)]$, the SABER 1.6 and 2.0 μ m emission channels will be utilized. The general form of the SEE for solving the OH non-LTE problem (Eq. 2.1), can be rewritten in matrix form,

$$\sum_{\upsilon'} \mathbf{R}_{\upsilon\upsilon'} \mathbf{n}_{\upsilon'} = \mathbf{Y}_{\upsilon}, \tag{5.10}$$

where, on the left side, $\mathbf{R}_{vv'}$ represents all pumping/quenching radiative and collisional terms, $\mathbf{n}_{v'}$ is the total density of OH(v), and Y_v is the chemical production term.

The $[O(^{3}P)]$ retrieval method relies on the assumption of OH chemical equilibrium at night, where the chemical production of OH by [H] and $[O_{3}]$ is in balance with chemical quenching by [OH] and $[O(^{3}P)]$,

$$Y = \sum_{\upsilon} f_{\upsilon} Y = k_P[H][O_3] = k_L[O(^3P)][OH], \qquad (5.11)$$

where f_{v} are branching ratios from Table 3.3. The chemical pumping rate is denoted by, k_{P} , and quenching rate, k_{L} . In Eq. 5.10, the pumping term is replaced for the quenching term. The SEE can be rewritten as follows,

$$[OH] \sum_{\upsilon'} \mathbf{R}_{\upsilon\upsilon'} \mathbf{p}_{\upsilon'} = k_L[O][OH] f_{\upsilon}, \qquad (5.12)$$

where $n_{l'}$ has been substituted for $p_{l'}[OH]$, where $p_{l'}$ is the normalized population for vibrational level v'. The OH density, [OH], appears on both sides of the SEE and, therefore, cancel out leaving the non-LTE solution for OH vibrational populations independent on total [OH]. Further, OH normalized vibrational populations are used to calculate VER in both OH emission channels and then, by taking their ratio, the [OH] dependence is, once

again, completely removed,

$$\frac{\text{VER}^{\text{Ch8}}}{\text{VER}^{\text{Ch9}}} = \frac{\sum A_{9,7}[\text{OH}(9)] + \sum A_{8,6}[\text{OH}(8)]}{\sum A_{5,3}[\text{OH}(5)] + \sum A_{4,2}[\text{OH}(4)]} = \frac{[\text{OH}](\sum A_{9,7}p_9 + \sum A_{8,6}p_8)}{[\text{OH}](\sum A_{5,3}p_5 + \sum A_{4,2}p_4)}.$$
(5.13)

The combination of Eqs. 5.12 and 5.13 allows for the retrieval of atomic oxygen using OH emissions without any a priori information about [OH]. Figure 5.1 displays the dependence



Figure 5.1: Volume Emission Rate (VER) ratios $\left(\frac{Ch8}{Ch9}\right)$ as a function of atomic oxygen density for four tangent heights: 80 km (top-left); 85 km (top-right); 90 km (bottom-left); 95 km (bottom-right). The colors are only used for aesthetic purposes.

of VER Ratio $\left(\frac{Ch8}{Ch9}\right)$ on atomic oxygen density for four tangent heights. Simulated VER ratios $\left(\frac{Ch8}{Ch9}\right)$ are nearly linearly dependent on atomic oxygen demonstrating that there is a unique solution for atomic oxygen density at each tangent height. Atomic oxygen can, therefore, be used as a fitting parameter between measured and simulated VER ratios. Our

retrieval approach will utilize these VER ratios for $\frac{Ch8}{Ch9}$ of measured and simulated signals and follow a similar methodology to Chahine,

$$[O(^{3}P)]_{i}^{n+1} = [O(^{3}P)]_{i}^{n} \cdot \left[\frac{\operatorname{VER}(\frac{\operatorname{Ch8}}{\operatorname{Ch9}})_{\operatorname{measured},j}}{\operatorname{VER}(\frac{\operatorname{Ch8}}{\operatorname{Ch9}})_{\operatorname{calculated},i}}\right].$$
(5.14)

An iterative forward fitting technique is used because the correlation (slopes in Figure 5.1) between VER Ratios and atomic oxygen will vary with each unique input nighttime atmosphere (i.e. temperature, pressure and total density) used when performing SABER retrievals. Since we do not know the correlation, but we do know that the dependence between VER ratios and atomic oxygen is linear, Eq. 5.14 allows us to "find" the true atomic oxygen density using an iterative process.

The suggested $[O(^{3}P)]$ retrieval method has several advantages: 1) the VER ratios are completely independent to the components of the chemical pumping term (the rate coefficient and collisional partners). Only the branching ratios, f_{v} in Table 3.3, for the respective vibrational levels influence these signals. 2) There is a nearly linear dependence between VER ratios and atomic oxygen allowing for a unique $[O(^{3}P)]$ solution per measured VER ratio, see Figure 5.1. 3) OH populations, p_{v} are independent to [OH]. This feature allows for $[O(^{3}P)]$ to be retrieved without a priori information about [OH] and influencing the retrieval of [OH].

5.5.2 Hydroxyl Module

After $O(^{3}P)$ is retrieved and p_{υ} are found, total [OH] can be retrieved from the VER of either OH channel 8 or 9 using the expression,

$$[OH] \sum_{\upsilon} A_{\upsilon,\upsilon'} p_{\upsilon} = VER_{\text{measured}}.$$
 (5.15)

On the left side, p_{v} is the normalized population of OH vibrational level, v, $A_{v,v'}$ are the known Einstein coefficients of bands contributing to the emission channel, and [OH] is the total OH density while on the right side the SABER measured VER. [OH] can be directly solved, as all other parameters are known.

In conclusion, the innovative retrieval approach, described in section 5.5.1 and 5.5.2, which was never used before, allows $O(^{3}P)$ to be easily estimated from the ratios of measured VERs and then fit one (or both) OH channel emissions with the OH density as a single unknown parameter.

5.5.3 Architecture of retrieval scheme



Figure 5.2: General scheme of two-channel retrieval method. See text for explanation.

The architecture of the retrieval approach for $O(^{3}P)$ and OH retrievals described above is

displayed by the flow diagram in Figure 5.2. The retrieval algorithm begins with calculations of the non-LTE populations using initial guess inputs of $O(^{3}P)$ and OH profiles, followed by calculations of the non-LTE limb radiances and volume emission rates for channel 8 and 9. The first condition checks whether $O(^{3}P)$ is close (converged) enough to the "true profile" based on a value of Sum of Squared Residuals (SSR) (Eq. (5.7)) between the measured and calculated VER ratios. If it is greater than the prescribed convergence criteria, a single relaxation calculation in the $O(^{3}P)$ retrieval module is performed using Eq. 5.14 to obtain an updated $O(^{3}P)$ VMR profile. Because $O(^{3}P)$ VMR strongly influences the OH populations, the non-LTE populations have to be recalculated after each iteration. This "loop" will continue until the measured and simulated VER ratios satisfy the convergence criteria (usually about 4-5 iterations). Upon exiting the $O(^{3}P)$ retrieval module, a flag is set so the algorithm "knows" that the next step is to perform an OH retrieval. The first and only step in the OH retrieval module is to follow eq. 5.15 to obtain the total OH density from either SABER Ch 8 or 9. Because OH normalized populations and VER ratios and independent to OH density, it is not necessary to check if $O(^{3}P)$ needs to be further retrieved. Finally, with the new OH profile, the retrieval algorithms is completed with the "true solutions" to $O(^{3}P)$ and OH total density.

5.5.4 Altitude Retrieval Range

Radiance contribution functions for the 2.0 μ m and 1.6 μ m channels are displayed in Figure 5.3. The various profiles represent the fraction of total radiation (x-axis) each altitude (y-axis) contributes along the LOS for each tangent height. The different color profiles represent the tangent heights at which the radiances were simulated. In both panels, for tangent heights above 80 km, a majority of the radiation is emitting from the associated tangent height or the altitudes above. However, both OH emission bands are not sensitive to OH molecules emitting from tangent heights below 80 km. This is a result of the OH density peak which typically resides between 77-83 km (see Fig. 3.2). For limb radiances below this density peak, the weighting function for emitting molecules at the tangent height



Figure 5.3: Ch8 (top) and Ch9 (bottom) radiance contribution functions. The calculations are perform over all altitude points, however, only every 5th contribution function is shown for clarity. Calculations were performed using a nighttime mid-latitude summer atmosphere. See text for details.

is small due to low density and excitation of OH. As a result, using SABER observations of OH emissions, OH cannot be retrieved below ~ 80 km. Figure 5.3 can be used to roughly define a lower boundary limit for atmospheric retrievals using OH SABER radiances.
The altitude range for retrieving $O({}^{3}P)$ and OH is also dependent on the quality of the SABER VER measurements. Figure 5.4 displays the SABER VER ratios for $\frac{Ch8}{Ch9}$. The horizontal green lines represent approximate retrieval boundaries. These VER ratios, which will be used for retrieving atomic oxygen, show robust quality between the altitudes of 83-98 km.

Figure 5.5 displays SABER VER for Ch8 (left-panel) and Ch9 (right panel) for nighttime scans taken on 10 October 2008 at various latitudes and longitudes. The red profiles



Figure 5.4: SABER VER ratio measurements taken for nighttime scans on 10 October 2008. Green lines depict the altitude range where $O(^{3}P)$ retrievals can be performed with reasonable SNR.

represent the Noise Equivalent Radiances (NER) which were calculated by averaging the emission rates above 110 km. In both panels, it is clear that the signal degrades quickly above 100 km and, with reference to the NER, no OH retrievals can be performed above 102 km using either SABER OH channel. The lower boundary of VERs is significantly more variable. Certain individual VER profiles in both panels display non-zero values only down to 83 km, while others can reach below 80 km. In general, the VERs quickly degrades



Figure 5.5: SABER VER measurements taken for nighttime scans on 10 October 2008. Left-panel: Ch8 (2.0 μ m); Right-panel: Ch9 (1.6 μ m). Red - Noise Equivalent Radiances (NER).

below 83 km. One may see that the VER peak for Ch9 is slightly lower than Ch8 as a result of OH quenching by $O(^{3}P)$. Ch9 emissions are more sensitive to $O(^{3}P)$ quenching with respect to Ch8 and, therefore, the emissions drop off sooner due to the rising $O(^{3}P)$ densities. For the case of VER ratios in Figure 5.4, if one OH emission channel has a slightly lower boundary than the other, VER ratios can be extremely large and produce nonphysical values. While OH retrieval using VERs can proceed down to 80 km, the $O(^{3}P)$ retrieval using VER ratios only appears to be feasible to 83 km. To avoid using noisy SABER measurements a conservative lower boundary limit will be set at 85 km and an upper boundary of 100 km for $O(^{3}P)$ and OH retrievals.

Two disadvantages using SABER measurements are: 1) the SABER VER ratios only have a high SNR over a limited altitude range (between 85-100 km). 2) the atomic oxygen density decreases rapidly as altitude decreases, posing difficulties in retrieving atomic oxygen at the lower altitudes. The following section will describe the OH retrieval module.

5.6 Self-consistent studies

A self-consistency study into the two channel retrieval algorithm allows investigation of the performance of the retrieval method in an effective and reliable manner. This includes estimating the errors associated to the retrieved parameters, in addition to, allowing qualitative and quantitative answers to be obtained for several important questions regarding the retrieval algorithm performance:

- Does the inverse algorithm produce biases in the presence of no noise on the measured signal and no errors in the forward model parameters?
- Does the solution depend on initial conditions?
- Is the relaxation algorithm stable/unstable, if so under which conditions?
- What are the other capabilities/limitations of the relaxation method (degree of signal fitting, convergence speed, etc)?
- Estimation of other error sources (detector noise, forward parameters, etc).

A perfect self-consistent retrieval algorithm would exhibit no dependence on initial conditions, produce no biases (always retrieve the original input parameters), show fast convergence speed with perfect signal fitting, and display no instability. Achieving this, however, is hardly possible in the real world problem since the physics of the forward problem, observation geometry of the experiment, and even the inverse problem itself degrades the information on the unknown parameters [Gille and Bailey, 1977].

The general procedure for a self-consistency test and error analysis can be described as follows:

1. Calculate the non-LTE limb radiances for some input atmosphere ("original parameter") and take them as the measured signal.

- 2. Change the input (forward model or atmospheric) parameter(s).
- 3. Solve the inverse problem.
- 4. Compare the retrieved and original parameters plus analyze the retrieval performance.

5.6.1 Self-consistency case studies

The following initial conditions were considered for the two channel $O(^{3}P)/OH$ retrieval problem: (high $O({}^{3}P)$ /high OH, high/low, low/high, low/low), where high/low is taken with respect to the true profiles of the $O(^{3}P)$ and OH parameters. The different combinations of starting condition were tested with varying magnitudes and different test atmospheres in an attempt to study the performance of the retrieval algorithm. In this section only few examples are discussed in detail that demonstrate the performance of the two-channel relaxation algorithm. For all calculations, inputs are taken from WACCM. Retrievals are performed on noiseless limb radiances. The effects of random noise, radiance bias and other sources of uncertainties are described in section 5.7. The first self-consistency test is for a climatological mid-latitude spring atmosphere as shown in Figure 5.6. There are four panels: the upper left panel shows the original, starting, and retrieved OH profiles; the upper right shows the same case case for $O({}^{3}P)$; the lower left and right panels show the differences ((retrieved-original)/original) in percent of OH and $O(^{3}P)$. For the first case, the starting conditions are OH = +30% and $O(^{3}P) = \pm 30\%$ over the retrieval altitude. By examining the lower panels showing the vertical profiles of retrieval error for the two different starting conditions, it is observed that for OH, the retrieved profile only differs by less than 0.5%over altitudes above 80 km, with higher error at altitudes below. The retrieved $O(^{3}P)$ agrees with the true solution to within 0.5% with the largest deviation coming from lower altitudes as well. It can also be seen that the vertical structure of the error profiles for $O(^{3}P)$, are quite similar but flipped in sign. The biases in the retrieved $O(^{3}P)$ profiles lean toward the starting conditions, whereas, those of the retrieved OH profile is reversed. This indicates that the solution is mildly dependent on the starting condition of $O(^{3}P)$. Similarly, when



Figure 5.6: Case 1: self-consistency test of the two-channel retrieval algorithm for a climatological mid-latitude spring atmosphere. The starting condition are OH +30% and O(³P) $\pm 30\%$. See text for discussion.

starting from OH = -30% (figure not shown), the profiles structure is identical to the results shown in 5.6, however, all results are flipped in sign. Observing the VER ratio fitting and convergence speed of this test is another way of examining the performance of the $O(^{3}P)$ retrieval algorithm. Figure 5.7 displays two panels: the top panel shows the VER ratio fitting for Ch8/CH9 ($\frac{2.0\mu m}{1.6\mu m}$) in terms of the ratio between measured and calculated VER ratio for the final retrieved $O(^{3}P)$ profile; the bottom panel shows the iteration number versus the SSR between the calculated and measured VER ratios, N represents the number of altitude points over the retrieval range, R_m and R_c denotes measured and calculated VER ratios, respectively. The VER ratios fit to within 0.2% at all altitudes. The high level of



Figure 5.7: Case 1: VER ratio fitting and convergence speed. See text for discussion.

VER ratio fitting can be further improved by using smaller values for the SSR convergence criteria. The OH VER fitting and its convergence speed for the retrieval of OH is not shown because only one iteration (see Eq. 5.15) is needed in the retrieval module to obtain the true solution. The next case, shown in Figure 5.8, was performed using a climatological polar summer atmosphere when the starting condition are, OH = -30% and $O(^{3}P) = \pm 30\%$. The $O(^{3}P)$ VMR for the polar summer condition are a couple orders of magnitude lower than case 1. Between 80-85 km the VMR ranges from 1e-6-1e-3 for case 2, where as, case 1 ranges from 1e-4-1e-2. It is important to investigate whether the extremely low VMR significantly influences the solution or retrieval performance. In this case, the OH error is within 2% of the true profile with largest values below 87 km. The $O(^{3}P)$ solution is within 1-2% of the true profile with the larger values also occurring below 87 km. Once again, a slight bias toward the starting the condition remains for $O(^{3}P)$ retrieval, however, below 85 km, the error profiles is similar, suggesting that the solution has very low sensitivity to the starting $O(^{3}P)$ VMR profile. The VER ratio fitting and convergence speed for case 2 showed similar results as case 1.

The previous two cases were perform under different atmospheric conditions with smooth climatogical profiles. In the following case, Figure 5.9, the peak of the true OH profile is several kilometers above the starting condition. Additionally, the starting $O(^{3}P)$ profile



Figure 5.8: Case 2: self-consistency test of the two-channel retrieval for a climatological polar summer atmosphere. The starting conditions are OH -10% and $O(^{3}P) \pm 30\%$. See text for discussion.

exhibits an upward trend which increases at a slower rate compared to the true $O(^{3}P)$. This case exhibits a more likely starting condition in the real retrieval, where the OH VMR peak varies throughout the night and $O(^{3}P)$ VMR vertical structure may differ by an order of magnitude. Looking at the lower panels, it is clear that the relaxation algorithm recovered the original profiles for both parameters. The OH and $O(^{2}P)$ profiles converged to within 1% above 79 km and between 2-10% below 79 km. Once again, the interdependence of the parameters is manifested in the mirroring effect of the error profiles. Also, there is no indication of instability of the algorithm that would produce artificial structures either in OH and $O(^{3}P)$ even for such extreme cases.

The VER ratio fit and convergence speed, Figure 5.10, are in the range of the two



Figure 5.9: Case 3: self-consistency test of the two-channel retrieval algorithm for a climatological mid-latitude spring atmosphere with an OH density peak shift to a lower altitude and $O(^{3}P)$ profile exponentially decreased as a function of altitude. See text for discussion.



Figure 5.10: Case 3: VER ratio fitting and convergence speed. See text for discussion.

previously shown cases 1 and 2.

For the final case, shown in Figure 5.11, the starting condition for the peak of the OH profile was place above the true solution, while the $O(^{3}P)$ starting profile exhibited an upward trend which increases at a faster rate relative to the true solution. Similar to case 3, the bottom panels shown convergence in both the OH and $O(^{3}P)$ profile to within 0.5%, except below 80 km, where it differs by 5% for both parameters. The VER ratio fit and



Figure 5.11: Case 4: self-consistency test of the two-channel retrieval algorithm for a climatological mid-latitude spring atmosphere with an OH density peak shift to a higher altitude and $O(^{3}P)$ profile exponentially increased as a function of altitude. See text for discussion.

convergence speed for case 4, Figure 5.12, are in the same range of the previous three cases.

The self-consistent studies, tested by the four different cases presented above for various atmospheres and $OH/O(^{3}P)$ starting conditions, demonstrate that the inversion algorithm



Figure 5.12: Case 4: VER ratio fitting and convergence speed. See text for discussion.

is self-consistent. The relaxation algorithm converge to the true solution without any instabilities for all test cases with a high degree of VER ratio and VER fitting. The retrieval algorithm also does not introduce any severe biases or artificial structures in the retrieved parameters for any of the different atmospheric conditions tested during these studies.

The two-channel retrieval shows dependence on the initial conditions only slightly for the O(³P) parameter. This bias is carried over to the OH retrieval module. The selfconsistency tests performed to find the maximum deviations of the initial profiles that would still converge to the true solution suggests maximum uncertainty exceeds $\pm 30\%$ for O(³P) and OH. Initial atmospheric profiles in real retrieval will be well within these limits, especially at the upper retrieval boundary.

5.7 Sensitivity and error analysis

In this section, the effect of the various sources of uncertainties on the retrieved $O(^{3}P)/OH$ are to be discussed. The total uncertainty of the retrieved parameters can be split into two categories 1) the random error, which gives a measure of the imprecision, specifically the random noise of the radiometer instrument (i.e SABER). and 2) the systematic error, which provides information on the inaccuracy or the bias of the inferred quantities. The

important sources of the systematic errors are instrument calibrations, non-LTE modeling parameters such as rate coefficients, and assumed atmospheric input parameters.

Table 5.1 shows the mean retrieval errors due to various sources for a single $O(^{3}P)/OH$ profile as well as the combined total error (i.e. the Root Sum Squared (RSS)). The values in the table are averages of estimated errors for four different seasons and latitudes which are included in the Appendix D. Errors for both $O(^{3}P)$ an OH are in percent.

The uncertainty of the retrieved parameters due to the random noise of the radiometer instrument was estimated first. Normally distributed noise was added to the noiseless calculated radiance with a standard deviation equal to the Noise-Equivalent-Radiances (NER) for each channel. The NER for channels 8 and 9 are 3.68×10^{-10} W/(cm²sr) and 6.51×10^{-10} W/(cm²sr), respectively. The NER in both channels drastically influence the O(³P) retrieval below 85 km and a moderate amount above 95 km. It also directly influences the OH VMR retrieval, where below 85 km, uncertainties reach >50%.

The first of the systematic tests considers pressure error. The pressure, P_o , is a SABER retrieval algorithm parameter which is fixed at 30 km. The pressure is varied within the estimated maximum range of $\pm 4\%$ [Remsberg et al., 2008]. These calculations are performed to isolate the pressure effect from temperature via the hydrostatic equation. Therefore, this error reflects only the influence of the P_o at the altitudes relevant to the two-channel retrieval. The effects of the varying pressure are minimal for O(³P) and OH above 85 km, and reach up to 15% below this altitude.

Next, the row labeled "T bias" was estimated by shifting the temperature profile at all altitudes, including ones outside of the retrieval range, by ± 5 K [Remsberg et al., 2008] and adjusting the pressure through the hydrostatic equation. The errors due to this bias are very large, especially for O(³P)/OH retrievals below 85 km. Above 85 km, errors still reach up to $\pm 20\%$ which makes kinetic temperature one of the largest contributors of uncertainty for retrieving O(³P)/OH in the MLT.

Next, the discussion turns to retrieval errors relating to uncertainties in the non-LTE

Random Errors						
		Altitude (km)				
Source of error	Param.	80	85	90	95	100
Random noise [*]	$O(^{3}P)$	± 135	± 5	± 5	±11	± 16
	OH	± 59	± 6	± 6	± 6	± 17
Systematic Errors						
P_0 bias ⁺	$O(^{3}P)$	±13	± 4	±1	± 2	± 3
	OH	± 15	± 9	± 4	± 4	± 4
T bias	$O(^{3}P)$	± 77	± 30	± 6	± 13	± 17
	OH	± 66	± 34	± 18	± 19	± 20
k_{VV} OH-N ₂	$O(^{3}P)$	± 85	± 28	± 3	±1	±1
	OH	± 63	± 17	±1	<1	<1
k _{VV} OH-O ₂	$O(^{3}P)$	± 89	± 63	± 17	± 8	± 4
	OH	± 59	± 25	± 2	<1	<1
k_{VE} OH-O ³ P	$O(^{3}P)$	± 5	±11	± 15	± 15	± 15
	OH	± 6	± 15	± 21	± 22	± 21
$k_L[OH][O]$	$O(^{3}P)$	<1	<1	<1	<1	<1
	OH	± 17	± 17	± 17	± 17	± 17
А	$O(^{3}P)$	± 19	± 6	± 1	± 3	± 3
	OH	± 22	± 5	± 3	± 4	± 4
Systematic RSS	$O(^{3}P)$	± 148	± 79	± 24	± 22	± 24
	OH	± 117	± 54	± 33	± 34	± 35
Total RSS	$O(^{3}P)$	± 167	± 79	± 25	± 25	± 27
	OH	± 138	± 54	± 35	± 35	± 38

Table 5.1: Mean retrieval errors and their sources

*SABER NER values for each channel respectively +Reference pressure at 30 km

pumping and quenching rates of the OH(v) levels. The source of uncertainty for V-V reaction between OH and N₂ depend on the accuracy of the V-V rate itself. Table 3 in Xu et al. [2012] provide a list of rate coefficients measured in the laboratory with their associated uncertainties for this reaction. From this table, an uncertainty was estimated for this rate and taken as $\pm 35\%$. We find that this reaction affects mostly O(³P) and OH at

85 km and below. The OH-N₂ reaction is weak and inefficient, however, at lower altitudes, where atomic oxygen density is extremely low and no longer a main quencher of OH, N₂ has a strong influence on $O(^{3}P)$ and OH retrievals.

The V-V collisional coefficient for the reaction between OH(v) and O_2 plays a crucial role in determining the populations of OH(v) levels as it is the dominant collisional quencher of OH over the entire retrieval range. An uncertainty of $\pm 35\%$ is assumed, which was estimated based on the list of measured rate coefficients for this reaction displayed in Table 3 of Xu et al. [2012]. The OH-O₂ reaction moderately influences the retrieval of $O(^{3}P)$ and very little for OH above 85 km. At 85 km and below, however, OH populations becomes extremely sensitive to O₂ and, therefore, largely influence the final solution.

Discussed earlier in chapter 5, the chemical quenching of OH in the form of $k_L[OH][O]$ can be used as the pumping term for OH if one assumes OH equilibrium. An uncertainty of \pm 20% is taken for this reaction which was based on the experimental studies performed by Westenberg et al. [1970] and Lewis and Watson [1980]. For all altitudes within the retrieval range, O(³P) is not influenced by the variation in the pumping rate because our technique for retrieving O(³P), which takes the ratio between OH populations of upper and lower levels, removes any dependence on chemical pumping terms. However, the effect is quite different for OH. For OH retrieval, our technique utilizes VERs which are directly dependent on the chemical pumping term and, therefore, the VERs are moderately sensitive to [OH], producing an error range of \pm 17% for all altitudes.

Finally, the spectroscopic parameters are studied for any influence on $O(^{3}P)/OH$ retrievals. By analyzing the spontaneous emission coefficients used in other OH models (Xu et al. [2012], Funke et al. [2012]), an uncertainty of \pm 5% is taken for all spontaneous emission coefficients. Similarly to other uncertainty parameters, above 85 km the emission coefficients have minimal influence on the $O(^{3}P)$ and OH retrievals. Below 85 km, uncertainty in retrieving either parameter is moderately large.

Overall, for altitudes above 85 km, the systematic sources dominate the contribution to

the total uncertainty. Above 85 km, the total RSS For $O(^{3}P)$ is estimated to be 25-27% while OH is estimated to be between 35-38%. The $O(^{3}P)$ and OH retrievals exceed errors of 50% at 85 km, and, at 80 km, are as high as 167% and 138% for $O(^{3}P)$ and OH, respectively. Because a high uncertainty at 85 km and below has been estimated, it is, therefore, not reasonable to retrieve $O(^{3}P)$ and OH below this altitude as the retrieved parameter may vary by a factor of 2.

In the next chapter, the results of the two-channel retrievals will be presented using SABER radiances.

Chapter 6: O(³P) and OH Retrieval Results and their Analysis

In this chapter the results of the self-consistent two-channel retrieval of $O(^{3}P)/OH$ from the V2.0 SABER data are presented. The qualitative and quantitative aspects of the retrieved $O(^{3}P)$ and OH VMR are discussed. The results will begin with the zonal density of the retrieved $O(^{3}P)$ for four seasons at all observed latitude between 80-95 km. These plots will be compared to the current SABER $O(^{3}P)$ densities over the same region. Following the discussion, retrieved $O(^{3}P)$ densities will be compared with results of the WACCM model, SCIAMACHY and OSIRIS instruments over the same latitude region for the fall season. Then, I will apply our model as well as other OH models to the two-channel algorithm, and examine their effects on retrieved $O(^{3}P)$ densities. After that, an examination of retrieved OH densities and its comparison with WACCM profiles will be presented. Finally, using the results of the two-channel algorithm, 4.3 μ m radiances are simulated and compared to SABER observations.

6.1 Daily global O(³P) densities for April 2009, August 2007, October 2008, and January 2008

The first four plots, Figures 6.1, 6.2, 6.3, and 6.4, show the daily zonal mean densities distributions of $O(^{3}P)$ obtained with the two-channel retrieval versus the current SABER $O(^{3}P)$ density, retrieved by Mlynczak et al. [2013]. The calculations for both retrievals are made using temperature, pressure, and VERs taken from SABER V2.0 and O₂ and N₂ are taken from WACCM. Atomic oxygen densities are in units of molec/cm⁻³ while densities

plots are scaled by 1e+11. The SABER database provides VERs which were derived from limb radiances using an Abel Inversion method [Mlynczak et al., 2014].

Figure 6.1-6.4 show the $O(^{3}P)$ density distributions of the two-channel (top-left) and current SABER (top-right) retrieved quantities on 10 October 2008, 20 January 2008, 05 April 2009, and 18 August 2007, respectively, at all observed latitudes during that night. The bottom panels shows their percent differences (from 85-95 km). In all cases the density distributions exhibit similar patterns. For example, in Figures 6.1 and 6.3, the oxygen densities show enhancements at the equator, while in Figure 6.2 both $O(^{3}P)$ densities show enhancements at mid-latitudes.



Figure 6.1: Nighttime atomic oxygen density distributions (in cm^{-3}) for SABER scan taken on 10 October 2008. Top-Left: atomic oxygen density retrieved using two-channel algorithm. Top-right: current SABER atomic oxygen density. Bottom: Atomic oxygen density difference in percent (SABER - retrieved)/retrieved.

Several noticeable differences can be observed in the plots of the current SABER and the retrieved $O(^{3}P)$. First, from 90-95 km, some small scattered regions exhibit a lower SABER $O(^{3}P)$ (upper-left region in Figures 6.2 and 6.3). In these cases, the SABER radiances have a degrading signal and, therefore higher error bars on the retrieved quantities.



Figure 6.2: Nighttime atomic oxygen density distributions (in cm^{-3}) for SABER scan taken on 20 January 2008. Top-Left: atomic oxygen density retrieved using two-channel algorithm. Top-right: current SABER atomic oxygen density. Bottom: Atomic oxygen density difference in percent (SABER - retrieved)/retrieved.

Secondly, the SABER atomic oxygen density between 90-95 km are, on average, higher than the retrieved ($O^{3}P$) by 10-50%. Figures 6.1 and 6.3 show a higher SABER O(^{3}P) between 10-30% for all altitudes while Figures 6.2 and 6.3 are higher between 10-50%, especially in the equatorial regions.

The atomic oxygen retrieved using the methodology for current SABER $O(^{3}P)$ and



Figure 6.3: Nighttime atomic oxygen density distributions (in cm^{-3}) for SABER scan taken on 05 April 2009. Top-Left: atomic oxygen density retrieved using two-channel algorithm. Top-right: current SABER atomic oxygen density. Bottom: Atomic oxygen density difference in percent (SABER - retrieved)/retrieved.

the two-channel algorithm both rely on modeling OH emissions. Despite different techniques, the OH relaxation mechanisms are similar with the exception of the OH-O(³P) reaction. Mlynczak et al. [2013], which provide the SABER database with the current $O(^{3}P)$ retrievals, uses a vibrationally independent rate coefficient of 5×10^{-11} cm³s⁻¹ for this reaction, whereas, the two-channel retrieval use the suggested rate coefficient of Sharma et al. [2015], and confirmed in a laboratory by Kalogerakis et al. [2016], which is 4-5 times higher. Mlynczak et al. [2013] found that using this high rate coefficient resulted in $O(^{3}P)$ densities that were nonphysical. However, using our retrieval technique, the higher rate coefficient for this reaction gives lower atomic oxygen values. In a further study, one needs



Figure 6.4: Nighttime atomic oxygen density distributions (in cm^{-3}) for SABER scan taken on 18 August 2007. Top-Left: atomic oxygen density retrieved using two-channel algorithm. Top-right: current SABER atomic oxygen density. Bottom: Atomic oxygen density difference in percent (SABER - retrieved)/retrieved.

to understand how revised atomic oxygen influences cooling and heating in the mesopause region in order to properly establish this balance.

A study performed by Kaufmann et al. [2014] showed that atomic oxygen derived from nighttime atomic oxygen green line limb emission measurements of he SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric Chartography) instrument on the European Environmental Satellite are, on average, 30% lower than current SABER retrievals. The retrieved atomic oxygen densities presented in this section are comparable to Kaufmann et al. [2014] and will be discussed further in the following section.

6.2 Comparison of retrieved O(³P) density with WACCM results, current SABER, OSIRIS, and SCIAMACHY retrievals

Figure 6.5 shows a comparison between SABER (this study), current SABER, OSIRIS, and SCIAMACHY, retrievals as well as WACCM result atomic oxygen densities for $20^{\circ}-40^{\circ}$ N and $40^{\circ}-60^{\circ}$ N in September 2005. Current SABER measurements are dervied from SABER OH 2.0 μ m radiances where an uncertainty in atomic oxygen retrievals is $\pm 25\%$ [Mlynczak et al., 2013]. SCIAMACHY measurements are derived from airglow green line radiances at 557.7 nm, emitted by the O(¹S) excited state. The overall uncertainty of atomic oxygen derived using SCIAMACHY measurements is 15%. OSIRIS measurements are derived from the O₂ A-band emissions [Sheese et al., 2011]. The WACCM model is an empirical, global model of the Earth's atmosphere from ground to space, calculating temperature and density profiles [Marsh et al., 2013]. The O(³P) two-channel retrievals presented in Figure 6.5 are



Figure 6.5: Zonal mean atomic oxygen density for Fall 2005 at (left) 20°-40°N and (right) 40°-60°N. The SCIAMACHY data were dervied from green line emission data, MSIS (?), and SABER (current) from OH 2.0 μ m emission.

taken from nighttime scans on 27 September 2005.

In both latitude bands, retrieved $O(^{3}P)$ peak between $(4-6) \times 10^{11} \text{ mol/cm}^{3}$, very similar

to SCIAMACHY results which peak around 6×10^{11} mol/cm³ in the left and right panels. Retrieved O(³P) fall within the error bars of SCIAMACHY O(³P) between 90-100 km for the right panel and 92-100 km for the left panel. Below 90 km, retrieved O(³P) show higher densities than SCIAMACHY and even current SABER around 85 km. Current SABER O(³P) retrievals generally are about 30% higher than retrieved atomic oxygen performed in this study and SCIAMACHY. In the left panel of Figure 6.5. however, the lower errors bars of SABER atomic oxygen overlap with retrieval errors bars for SCIAMACHY and our results above 90 km. Additionally, SABER O(³P) agree very with all O(³P) profiles in both panels below 90 km. O(³P) retrievals derived from OSIRIS measurements are about 10% lower than SCIAMACHY and our O(³P) retrievals above 90 km, but fall with the error range below this altitude. Finally, O(³P) calculated by WACCM is generally 10-20% lower than all retrieved quantities in both panels.

6.3 Comparison of retrieved O(³P) using different OH models

Figure 6.6 displays retrieved $O(^{3}P)$ using the two-channel algorithm for different OH models. Four days are plotted: (top-left) 05 April 2009 at latitude 0°N; (top-right) 20 January 2008 at latitude 70°S; (bottom-left) 10 October 2008 at latitude 45°N; and (bottom-right) 18 August 2007 20°S. In addition to the OH model described in Chapter 3, three other previous OH model rate sets were implemented in our model and the subsequently retrieved atomic oxygen densities are compared. We adopted OH model rate sets which have been described by: (red) Adler-Golden [1997], (blue) Funke et al. [2012], and (green) Xu et al. [2012]. See section 3.5 and Table 3.6 for a description of the different OH model rate sets. $O(^{3}P)$ densities are in units of mol/cm³ and are scaled by 1e+11.

In all cases, the retrieved $O(^{3}P)$ exhibit similar vertical structure, albeit different $O(^{3}P)$ densities values. A brief description of the results which were obtained using different



Figure 6.6: Comparison of atomic oxygen density using four different OH model rate sets at various latitudes and seasons. Retrievals were performed using the same two-channel algorithm. Black - This Study; Red - Adler-Golden [1997]; Blue - Funke et al. [2012]; Green - Xu et al. [2012].

OH model rate sets will be presented from highest retrieved $O(^{3}P)$ to lowest. First, The collisional rate coefficients used in Xu et al. [2012] are similar to the ones used by Mlynczak et al. [2013] to retrieve the current $O(^{3}P)$ SABER densities. The authors took branching ratios for the OH-N₂ and OH-O₂ reactions from Adler-Golden [1997], used a single-quantum process for the OH-N₂ reaction, a multi-quantum process for OH-O₂, and sudden death quenching for OH-O(³P) with a rate of 5×10^{-11} cm⁻³sec⁻¹. The low OH-O(³P) quenching rate keep vibrational levels highly excited especially v = 4 and 5, where radiative transitions from these levels are main contributors to 1.6 μ m emission. This results in low VER ratios which cause high atomic oxygen retrieved. The Xu et al. [2012] model retrieved is by far the largest $O(^{3}P)$, exceeding densities of 15×10^{11} mol/cm³.

Our OH model used in this study has been described in detail in Chapter 3. To briefly

summarize our OH model, chemical branching ratios are taken from Adler-Golden [1997], OH-N₂ is single-quantum, OH-O₂ is multi-quantum, and the new mechanism is used for the OH($v \ge 5$)-O(³P) reaction, with suggested rate coefficient 2.3×10^{-10} cm⁻³sec⁻¹, while a sudden death quenching is used for OH(v < 5)-O(³P), with a rate of 5×10^{-11} cm⁻³sec⁻¹. The higher rate coefficient for the OH($v \ge 5$)-O(³P) reaction is the main difference between our OH model and Xu et al. [2012]. This treatment quenches the vibrational levels, v = 5-9, at a faster rate, especially v=5 where the OH-O(³P) reaction is the dominant quencher. More efficient quenching at v=5 increases the VER ratio and, as a result, lower atomic oxygen is retrieved.

The Adler-Golden [1997] model uses similar N₂ and O₂ relaxation mechanisms, rate coefficients, and chemical branching ratios as our OH model. The OH-O(³P) reaction, however, is treated as a sudden death quenching using a vibrationally independent rate coefficient of 2.0×10^{-10} cm⁻³sec⁻¹. Such a high rate coefficient for all OH(v) levels results in more quenching of excited OH. Compared to our OH model, the "indirect" mechanism, which has a similarly high rate coefficient as the one used by Adler-Golden [1997], is only applied to OH($v \ge 5$). As a result, vibrational levels, v = 4 and 5, which are sensitive to 1.6 μ m emissions, are more quenched using the Adler-Golden [1997] model and have a higher VER ratio which causes lower O(³P) densities to be retrieved.

The Funke et al. [2012] model is the most different of the four OH models tested. The branching ratios are taken from Dodd et al. [1994], which include chemical pumping for all OH vibrational levels. The OH-N₂ and OH-O₂ reactions are treated as a single-quantum process and the OH-O(³P) reaction is treated as a sudden death process with a high rate coefficient of 2.2×10^{-10} cm⁻³sec⁻¹. Using rate coefficients from the Funke et al. [2012] resulted in lowest O(³P) density retrievals for all four test cases. A number reasons cause this low atomic oxygen retrieval: 1) OH-O₂ reaction, which is the dominant quencher of OH, is single-quantum, compared to a multi-quantum process which the previous models use. This treatment keeps the upper vibrational OH levels, v = 7-9, highly excited and

increases the VER ratio, which causes lower atomic oxygen densities to be retrieved. 2) The branching ratios are more evenly distributed among the OH vibrational levels compared to the ones provided in Adler-Golden [1997]. The upper levels have less pumping and the lower levels have more pumping, which will decreases the VER ratio and should retrieve less atomic oxygen. However, the Funke et al. [2012] model uses a high rate coefficient for the OH-O(³P) reaction which further quenches the lower levels. The OH-O(³P) quenching and the single-quantum OH-O₂ reaction offsets the effects of the branching ratios which results in even lower atomic oxygen.

Among the three models which retrieve reasonable $O(^{3}P)$ densities (our model, Adler-Golden [1997], and Funke et al. [2012]), only our model incorporates a mechanism which enhances 4.3 μ m emissions. Later in this chapter, further validation of retrievals based on our model will be presented by analyzing SABER 4.3 μ m emissions.

6.4 Nightly zonal OH densities: comparison with model results and other observations

Figures 6.7 and C.1 show the zonal mean density distributions of OH ground state obtained using the (black) two-channel retrieval versus (red) WACCM for two nights: 05 April 2009 and 18 August 2007 (see Appendix for 20 January 2008 and 10 October 2008). Each night displays OH(v=0) results averaged over 4 latitude bins: (top-left) 0-5°N, 40-45°N, 40-45°S, and 70-75° North or South depending on the month. The number of profiles averaged is given in the plot title. OH(v=0) densities are displayed in units of mol/cm³. Figure 6.8 displays the averaged residual OH(v=0) densities for each latitude bin ((WACCM -RETR)/RETR) in percent. The differences between the retrieved and WACCM OH(v=0)densities are generally the same for all four nights nights. Figures 6.8 displays OH(v=0) is very similar to WACCM, where WACCM density differences are bewteen 0-50% larger than retrieved values for all four latitude bins. Below 87 km, the WACCM OH(v=0) density



Figure 6.7: Comparison of zonal OH ground state density on (top) 05 April 2009 and (bottom) 18 August 2007 in four latitude bins: 0-5° N, 40-45° N, 40-45° S, 70-75° S. Black - This study. Red - WACCM.

is also consistently higher than OH(v=0) retrieved by at least a factor of 2-3 for various nights. It must be stressed that the WACCM model calculates OH ground state densities assuming "sudden" death quenching for all collisional processes. The vibrationally excited states of OH(v) have no chemical lifetime in the WACCM model and, therefore, the OH densities which are calculated may be biased toward its ground state.



Figure 6.8: Residuals (WACCM - Retrieved)/Retrieved) of OH(v=0) densities for four latitude bins: Green-0-5°N; Blue-40-45°N; Magenta-40-45°S; Orange-70-75°N&S. See text for description.

Mast et al. [2013] retrieved absolute OH densities for vibrational levels v=8+9 using SABER Ch8 VERs. The authors took advantage of the fact that the Einstein coefficients for the $9\rightarrow7$ and $8\rightarrow6$ vibrational transitions, who's emissions dominate the SABER 2.0 μ m channel, are roughly the same (110 s⁻¹ and 115 s⁻¹, respectively, see Table 3.2). Using the formula for VER, Eq. 3.13, the combined absolute density of OH(v=8+9) can be determined if the Einstein coefficients and VERs are known.

Figure 6.9 (left-panel) displays the absolute nighttime densities derived from the twochannel algorithm averaged over 4 nights for 2008. The right-panel of this figure displays results presented in Mast et al. [2013] for the entire year of 2008. Massive retrievals for OH were not possible due to the time constrains of this study, however, the magnitude of retrieved OH(v=8+9) densities in Figure 6.9 can still be compared. There are several similarities between both plots. First, both OH(v=9+8) densities exhibit equatorial peaks around 87 km and reach maximum densities of 900 cm⁻³ and 1000 cm⁻³ for the twochannel algorithm results and for results of Mast et al. [2013], respectively. Also, both plots exhibit a secondary peak in the mid-latitude northern hemisphere region. Absolute densities peak around 87 km with densities of 900 cm⁻³. Above 90 km, both retrieved quantities experience similar decreasing trends in absolute densities. Around 100 km, both densities are displaying magnitudes of about 100 cm⁻³. Below 85 km the retrieved OH(v=9+8)



Figure 6.9: Comparison of retrieved OH(v=9+8) absolute densities with Mast et al. [2013] for 2008. Left - This study; Right - Mast et al. [2013]. Absolute densities are in units of (cm^{-1}) . See text for description.

densities, however, decrease at a steadier rate than the ones derived by Mast et al. [2013]. At 80 km, the right-panel has absolute densities of 50 cm⁻¹, while the left-panel has 200 cm⁻¹. The results presented in Figure 6.9 help validate the OH densities retrieved using the two-channel algorithm, especially OH(v=9+8).

Pickett et al. [2006] studied satellite measurements of thermal emission from the 2.5 THz rotational lines in the ground vibrational state of OH using the Aura MLS (Microwave Limb Sounder) instrument during the nighttime on 22 June 2005. The left panel in Figure 6.10 show our OH(v=0) density retrieval results using the two-channel algorithm for the same night while the right panel displays OH(v=0) density observations by Pickett et al. [2006].

To perform OH(v=0) retrievals below 85 km, retrieved $O(^{3}P)$ from 85-100 km was merged with WACCM $O(^{3}P)$ below this altitude range for similar latitudinal and seasonal conditions. Then using Eq. 5.15, OH density can be retrieved. SABER observations during this night cover a smaller region compared to MLS observation. The red square plotted in the right panel of Figure 6.10 represents the SABER coverage overlap with MLS observations during that night. The retrieved OH densities using the two-channel



Figure 6.10: Comparison of retrieved ground state OH density distributions with Pickett et al. [2006] on June 22, 2005. Left-This study using SABER OH observations. Right-Pickett et al. [2006] using zonal mean MLS observations. See text for description.

algorithm exhibit similar features to the MLS OH observations. The OH densities are very similar in concentration, showing roughly between $(1-1.5) \times 10^6 \text{ mol/cm}^3$ between 80-81 km. Between the latitudes 40° S- 20° N, the retrieved OH densities show a slight increase in peak density from the southern latitudes to the northern ones, especially around 20° N. The MLS observation show the same behavior but more prominently. The MLS observations, however, show an OH peak that broadens almost 10 km, from 75-85 km, whereas our retrievals only exhibit at 1-2 km broadening. Because OH is mostly in its ground state up to 80 km, SABER observations, which can only observe excited OH, cannot retrieve any OH densities below this threshold. Despite its limitations, the retrieved concentrations are similar between 80-82 km for both measurements.

Previous studies using ground-based LIDAR measurements also observed mesospheric OH densities. These LIDAR measurements detect resonant fluorescence of OH in the UV and are sensitive to OH in the ground vibrational state. Studies performed by Brinksma et al. [1998] at Table Mountain in Wrightwood, CA saw a night layer in mesopsheric OH near 82 km, similar to MLS and SABER observations. LIDAR measurements also observed a narrow 1.6 km wide OH denisty layer, which is consistent with retrieved SABER densities. LIDAR measurements, however, were not performed on the same date and time as MLS and SABER observations.

The difference between SABER measurements and those observed by MLS and LIDAR is that SABER can only observe OH(v) in a vibrational excited state, whereas MLS and LIDAR can observe OH ground state emission. Our suggested OH model, however, has chemical balance for total OH built in and, therefore, allows observing fitted emissions from excited states as well as its ground state. Comparing with direct ground state observation such as Pickett et al. [2006] and Brinksma et al. [1998] gives additional validation of our model.

Overall, the retrieved OH densities demonstrate that: 1) the absolute density of $OH(\nu=9+8)$ are comparable to results presented by Mast et al. [2013]. 2) The ground OH densities are of similar magnitude to results obtain by Pickett et al. [2006] in additional to, 3) similar density widths discussed by Brinksma et al. [1998] using LIDAR observations.

6.5 CO₂ 4.3 μ m radiation calculated using two-channel retrieval results of O(³P) and OH

In Chapter 4, WACCM atmospheric inputs were used to simulate 4.3 μ m emissions using our OH/CO₂ non-LTE nighttime radiative transfer model. We show that including the new mechanism suggested by Sharma et al. [2015] significantly enhanced simulated 4.3 μ m emissions and agree very well with SABER observations. In the following section, we present residuals for 4.3 μ m emissions using O(³P)/OH inputs taken from the SABER database and results taken using the two-channel algorithm. Additional inputs such as CO₂, O₂, and N₂ are taken from WACCM while kinetic temperature and pressure are retrieved from the 15 μ m CO₂ channel [Mertens et al., 2001].



Figure 6.11: Residual CO₂ 4.3 μ m radiance (simulated-measured)/measured using O(³P) from SABER and OH from WACCM. Results are shown for four days: (top-left) 05 April 2009; (top-right) 18 August 2007; (bottom-left) 10 October 2008; (bottom-right) 20 January 2008.

Figure 6.11 displays 4.3 μ m residuals plotted for 4 nights across 4 different seasons using inputs of O(³P) retrieved by Mlynczak et al. [2014] and OH calculated by WACCM [Marsh et al., 2013]. In all four panels, our CO₂ non-LTE model agrees with SABER measurements to within ±30% for a majority of latitudes and altitudes. Clear under-predictions of 30% are visible between 80-85 km and up to 50% in the top-panel panel in polar regions. Overall, there is relatively good agreement with SABER observations using these O(³P)/OH inputs.

Figure 6.12 displays 4.3 μ m residuals for the same 4 nights as above now using retrieved O(³P) and OH from the two-channel algorithm as inputs to the CO₂ non-LTE model. In

all four panels, our non-LTE model agrees with SABER measurements to within $\pm 10\%$ over the vast majority of latitudes and altitudes. Significant under-predictions in the polar regions no longer are seen. Only the night of 05 April 2009 (top-left panel) we see overprediction of 20-30%, which occurs in the southern latitudes. It is clear that Figure 6.12 displays better agreement with SABER observations compared to Figure 6.11.



Figure 6.12: Residual CO₂ 4.3 μ m radiance (simulated-measured)/measured using O(³P)/OH density from two-channel algorithm. Results are shown for four days: (top-left) 05 April 2009; (top-right) 18 August 2007; (bottom-left) 10 October 2008; (bottom-right) 20 January 2008.

Overall, our nighttime forward model produces 4.3 μ m radiance residuals to within $\pm 10\%$ when both retrieved O(³P) and OH are used as inputs. These results demonstrate that, in addition to the new mechanism of CO₂ 4.3 μ m pumping suggested by Sharma et al.

[2015] presented in Chapter 3, using $O(^{3}P)$ and OH retrievals as inputs have further refined the 4.3 μ m emission model compared to using using current SABER $O(^{3}P)$ and WACCM OH. The excellent agreement between simulations and measurements allows us to proceed to the next step, which is to study the possibility of retrieving nighttime CO_{2} densities.

Chapter 7: Retrieval of Nighttime CO₂ VMR from SABER Limb Radiances

7.1 Chapter Overview

In the following chapter, a method for single channel nighttime CO_2 retrieval will be described. A self-consistent study will be performed under ideal conditions, then its feasibility using real SABER limb radiances will be discussed. Finally, first retrievals of nighttime CO_2 from SABER limb radiances will be presented.

7.2 Characteristics of the SABER CO_2 4.3 µm channel for nighttime conditions

Figure 7.1 shows the normalized radiance contribution functions for SABER Ch7. For upper tangent heights from 90-95 km, the normalized contribution function is maximized because of the semi-optically thin conditions. As a result, tangent height are very well seen from the point of view of spacecraft observations and contribute the most along the LOS. At lower altitudes the optical depths become thicker, therefore, radiances emitting at lower tangents contribute less relative radiance and receive non-negligible contributions from higher altitudes. The optically thick regions cause the peak contribution functions to slightly decease with altitude, as seen from 70-85 km. Otherwise, contribution functions gradually increase which is a direct results of the CO_2 molecules becoming more optically thin at higher altitudes.

Figure 7.2 displays the Jacobians in respect of CO_2 VMR on 4.3 μ m emissions for both day and nighttime conditions. Each individual profile represents a forward run calculation where CO_2 is perturbed by +20% (with a 1.5 km Gaussian width) at the respective altitudes



Figure 7.1: Ch7 normalized radiance contribution functions. The calculations are performed on a 1km vertical grid, however, only every 5th contribution function is shown for clarity. Calculations are performed for a mid-latitude nighttime atmosphere.

displayed in the legend. The x-axis displays the 4.3 μ m residuals of radiance calculated using a perturbed and unperturbed CO₂ profile for each respective altitude layer. For daytime conditions (top-panel), when CO₂ is perturbed by 20% at various altitudes, it has a positive influence on the limb radiance on or near the associate altitude. These perturbations increase Channel 7 radiances between 5-8% from 75-100 km. Daytime 4.3 μ m emissions are relatively sensitive to the 626 CO₂ molecule, making CO₂ retrieval feasible from this emission channel. For nighttime conditions (bottom-panel), however, the story is different. With the lack of solar pumping, which is the dominant source of excitation for CO₂(v_3) during the day, nighttime CO₂(v_3) is driven by absorption of radiation from lower altitudes and collisional processes. Overall, compared to the daytime, 4.3 μ m emissions have much lower sensitivity to CO₂ VMR, by a factor of 2-3, than during the night. Additionally, perturbations of CO₂ VMR at 80 km and above have a negative influence on 4.3 μ m emissions at higher altitudes. When CO₂ is increased at lower altitudes, it provides higher absorption



Figure 7.2: Sensitivity of 4.3 μ m emissions to variations to CO₂ density for daytime (top) and nighttime (bottom) at various altitudes. CO₂ density is taken from WACCM in both panels.

of upwelling radiation at those altitude, reducing the amount of upwelling flux that reaches upper altitudes. This directly reduces the amount of upwelling radiation that would nor-



Figure 7.3: Sensitivity of vibrational temperature on CO_2 density for the $CO_2(00011)$ fundamental band. Black - kinetic temperature; Red-CO₂ normal case; Green- CO_2 decreased by 30% from 65-100km; Blue- CO_2 increase by 30% from 65-100 km. See text for discussion.

mally excite the CO₂ molecule above 80 km. Because upwelling radiation is one of the key excitation mechanism for CO₂(v_3 =00011) fundamental band, vibrational populations of the v_3 level decrease and molecules emit less radiation. This effect can be seen more directly in Figure 7.3 which displays CO₂ VMR influence on vibrational temperatures (populations) of the fundamental band for the main CO₂ isotope. The black profile represents the kinetic temperature, the red profile displays vibrational temperatures of CO₂(00011) using a smooth CO₂ profile, and the green and blue profiles display vibrational temperatures of 626 CO₂(00011) when CO₂ is perturbed from 65-95 km by -30% and +30%, respectively. In general CO₂(00011) departs from LTE (when T_{vib} starts departing from T_{kin}), around 60 km as upwelling radiation and V-V collisions give significant contribution to CO₂(00011) compared to V-T processes. Between 80-100 km, the "direct" and "indirect" mechanisms are active and create the bump feature of the vibrational temperatures over this altitude range. Vibrational temperatures of CO₂(00011) decrease above 72 km when CO₂ increases
(blue) and the opposite effect occurs when CO_2 decreases (green). The low sensitivity of Ch7 radiance on CO_2 VMR at night in addition to the negative feedback of CO_2 at higher altitudes may pose major problems for nighttime CO_2 retrieval.

7.3 The CO₂ Retrieval Algorithm

In this section, we describe our tests of applying the daytime CO_2 retrieval algorithm presented in Rezac et al. [2015] for nighttime conditions. Rezac et al. [2015] used Chahine's method for limb radiance fitting, previously discussed in section 5.3, and including the following feedback formula,

$$\left[\mathrm{CO}_{2}\right]_{i}^{n+1} = \left[\mathrm{CO}_{2}\right]_{i}^{n} \cdot \left[\frac{\mathrm{L}_{\mathrm{measured},i}}{\mathrm{L}_{\mathrm{calculated},j}}\right],\tag{7.1}$$

where $L_{measured}$ represents the SABER limb radiance at altitude i, $L_{calculated}$ is the calculated limb radiance at altitude j, and n is the iteration number. Figure 7.1 shows that 4.3 μ m day and nighttime emission is most sensitive to variations of CO₂ density at the tangent height and, therefore, Rezac et al. [2015] applied Eq. 7.1 when i=j. For the nighttime CO₂ retrievals, we will apply the same approach.

The CO₂ retrieval approach will work as following: 1) for the input model of T(p) and N₂, O₂, and O(³P) densities, we will retrieved the OH/O(³P) using the two-channel selfconsistent algorithm described in Chapter 5 from SABER 1.6 and 2.0 μ m OH emissions, 2) initial model CO₂ densities supplemented with the retrieved OH/O(³P) densities will be used as inputs for simulating the 4.3 μ m emission and self-consistent CO₂ single channel retrieval will be performed. The iteration process will continue until the reliable convergence criteria based on prescribed differences between measured and simulated radiance in the 4.3 μ m channel will be reached. Because OH emissions are insensitive to CO₂ VMR, O(³P) and OH do not need to be retrieved again after CO₂ has reached its converged solution.

7.4 Self-consistency tests: two case studies

Two initial conditions were considered for the single channel CO_2 retrieval problem: high and low CO_2 density with respect to the true CO_2 profile. For all calculations, all inputs are taken from WACCM and retrievals are performed on noiseless radiances. We show in Figure 7.4 the first self-consistency test for a climatological mid-latitude spring atmosphere. There are four panels: the upper left panel shows the original starting, and retrieved CO_2 profiles; the upper right shows the CO_2 residuals (retr-orig)/orig in percent; the bottom left is the limb radiances fitting for Ch7 in terms of the ratio between calculated and measured limb radiances for the retrieved CO_2 profiles; the bottom right shows the iteration number versus the SSR between the calculated and measured limb radiances. For this case, the starting conditions are $CO_2 = \pm 30\%$ over the retrieval altitude range (65-95 km). By examining the top-right panel, one may see that the CO_2 retrieved profiles only differs by $\pm 1\%$ for the +30% case and $\pm 3\%$ for the -30% case. The former case appears to have no obvious biases in the retrieved results, however the latter case has a slight bias toward the starting condition. Also, in both cases, the retrieved profiles show more deviation from the true solution at higher altitudes. This feature is due to the negative feedback effect discussed in the previous section, which causes lower 4.3 μ m emission sensitivity to CO₂ variation. This effect is seen more directly in the bottom-left panel showing the ratios between calculated and measured limb radiances. Signals at lower altitudes are far more sensitive to CO_2 , where a $\pm 30\%$ perturbation to CO₂ between 65-95km can influence the limb radiance between 8-10%, similar to daytime conditions. From 80-92 km, however, this sensitivity decreases to only 3%. Finally, perturbations of CO_2 at all altitudes cause opposite effect to the limb radiance above 92 km, where an increase in CO_2 , decreases the calculated limb radiance. Despite these effects, the retrieval algorithm does converge to its true solution after 16-24 iterations (bottom-right panel). In theory, the algorithm works, however, the sensitivity of these emissions on CO_2 variations will create difficulties in obtaining feasible retrievals, as will be discussed below.

The goal of the second case of our study is to simulate a real CO_2 retrieval for nighttime



Figure 7.4: Self-consistency test of the single channel CO_2 retrieval algorithm for a climatological mid-latitude spring atmosphere. The starting condition are $CO_2 \pm 30\%$. See text for discussion.

conditions. Figure 6.12 displays the 4.3 μ m residual where, on average, our CO₂/OH model using O(³P)/OH retrieved parameters agree with SABER measured limb radiances to within ±10%. The second case study will be executed in a different way as above. Above, the CO₂ starting position was set to ±30% relative to the original profile where the goal was to retrieve the original profile and observe the radiance ratio converge to unity. This case, however, will start with the original CO₂ profile and set the measured limb radiance to ±10% relative to the initial calculated limb radiance. The bottom-left panel of Figure 7.5 displays the starting conditions for the two cases. The retrievals converged within 8-10 iterations (bottom-right) and the radiance ratios approached unity to with 1%. The vertical



Figure 7.5: Self-consistency test of the single channel CO₂ retrieval algorithm for a climatological mid-latitude spring atmosphere. The starting condition are $I_m = \pm 10\%$. See text for discussion.

profiles of CO₂ are displayed in the top-left panel, where the dashed blue profile represents the starting condition in both cases. The red and magenta profile are the retrieved solutions for their respective cases. The top-right panel shows the CO₂ residuals in percent. The red profile, which represents the $\pm 10\%$ starting condition of the measured limb radiance, calculated CO₂ profile between 25-100% higher than the original profile. The magenta profile, which represents the $\pm 10\%$ case, calculated a CO₂ profile 25-50% lower than the original one. With only a $\pm 10\%$ difference between measured and simulated limb radiance, the CO₂ may vary by 25% at the lowest altitudes to a factor of 2 above 80 km. This is directly a result of the low sensitivity of 4.3 µm emission on CO₂ variations. This test obviously demonstrates that even with inputs of O/OH retrieval from two other channels and a small $\pm 10\%$ initial difference between simulated and measured 4.3 μ m radiance, which is the case for a majority of retrievals, we will be unable to retrieve realistically looking CO₂ densities, even if we achieve good signal fitting. In the following section, two sample SABER retrievals are performed and discussed.

7.5 First retrievals of nighttime CO_2 VMR

Two SABER retrievals of nighttime CO_2 are presented in Figure 7.6. Both cases were performed for mid-latitude SABER scans on 05 April 2009: case 1, latitude 44°N, longitude 330; case 2, latitude 43°N, longitude 182. The top-left panel displays the CO_2 profiles for case 1 (red and black) and case 2 (blue and green). The WACCM profiles represent the starting condition for each case and the Retrieved profiles represents the final solution using the single-channel algorithm. The top right panel shows the CO_2 residuals in percent between the retrieved and WACCM VMRs. The bottom left panel displays the ratio between measured and calculated limb radiances. Starting conditions are shown in blue and black for the respective cases using WACCM profiles. Final radiance are in red and green. The bottom-right panel shows the rate of convergence.

Case 1 shows excellent limb radiance residuals, to within $\pm 5\%$, for the starting condition (black; bottom-left). Convergence is easily reached after 8 iterations and the retrieved CO₂ profile (red; top-left) displays a similar vertical structure to the WACCM starting condition (black; top-left). The CO₂ residuals display differences no larger than 15% compared to WACCM from 65-95 km. Case 1 is an ideal scenario where initial conditions are in excellent agreement with the measured signal, allowing reasonable CO₂ retrievals.

Case 2, however, is a more probable scenario where initial conditions produce calculated limb radiances which agree with SABER measurements to within $\pm 10-15\%$. This initial radiance ratio, which over-predicts SABER measurements between 2-12\%, is displayed in the bottom-left panel (blue) while the final retrieved radiance is given in green. Such as case



Figure 7.6: Sample CO_2 nighttime retrievals. Top-left: CO_2 VMR profiles in ppmv; Topright: CO_2 residuals (retrieved-WACCM)/WACCM) in percent; Bottom-left- Ch7 radiance ratio; Bottom-right- Convergence speed. See text for discussion.

produces a very different CO₂ profile (green) comapared to WACCM (blue) as seen in the top-left panel. The calculated limb radiance is consistently over-predicting the measured signals, therefore, following Chahine's method, to better match the signals, CO₂ VMR needs to decrease. The final solution, however, is significantly less than WACCM by 10-90% between 65-95 km, a much more drastic difference than Case 1. The severe decrease in CO₂ VMR is a product of only a 12% over-prediction in the SABER limb radiance, whereas Case 1 was less than $\pm 5\%$. The radiance ratio profile (green) in the bottom-left panel approaches unity up to 85 km. Above this altitude, a steady decrease of these ratios is seen. This feature is a result of the negative feedback effect pronounced at higher

altitudes, as displayed in Figure 7.2. Once again, the low sensitivity of 4.3 μ m emissions on CO₂ variation, especially at the higher altitudes poses major issues for single-channel CO₂ nighttime retrieval. In both cases, 4.3 μ m calculated limb radiance are in good agreement with SABER measurements, however, only in the case where initial conditions produce near unity radiance ratios that reasonable CO₂ retrievals are possible.

7.6 Future Study: Discussion of the feasibility for retrieval of O(³P), OH, CO₂ and temperature from SABER nighttime observations

It is clear from results presented in section 7.5 that a single-channel algorithm for retrieving nighttime CO_2 VMR is not feasible for a vast majority of SABER scans (see Figure 7.5). This section will discuss potential methods to improve CO_2 retrieval viability.

Rezac et al. [2015] showed that the daytime CO₂ 4.3 μ m and 15 μ m radiances, which both strongly depend on CO₂ in the MLT, are also strongly coupled due to hydrostatic equilibrium and, therefore, applied a self-consistent two-channel algorithm to retrieve daytime CO₂ density and temperature/pressure simultaneously from these SABER emission observations. This approach significantly improves the accuracy of the retrieved products for daytime. We, therefore, would like to discuss the opportunity of this approach to be applied for nighttime conditions. For example, the green curve in Figure 7.6 shows a low retrieved CO₂ VMR which, in the context of a two-channel CO₂/T(p) algorithm, will be used as input for temperature retrieval from 15 μ m emissions. The lower CO₂ will produce low 15 μ m emission and will subsequently retrieve a higher temperature and pressure (through hydrostatics) and, therefore, lead to a higher emission in the 4.3 μ m channel. Following this, we might not need to retrieve such a low CO₂ VMR. Because of the coupling effect between CO₂ and temperature/pressure, a two-channel retrieval algorithm is needed to accurately retrieve these nighttime parameters. Since the 15 μ m emission is nearly independent of the insolation conditions, nighttime temperature retrievals should not show any significant



Figure 7.7: Sensitivity of 15 (Ch1) and 4.3 (Ch7) m emissions on CO_2 VMR and Temperature. Top-left- Temperature/Ch1; Top-right- Temperature/Ch7; Bottom-left- CO_2 /Ch1; Bottom-right- CO_2 /Ch7. See text for discussion.

convergence problems up to about 95-100 km. This is illustrated in the top-left panel of Figure 7.7, which displays the sensitivity of 15 μ m nighttime emissions to temperature.

The right panels of Figure 7.7 show nighttime 4.3 μ m sensitivity to temperature (topright) and CO₂ VMR (bottom-right). The reaction of Ch7 signals to temperature behaves differently at nighttime compared to daytime conditions. Most notably, perturbations of temperature at 50 and 60 km (red and green profiles, respectively) have between at 5-10% influence on 4.3 μ m emissions. The bottom-right panels displays the same effect as Figure 7.2, showing the negative feedback for CO₂ molecules at higher altitudes. Overall, the sensitivity of nighttime Ch7 on temperature is comparable to that of CO₂. This effect, which is not seen during the daytime, cannot be ignored when performing nighttime retrievals. We can take advantage of this effect and develop an alternative method for obtaining reliable nighttime CO_2 VMRs. This method involves switches the SABER channels and using Ch1 for CO_2 retrieval and Ch7 for temperature retrieval. In Figure 7.7, it is clear that Ch1 radiances, similar to Ch7, are more sensitivity to temperature compared to CO_2 . It is also easily seen in the bottom-left panel of this figure that CO_2 does not show any negative feedback on Ch1 radiances. This feature will allow more stable convergence when performing real retrievals. Rigorous checking of this idea will be done in a future study. For the remainder of this discussion, however, we will adhere to Ch1 for temperature retrieval and Ch7 for CO_2 retrieval.



Figure 7.8: Sensitivity of 15 μ m emissions on O(³P). Black - O(³P) Normal; Red - O(³P) increased by 30%.

Figure 7.8 displays the sensitivity of 15 μ m emission on O(³P) VMR. The right-panel displays limb radiance residuals when a normal O(³P) is used versus O(³P) which has been increase by 30% between 80-100 km. It is clear from this figure that the SABER CO₂ 15 μ m channel, which is traditionally used to retrieve kinetic temperature, is significantly influenced by $O(^{3}P)$, increasing by 10% between 80-100 km. The $CO_{2}+O(^{3}P)$ reaction is one of the dominant pumping mechanism for the v_{2} fundamental which emits at 15 μ m. Current SABER temperature retrievals are performed using model CO_{2} and $O(^{3}P)$ retrieved by Mlynczak et al. [2014], which are 30% higher than other studies [Kaufmann et al., 2014]. With new $O(^{3}P)$ densities retrieved from this study, it is clear from Figure 7.8 that new temperatures also need to be updated and a four-channel retrieval algorithm is inevitable.

With the addition of temperature to the retrieval algorithm, $O(^{3}P)$ and OH will need to be updated after every temperature correction (see section 5.7 for $O(^{3}P)/OH$ retrieval sensitivity to temperature). Although $O(^{3}P)/OH$ retrievals are independent to the CO_{2} VMR, various collisional rate coefficients and chemical pumping terms are dependent on temperature as well as the effect of hydrostatics. Therefore, a self-consistent, simultaneous four-channel retrieval algorithm will have to be developed which combines these two independent two-channel retrieval approaches together. The four-channel approach (see Figure 7.9 for flow diagram) will work as following: 1) for the initial model of atmospheric pressure and temperature (p/T), CO_2 , $O(^{3}P)$ and OH densities, the two-channel self-consistent $OH/O(^{3}P)$ will be retrieved from the 1.6 and 2.0 μm OH emissions, 2) initial model p/T and CO_2 densities supplemented with the retrieved $OH/O(^{3}P)$ densities will be used as inputs for simulating the 4.3 and 15 μ m emission and self-consistent p/T and CO₂ retrieval will be performed, 3) updated p/T data will replace model data used in step 1, and new $OH/O(^{3}P)$ will be retrieved, 4) updated p/T, CO_{2} and $OH/O(^{3}P)$ will replace those used in step 2 and new p/T and CO_2 will be retrieved. The iteration process will continue until the reliable convergence criteria based on prescribed differences between measured and simulated radiance in all 4 channels will be reached.

Overall, it is very promising that adding a temperature module to the retrieval algorithm will further improve calculated 4.3 μ m emissions and allow reliable CO₂ retrievals. The fourchannel algorithm described above is the most probable way of solving the problem and will be the concentration for a future study.



Figure 7.9: General scheme of four-channel retrieval method. See text for explanation.

Chapter 8: Summary

Over the last 15 years, SABER/TIMED has been continuously observing the mesospherelower thermosphere (MLT) in limb viewing geometry in several infrared wavelengths. Previous studies showed the emission generating mechanisms of some measured signals, such as nighttime CO₂ 4.3 μ m and OH 1.6 and 2.0 μ m radiances, remain a mystery and thus the data products are either still completely unprocessed or not accurate enough, preventing SABER from reaching its full capabilities. In this study, new OH and CO₂ non-LTE models were developed, which include the new "indirect" mechanism suggested by Sharma et al. [2015], and applied to the nighttime limb emissions measured by the SABER instrument.

In chapter 3, a new OH(v) non-LTE model was developed and OH(v) populations and emissions were compared with measurements taken from various ground and space based instruments. The main conclusions regarding this study are as follows:

- Including the new energy transfer channel into our OH non-LTE model of the nighttime MLT emissions produces OH(ν) density distributions which are in good agreement with ground and space observations in the mesosphere. Our results also reproduce SABER (Channel 8)/(Channel 9) VER ratio measurements.
- Other models (see Chapter 3) do not reproduce the SABER measured VER ratios of the OH 1.6 and 2.0 μm channels and the ground and space measurements of the OH(v) densities.

In chapter 4, the CO₂ model was linked with our OH model. We studied in detail the impact of the "direct" and "indirect" mechanisms on the $CO_2(v_3)$ emissions and compared our calculations with the SABER/TIMED nighttime 4.3 μ m CO₂ limb radiances of the MLT. The main conclusions regarding this study are as follows:

- The "direct" mechanism alone with three-quantum efficiency for the OH+N₂ reaction (model of López-Puertas et al. [2004]) reproduces SABER 4.3 μ m emissions to within a 10-30% difference range. The model of López-Puertas et al. [2004], however, does not reproduce either the SABER measured VER ratios of the OH 1.6 and 2.0 μ m channels or the ground and space measurements of the OH(v) densities.
- Our model, which includes the new "indirect" channel, produces significant enhancement of the 4.3 μm CO₂ emission and agrees with observations to within 10-30% in additional to producing OH(v) density distributions which are in good agreement with both SABER limb OH emission measurements and the ground and space observations in the mesosphere.
- The new mechanism accounts for most of the discrepancies between measured and calculated 4.3 μm emission for various atmospheric situations, leaving relatively little room for other processes, suggesting that the missing nighttime mechanism of CO₂(v₃) pumping has finally been identified.

In chapter 5, A self-consistent method for a two-channel retrieval of the $O(^{3}P)/OH$ Volume Mixing Ratio (VMR) from broadband measurements of non-LTE emissions at 2.0 and 1.6 μ m was developed using the new OH non-LTE model. This model was then applied to nighttime limb emissions measured by the SABER instrument. The main conclusions regarding the self-consistency, sensitivity and error analysis of the two-channel algorithm are as as follows:

- Retrievals using synthetic radiances show that reasonable starting conditions (within ± 30% on the OH VMR and ± 30% in O(³P)) allow a stable two-channel inference of OH/O(³P) in a self-consistent fashion. The study further revealed that the retrieved profiles are nearly independent of the starting O(³P) and OH VMR profile.
- The error analysis performed showed that for altitudes above 85 km, the systematic parameters dominate the contribution to the total uncertainty. For O(³P), the total

uncertainty is estimated to be 25-27%, while OH is estimated to be between 35-38% above 85 km. Below 85 km, the $O(^{3}P)$ and OH retrievals exceed errors of 50% at 85 km, and are as high as 167% (more than a factor of 2), at 80 km.

In chapter 6, we discussed results of the two-channel retrieval algorithm which was applied to the v2.0 SABER measured radiances and yielded new products for the SABER mission. Zonal mean profiles of $O(^{3}P)$ and OH densities were compared with retrieval results from current SABER and other MLT instruments. The main conclusion are as follows:

- Retrieved O(³P) densities exhibit peak values on the order of (5-6)×10¹¹ mol/cm³, very similar to SCIAMACHY results which peak around 6×10¹¹ mol/cm³. Atomic oxygen calculated by WACCM, however, is about 20% lower and current SABER densities are about 30% higher.
- Comparison of WACCM and retrieved OH ground state densities showed that above 87 km, the retrieved ground state OH is somewhat similar to WACCM to within ±50%. Below 87 km, however, the retrieved OH(v=0) density is lower than OH WACCM by at least a factor of 2-3 for various nights.
- The absolute density of OH(\nu=9+8) are comparable to results presented by Mast et al. [2013]. The total OH densities are of similar magnitude to results obtain by Pickett et al. [2006] in additional to similar density widths discussed by Brinksma et al. [1998] using LIDAR observations.
- Our nighttime forward model produces the most accurate CO₂ 4.3 μ m residuals when both retrieved O(³P) and OH are used as inputs. In all cases, our non-LTE model agrees with SABER measurements to within ±10% over the vast majority of latitudes and altitudes.

Finally, in chapter 7, a method for single channel nighttime CO_2 retrieval was presented. A self-consistent study was performed under ideal conditions, and its feasibility using SABER limb radiances was discussed. The main conclusions regarding this study are as follows:

- The low sensitivity 4.3 μ m radiance to CO₂ VMR at night in addition to the negative feedback of CO₂ at higher altitudes poses major problems for nighttime CO₂ retrieval.
- Radiance residuals need to have less than a 5% difference in order to allow to retrieve reasonable CO₂ VMR for nighttime conditions using a single channel algorithm.
- A single-channel algorithm for retrieving nighttime CO₂ VMR is not feasible for a vast majority of SABER scans. Potential methods to improve CO₂ retrieval viability need to be considered.
- Adding a temperature module to the retrieval algorithm will further improve calculated 4.3 μm emissions and allow reliable CO₂ retrievals. The four-channel algorithm described in section 7.6 is the most probable way of solving this problem and will be the concentration for a future study.

A.1 Measurement Geometry



Figure A.1: Limb viewing geometry

The limb scanning technique has been well studied since the early 1970s (Gille and House [1971], Gille and Bailey [1977]). The limb viewing geometry which SABER utilizes is illustrated in Figure A.1. For the case of an infinitesimal FOV, as the satellite performs its limb viewing scans, there is no radiance contribution below the tangent height, which is a point along the Line of Sight (LOS) that is closest to the surface. In addition, the geometrical lengths along the LOS are much longer through the tangents points than any other altitude layer ensuring that most of the contribution of the emitting molecules originate from the tangent layer. These factors can allow the weight functions (rate of change of transmittance over the vertical coordinate, $dt(\nu)/dz$, see Eq. A.9) to be relatively narrow and sharply peaks at the tangent layers, particularly for optically thin situations, resulting in a high vertical resolution. The cold background of space is another advantage that counters any needs to remove background radiation, which simplifies the analysis of limb measured radiance. There are a couple negative factors, however, which the limb geometry technique introduce. The effect of the finite FOV on the vertical resolving power causes the weighting function to be broadened and, under non-LTE conditions, the weighting functions tend to be broader below the tangent height than the LTE counterparts.

A.2 Basic Relations for non-LTE radiance modeling

The forward model applied in this study to simulate non-LTE limb radiances observed by SABER consists of two parts: 1) solving the non-LTE problem (described in Chapter 2) which determines the vibrational populations at each vertical grid point for an atmospheric scenario and 2) calculating the limb radiance. This section describes the method of calculating non-LTE radiance for limb viewing geometry where previous calculated populations (Chapter 2) are applied. To retain maximum accuracy, a Line-By-Line (LBL) technique is used for calculating limb radiance. Spherically symmetric atmosphere is also assumed with a homogeneous distribution of pressure, temperature, a trace gas densities in each spherical shell.

The total signal, N_{ch} , measured in a particular channel of the SABER instrument at a given tangent altitude, h, can be expressed as

$$N_{ch}(h) = \int_{\Delta\nu} I(\nu, h) f(\nu) d\nu \tag{A.1}$$

where the integration is performed over $\Delta \nu$ which represents the frequency range of channel spectral response function, $f(\nu)$. The monochromatic intensity of limb radiation $I(\nu,h)$ can be written in two equivalent forms

$$I(\nu,h) = \int_{x}^{x_{obs}} \chi(\nu,x) S(\nu,x) \exp\left(-\int_{x}^{x_{obs}} \chi(\nu,x') dx'\right) dx$$
(A.2)

$$I(\nu,h) = \int_{x}^{x_{obs}} \eta(\nu,x) \exp\left(-\int_{x}^{x_{obs}} \chi(\nu,x') dx'\right) dx$$
(A.3)

where h is the tangent height, x is the coordinate along the LOS (see Figure A.1), x_{obs} is the location of the observer and $S(\nu)$, is the source function, Eq. 2.12 for a single line or, in a more general case, Eq. 2.15 for over-lapping lines. In this study, we rely on non-overlapping ro-vbrational lines. The source function for overlapping lines, Eq. 2.15, is the ratio between the total emissivity, $\eta(\nu, x)$, and absorption, $\chi(\nu, x)$, which includes contribution from the continuum.

For a many trace gases (i.e. CO_2 , H_2O , O_3), the source function is stable and Eq. A.2 is utilized for solving the radiative transfer equation. In certain cases, however, under non-LTE conditions, an inversion of populations between the ground and upper levels occur, also known as the lasering effect. We are rigorously considering stimulated emission and in the lasering case, where the population of the upper level is beginning to be comparable to higher than lower level, the absorption coefficient of a single line can approach zero the source function in Eq. 2.12 can be infinite and the radiative transfer calculation in Eq. A.2 cannot proceed. However, Eq. A.3, which is expressed in terms of only the emissivity coefficient can still be utilized to produce a stable solution. Further details of possible treatments of laser bands is discussed in Gusev [2002].

The total emissivity and absorption coefficients are reproduced here again from section 2.2 and are expressed as follows,

$$\eta(\nu) = \sum_{ij} \frac{h\nu_{ij}}{4\pi} n_i A_{ij} \vartheta_{ij}(\nu), \qquad (A.4)$$

$$\chi(\nu) = \sum_{ij} \frac{h\nu_{ij}}{4\pi} (n_j B_{ji} - n_i B_{ij}) \varphi_{ij}(\nu),$$
(A.5)

where $\vartheta_{ij}(\nu)$ and $\varphi_{ij}(\nu)$ are emission and absorption line shape functions, respectively. The indices, *i* and *j*, correspond each to the pair of ro-vibrational levels, $i \rightarrow v'j'$ and $j \rightarrow v'j'$ v_j , where the primed notation represents the upper level of the transition. The Einstein coefficients are expressed as A_{ij} , B_{ij} , and B_{ji} and v_{ij} is the line center frequency. The line shape functions are modeled based on the Voigt function and we assume complete frequency redistribution, where emission and absorption line shape functions are assumed equal, i.e. $\vartheta_{ij}(\nu) = \varphi_{ij}(\nu)$. To avoid under-sampling of narrow Doppler line cores, a fine wavenumber grid $(10^{-3} \text{ cm}^{-1})$ is used that spans the entire band pass of the SABER channel selected.

The exponential term in Eqs. A.3 and A.2 plays a fundamental role in radiative transfer, and is known as the transmittance,

$$t_{\nu}(x, x_{obs}) = \exp\bigg(-\int_{x}^{x_{obs}} \chi(\nu, x') dx'\bigg).$$
(A.6)

This expression can take a more compact form by defining optical thickness, τ_{ν} ,

$$\tau_{\nu}(x, x_{obs}) = \int_{x}^{x_{obs}} \chi(\nu, x') dx'.$$
(A.7)

Then the radiative transfer equation (A.3 & A.2) can be written as follows

$$I(\nu, h) = \int_{x}^{x_{obs}} S(\nu, x') W_{\nu}(x') dx$$
 (A.8)

where

$$W_{\nu}(x) = \frac{dt_{\nu}(x)}{dx} \tag{A.9}$$

is the weighting function. The weighting function governs the quality of information which can be extracted from the radiance measurement and its vertical smoothing. In general, Eqns. (A.6)-(A.9) present the idea of how to calculate limb radiance. These equations also can take a discretized form to solve the problem directly in addition to differential methodologies (see Gusev [2002]).

Appendix B: OH Einstein Coefficients

The following tables are calculated Einstein coefficients for the additional state band transitions considered in our OH model: $X^2\Pi_{3/2} \rightarrow X^2\Pi_{1/2}, X^2\Pi_{1/2} \rightarrow X^2\Pi_{3/2}$, and $X^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$.

v'v	0	1	2	3	4	5	6	7	8	$\sum A(s^{-1})$
1	0.3600									0.3600
2	0.1704	0.4965								0.6669
3	0.0181	0.4351	0.4864							0.9396
4	0.0022	0.0632	0.7342	0.3923						1.1919
5	3.3e-4	0.0097	0.1375	1.021	0.2641					1.4326
6	6.1e-5	0.0018	0.0258	0.2385	1.26	0.1399				1.6661
7		3.9e-4	0.0056	0.0533	0.3605	1.421	0.0477			1.8885
8			0.0014	0.0136	0.0941	0.4979	1.476	0.0048		2.0878
9				0.0040	0.0248	0.1468	0.6539	1.386	0.0133	2.2288

Table B.1: Einstein Coefficients $A_{\nu' \to \nu}$ for $X^2 \Pi_{3/2} \to X^2 \Pi_{1/2}$ state band transitions

Table B.2: Einstein Coefficients $A_{\nu' \to \nu}$ for $X^2 \Pi_{1/2} \to X^2 \Pi_{3/2}$ state band transitions

v'v	0	1	2	3	4	5	6	7	8	$\sum A(s^{-1})$
1	0.1442									0.1442
2	0.1307	0.1594								0.2901
3	0.0147	0.3267	0.1112							0.4526
4	0.0017	0.0511	0.5374	0.0508						0.6410
5	2.5e-4	0.0078	0.1102	0.7251	0.0166					0.8599
6	4.4e-5	0.0013	0.0208	0.1889	0.8623	0.0353				1.1086
7		2.8e-4	0.0044	0.0429	0.2814	0.9291	0.1212			1.3793
8			0.0011	0.0107	0.0755	0.3816	0.9804	0.2727		1.7220
9				0.0031	0.0226	0.1171	0.4910	0.7809	0.4637	1.8784

v'v	0	1	2	3	4	5	6	7	8	$\sum A(s^{-1})$
1	17.47									17.470
2	10.34	23.79								34.130
3	1.123	27.60	22.46							51.183
4	0.1345	4.119	48.67	16.75						69.673
5	0.0194	0.6250	9.413	70.73	9.707					90.494
6	0.0033	0.1099	1.743	17.15	91.10	4.181				114.287
7		0.0227	0.3636	3.780	27.20	107.1	2.754			141.217
8			0.0874	0.9211	6.982	39.38	115.4	7.443		170.213
9				0.2514	1.999	11.35	54.12	111.2	18.76	197.680

Table B.3: Einstein Coefficients $A_{\nu' \to \nu}$ for $X^2 \Pi_{1/2} \to X^2 \Pi_{1/2}$ state band transitions

Appendix C: Additional Retrieved OH Densities

Figure C.1 displays additional retrieved OH(v=0) densities comparisons with WACCM calculations for 20 January 2008 and 10 October 2008.



Figure C.1: Comparison of zonal OH(v=0) density on (top) 20 January 2008 and (bottom) 10 October 2008 in four latitude bins: 0-5° N, 40-45° N, 40-45° S, 70-75° N. Black - This study. Red - WACCM.

Appendix D: Error Analysis for Individual Days and Latitudes

Random Errors											
		Altitude (km)									
Source of error	Param.	80	85	90	95	100					
Random noiso*	$O(^{3}P)$	5	2	1	4	16					
Random noise	OH	75	4	2	2	4					
Systematic Errors											
D hing+	$O(^{3}P)$	± 26	<1	±1	± 2	±3					
1 0 Dias	OH	± 24	± 5	±4	± 4	±4					
This	$O(^{3}P)$	± 58	±1	± 6	± 10	± 14					
1 Dias	OH	± 46	± 18	± 15	± 16	± 18					
CO ₂ bing	$O(^{3}P)$	<1	<1	<1	<1	<1					
002 bias	OH	<1	<1	<1	<1	<1					
kana OH Na	$O(^{3}P)$	± 59	± 8	± 3	± 2	±1					
$K_V V O \Pi - W_2$	OH	± 35	± 4	<1	<1	<1					
kur OH Os	$O(^{3}P)$	± 96	± 29	± 17	±11	6					
	OH	± 38	± 6	±1	<1	<1					
kup OH O ³ P	$O(^{3}P)$	± 17	± 16	± 15	± 15	± 16					
	OH	± 21	± 21	± 22	± 22	± 22					
	$O(^{3}P)$	<1	<1	<1	<1	<1					
	OH	± 21	± 21	± 22	± 22	± 22					
Δ	$O(^{3}P)$	± 37	± 1	± 2	± 3	± 3					
Л	OH	± 53	± 2	±4	± 4	±4					
Systematic BSS	$O(^{3}P)$	± 135	± 34	± 23	± 21	± 22					
	OH	± 95	± 35	± 35	± 35	± 36					
Tatal DCC	$O(^{3}P)$	± 135	± 34	± 23	±21	± 27					
10tal R55	OH	±121	± 35	± 35	± 35	± 36					

Table D.1: 03 April 2009 Lat000

*SABER NER values for each channel respectively

 $^+\mathrm{Reference}$ pressure at 30 km

Random Errors										
		Altitude (km)								
Source of error	Param.	80	85	90	95	100				
Dandom noiso*	$O(^{3}P)$	±100	± 18	± 18	± 20	N/A				
Random noise	OH	±100	± 16	± 20	± 16	N/A				
Systematic Errors										
P. bins+	$O(^{3}P)$	± 8	± 9	± 2	± 3	± 3				
1 0 Dias	OH	± 12	± 13	±4	± 4	± 4				
T bise	$O(^{3}P)$	± 50	± 80	±11	± 20	± 24				
1 0105	OH	± 43	± 55	± 22	± 23	± 25				
CO ₂ bias	$O(^{3}P)$	<1	<1	<1	<1	<1				
002 bias	OH	<1	<1	<1	<1	<1				
kuu OH Na	$O(^{3}P)$	± 81	± 59	± 2	<1	<1				
$K_V V O \Pi - W_2$	OH	± 44	± 35	<1	<1	<1				
kuu OH Oa	$O(^{3}P)$	± 60	>100	± 12	± 3	±1				
$K_V V OII-O_2$	OH	24	47	1	<1	<1				
kup OH O ³ P	$O(^{3}P)$	<1	± 1	± 14	± 15	± 14				
KVE OII-O I	OH	<1	± 2	± 21	± 22	± 21				
$k_{\rm T}[OH][O]$	$O(^{3}P)$	<1	<1	<1	<1	<1				
	OH	± 16	± 16	± 16	± 16	± 16				
Δ	$O(^{3}P)$	± 12	± 13	± 2	± 4	±4				
Π	OH	±10	± 12	± 4	± 4	± 4				
Systematic BSS	$O(^{3}P)$	± 113	± 141	± 21	± 25	± 28				
Systematic Roo	OH	± 69	± 83	± 34	± 36	± 36				
Total DSS	$O(^{3}P)$	± 150	± 142	± 27	± 32	± 28				
10tal hos	OH	± 121	± 84	± 39	± 39	± 36				

Table D.2: 09 January 2008 Lat-070

*SABER NER values for each channel respectively

 $^+\mathrm{Reference}$ pressure at 30 km

Random Errors										
		Altitude (km)								
Source of error	Param.	80	85	90	95	100				
Dandom noico*	$O(^{3}P)$	±100	±1	± 2	± 9	±11				
Random noise	OH	± 22	± 4	± 2	± 3	± 18				
Systematic Errors										
D. biast	$O(^{3}P)$	± 12	± 4	<1	± 2	±3				
1 0 Dias	OH	± 15	± 8	± 4	± 4	± 4				
This	$O(^{3}P)$	>100	± 16	± 3	± 9	± 15				
I DIAS	OH	± 92	± 29	± 19	± 19	± 20				
CO ₂ bing	$O(^{3}P)$	<1	<1	<1	<1	<1				
002 bias	OH	<1	<1	<1	<1	<1				
kana OH Na	$O(^{3}P)$	>100	± 20	± 5	± 3	±1				
$K_V V O \Pi - W_2$	OH	± 92	± 13	± 2	±1	<1				
kuu OH Oa	$O(^{3}P)$	>100	± 55	± 22	± 12	± 6				
$K_V V OII-O_2$	OH	± 94	± 22	± 5	±1	<1				
$k_{\rm WR}$ OH O ³ P	$O(^{3}P)$	<1	± 16	± 16	± 16	± 16				
	OH	<1	± 20	± 21	± 22	± 22				
	$O(^{3}P)$	<1	<1	<1	<1	<1				
	OH	± 16	± 16	± 16	± 16	± 16				
Δ	$O(^{3}P)$	± 16	± 6	<1	± 2	± 3				
Π	OH	± 16	± 2	± 3	± 4	± 4				
Systematic BSS	$O(^{3}P)$	± 174	± 63	± 27	± 22	± 23				
	OH	± 162	± 47	± 33	± 33	± 34				
Total PSS	$O(^{3}P)$	± 200	± 63	± 27	± 23	± 25				
	OH	± 163	± 47	± 33	± 33	± 38				

Table D.3: 15 September 2008 Lat045

*SABER NER values for each channel respectively

+Reference pressure at 30 km $\,$

Random Errors										
		Altitude (km)								
Source of error	Param.	80	85	90	95	100				
Dandom noico*	$O(^{3}P)$	± 65	± 2	± 2	±14	± 21				
Random noise	OH	±41	± 2	± 3	± 5	± 30				
Systematic Errors										
D bisc+	$O(^{3}P)$	± 8	± 5	±1	± 2	± 3				
r ₀ blas	OH	± 12	± 10	± 4	±4	± 4				
Thiss	$O(^{3}P)$	>100	± 25	± 5	± 13	± 17				
1 Dias	OH	± 84	± 34	± 19	± 19	± 20				
CO ₂ biag	$O(^{3}P)$	<1	<1	<1	<1	<1				
CO_2 bias	OH	<1	<1	<1	<1	<1				
Less OH N	$O(^{3}P)$	>100	± 26	± 5	±1	±1				
K_{VV} OII-N ₂	OH	± 82	± 17	± 2	<1	<1				
kana OH Oa	$O(^{3}P)$	>100	± 68	± 19	±8	± 4				
$K_V V O \Pi O 2$	OH	± 82	± 28	± 3	<1	<1				
$h_{\rm exp} \cap \Pi \cap {}^{3}\mathrm{D}$	$O(^{3}P)$	±1	± 14	± 16	± 16	± 16				
K_{VE} OII-O F	OH	±1	± 17	± 21	± 22	± 22				
	$O(^{3}P)$	<1	<1	<1	<1	<1				
	OH	± 16	± 16	± 16	± 16	± 16				
Δ	$O(^{3}P)$	± 12	± 7	±1	±3	±4				
A	OH	±10	± 4	± 3	± 4	±4				
Systematic PSS	$O(^{3}P)$	± 173	± 78	± 25	± 22	± 24				
Systematic Roo	OH	± 144	± 53	± 33	± 33	± 34				
Total DSC	$O(^{3}P)$	± 184	± 78	± 25	± 26	±31				
10tal noo	OH	± 149	± 53	± 33	± 33	± 45				

Table D.4: 27 June 2010 Lat -020

*SABER NER values for each channel respectively +Reference pressure at 30 km

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Curriculum Vitae

Peter A. Panka

Personal Information

EMAIL: ppanka@masonlive.gmu.edu

Education

George Mason University, Fairfax, VAThesis: "New Non-LTE Model of OH and CO2 Emission in the Mesosphere-Lower Thermosphere and its Application to retrieving Nighttime Parameters" Advisor: Dr. Erdal Yiğit GPA: 3.77/4MAY 2014Master of Science in PHYSICS George Mason University, Fairfax, VA Advisor: Dr. Erdal Yiğit GPA: 3.77/4MAY 2011Bachelor of Science in Astronomy University of Massachusetts-Amherst, Amherst, MA GPA: 3.4/4	October 2017	Doctor of Philosophy in Physics		
 Thesis: "New Non-LTE Model of OH and CO₂ Emission in the Mesosphere-Lower Thermosphere and its Application to retrieving Nightime Parameters" Advisor: Dr. Erdal Yiğit GPA: 3.77/4 MAY 2014 Master of Science in PHYSICS George Mason University, Fairfax, VA Advisor: Dr. Erdal Yiğit GPA: 3.77/4 MAY 2011 Bachelor of Science in Astronomy University of Massachusetts-Amherst, Amherst, MA GPA: 3.4/4 		George Mason University, Fairfax, VA		
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GPA: 3.4/4		University of Massachusetts-Amherst, Amherst, MA		
		Gpa: 3.4/4		

Sept 2014 - Oct 2017	PhD Thesis, George Mason University and NASA Goddard
	Space Flight Center
	Studying Non-Local Thermodynamic Equilibrium in OH and
	CO_2 in the Mesosphere-Lower Thermosphere
	Developing a nighttime model which simultaneously retrieves
	CO ₂ , O(³ P), and OH concentrations using data from SABER
	instrument on TIMED satellite (C language)
Spring 2014	Research Assistant, George Mason University, Fairfax, VA
	Studied tidal bulges on exoplanets due to their host stars
	Determined if bulge amplitude of close-in planets are detectable
	in light curves with current/future space telescopes
	Constrain planetary interior compositions
Fall 2012	Research Assistant, George Mason University, Fairfax, VA
	Used a Radiative-Convective model to produce temperature-
	pressure profiles of exoplanets Gliese 581c and 581d $$
Sep. 2010 - May 2011	Researcher/Senior Thesis, University of Massachusetts-
	Amherst, MA
	Studied elliptical galaxy evolution using Hubble Space Tele-
	scope data from two different types of catalogues (morphologi-
	cal classification and specific star formation rate)

Research & Work Experience

Research & Work Experience (Cont.)

Jun. 2010 - Aug. 2010	Research Intern , University of Massachusetts-Amherst, MA Worked directly with a postdoc in the Astronomy Department to study elliptical galaxies evolution from redshift 1 to 0
Jan. 2010 - May 2010	Research Assistant , University of Massachusetts-Amherst, MA
	Studied the Initial Mass Function and challenged its universal- ity under academic advisor
	Used IRAF to determine size of dust clouds in H-alpha regions
JUN 2009 - AUG 2009	Besearch Intern University of Massachusetts-Amberst MA
JUN. 2009 - AUG. 2009	Studied elliptical galaxy evolution using Hubble Space Tele-
	Determined if galaxies between redshift 1 and 0 were color gra- dients (size variation with different wavelengths)

Teaching Experience

Jun. 2012 - May 2013	Graduate Teaching Assistant, George Mason University,
	Fairfax, VA
	College Physics Lab (PHYS 244)
	Topics covered: Kinetic/Potential Energy, Kinematic
	Motion, Projectile Motion, Torque, Friction, Newton's
	Laws
	College Physics Lab (PHYS 246)
	Topics covered: Electric Fields, Circuits, Ohms Law, RC
	Decay, Optics, Photoelectric Effect
	Astronomy Lab (ASTRO 114)
	Topics covered: Stellar Classification, Galaxy Redshift,
	H-R Diagrams, Pulsars, Exoplanets
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Observing Experience

Sep. 2013 - Present	KELT North/South Follow-Up Member, George Ma-
	son University, Fairfax, VA
	Detect light curves of exoplanets using the George Mason
	Observatory
	Specs: 0.8m Cassegrain, CCD Camera: STX 16803,
	Filter Wheel: FW7-STX
	KELT (Kilo-degree Extremely Little Telescope) team has a
	catalog of potential exoplanets needed for follow-up obser-
	vations

Outreach

Fall & Spring 2014-2016	Observatory Tour Guide , George Mason University, Fair-
	fax, VA
	Public and private guided tours of George Mason Observa-
	tory
Aug. 2013/14 & Jan. 2014	Astronomy Teacher, Seoul Science High School, Seoul,
	Korea
	Taught several one week astronomy courses in Engligh to
	high school students
	Topics covered: Stellar Classification, Galaxy Redshift, H-R
	Diagrams, Pulsars, Exoplanets

Fellowships and Awards

Nov. 2017 - Present	NASA Postdoctoral Program Fellowship
Sept. 2016 - Aug. 2017	NASA Earth and Space Science Fellowship (NESSF)
June 2009 & 2010	NASA Space Grant Fellowship

Computer Skills

Advanced Knowledge: C, IDL, LINUX, ubuntu, LATEX, Excel Basic Knowledge: PYTHON, Matlab

Presentations

Panka, P. A., "New model for nighttime CO₂ infrared emissions in the middle and upper atmosphere", Heliophysics Science Division Director's Seminar. NASA Goddard Space Flight Center. Greenbelt, MD. 28 January 2017.

Conferences

JUNE 2017 CEDAR, Keystone Resort, Keystone, CO

- APRIL 2017 European Geosciences Union General Assembly 2017, Vienna, Austria
- DECEMBER 2016 American Geophysical Union, San Francisco, CA
 - APRIL 2016 European Geosciences Union General Assembly 2016, Vienna, AustriaJUNE 2015 CEDAR, University of Washington, Seattle, WA
 - APRIL 2014 Habitable Worlds, Space Telescope Science Institute, Baltimore, MD

Conference Reports

- Panka, P. and Kutepov, A. and Kalogerakis, K. and Janches, D. and Feofilov, A. and Rezac, L. and Marsh, D. and Yigit, E., "New non-LTE model of OH(v) in the mesopshere/lower thermosphere", EGU General Assembly Conference Abstracts, Oral Presentation, Vienna, Austria, April 2017
- Panka, P. A., Kutepov, A. A., Kalogerakis, K. S., Janches, D., Russell, J. M., Rezac, L., Feofilov, A. G., Mlynczak, M. G., Yigit, E., "New Model of the night-time CO₂ 4.3 μm emissions in the mesosphere/lower thermosphere", Abstract #183480 presented at 2016 Fall Meeting, AGU San Francisco, Calif., 12-17 Dec. 2016
- Panka, P. A., Kutepov, A. A., Feofilov, A. G., Rezac, L., Janches, D., "Modeling the night-time CO₂ 4.3 μm emissions in the mesosphere/lower thermosphere", Geophys. Res. Abstr., 18, EGU2016-9192-1, EGU General Assembly, April 2016
- Panka, P., Yigit, E., Kutepov, A., Janches, D., Study of Vibrational-Vibrational (V-V) Energy Exchanges Between CO₂ Isotopes in the Middle and Upper Atmosphere of Earth and Mars, CEDAR conference, Poster, June 2015
- Dawkins, E., Janches, D., Kutepov, A., Feofilov, A., Panka, P., CO₂ in the MLT: constraining the CO₂(ν₂)-O quenching rate coefficient, CEDAR conference, Poster, June 2015

Publications

- Panka, P. A., Kutepov, A. A., Kalogerakis, K. S., Janches, D., Russell, J. M., Rezac, L., Feofilov, A. G., Mlynczak, M. G., and Yiğit, E.: Resolving the mesospheric night-time 4.3 μm emission puzzle: comparison of the CO₂(v₃) and OH(v) emission models, Atmos. Chem. Phys., 17, 9751-9760, https://doi.org/10.5194/acp-17-9751-2017, 2017.
- Saxena, P., Panka, P., Summers, M., The Observational Effects and Signatures of Tidally Distorted Solid Exoplanets, MNRAS (February 2015) 446 (4): 4271-4277