The Development of an Infrared Laser Heterodyne Radiometer to Search for Methane in the Atmosphere of Mars

Second Year Report

Richard L. Passmore

Atmospheric, Oceanic and Planetary Physics
University of Oxford

Supervisors: Dr. Neil E. Bowles
and Dr. Kevin M. Smith (Rutherford Appleton Laboratory)

Word Count: \(\sim 11,500\)

August 2010
Abstract

Recent observations of the Martian atmosphere have revealed evidence of trace amounts of methane (CH$_4$). Measurements from orbiter-based missions (such as Mars Express) and ground-based instruments indicate an average methane mixing ratio of approximately 10 ppbv. The source of the methane is at present unknown, but its detection has generated much interest in the Mars science community. Theories contributing to its origin include volcanic activity, cometary and meteoric delivery, a subsurface serpentinization reaction, and perhaps most excitingly, biological activity.

The aim of this research is to investigate the viability of remote sensing using a passive mid-infrared laser heterodyne radiometer (LHR) to detect methane in the Martian atmosphere. The LHR technique allows spectral measurements to be performed at high resolutions (up to 0.005 cm$^{-1}$) over a narrow spectral range ($\sim$ 10 cm$^{-1}$) when a distributed feedback quantum cascade laser (QCL) is used as local oscillator. Initial test results performed on a 7.7 μm QCL are detailed. These results provide the primary spectral tuning range for the LHR. The benefits of the LHR currently under development, including its compact lightweight design, are also discussed in relation to existing remote sensing spectral instruments.
## Contents

1 Introduction 1

2 Atmospheric Observations of Methane 4  
2.1 Methane in the Martian Atmosphere 4  
2.1.1 Mapping the Methane 4  
2.1.2 Difficulties Observing Extra-Terrestrial Methane 9  
2.1.3 Possible Sources and Sinks of the Martian Methane 10  
2.2 Remote Sensing of Methane in Earth’s Atmosphere 13

3 The Laser Heterodyne Radiometer 15  
3.1 Heterodyne Detection 15  
3.2 Using a Quantum Cascade Laser as Local Oscillator 16  
3.2.1 The QCL Advantage 16  
3.3 LHR Instrument Design 17  
3.3.1 Block Diagram 17  
3.3.2 Instrument Sensitivity and Noise Performance 19  
3.4 Comparing the LHR with a Fourier Transform Spectrometer 20

4 QCL Setup and Initial Test Results 22  
4.1 Initial Breadboard Design 22  
4.2 QCL Performance at 7.7 µm 24  
4.2.1 Characterising the Beam Profile 26

5 Atmospheric Radiative Transfer Calculations 27  
5.1 RADTRANS 27  
5.2 Simulating the Martian Atmosphere at 7.7 µm 28  
5.2.1 Simulations at LHR Resolutions 28  
5.2.2 Comparing the LHR with other Instruments 30  
5.2.3 Simulating Seasonal Changes on Mars 33  
5.2.4 LHR Noise Performance Simulations 35  
5.3 Nemesis 36
Chapter 1

Introduction

In the last few years, several research teams have reported, by remote infrared spectroscopy, the detection of trace quantities of methane in the atmosphere of Mars. Ground-based [Krasnopolsky et al., 2004, Mumma et al., 2009] and space-based instruments like the Planetary Fourier Transform spectrometer on Mars Express [Formisano et al., 2004] have measured low levels of methane (global average mixing ratio of 10 ppbv) in the Martian atmosphere. The origin of the methane is still unknown, but much speculation as to its source has arisen. Some attribute past hydrothermal activity and cometary impacts to the levels of methane seen today [Krasnopolsky et al., 2004], while some suggest it may be biologically produced by Martian bacteria or microorganisms [Boston et al., 1992]. Whatever the cause, all agree that higher resolution measurements of the atmosphere, preferably from Mars orbit, need to be carried out to confirm the presence of the gas. So far, the majority of studies have utilised Fourier transform spectrometers; both from telescopes on Earth, and satellites in orbit around Mars. Earth based instruments have the advantage of high spectral resolution (e.g. CSHELL, an echelle spectrograph, on the IRTF has a resolution of 0.076 cm$^{-1}$), but have poor spatial resolution. The other disadvantage is the presence of terrestrial absorption lines in the measured spectrum, which have to be removed. Instruments on orbiter missions have the advantage of proximity to the Martian surface, the absence of telluric absorption and provide good spatial resolution. However the current generation of instruments only have moderate spectral resolution (e.g. the FTS on Mars Express has a resolution of 1.3 cm$^{-1}$). Usually, this is a result of the instrument’s limitation due to size and mass restrictions. To achieve a high spectral resolution in an instrument such as Fourier transform spectrometer (FTS), a large optical path difference is required, which results in a complex and high mass instrument. For example, the mass of the MIPAS instrument on the ESA ENVISAT satellite in low Earth orbit, which has a spectral resolution of 0.035 cm$^{-1}$, is 327 kg [Endemann, 1999], whereas the PFS instrument on Mars Express is 30.9 kg [Formisano et al., 2005]. The reason a high resolution FTS has not already been sent to Mars is because the bulk composition of the atmosphere has already been surveyed and a further scientific case has not been made that justified a large, and very heavy, instrument.

The detection limits of current instruments used to detect Martian methane lie below the requirements for an unambiguous determination of concentration mapping and distri-
bution. Recent advances in tunable laser heterodyne spectro-radiometry that are based on mid-infrared solid state laser sources may offer an opportunity for methane observation in the Martian atmosphere with enhanced detection sensitivity.

Although laser heterodyne spectroscopy is not a new idea (e.g. Menzies, 1976, Lenth, 1983) the recent development and maturation of mid-infrared quantum cascade lasers (QCLs) offer the prospect of major improvement in radiometer’s capabilities relevant to space deployment. This report details current work on a quantum cascade laser-based heterodyne radiometer (LHR) for the potential of measuring methane in the Martian atmosphere by remote sensing. This involves adapting an existing 10 µm laser breadboard design [Weidmann et al., 2007a] to operate at 7.7 µm in order to target the ν4 fundamental band of methane centred at 1306 cm⁻¹. Performing as the local oscillator, the QCL is at the heart of the LHR. Incoming radiation from the scene, in this case the Martian atmosphere, is mixed with the radiation from the local oscillator, which is then detected at the photodiode. The output signal contains an oscillating part consisting of the difference frequency, which is then converted into the RF in order to analyse it more easily. By changing the input current of the laser, its output wavelength can be tuned to match the incoming radiation allowing the identification of spectral features. QCLs are an ideal local oscillator for this instrument as they allow continuous frequency tuning over a specific spectral window, provide the necessary optical power and have high spectral purity [Weidmann et al., 2007b]. They also have the advantage of being extremely compact and reliable devices.

LHRs have the benefit of high sensitivity, high spatial resolution and ultrahigh spectral resolution down to, and even below, 0.005 cm⁻¹. During the retrieval of terrestrial atmospheric ozone profiles, Weidmann et al. [2007b] concluded that a carefully selected specific high resolution microwindow provided as much information as a medium resolution radiometer covering a broad spectral range. This major advantage favours the development of a compact and lightweight LHR instrument over the current large and heavy Fourier transform spectro-radiometers.

The bulk of the experimental work of this project is being performed at the Molecular Spectroscopy Facility (MSF) at the Rutherford Appleton Laboratory (RAL), with preparation and calibration work carried out at Oxford. Chapter 4 outlines the installation of a 7.7 µm QCL and details the tests carried out to determine its performance and spectral tuning range. The next phase of laboratory work involves assessing the instrument’s ability to measure methane gas transmission through small gas cells. Subsequently the gas cell facilities at RAL will be used to reproduce a representative Martian atmospheric path, including typical dust and condensate loadings using specialised aerosol cells. This will test the instrument’s discrimination of overlapping spectral features and sensitivity to contamination from the dust present in the Martian atmosphere. Also a side-by-side spectroscopic comparison of the LHR and a high resolution Fourier transform IR spectrometer will be carried out. This will evaluate the performance of the LHR against an existing laboratory spectrometer. Con-
sideration will also be made to further miniaturise the instrument, an important factor for flight consideration.

This report also focuses on previous work regarding atmospheric methane detection. The published data for Mars has been used to perform atmospheric simulations containing trace amounts of methane under known atmospheric conditions, the results of which are detailed in chapter 5. Spectra have been produced using the Oxford Planetary radiative transfer modelling code, RADTRANS [Irwin et al., 1997], using profiles of Mars obtained from COSPAR and the Mars Climate Database (MCD). These databases contain information about temperature, pressure and the volume mixing ratios of the major gases present in the Martian atmosphere. Sensitivity studies have also been carried out. Spectra were simulated at the $\nu_4$ CH$_4$ band at resolutions of 0.005 cm$^{-1}$ and 0.1 cm$^{-1}$ with and without traces of methane, matching the operating modes of the LHR.

Finally, the plans for future work on this project are outlined in chapter 7.
Chapter 2

Atmospheric Observations of Methane

Methane in the atmosphere of Mars has been a major topic of interest for many over the last few years. A summary of the scientific studies to date to detect methane are discussed in this chapter. Information regarding the methane molecule can be found in appendix B.

2.1 Methane in the Martian Atmosphere

Studies to detect trace gases in the Martian atmosphere began many decades ago. Using Mariner 6 and 7 infrared spectrometer data, Horn et al. [1972] placed an upper limit of atmospheric CH$_4$ at 3.7 ppm in their study of the $\nu_3$ fundamental band. Later, the Mariner 9 orbiter (1971) observed Mars and focused on the $\nu_4$ CH$_4$ band, but did not detect the IR absorption of methane. This resulted in an upper limit of 20 ppb being placed on the gas [Maguire, 1977].

While viewing Mars in June 1988 using the Fourier Transform Spectrometer at the Kitt Peak National Observatory, Arizona, Krasnopolsky et al. [1997] indicated a potential detection of methane in the Martian atmosphere. They were observing in the 2650 – 2800 cm$^{-1}$ spectral range searching for HDO (Hydrogen Deuterium Oxide). Methane was detected as a by-product of their study, with a measured concentration of 70 $\pm$ 50 ppb, which was below the 2$\sigma$ limit of the instrument.

Lellouch et al. [2000] observed Mars in July 1997 between 2.4 – 4.5 $\mu$m using the short-wavelength spectrometer on the ESA Infrared Space Observatory (ISO). They did not detect methane in its strong $\nu_3$ band centred at 3.3 $\mu$m, with an upper limit of 50 ppb.

Krasnopolsky et al. [2004] in January 1999, used the Fourier Transform Spectrometer (FTS) of the Canada-France-Hawaii Telescope, located near the Mauna Kea Observatory in Hawaii, to record the Martian spectrum between 2840 and 3020 cm$^{-1}$ with a resolving power of 180,000 ($\Delta\nu = 0.016$ cm$^{-1}$). They reported the detection of methane, after the summation
of the 15 strongest CH$_4$ transitions, at a 3.7σ level. They concluded a CH$_4$ mixing ratio of 10 ± 3 ppb. This method of detection has the advantage of providing very high spectral resolution. However, it has limitations that include a lack of spatial resolution, and the presence of terrestrial absorption lines in the spectra which have to be removed.

Formisano et al. [2004] observed the Martian atmosphere in January, February and May 2004, using the Planetary Fourier Spectrometer (PFS) on Mars Express. The instrument has a spectral resolution of 1.3 cm$^{-1}$ and a spatial resolution of about 10 km at pericentre. They concentrated on the $\nu_3$ methane fundamental band as the SNR of the Mars Express PFS is much greater in the region around 3000 cm$^{-1}$. Data from 16 orbits were summed and used to calculate a mean CH$_4$ mixing ratio of 10 ± 5 ppb. Figure 2.1 shows a PFS spectrum obtained in the 3000-3030 cm$^{-1}$ region. In order to fit the data to known methane abundances, simulated spectra have been overlaid containing varying amounts of CH$_4$. There are advantages to using space based instruments to collect data, which include proximity to the Martian Surface and the absence of telluric absorption. However, the PFS also has disadvantages which include only a moderate resolving power of 2300 ($\Delta$ν = 1.3 cm$^{-1}$) and a spectral sampling of 1 cm$^{-1}$. There was also a major dust storm in development during the measurement period that could have affected the retrievals.

Figure 2.1: An averaged spectrum of the Martian atmosphere between 3000 – 3030 cm$^{-1}$ recorded by the PFS on Mars Express between January–February 2004 (black curve), with ±1σ confidence (red lines). The SNR is about 1300. Methane is identified at 3018 cm$^{-1}$. There are three water lines (at 3003.5, 3022, and 3026 cm$^{-1}$) and two solar lines (at 3012 and 3014 cm$^{-1}$). The continuum slope is due to water ice clouds in the atmosphere. The small peak at the left of the main solar line is due to instrumental response function. Also shown are simulated methane spectra computed at concentrations of 0 ppbv (green curve) and 10, 20, 30, 40, and 50 ppbv (violet curves). The simulated spectra have been computed for 6.7 mbar of CO$_2$, including 350 ppm of H$_2$O, along with dust and water ice clouds. The temperature profile obtained from simultaneous measurements in the thermal radiation was used [Formisano et al., 2004].
Mumma et al. [2004] used CSHELL on The NASA Infrared Telescope Facility (IRTF), located at Hawaii’s Mauna Kea Observatory, in March 2003, and Phoenix (a near-IR spectrometer) on Gemini South, located in the Chilean Andes, in May 2003. CSHELL and Phoenix are cryogenic infrared echelle spectrographs [Greene et al., 1993, Hinkle et al., 1998]. A slit was situated along the central meridian of the disk and the spectra were recorded as a function of latitude. A partial mapping of the Martian disk was obtained as the planet rotated. The 3020 – 3040 cm\(^{-1}\) spectral range was observed with a spectral resolution higher than \(10^4\) (CSHELL has a resolution of 0.076 cm\(^{-1}\) [Wiedemann et al., 2001]). Large volumes of methane were detected in two specific areas, both close to the equator, with Eastern longitudes of 300°, in March 2003, and about 60°, in May 2003. From the IRTF data, a maximum CH\(_4\) mixing ratio of 250 ppb was concluded. From the data obtained at Gemini South, a value of 60 ppb CH\(_4\) was established at the location of maximum intensity. This method gave Mumma and his team the advantage of high spectral resolution with some spatial resolution. However, these observations provided only a tentative detection of methane on Mars.

Then, between January and March 2006, Mumma et al. [2009] observed localised sources of methane on Mars. High-dispersion IR spectrometers located at the Mauna Kea Observatory were used: CSHELL on IRTF and The Near Infrared Spectrometer (NIRSPEC) on Keck II. Again the spectrometers featured a long entrance slit that was held to the central meridian of Mars (figure 2.2A) while spectra were taken sequentially in time. Pixelated spectra were acquired simultaneously at neighbouring positions along the entire slit length for each observation, which provided 35 spectra at 0.2 arc second intervals when Mars’ diameter was 7 arc seconds. The data were binned to provide latitudinally resolved spectra, and then in time (longitude) to improve the signal to noise ratio. These spectra are shown in figure 2.2B and 2.2C respectively. During Mars’ northern midsummer, an extended plume of methane was detected, containing approximately 19,000 metric tons of CH\(_4\) (Figure 2.3, profile d) with an estimated source strength greater than 0.6 kg per second. In Figure 2.4, Mumma et al. [2009] use their midsummer 2003 data to construct a high resolution map where CH\(_4\) is particularly enhanced over several localised areas.

Simulations by Lefèvre and Forget [2009] attempt to recreate the localised methane sources observed by Mumma et al. [2009]. They conclude that an atmospheric lifetime of less than 200 days is necessary to reproduce the same local levels of detected methane. This results in a loss of CH\(_4\) 600 times faster than calculated by standard photochemistry in order to maintain the same amount of methane in the atmosphere.
Figure 2.2: Detections of CH₄ and water vapour on Mars on March 19th and 20th, 2003. (A) Mars is shown as it appeared at the mean time of the R0 and R1 observations. The subsolar (*) and sub-Earth (+) points are marked, along with several prominent features. The entrance slit of the spectrometer was oriented north-south on Mars along the central meridian and is shown to scale. (B) Spectra taken on March 20th were extracted at 11 equal intervals (0.6 arc sec each) along the slit (ranging from 70°N to 70°S), after binning over longitudes 277° to 323°W. (C) Spectra taken on March 19 are binned over the longitude range from 289° to 335°. Spectral lines of H₂O (three lines, short dashes) and CH₄ (long dashes) are seen. (D and E) show residual intensities in a greyscale format, and show the spatial distribution of the gases with latitude [Mumma et al., 2009].
Figure 2.3: Geographic and temporal variability of Martian methane. Latitudinal profiles of CH₄ mixing ratios for different longitudes and seasons are shown; the width of the colour band represents the ±1σ confidence. The aero-centric seasons (Lₘ) are early northern spring (a: 17°), early northern summer (b and c: 122°), and late northern summer (d: 155°). Data is obtained from spectra centred at the indicated meridian longitude (CML) [Mumma et al., 2009].

Figure 2.4: High resolution map constructed from IR data from ground based observations of Mars in 2003. Regions are highlighted where methane appears noticeably localised in northern midsummer (A, B₁ and B₂) and their relationship to mineralogical and geomorphological domains [Mumma et al., 2009].
2.1.1 Mapping the Methane

Lefèvre and Forget [2008] used the Mars LMD global circulation model (GCM) to simulate Mars’ atmosphere in order to better understand how the observed variations in seasonal methane could occur. Figure 2.5 shows the results of methane distribution throughout the atmosphere at $L_a = 0 - 30^\circ$ obtained at vernal equinox after a quasi-stationary state was reached. It shows that methane is almost uniformly mixed up to an altitude of 70 km at mid-latitudes, but above that the mixing ratio decreases quickly as a result of photolysis. The simulation was initialized with a uniform CH$_4$ mixing ratio of 14 ppbv, which corresponds to the yearly average measured by the Planetary Fourier Spectrometer (PFS) onboard Mars Express [Geminale et al., 2008]. This value is used in chapter 5 in several simulated models of the Martian atmosphere.

![Figure 2.5: Zonal mean mixing ratio of methane computed at L$_a$ = 0 - 30° using the LMD GCM [Lefèvre and Forget, 2008].](image)

Using data from the thermal emission spectrometer (TES) onboard Mars Global Surveyor (MGS) Fonti and Marzo [2010] map the methane concentration and evolution over three Martian years (the second half of MY24, MY25, MY26 and the first half of MY27). Their research exclusively targets the $\nu_4$ Q-branch of methane at 1306 cm$^{-1}$. TES operates in two modes, providing spectral resolutions of 12.5 and 6.25 cm$^{-1}$, with 5 and 10 cm$^{-1}$ spectral sampling, respectively. An analysis of the data was performed by comparing it with a set of synthetic spectra (produced using the radiative transfer code MODTRAN). Their conclusions show that the methane is distributed seasonally with the maximum global average abundance seen in northern autumn ($33 \pm 9$ ppbv). This is contrasted with a decrease in winter to its lowest level ($5 \pm 1$ ppbv), followed by an increase in spring, and a further rise in summer. This suggests that the methane in the atmosphere has a lifetime of < 1 year. Simulations of these results are performed in section 5.2.2, and suggest that a confident determination of methane at these low resolutions is highly unlikely.
NASA’s Mars Science Laboratory (MSL) rover, scheduled for launch in late 2011, will house the Tunable Laser Spectrometer (TLS) that will perform precision measurements of oxygen and carbon isotope ratios in carbon dioxide (CO$_2$) and methane (CH$_4$) in the atmosphere over one Martian year in order to distinguish between a geochemical and a biological origin. Also, the onboard Analytical Laboratory is designed achieve a more detailed investigation of biological habitability [Atreya et al., 2007].

The Mars Trace Gas Mission (TGM) orbiter due for launch in 2016 is part of ESA’s ExoMars mission in collaboration with NASA as part of the Mars Exploration Joint Initiative (MEJI). The orbiter will deliver the ExoMars static lander and then proceed to map the sources of methane and other gases on Mars and in doing so, help select the landing site for the ExoMars rover to be launched in 2018.

2.1.2 Difficulties Observing Extra-Terrestrial Methane

Zahnle et al. [2010] discuss the difficulty in detecting methane on Mars from Earth due to telluric contamination. They highlight observations made by Mumma et al. [2009] in 2003 when Mars was approaching Earth. Martian $^{12}$CH$_4$ lines would have blue shifted into near coincidence with strong terrestrial $^{13}$CH$_4$ lines. Also, weak H$_2$O and strong CO$_2$ lines overlap the $^{12}$CH$_4$ P2 line. The CSHELL instrument would be unable to differentiate these lines without greater resolving power. These issues would have posed problems during data reduction and retrieval stages, and as a result, the observed methane reported could have been a result of errors. Zahnle et al. [2010] conclude that there is as yet no compelling evidence for methane on Mars, and that the upper limit may be as small as 2 ppb.

Since publishing their paper in 2009, Mumma et al. have been working on the next phase of their investigation; performing higher resolution measurements using three ground-based telescopes to map Mars in multiple gases over the majority of the Martian year (Mumma, private communication).

2.1.3 Possible Sources and Sinks of the Martian Methane

Possible Sources

The recent evidence indicating that there are trace amounts of methane in the atmosphere of Mars has led many to speculate as to its origin. Atreya et al. [2007] argue that volcanoes are most likely not responsible, as they have been extinct for hundreds of millions of years. Also, if they were the source of the methane, they would also have expelled vast amounts of sulphur dioxide (SO$_2$), and no evidence of sulphur compounds in the Martian atmosphere has been found. Therefore, the volcanic origin of the methane is doubtful. Lyons et al. [2005] discuss the production of methane by fluid-rock interaction in the Martian crust. Its detection could indicate active magma on the planet. They conclude that the low temperature alteration of basaltic crust by carbon-bearing hydrothermal fluid can produce a CH$_4$
flux of $1 \times 10^7$ moles per year. It has also been suggested that methane could form in liquid water under a layer of permafrost by serpentinization of olivine, assuming the presence of CO$_2$ [Oze and Sharma, 2005, Atreya et al., 2007]. The methane could have originated off-world and been delivered by comets, meteorites and interplanetary dust. However, as Krasnopolsky et al. [2004] calculate, this could not be the primary source, as this method equates to only 6% of the detected methane.

Krasnopolsky [2006] acknowledge that geological sources of methane are possible, but conclude that the lack of current volcanism, hydrothermal activity, hot spots, and the low levels of out-gassing from the interior limit these as the only source of the methane. The possibility of methane producing bacteria or microorganisms has been suggested by a number of authors [Boston et al., 1992, Weiss et al., 2000, Krasnopolsky et al., 2004]. Max and Clifford [2000] suggest methanogenic bacteria could be present in a possible liquid saline groundwater layer at a depth of around 6 km. The chemical reactions involved in microbe metabolism, from Atreya et al. [2007], are:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad (2.1)$$

$$4CO + 2H_2O \rightarrow CH_4 + 3CO_2 \quad (2.2)$$

Brown et al. (2010) suggest that a serpentinization process could be a source for methane at the Nili Fossae region as part of a Basalt Clay-Carbonate 2-step alteration reaction. Boston et al. [1992] consider a possible scenario involving hydrothermal habitats below the Martian surface; an illustration is seen in figure 2.6. Methane is then released at localised sources at the surface, known as hot spots [Wong et al., 2003].

![Figure 2.6: Illustration of a possible hydrothermal habitat on Mars. The circulation of water is forced by the pressure of a temperature gradient [Clifford, 1991]. Reduced volcanic gases are carried upward while oxidized and organic materials are carried downward [Boston et al., 1992].](image)
Possible Sinks

Methane is primarily broken down by photochemical reactions in the upper atmosphere. These reactions are listed in figure 2.7. The total photochemical loss of CH\(_4\) in the Martian atmosphere is equal to \(2.2 \times 10^5\) cm\(^{-2}\) s\(^{-1}\), or 270 tons per year, with a lifetime of approximately 340 years [Krasnopolsky et al., 2004], and as a result would require a continuous CH\(_4\) source to maintain current levels. The methane lifetime on Mars is long enough to allow for winds and diffusion to mix the gas into the atmosphere homogeneously, so the large deviations in observed methane levels over the planet were unexpected [Mumma et al., 2009]. This suggests that the CH\(_4\) originates from localised sources.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient (cm(^3) s(^{-1}))</th>
<th>Column rate (cm(^{-2}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4) + h(v) (1216 Å) (\rightarrow) products</td>
<td>(-)</td>
<td>(1.0 \times 10^5)</td>
</tr>
<tr>
<td>CH(_4) + OH (\rightarrow) CH(_3) + H(_2)O</td>
<td>(2.45 \times 10^{-12} \exp(-1775/T))</td>
<td>(1.0 \times 10^5)</td>
</tr>
<tr>
<td>CH(_4) + O (\rightarrow) CH(_3) + OH</td>
<td>(8.3 \times 10^{-12}(T/300)^{1.56} \exp(-4270/T))</td>
<td>(1.2 \times 10^4)</td>
</tr>
<tr>
<td>CH(_4) + O(^1)D (\rightarrow) CH(_3) + OH</td>
<td>(1.5 \times 10^{-10})</td>
<td>(560)</td>
</tr>
<tr>
<td>Total</td>
<td>(2.8 \times 10^5)</td>
<td>(1.6 \times 10^5)</td>
</tr>
</tbody>
</table>

Figure 2.7: Reactions for the photochemical loss of methane in the Martian atmosphere. Column rates for the reactions are calculated using the photochemical models of Nair et al. [1994, Fig.15] and Krasnopolsky [1995, Fig.2a] in the left and right columns, respectively. The main process is photolysis by solar Lyman-alpha radiation. This occurs at around 80 km [Krasnopolsky et al., 2004].

There is recent research that suggests that methane concentrations decrease at regions of local dust storm activity. Studies performed by Farrell et al. [2006] demonstrate that Martian dust devils and large dust storms generate large-scale electric fields. These E-fields have the ability to produce major electron drift motions that are capable of dissociating any trace CH\(_4\) in the ambient atmosphere, therefore acting as a sink of methane. Figure 2.8 shows the relationship between electrostatic field and methane destruction. As the E-field increases, the CH\(_4\) destruction time geometrically decreases. For large E-fields the CH\(_4\) destruction rate is approximately 1000 seconds.

Atreya et al. [2006] consider that at the surface, H\(_2\)O\(_2\) could serve as a strong oxidiser that could accelerate the loss of methane from the atmosphere (see section 5.4 for more information on H\(_2\)O\(_2\) detection on Mars).
Figure 2.8: Methane destruction as a function of electrostatic field, assuming a methane concentration of 10 ppb [Farrell et al., 2006].

2.2 Remote Sensing of Methane in Earth’s Atmosphere

Methane sources on Mars are currently the topic of much speculation. On Earth however, there is much conclusive data on the topic. The first unambiguous detection of methane in Earth’s atmosphere was that of Migeotte [1948], who observed its infrared absorption bands in the solar spectrum. Methane is the most abundant organic chemical in Earth’s atmosphere [Cicerone and Oremland, 1988]. The global average amount of methane in the atmosphere in 2005 was measured at $1,774.62 \pm 1.22$ ppb [Forster et al., 2007].

There are many sources of methane on Earth, the most significant of these include: Microorganisms called methanogens produce large amounts of methane as they respire; they are responsible for anaerobic decomposition in wetlands and irrigated rice paddies [Matthews and Fung, 1987]. Methane is also produced by enteric fermentation in animals, decomposition in landfills, and a contribution by termites. Abiogenic sources of methane include: Natural gas production and consumption, the mining and processing of coal, biomass burning, and the release from the breakdown of clathrates. Methane lifetime on Earth is approximately 9 to 10 years [Rowland, 1985] and is destroyed predominantly in the troposphere by the chemical reaction with the hydroxyl radical OH:

$$CH_4 + OH \rightarrow CH_3 + H_2O$$  \hspace{1cm} (2.3)

The OH radical is extremely short-lived in the troposphere, reacting primarily with CO or CH$_4$ on time scales of 10 seconds or less [Fung et al., 1991].

A number of instruments have measured the concentration of methane in Earth’s atmosphere from orbit. One of them is the Infrared Atmospheric Sounding Interferometer (IASI) [Phulpin et al., 2007] which is a nadir-looking Fourier transform spectrometer on board the MetOp-A platform orbiting at about 820 km. IASI is designed to study atmospheric com-
position and meteorology, and provides global coverage of Earth twice a day. It measures outgoing radiation from Earth between 645 and 2760 cm\(^{-1}\) (15.5 to 3.6 \(\mu\)m) with a spectral resolution of 0.5 cm\(^{-1}\). IASI has dimensions 1.2 m x 1.1 m x 1.3 m and a mass of 236 kg [EUMETSAT]. Methane has been measured with normalised mixing ratios ranging from 1,742 ppb in tropical regions to 2,101 ppb at high northern latitudes [Razavi et al., 2009].

The Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY (SCIAMACHY) and the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) instruments onboard ESA’s ENVironmental SATellite (ENVISAT) are designed to perform global measurements of trace gases in the troposphere and stratosphere [ESA Earthnet: ENVISAT]. SCIAMACHY operates at resolutions of 0.24 nm to 1.5 nm and has a mass of 198 kg [Nett et al., 2001]. The MIPAS instrument has a spectral resolution of 0.035 cm\(^{-1}\) and a mass of 327 kg [Endemann, 1999].
Chapter 3

The Laser Heterodyne Radiometer

Laser heterodyne radiometers (LHRs) have been successfully demonstrated for atmospheric studies of stratospheric ozone on Earth [Weidmann et al., 2007a]. The ultrahigh spectral resolution of the instrument allows fully resolved narrow molecular absorption line-shapes, which contain information on vertical concentration profiles. It has been shown that a carefully selected specific high resolution micro-window provides as much vertical profile information as a medium resolution radiometer covering a broad spectral range [Weidmann et al., 2007a]. In addition to the high spectral resolution, the LHR is also extremely compact (the prototype has a dimension of 0.75 m x 0.75 m, and a mass of 10 kg, depending on configuration) and robust, so has a significant advantage when targeting specific trace species over larger instruments such as high-resolution Fourier Transform spectrometers. For example, the total mass of the Planetary Fourier Spectrometer (PFS) instrument on Mars Express is 30.9 kg [Formisano et al., 2005].

With further development and integration, using for example hollow waveguide (HWG) technology [CEOI Remote Sensing Brochure], the size of the core instrument can be dramatically reduced. A dimension of approximately 7 cm x 7 cm, with a mass of 0.2 kg, excluding calibration targets and external telescope should be achievable [Weidmann, CEOI Technology Showcase 2010].

3.1 Heterodyne Detection

The heterodyne method down-converts the received signal to a lower, intermediate frequency (IF) signal, in order to process it more easily by mixing the incident radiation with that from the local oscillator (LO) at the detector with a nonlinear response (see Menzies, 1976, Teich, 1985 for more details):

$$A_S \cos(\omega_S t) A_{LO} \cos(\omega_{LO} t) = \frac{A_S A_{LO}}{2} \{ \cos(\omega_S + \omega_{LO}) \cdot t + \cos(\omega_S - \omega_{LO}) \cdot t \}$$

(3.1)

The IF signal is then amplified without degradation of the signal-to-noise ratio (SNR), which allows efficient spectral multiplexing [Weidmann et al., 2007a]. A low pass-filter then attenuates the high frequency signals, before the signal is demodulated and analysed (see
section 3.3 for detailed information). The heterodyne technique provides a signal gain to a weak input source that is many times more powerful than direct detection, without involving optical amplification. Notable accomplishments of planetary atmospheric retrievals from IR heterodyne measurements using a CO$_2$ laser as local oscillator are discussed in Kostiuk and Mumma [1983].

3.2 Using a Quantum Cascade Laser as Local Oscillator

At the heart of the current generation infrared LHR is the use of a Quantum Cascade Laser (QCL) as the local oscillator (LO). The majority of previous spectroscopy studies using the IR heterodyne technique have been carried out with a CO$_2$ gas laser as the LO source (e.g. Kostiuk and Mumma, 1983). However, the invention of mid-infrared quantum cascade lasers (QCLs) [Faist et al., 1994] has offered a new alternative. QCLs allow high spectral resolution (0.005 cm$^{-1}$) measurements coupled with a wide spectral tuning range (10 cm$^{-1}$). They are an ideal local oscillator for this instrument as they emit with high spectral purity [Weidmann et al., 2007a] and the necessary optical power in the mid-infrared region where characteristic spectral lines of interest lie.

3.2.1 The QCL Advantage

The major feature of QCLs, which has been exploited for absorption spectroscopy, is their ability to be continuously tuned in frequency. The spectral coverage of a heterodyne receiver is determined by the LO frequency, the bandwidth of the photomixer and the related electronics. QCLs also have the advantage of being extremely compact, robust and reliable devices which make them ideal candidates for flight and satellite deployment.

Quantum cascade lasers differ in a fundamental way to normal semiconductor lasers. In conventional diode lasers, one photon is created for each electron that recombines with a hole in the active region. In quantum cascade lasers, once an electron has emitted a photon, it is recycled by injection into an identical neighbouring stage, where it is free to produce another photon. This process is repeated resulting in the electrons cascade down an energy staircase, created by an applied voltage, successively emitting photons at each step. These steps consist of coupled quantum wells in which population inversion between the discrete excited states of the conduction band is achieved via tunnelling control [Faist et al., 1994]. This cascade effect gives QCLs the ability to outperform diode lasers operating at the same wavelength. The wavelength of a convention laser is determined by the chemical composition of the material used to construct the laser. However, QCLs can emit at different wavelengths using the same combination of materials (gallium and aluminium compounds) by changing the thickness of the quantum wells during fabrication.
3.3 LHR Instrument Design

This section details the components of the LHR and discusses the issue of the instrument’s sensitivity and noise performance.

3.3.1 Block Diagram

Figure 3.2 is a block diagram of the components that make up the prototype LHR instrument. Output radiation from the laser is focused by an off-axis paraboloidal mirror onto a mixing plate. Incoming radiation from the scene (i.e. the Martian atmosphere) is then superimposed with radiation from the local oscillator (LO), i.e. the QCL, onto the quarter-wave mixing plate (R = 25%). During this stage it is important that both beams are aligned and spatially coherent in order to obtain maximum mixing efficiency. The resultant radiation is focused onto a mercury cadmium telluride (MCT) photodiode (photomixer) where the two input beams are combined. The photomixer is sensitive to incident light and responds by producing charge carriers from bound states [Menzies, 1976]. These freed charge carriers are then able to move in an electric field, producing a current. The output photocurrent is proportional to the total optical input signals, and therefore proportional to the square of the electric field amplitude. It is made up of two parts; a constant (zero-frequency) part that is proportional to the sum of the LO and incoming source frequencies; and an oscillating frequency component (a beat pattern) made up of the difference between the two beams [Encyclopedia of Laser Physics and Technology]. This oscillating component, modulating in
the RF domain, is known as the intermediate frequency (IF).

To calibrate the system, a short length gas cell (5 cm) can be inserted between the mixing plate and the photomixer containing a known gas whose spectral lines can be checked against a line list contained in the HITRAN database.

Now in the RF domain, the DC component of the signal is rejected and used for alignment and power monitoring. The signal is then amplified by two amplifiers: a 10 MHz to 1 GHz amplifier and a 1 GHz to 3 GHz amplifier, each with a 30 dB gain. The high gain output then passes through a low-pass filter that permits low frequency signals while attenuating high frequencies. The output low frequency signal is then passed to a square-law detector. A square-law detector is a demodulator whose output voltage $V_0$ is proportional to the square of the AC input voltage $V_i$. Therefore, $V_0$ is proportional to the input signal power:

$$V_0 = nV_i^2 = nP_i \quad \text{or} \quad P_i \propto V_0$$

where $n$ is the constant of proportionality. The square-law detector consists of a Schottky diode which is used to measure signal intensity. The low frequency signal is then demodulated by a digital signal processing (DSP) lock-in amplifier, and finally analysed by an analogue-to-digital converter. This setup allows the design of the LHR to be kept as simple as possible with minimum mass (approximately 10 kg), and provides an overall spectral resolution of 0.1 cm$^{-1}$.

Alternatively, a second heterodyne stage can be added to the setup allowing the use of an acousto optical spectrometer (AOS). This way the intermediate frequency (IF) can be analysed directly, allowing for higher spectral resolution ($\sim 0.005$ cm$^{-1}$). The AOS is based on the principle of diffraction of light at ultrasonic waves [Uchida and Niizeki, 1973]. The IF signal drives a piezoelectric transducer which generates an acoustic wave in a crystal (a Bragg-cell). This wave then creates a periodic variation of the refractive index, inducing a phase grating [Gál, 2005]. The crystal is illuminated by a monochromatic light source, i.e. a collimated laser beam, which is diffracted. The angle of diffraction is dependent on the
input frequency, which is proportional to the grating constant. The deflected light is then imaged onto a linear diode array (CCD) where the analogue signal is converted into a digital spectrum. The resolution of the AOS is dependent on the crystal and the focal length of the optics. Even though the AOS has the advantage of increasing the spectral resolution of the LHR, it has the disadvantage of adding further mass (approximately 7 kg) to the overall design, as well as complexity and increased power requirements.

A general purpose interface bus (GPIB) connected to a computer installed with LABVIEW software is used to control the instrument’s hardware: the temperature controller, current source, the lock-in amplifier, a waveform generator and a digital oscilloscope [Weidmann et al., 2007a].

3.3.2 Instrument Sensitivity and Noise Performance

There are several contributions to noise in the system. Shot noise is a quantum noise caused by fluctuations of the detected photons. Its power spectral density is proportional to the average optical power. Also, dark noise from the photodetector occurs when no photons are incident on the detector and is due to the random generation of electrons and holes within the detector that are then swept by the electric field that is applied to the diode [Optical Technologies]. Thermal noise, or Johnson noise, is produced regardless of an applied voltage, and is generated by the random thermal agitation of electrons inside a conductor at equilibrium [Johnson, 1928]. The instrument’s electronics also introduce an additional noise element.

The noise equivalent power (NEP) is defined as the power required being incident on the detector to generate an output of an amount equal to the RMS noise [Wilson et al., 2009]. The NEP for an ideal heterodyne radiometer is given by the following equation:

\[
NEP = \frac{h \nu}{\eta \sqrt{B \tau}}
\]  

(3.3)

where \( h \) is the Planck constant, \( \nu \) is the frequency, \( \eta \) is the heterodyne efficiency, \( B \) is the bandwidth of the receiver and \( \tau \) is the integration time. The equation for NEP only takes into account the limited shot-noise induced by the local oscillator. If the power from the local oscillator is high enough, the shot noise power spectral density will exceed that of all other noise, therefore the excess noise from the background and signal source, can be neglected. The NEP improves at longer wavelengths as it is dependent on the LO frequency. This gives a QCL-based LHR operating at 7.7 \( \mu m \) an advantage to observe the \( \nu_4 \) \( CH_4 \) band, over a 3.3 \( \mu m \) based LHR designed to observe the \( \nu_3 \) \( CH_4 \) band. Assuming a heterodyne efficiency of 50%, and an integration time of 1 second, the NEP for a 7.7 \( \mu m \) QCL-based LHR at resolutions of 0.1 \( cm^{-1} \) and 0.005 \( cm^{-1} \), are \( 2.84 \times 10^{-15} \) W and \( 6.35 \times 10^{-16} \) W respectively.
The noise equivalent radiance (NER) can be calculated from the NEP, and is given by

\[ NER = \frac{NEP}{A\Omega R} \quad (3.4) \]

where \( A \) is the collecting area of the telescope, \( \Omega \) is the solid angle and \( R \) is the spectral resolution of the instrument measured in wavenumbers. Assuming a telescope aperture diameter of 0.1 m and \( \Omega = 0.049 \) sr, the NER for the LHR at resolutions of 0.1 cm\(^{-1}\) and 0.005 cm\(^{-1}\), are \( 7.46 \times 10^{-15} \) W cm\(^{-2}\) sr\(^{-1}\)/cm\(^{-1}\) and \( 3.33 \times 10^{-14} \) W cm\(^{-2}\) sr\(^{-1}\)/cm\(^{-1}\) respectively. These noise values are plotted on simulated Martian methane spectra in chapter 5 for evaluation.

The power received by an ideal heterodyne radiometer from a blackbody source at temperature \( T \) is

\[ P = \frac{1}{2} I(\nu, T) \lambda^2 B \quad (3.5) \]

where \( I(\nu, T) \) is the Planck equation and \( \lambda^2 \) is the throughput of a single spatial mode. The one-half factor accounts for the radiometer’s sensitivity to polarisation. The minimum brightness temperature difference the radiometer can detect is therefore

\[ T_{\text{min}} = \frac{h \nu}{k \log(\eta B z + 1)} \quad (3.6) \]

Noise temperature is used to as a way of representing the noise in a system in terms of a temperature. It is not the physical temperature of the instrument, but rather an equivalent temperature (measured in Kelvins) proportional to the noise power. Figure 3.3 shows a contour plot of the minimum detectable temperature difference as a function of the radiometer bandwidth and the integration time. The plot was produced for a shot-noise limited heterodyne radiometer operating at 7.7 \( \mu \)m, with a 50% photomixer heterodyne efficiency, estimated from previous work by Weidmann et al. [2007a] during testing of a 10 \( \mu \)m QCL manufactured by Hamamatsu Photonics.

### 3.4 Comparing the LHR with a Fourier Transform Spectrometer

Current high-resolution IR instruments are typically based on Fourier transform spectrometers. These instruments require large optical path differences to achieve a high spectral resolution, which result in their large physical size and mass (e.g. a Bruker IFS 125HR FTS has a length of 6 m). The design of the LHR allows for a compact and lightweight (approx. 10 kg) instrument. The current quantum cascade laser-based LHR at the MSF has a dimension of 0.75 m x 0.75 m and there is potential for miniaturization through optical integration. Weidmann et al. [2007b] also demonstrate that a carefully selected specific high resolution microwindow provides as much information as a medium resolution radiometer covering a broad spectral range. This additional feature is another advantage that favours
Figure 3.3: The minimum detectable brightness temperature difference for a shot noise limited infrared heterodyne radiometer operating at 7.7 μm with a 50% heterodyne efficiency.

the development of the LHR instrument over current Fourier transform spectrometers.

When performing surveys of planetary atmospheres, a Fourier transform spectrometer is an ideal instrument. It can look over a wide spectral range in order to identify many constituents in the atmosphere. But to target a particular molecule, such as methane, then a more specialised instrument, such as the LHR, is better suited. The equation for the SNR of a FTS is

\[ SNR_{FTS} = I(\nu, T) U \xi \Delta \nu D^* \sqrt{\tau(A_D)} \]  

(3.7)

where \( I(\nu, T) \) is the Planck equation, \( U \) is the FTS throughput, \( \xi \) is the efficiency, \( \Delta \nu \) is the resolution, \( D^* \) is the detectivity, and \( A_D \) is the physical area of the detector element. Comparing the SNR of the FTS to the SNR of the LHR we get

\[ \frac{SNR_{HET}}{SNR_{FTS}} = \frac{c^2 \sqrt{A_D}}{2h U \xi D^*} \frac{1}{\nu^3 \sqrt{\Delta \nu}} \]  

(3.8)

The first term is a constant, the second term is related to the performance of the FTS, and the last term shows that heterodyne radiometry is more favourable at higher resolutions. Typical specifications for a commercial FTS are: \( A_D = 1 \text{ mm}^2 \), \( U = 0.01 \text{ cm}^2 \text{ sr} \), \( \xi = 0.1 \), and \( D^* = 8 \times 10^{10} \text{ cm} \sqrt{\text{Hz W}^{-1}} \) [Weidmann et al., 2007a]. Using these values and assuming a heterodyne photomixer of 50% efficiency, it can be shown that a laser heterodyne radiometer operating in the 7.7 μm region of the spectrum performs better than a FTS at resolutions greater than 0.02 cm\(^{-1}\). The spectral coverage of the FTS is around 500 times wider than the LHR, but the resolution of the LHR is superior to that attainable by most FTS instruments.
Chapter 4

QCL Setup and Initial Test Results

Work involves adapting an existing 10 μm quantum cascade laser (QCL) LHR prototype setup that has been used to measure ozone in the Earth’s atmosphere [Weidmann et al., 2007a], for future use in measuring methane gas in the Martian atmosphere. The 7.7 μm QCL-based LHR will be used to target the ν4 fundamental methane band centred around 1306 cm⁻¹. The QCL acts as the local oscillator of the system and can be tuned in frequency, by changing the input current, to match the incoming radiation from the scene allowing spectral signatures to be picked out; this is analogous to the way a radio is tuned in the RF domain. The testing that is detailed in this chapter was performed at the Molecular Spectroscopy Facility (MSF) of the Rutherford Appleton Laboratory (RAL).

4.1 Initial Breadboard Design

The QCL used is manufactured by Hamamatsu Photonics and has been designed to operate at a central output wavelength of 7.7 μm (~ 1300 cm⁻¹), with a typical output power of 40 mW. It is installed on a custom mound (figure 4.1) that provides heat extraction via conduction, and also the electric wiring required to supply the laser with a current. The QCL and mount are housed in a liquid nitrogen cryostat where its temperature can be monitored using a ± 0.5 mK temperature controller. In order to use the QCL it must be cooled using liquid nitrogen to a temperature of around 90 K. After new research and development, QCLs are now being manufactured that can operate at room temperature; however when this project began 7.7 μm QCLs were not commercially available. During tests the input current was limited to maximum of 400 mA in order to safely assess the QCL setup. The manufacturing specifications list a maximum operating current of 600 mA.

The QCL test setup shown in figure 4.2 was used to assess the performance and tuning range of the laser output. The equipment used comprises of a current source (Lightwave LDX-3232 High Compliance Quantum Cascade Laser Diode Driver), a cryogenic temperature controller (LakeShore Model 340), a laser spectrum analyser (Bristol 721B-MIR) and a
power meter. The optical bench consists of mirrors and a collimator used to focus the beam onto a detector (an IR camera). Optical alignment was carried out using a visible laser at 635 nm.

Once aligned, the beam was narrowed using a beam reducer, made from two off-axis paraboloids, and focused into a spectrum analyser. The spectrum analyser, operating in wavelength meter mode, is used to automatically characterize the spectrum of the QCL. Spectral features are measured in real-time up to a resolution of 2 GHz (0.067 cm\(^{-1}\)) and the results are output to a computer.

Figure 4.1: The 7.7 \(\mu\)m QCL installed on a custom mount.

Figure 4.2: The QCL workbench test setup at RAL.
4.2 QCL Performance at 7.7 µm

Using the spectrum analyser in wavelength meter mode the tuning range of the QCL output can be determined. A current is applied to the QCL until stimulated emission of photons is achieved and can be detected. This is attained at around 320 mA, where an output power of approximately 30 µW is detected. Increasing the current rapidly increases the power output from the laser. Figure 4.3 shows the power versus current curve measured for the 7.7 µm QCL. During testing, 400 mA was the maximum current that was supplied, which produced an output beam of 1.86 mW.

Figure 4.3: I-V curve for the 7.7 µm QCL.

Figure 4.4 is a graph of the current applied to the QCL against output wavenumber at various temperatures. The graph shows that as the current is increased, the output wavenumber from the QCL decreases (i.e. wavelength increases). Instabilities in maintaining a constant QCL temperature also affect the output performance of the QCL. The current supplied to the QCL causes its temperature to increase, which in turn also decreases the output wavenumber of the laser. The QCL has been demonstrated to operate at temperatures varying from 90 K to 110 K (ΔT = 20 K), depending on the input current. Further work is required to determine the limit of how fast the laser can be scanned, allowing for it reach thermal equilibrium, with each adjustment of the current.

Figure 4.5 is a high resolution simulated methane spectrum showing the features of the \( ν_4 \) fundamental band with the maximum and minimum QCL output wavenumbers highlighted in order to determine the tuning range for the laser.
Figure 4.4: Graph of applied current against QCL output wavenumber. Trend lines show the QCL operating at various temperatures.

Figure 4.5: High resolution (0.001 cm$^{-1}$) simulated CH$_4$ spectrum from 1296 - 1308 cm$^{-1}$ (approximately 7.7 μm) at a pressure of 1 mbar, temperature of 296 K, with a path length 5 cm. The QCL tuning range is shown in blue.
4.2.1 Characterising the Beam Profile

The QCL beam was focused onto a detector (IR camera) in order to characterise the beam profile. These tests were performed with an input current of 328.5 mA with the temperature stabilised at 88.2 K. A low forward current was used to reduce the power output from the laser, and insured that the beam was not saturating the CCD array. An image of the beam was then captured and transferred to a computer. Using Origin 8.0, the beam image was imported as a matrix for analysis. Figure 4.6 shows a 2D and 3D beam profile with the background CCD noise removed in order to produce a much cleaner image profile. This was achieved by recording the output from the detector with no beam incident on it, and subtracting it from the images with the beam present. Although these tests are still incomplete the results so far show that the beam is well focused and of good quality.

Further beam profile testing to be carried out includes characterising the beam’s $M^2$ value [Siegam, 1997]. This is a measure of how close the beam is to a perfect Gaussian single mode beam. Also, a “power in the bucket” (PIB) curve will be plotted. This shows the fractional power of a given beam diameter versus its actual diameter, and is useful for displaying how much of the total beam power is focused in its central lobe. Additionally, the kurtosis parameter can give information about the sharpness of the beam profile.

![QCL beam profile in 2D and 3D](image)

Figure 4.6: QCL beam profile in 2D (left) and 3D (right).
Chapter 5

Atmospheric Radiative Transfer Calculations

Atmospheric modelling enables the fundamental methane regions of the spectrum to be studied in detail, which subsequently determines the focus for experimental efforts in the laboratory. This chapter describes the use of radiative transfer modelling to simulate the atmosphere of Mars using known conditions.

The spectral radiance measured after radiation has passed through the atmosphere from the surface is given by the equation of radiative transfer [Goody and Yung, 1989]:

\[ L^1 = \int_0^\infty B(z) \frac{dz(z, \infty)}{dz} dz + B(0) \tau(0, \infty) \]

5.1 RADTRANS

RADTRANS [Irwin et al., 1997] is a Radiative Transfer modelling program used to study simulated planetary atmospheres. RADTRANS can simulate a range of environments from simple single gas atmospheres to multi-gas multi-layer atmospheres with particle scattering. The RADTRANS model calculates the transmission, absorption or thermal emission spectra of a gaseous path using one of three spectral models: Line-by-line, Band or Correlated-k. Depending on the spectral model selected, information is read in either from a line database, an averaged band parameter, or k-distribution table. The input files containing the atmospheric profiles include all the information needed to model the atmosphere of a planet. The Mars atmospheric profiles used in this report were obtained from the Committee on Space Research (COSPAR) [Kliore, 1982] and the Mars Climate Database (MCD) [Lewis et al., 1999] (see appendix D for more information). The profiles contain information about Martian atmospheric temperatures and pressures in relation to height from the surface. Also included are the atmospheric abundances of the major gases, in terms of their volume mixing ratio (vmr), present in Mars' atmosphere, including CO₂, CO, N₂ and H₂O. The spectroscopic parameters containing the intensities and line positions of the peaks of the individual gases were taken from the HITRAN 2004 (High Resolution Transmission) database. HITRAN is
a very comprehensive database used for calculating atmospheric molecular transmission and radiance from the microwave through to the UV region of the spectrum [Rothman et al., 2005].

RADTRANS is used in this project to model the ν4 fundamental methane band and incorporate its spectrum with that of the Martian atmosphere. The results of these simulations are used to direct and improve laboratory measurements. These simulations have helped in planning upcoming gas cell studies. They have also been used to check the noise performance of the quantum cascade laser (see section 5.2.4). Simulations of the Martian atmosphere are also useful for determining the information content for the quantum cascade laser range. This forms part of the future work for this project (see chapter 7).

5.2 Simulating the Martian Atmosphere at 7.7 μm

Atmospheric profiles were obtained from the Mars Climate Database (MCD) for Mars Year 24 (MY24) (12:00 local time) for a dust and averaging solar flux scenario. MY24 data is designed to mimic Mars as observed by Mars Global Surveyor between 1999 to June 2001. Coordinates chosen for study were 22.5°N, 73.1°E (in the Nili Fossae region) for months 4 (Ls = 90° – 120°), Mars’ summer, and for month 10 (Ls = 300° – 330°). These months were chosen in order to investigate how seasonal variations in water vapour influences detection of methane. The Nili Fossae region was selected as recent evidence suggests it to be one of several localised areas where methane is notably enriched [Mumma et al., 2009].

A concentration of methane was added to the profiles using results from LMD general circulation model (GCM) simulations by Lefèvre and Forget [2008]. Their model is initialised (at Ls = 0 – 30°) with a uniform methane mixing ratio of 14 ppbv, corresponding to the yearly averaged value measured by the Planetary Fourier Spectrometer (PFS) onboard Mars Express [Geminale et al., 2008]. At low and mid-latitudes the methane is almost uniformly mixed up to 70 km. Above 70 km its mixing ratio decreases rapidly due to the action of photolysis, reaching 0 ppbv at 120 km. Using this data, a constant methane concentration of 14 ppbv was added to the Martian atmospheric profiles from 0.01 km to 70 km, after which 0 ppbv was used.

5.2.1 Simulations at LHR Resolutions

Martian spectra have been calculated in the nadir and limb viewing modes using the RADTRANS line-by-line model. Although, the results presented are a sample of the simulated spectra calculated that focus on limb measurements at a tangent height of 22 km from the local surface, unless otherwise stated. Spectra in figures 5.1 and 5.2 have been simulated at the two main operating resolutions of the LHR, 0.1 cm⁻¹ and 0.005 cm⁻¹ depending on configuration, and highlight the difference resolution has on the identification of spectral

28
features. Spectra were produced with and without methane for comparison. The black Mars spectrum contains CO$_2$, CO, N$_2$ and H$_2$O, but no CH$_4$. The main H$_2$O feature has been coloured blue and labelled for visual purposes. The red spectrum has been calculated under the same conditions as the black Mars spectrum, but with 14 ppb CH$_4$ added.

The spectra clearly show the peak methane radiance at 1306 cm$^{-1}$, corresponding to the centre of the $\nu_4$ fundamental band. Note that corrections have not been made for Doppler shift due to the motion of the spacecraft.

Figure 5.1: Simulated Mars spectrum of resolution 0.1 cm$^{-1}$, measured at a limb height of 22 km from the surface at the Nili Fossae region during month 4 of Mars Year 24.

Figure 5.2: Simulated Mars spectrum of resolution 0.005 cm$^{-1}$, measured at a limb height of 22 km from the surface at the Nili Fossae region during month 4 of Mars Year 24. Note the difference in vertical scale compared to figure 5.1.

The higher resolution (0.005 cm$^{-1}$) spectrum shows an increase in the detected radiance by a factor of 10. The CH$_4$ lines are now more prominent from the CO$_2$ and H$_2$O lines than they were at a resolution of 0.1 cm$^{-1}$. This demonstrates that high resolution instruments are an advantage when studying weak spectral features in the Martian atmosphere in order
In order to see the effect that spectral resolution has on calculations, Mars spectra were calculated at a range of resolutions, varying from 0.005 cm\(^{-1}\) to 1.5 cm\(^{-1}\) at intervals of 0.005 cm\(^{-1}\). The methane was then separated from the background Martian spectra and the value of the peak methane radiance, occurring at 1306 cm\(^{-1}\), was selected. These peak methane values were then plotted against their corresponding resolutions, as shown in figure 5.3. It can be seen that the methane radiance drops quickly with decreasing resolution. This plot is useful in determining the required minimum resolution of an instrument in order to convincingly detect methane on Mars.

![Chart](image)

**Figure 5.3:** Plot of the maximum methane radiances against spectral resolution for a Mars Climate Database atmosphere. The peak CH\(_4\) value, at the centre of the \(v_4\) fundamental band (1306 cm\(^{-1}\)) is calculated and plotted at resolutions from 0.005 cm\(^{-1}\) to 1.5 cm\(^{-1}\) at intervals of 0.005 cm\(^{-1}\).

### 5.2.2 Comparing the LHR with other Instruments

In order to highlight the spectral modes of the LHR, compared to instruments that have been used to study the Martian atmosphere, spectra were produced at different resolutions matching these instruments. Resolutions of 0.005 cm\(^{-1}\) and 0.1 cm\(^{-1}\) correspond to the two main operating resolutions of the LHR (figures 5.4 and 5.5 respectively). A resolution of 1.3 cm\(^{-1}\) corresponds to the Planetary Fourier Spectrometer (PFS) instrument onboard Mars Express (figure 5.6) and 6.25 cm\(^{-1}\) corresponds to the high resolution mode used by the Thermal Emission Spectrometer (TES) onboard Mars Global Surveyor (figure 5.7). Spectra were simulated with a nadir viewing geometry to compare with these other instruments. The dark blue spectra represent a Mars atmosphere with no methane present and the red spectra are calculated with 14 ppb methane. All spectra are producing using data from the MCD during Mars Year 24, month 4.
Figure 5.4: Simulated Mars spectra calculated at a spectral resolution of 0.005 cm$^{-1}$ with 14 ppb methane (red spectrum) and without methane (dark blue spectrum) measured in the nadir, 230 km from the surface at the Nili Fossae region. 0.005 cm$^{-1}$ corresponds to the resolution of the LHR employing the use of an acousto optical spectrometer to directly analyse the intermediate frequency (IF).

Figure 5.5: Simulated Mars spectra calculated at a spectral resolution of 0.1 cm$^{-1}$ with 14 ppb methane (red spectrum) and without methane (dark blue spectrum) measured in the nadir, 230 km from the surface at the Nili Fossae region.
Figure 5.6: Simulated Mars spectra calculated at a spectral resolution of 1.3 cm$^{-1}$ with 14 ppb methane (red spectrum) and without methane (dark blue spectrum) measured in the nadir, 230 km from the surface at the Nili Fossae region.

Figure 5.7: Simulated Mars spectra calculated at a spectral resolution of 6.25 cm$^{-1}$ with 14 ppb methane (red spectrum) and without methane (dark blue spectrum) measured in the nadir, 230 km from the surface at the Nili Fossae region.
As in the previous section, these spectra highlight the advantage of higher resolution instruments. At a resolution of 1.3 cm$^{-1}$, individual spectral lines can no longer be identified and searching for methane becomes more difficult. Also, a major measurement problem highlighted as a result of the simulations is the spectral identification of methane from the other gases in the Martian atmosphere at 7.7 μm (mainly consisting of carbon dioxide and water vapour). The $\nu_3$ fundamental band of methane (centred at 3019 cm$^{-1}$) was instead used by PFS to determine a concentration of 10 ppb CH$_4$ [Formisano et al., 2004].

Figure 5.7 is a simulated Mars spectrum at the highest resolution of the TES instrument. It shows that a weak methane signature from the Martian atmosphere cannot be detected convincingly at this resolution. This result questions the data obtained by Fonti and Marzo [2010] (see section 2.1.1). Instead, the data may be correlated to changes in water vapour abundance. The issue of seasonal atmospheric water vapour is discussed in the next section.

5.2.3 Simulating Seasonal Changes on Mars

Figure 5.8 shows an emission spectrum covering the spectral range from 1300 – 1310 cm$^{-1}$ at a high resolution of 0.005 cm$^{-1}$ for the Nili Fossae region on Mars during month 4 (Mars summer) of Mars Year 24. Figure 5.9 shows a spectrum for the same Mars region calculated during month 10 (Mars winter) of Mars Year 24. Both spectra contain a constant 14 ppb CH$_4$ between 0 and 70 km. The methane features are highlighted in red for visibility from the rest of the spectrum.

Differences in line intensities between the two spectra are a result of seasonal water vapour variations on Mars. Concentrations of water vapour are greatest during summer months [Smith, 2002] when the frozen water at the polar caps sublimes into the atmosphere. Water vapour has strong spectral features near the same $\nu_4$ fundamental band of methane which makes identification more difficult during winter months.
Figure 5.8: High resolution (0.005 cm$^{-1}$) spectrum for the Nili Fossae region during month 4 (Summer) of Mars Year 24. The spectrum is calculated in the limb at a tangent height of 22 km from the local surface. The methane features (in red) are highlighted from the rest of the spectrum.

Figure 5.9: High resolution (0.005 cm$^{-1}$) spectrum for the Nili Fossae region during month 10 (Winter) of Mars Year 24. The spectrum is calculated in the limb at a tangent height of 22 km from the local surface. The methane features (in red) are highlighted from the rest of the spectrum.
5.2.4 LHR Noise Performance Simulations

RADTRANS simulations have also been used to check the noise performance of the quantum cascade laser, the key component of the laser heterodyne radiometer. Figures 5.10 and 5.11 show simulated Martian methane spectra with the background gases removed for clarity, overlaid with the noise equivalent radiance (NER) for the LHR operating at resolutions of 0.1 cm\(^{-1}\) and 0.005 cm\(^{-1}\) respectively. Note that the noise plotted only considers the limited shot-noise induced by the local oscillator, and not the additional noise components discussed in section 3.3.2, thereby representing a best case scenario. The results confidently show that the signal from the methane is above that of the noise of the QCL, indicating strong prospects for detecting Martian methane at 7.7 \(\mu\)m using a QCL-based LHR.

Figure 5.10: Simulated CH\(_4\) (14 ppbv) spectrum at a resolution of 0.1 cm\(^{-1}\). The LHR instrument NER = \(7.46 \times 10^{-15}\) W cm\(^{-2}\) sr\(^{-1}\) cm\(^{-1}\) (represented by the blue dotted line).

Figure 5.11: Simulated CH\(_4\) (14 ppbv) spectrum at a resolution of 0.005 cm\(^{-1}\). The LHR instrument NER = \(3.33 \times 10^{-14}\) W cm\(^{-2}\) sr\(^{-1}\) cm\(^{-1}\) (represented by the blue dotted line).
5.3 Nemesis

Nemesis [Irwin et al., 2008], which stands for Non-linear optimal Estimator for Multivariate spectral analysis, is used for atmospheric retrievals and utilises code derived from RADTRANS to generate radiative transfer models. The next work in this project involves further noise performance calculations and error analysis, and so far, line-by-line models have been used in calculating RADTRANS spectra. These are slow calculations to compute and therefore a faster method is preferred. This can be achieved through the use of correlated k-models. They have the same speed advantages of band models but can be additionally used for scattering calculations. The model uses pre-calculated k-tables compiled for individual gases using data from the HITRAN 2004 database [Rothman et al., 2005]. Tables have been generated for CO₂, H₂O and CH₄ using Calc_ktable.

So far, Nemesis has only been run for 1 iteration in order to check that the line-by-line model agrees with the correlated-k model. Figure 5.12 contains a Nemesis spectra fitted from Mars COSPAR data at 214 K (blue line). Also displayed is a 214 K black body spectrum (black dotted line) and a line-by-line Mars COSPAR spectrum (red line) calculated using RADTRANS. Both emission and transmission spectra were produced using RADTRANS and combined to ensure both contributions to the Martian atmosphere were included. As shown, both RADTRANS and Nemesis spectra are in agreement.

After work is complete on the construction of the LHR, and spectral measurements have been carried out, the Nemesis code will be used to perform retrievals on the collected data.

![Figure 5.12: Nemesis Mars spectrum calculated at a temperature of 214 K and a resolution of 0.1 cm⁻¹ (blue spectrum). A blackbody spectrum at 214 K is shown for comparison (black dotted line).](image)
5.4 Simulating other Potential Trace Gases in the Martian Atmosphere

Another important trace gas that has been reported to be present in the Martian atmosphere is hydrogen peroxide ($\text{H}_2\text{O}_2$). In September 2003, Clancy et al. [2004] measured the 362.156 GHz absorption spectrum of $\text{H}_2\text{O}_2$ in the Martian atmosphere using the James Clerk Maxwell Telescope (JCMT) sub-millimetre facility on Mauna Kea, Hawai‘i. Using the data obtained and performing a radiative transfer analysis, they determined an average $\text{H}_2\text{O}_2$ volume mixing ratio of $18 \pm 4$ ppbv, including retrieval uncertainties, in the lower atmosphere (0–30 km). This observation of $\text{H}_2\text{O}_2$ signifies the first extra-terrestrial atmospheric detection of a key catalytic chemical.

$\text{H}_2\text{O}_2$ has been proposed as a potential oxidizer of the Martian surface, responsible for sterilising the soil down to a few metres [Bullock et al., 1994]. It is believed to be formed from the following two-step reaction:

\[
\text{H} + \text{O}_2 + \text{CO}_2 \rightarrow \text{HO}_2 + \text{CO}_2 \quad (5.2)
\]

\[
\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (5.3)
\]

$\text{H}_2\text{O}_2$ subsequently photodissociates through the following reaction [Encrenaz et al., 2002]:

\[
\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH} \quad (5.4)
\]

Using a value of 18 ppbv, $\text{H}_2\text{O}_2$ has been simulated between 1260 and 1320 cm$^{-1}$, using the RADTRANS line-by-line model (figure 5.13). Following this, $\text{H}_2\text{O}_2$ was incorporated into simulations of the Martian atmosphere, which include 14 ppbv CH$_4$. Results show that $\text{H}_2\text{O}_2$ lines are present in the same spectral region as the $v_4$ CH$_4$ fundamental band and in fact overlap lines of CO$_2$, H$_2$O and most importantly CH$_4$ (figure 5.14). $\text{H}_2\text{O}_2$ also occurs at similar quantities and intensities to CH$_4$ in the Martian atmosphere. This poses a potential problem for confident methane identification and requires further high resolution investigations of $\text{H}_2\text{O}_2$ to determine if there is any interaction between the two trace gases.
Figure 5.13: Simulated $H_2O_2$ spectrum at a resolution of 0.005 cm$^{-1}$, measured at a limb height of 22 km from the surface at the Nili Fossae region.

Figure 5.14: Simulated Mars spectrum at a resolution of 0.005 cm$^{-1}$ containing $H_2O_2$ (18 ppbv) and $CH_4$ (14 ppbv), measured at a limb height of 22 km from the surface at the Nili Fossae region.
Chapter 6

Conclusions

The recent detection of methane in the atmosphere of Mars has become an important topic of investigation. Many are speculating as to its origin; some theorise that geological activity is the cause, while others consider the possibility of a biological source. Future missions are being planned and new spectroscopic techniques are being developed that will provide better data and determine the origin of the gas. This report has considered the possibility of observing and measuring methane in the Martian atmosphere using laser heterodyne radiometry with the use of a quantum cascade laser as local oscillator. Work consisted of simulated spectra produced using radiative transfer calculations, laser beam testing and analysis, and the optical and mechanical design of the LHR breadboard layout.

Radiative transfer calculations focused on one of the strongest fundamental bands of CH$_4$, the $\nu_4$ band centred at 7.7 $\mu$m (1306 cm$^{-1}$ wavenumbers), as the quantum cascade laser used in the laboratory was manufactured to operate at this wavelength. The atmospheric simulations of the Martian atmosphere show how challenging methane on Mars is to detect, and identification is further complicated at lower resolutions. Results conclude that the spectral resolution of the instrument is a critical factor when planning observations of the Martian atmosphere. The simulations also indicate that seasonal water vapour is an issue that must be considered as it has strong spectral features around the same region as the $\nu_4$ fundamental methane band. Water vapour contaminates the signal and makes methane detection more difficult. These models are helping by focusing efforts in the laboratory to construct of a Mars-like atmosphere in a gas cell, and subsequent spectral analysis using the LHR.

Initial QCL beam profile testing showed positive results, with the laser providing a good quality and well-focused beam. Based on noise calculations of the 7.7 $\mu$m QCL, this type of local oscillator at the heart of the LHR seems an ideal choice for high-resolution spectroscopy where high sensitivity is required. QCLs are extremely compact, robust and reliable devices and have the advantage of continuous frequency tuning over a specific spectral window. An instrument like the LHR can provide the high spectral resolution that is required for atmospheric studies, with the many advantages it brings over conventional spectrometers.
Chapter 7

Future Work

This chapter details the work planned over the following year. Before the next stage of testing begins, a draft paper for submission to Space Science Reviews will be completed which will contain information content analysis for the instrument.

In order for the LHR to be assessed on its ability to pick out the spectral features of methane from background gases, a gas cell containing Mars-like atmosphere will need to be fabricated in the laboratory. Subject to availability of equipment at RAL, the design and preparation of this work will be carried out in Oxford. A gas cell with a path length of 0.3 m and an internal diameter of 34 mm will be used in which the Martian atmosphere will be replicated. A small volume of methane gas (approximately 10 ppb) will then be introduced into the cell. Planning and testing involving the gas cell at this early stage will highlight the difficulties in measuring, introducing and controlling volumes of the different gases, ready for the later experiments with the fully constructed LHR. As the 7.7 µm spectral region has very few and weak CO$_2$ lines, a validation of the lines documented in the HITRAN database will be carried out using either the same gas cell, or a multipass cell that will provide a longer path length.

Additional QCL beam profile testing will be conducted at RAL that includes characterising the beam's $M^2$ value and producing a "power in the bucket" (PIB) curve. Also, further work is required on maintaining a stable QCL temperature. Reassembly of the LHR will then commence, including spectral calibration with a small gas cell (5 cm) containing pure methane, and radiometric calibration with hot and cold black bodies.

The LHR’s noise performance will be assessed and spectral capabilities tested using the gas cell mentioned earlier. The gas cell will also be cooled to temperatures varying from 150 K to 250 K to simulate the Martian atmosphere at a range of altitudes and latitudes. Aerosols will also be added at a later stage that will represent typical atmospheric dust concentrations. Output signals from the LHR will be processed and wavelength calibrated transmission spectra will be produced. The instruments sensitivity and discrimination of overlapping spectral features will be analysed under these varying conditions.
During testing of the LHR, a side-by-side spectroscopic comparison will be carried out against a high resolution Fourier transform IR spectrometer (a Bruker 125HR operating at a spectral resolution of 0.005 cm$^{-1}$). This will evaluate the performance of the LHR against an existing laboratory spectrometer. If methane can be detected using the LHR as well as the FTS successfully consideration will then be made for developing the instrument further in order to make remote sensing measurements of the Martian atmosphere.
### Timeline of Work

<table>
<thead>
<tr>
<th>Task</th>
<th>2010</th>
<th>2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>Draft of paper for submission + information content analysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Construct a Mars-like atmosphere (+ 10 ppb CH₄) in a gas cell</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Validate CO₂ database lines</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Further beam profile testing of the Quantum Cascade Laser (QCL)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Reassemble the Laser Heterodyne Radiometer (LHR)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectral calibration using small gas cell of CH₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&amp; radiometric calibration with hot and cold blackbodies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test the noise levels of the LHR and compare with predicted models</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perform spectroscopic measurements with the LHR using the constructed gas cell</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perform additional measurements on the gas cell using a FTS and compare with LHR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Assess the data collected</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Recreate Martian atmospheric dust in the gas cell using aerosols</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test a range of silicates in the aerosol chamber</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add the aerosol to the Mars cell and perform spectral measurements</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Write-up thesis</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Acknowledgments

Thanks go to my supervisor Dr Neil Bowles for his continued support and guidance over the last two years, and to Damien Weidmann and Kevin Smith of the Rutherford Appleton Laboratory for their supervision during my time at the Molecular Spectroscopy Facility. Thanks also goes to Gary Williams for his technical support during the time I have spent working at RAL. Appreciations also go to Nick Teamby and Ramin Lolachi for their advice on running RADTRANS and Nemesis, to David Mulholland for our discussions relating to Martian water vapour, and to Ian Thomas and Jo Barstow for help in defeating IDL gremlins. A further thank you goes to the Science and Technology Facilities Council (STFC) for funding this work at AOPP and RAL.
Bibliography


ESA Earthnet: ENVISAT. URL http://envisat.esa.int.

EUMETSAT: Monitoring Weather and Climate from Space. URL http://www.eumetsat.int.


The HITRAN Database. URL http://www.cfa.harvard.edu/hitran.


Appendix A

Mars

A.1 Mars Facts and Figures

Planetary and atmospheric parameters for Mars, and their corresponding terrestrial values, are displayed in table A.1. The principal constituents of the atmosphere of Mars are shown in table A.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mars</th>
<th>Earth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equatorial Radius</td>
<td>3396 km</td>
<td>6378 km</td>
</tr>
<tr>
<td>Mass</td>
<td>$6.42 \times 10^{23}$ kg</td>
<td>$5.976 \times 10^{24}$ kg</td>
</tr>
<tr>
<td>Mean Density</td>
<td>$3.95 \times 10^3$ kg m$^{-3}$</td>
<td>$5.52 \times 10^3$ kg m$^{-3}$</td>
</tr>
<tr>
<td>Surface Gravity</td>
<td>3.72 m s$^{-2}$</td>
<td>9.81 m s$^{-2}$</td>
</tr>
<tr>
<td>Surface Pressure</td>
<td>600 Pa (variable)</td>
<td>101,300 Pa</td>
</tr>
<tr>
<td>Surface Temperature</td>
<td>140 – 300 K</td>
<td>230 – 315 K</td>
</tr>
<tr>
<td>Mean Orbital Radius</td>
<td>$227.9 \times 10^6$ km</td>
<td>$149.6 \times 10^6$ km</td>
</tr>
<tr>
<td>Orbital Period</td>
<td>687 days</td>
<td>365.25 days</td>
</tr>
<tr>
<td>Mean Orbital Velocity</td>
<td>24.13 km s$^{-1}$</td>
<td>29.79 km s$^{-1}$</td>
</tr>
<tr>
<td>Inclination of the Orbital Plane</td>
<td>1.85°</td>
<td>0.0°</td>
</tr>
<tr>
<td>Orbital Eccentricity</td>
<td>0.0034</td>
<td>0.0167</td>
</tr>
<tr>
<td>Rotation Period</td>
<td>24.62 hours</td>
<td>24 hours</td>
</tr>
<tr>
<td>Planetary Obliquity</td>
<td>25.19°</td>
<td>23.45°</td>
</tr>
</tbody>
</table>

Table A.1: Planetary and atmospheric parameters for Mars and Earth [Read and Lewis, 2004]

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>95.32%</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2.7%</td>
</tr>
<tr>
<td>Ar</td>
<td>1.6%</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.13%</td>
</tr>
<tr>
<td>CO</td>
<td>0.07%</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Approx. 0.03%</td>
</tr>
</tbody>
</table>

Table A.2: Principal constituents of the atmosphere of Mars [Forget et al., 2008]
A.2 Thermal Structure of the Martian Atmosphere

Most of the mass of Mars’ atmosphere is confined to the troposphere (0 – 50 km). In this layer the temperature falls off rapidly with increasing altitude. This trend can be seen in figure A.1. A ‘ozone layer’ like the one in Earth’s atmosphere, is absent from Mars. Between 60 and 120 km the thermal profile stabilises due to the absorption of solar radiation in the near IR by carbon dioxide. Above 120 km is the thermosphere, where the few molecules that are present are exposed to the most energetic photons of intense UV radiation, which dissociates them and warms them significantly [Forget et al., 2008].

Figure A.1: Vertical temperature profile of the Martian atmosphere. The data were obtained from the Mars Climate Database for the northern hemisphere (at coordinates 48.8°N, 0°E). The red profile represents a Martian summer and blue a Martian winter. MY24 Month 4 (M04) $L_s = 90° - 120°$. MY24 Month 10 (M10) $L_s = 300° - 330°$. 
A.3 The Water Cycle on Mars

Martian atmospheric water vapour is important to consider because H$_2$O has strong spectral features around the same areas as the main fundamental methane bands. H$_2$O can contaminate the methane signal, making detection difficult, particularly at low resolutions.

The annual water cycle on Mars as observed by the Thermal Emission Spectrometer (TES) on Mars Global Surveyor (MGS) is shown figure A.2. The quantity of water vapour in the Martian atmosphere is expressed in ‘precipitable microns’$^1$. The results show a strong maximum in the summer of the northern hemisphere. A peak water column of approximately 100 pr-$\mu$m was attained in each of the two Martian years observed poleward of 80°N latitude at $L_s = 110^{-}-120^\circ$ [Smith, 2002]. The maximum column abundance during the southern mid-summer reached a maximum of 50 pr-$\mu$m. Low water abundances are observed during fall and winter at middle and high latitudes of both hemispheres. Figure A.3 is a plot the change in seasonal atmospheric water vapour, for the northern and southern hemisphere. Recent work by Fouchet et al. [2007] using data from the PFS/LW on Mars Express concludes a substantially drier water cycle. They measure a maximum water column at high latitudes in northern summer of $\sim$60 pr-$\mu$m. They identify a flaw in the TES data, but advise that it still be used because it is a more complete dataset, after a revision to lower the column abundances is performed.

Figure A.2: The column abundance of water vapour as a function of season ($L_s$) and latitude as observed by TES. Water vapour abundance is shown for the Mars Global Surveyor (MGS) mapping period between $L_s = 104^\circ$, March 1st, 1999 and $L_s = 137^\circ$, March 28th, 2001. Results include only daytime data (local time $\sim$14:00) where the surface temperature is $>220$ K. Results have been zonally averaged into bins that are 2° wide in latitude and 2° wide in $L_s$. The total water column integrated perpendicularly from the surface to infinity is shown. The data has not been topographically scaled. Contours show a smoothed representation of the results [Smith, 2002].

$^1$A precipitable micron (pr-$\mu$m) is a measure of the water depth in a column of atmosphere if it could be condensed at the surface. 1 pr-$\mu$m = 3.34 x $10^{18}$ cm$^{-2}$ [Wolfram Research]
Figure A.3: The annual cycle of water vapor on Mars as observed by the Thermal Emission Spectrometer (TES) on Mars Global Surveyor (MGS). The total amount of atmospheric water vapor is plotted for each season for the northern hemisphere (dashed line), the southern hemisphere (dotted line), during one Martian year (March 1999 to March 2001). Seasons are expressed as $\Delta L_s$ (solar longitude) from spring equinox ($L_s = 0^\circ$ for the northern hemisphere and $L_s = 180^\circ$ for the southern hemisphere) [Smith, 2002].
Appendix B

The Methane Molecule

Methane (CH$_4$) is a spherical top molecule with four identical moments of inertia. It absorbs and radiates in the infrared by the excitation of the bonds between constituent atoms. This leads to internal vibrational and rotational transitions, resulting in a characteristic spectrum. CH$_4$ consists of five atoms, resulting in nine degrees of freedom corresponding to nine normal vibrations: four stretching modes and five bending modes [Bowles, 2003]. The stretching modes consist of the $\nu_1$ non-degenerate symmetric stretch (centred at 2917 cm$^{-1}$) and $\nu_3$ triply degenerate anti-symmetric stretch (3019 cm$^{-1}$). The bending modes consist of the $\nu_2$ doubly degenerate (1534 cm$^{-1}$) and the $\nu_4$ triply degenerate (1306 cm$^{-1}$) [The HITRAN Database]. However, only the $\nu_3$ and $\nu_4$ bands are infrared active, these are shown in figure B.1, and are the focus of methane detection for this project. The central vibration frequencies can be split into three branches; a central Q branch, which has no change in its total angular momentum quantum number ($\Delta J = 0$), the P branch to the left of the Q branch, which has a change in rotational quantum number of $\Delta J = -1$, and the R branch to the right, which has a change in rotational quantum number of $\Delta J = +1$ [Bowles, 2003]. The observed PQR structure is a result of the simultaneous vibration and rotation of the molecule.

The following information on the molecule is listed in the HITRAN database: The molecular mass of CH$_4$ is 16.0426 g/mol; it has a freezing point of -182.5 °C and a boiling point of -161.5 °C.
Figure B.1: A synthetic methane spectrum showing the main fundamental bands calculated using RADTRANS and using data from the HITRAN 2004 database covering the 500 – 4000 cm\(^{-1}\) spectral range at a resolution of 5 cm\(^{-1}\). Calculations were performed on a simulated gas cell of path length 30 cm containing 10 ppb of CH\(_4\) at a pressure of 10 mbar and at a temperature of 150 K.

**Spectral Line Strength**

The intensity of the spectral lines are determined by several factors: the transition probability of the system, the population of energy states and the path length of the sample; the greater the distance the radiation beam traverses, the more energy will be absorbed from it [Banwell and McCash, 1994].

**Spectral Line Shape**

The line shape determines the wavenumber dependence of a spectral feature in the vicinity of the line position. When a spectrometer resolves lines, they do not appear as infinitely narrow features, but are instead spread over a finite wavenumber range. There are several mechanisms that are responsible for the line shape: One is the natural line broadening due to the molecule’s fundamental quantum mechanical nature, and the other is a function of the environment of the molecules (Doppler and Lorentz broadening) [Hanel et al., 2003]. Doppler broadening is temperature dependent and is due to the molecule’s translational motion and distortions induced by the presence of other molecules. Lorentz (collision) broadening is a function of both pressure and temperature [Beer, 1992].
Appendix C

Additional LHR Component Descriptions

Mercury Cadmium Telluride (MCT) Detector

In order to detect the incoming infrared radiation from the scene and the local oscillator a MCT detector is used. The band-gap energy can be tuned to allow multi-spectral detection that provides high detectivity with high quantum efficiency (60 - 75%).

Sideband

A sideband consists of a band of frequencies that contain power as an outcome of the modulation process, which are higher or lower than the carrier frequency. Sidebands include all the Fourier parts of the modulated signal, excluding the carrier. The receiver must eliminate the high frequency components, by applying a low-pass filter, and demodulate the signal in order to recover the required information.

Schottky Diode

The Schottky diode is a semiconductor diode that has a low forward voltage drop. A small voltage drop occurs across the terminals of the diode when a current passes through it, due to the internal resistance of the diode [Horowitz and Hill, 1989]. The voltage drop of a Schottky diode is approximately 4 times less than that of a normal silicon diode. This characteristic can lead to faster switching speeds and improved system efficiency. These are achieved as a result of its design; conventional diodes use a semiconductor-semiconductor junction as a barrier, while a Schottky barrier constructed from a metal-semiconductor junction is used in a Schottky diode. Switching times are on the order of hundreds of picoseconds for small signal diodes.

One of the most important distinctions between a Schottky and conventional diode is the reverse recovery time, when the diode switches to and from a conducting and non-
conducting state. A conventional diode can have a reverse recovery time of a few hundred nanoseconds; however Schottky diodes do not have a recovery time. Limitations of Schottky diodes include relatively low reverse voltages, 50 V and lower, and a high reverse leakage current which leads to thermal instability with increasing temperature.
Appendix D

Mars Atmospheric Profiles

The COSP AR Database

The COSP AR International Mars Reference Atmosphere profile [Kliore, 1982] for northern summer was used to produce RADTRANS simulations, some of which are included in this report. The profile contains 51 evenly separated vertical layers, every 2 km, from the surface to an altitude of 100 km. The data used to construct the COSP AR profile was obtained during the NASA Viking missions. The profile contains CO$_2$ (0.95321%), O$_2$ (0.0013%), CO (700 ppm), H$_2$O (300 ppm) and O$_3$ (120 ppb). At the surface the atmospheric pressure is 6.36 mbar and the temperature is 214 K. The pressure decreases exponentially with altitude until it reaches almost 0 mbar at 100 km. The temperature decreases linearly until it reaches 139 K at 100 km.

The Mars Climate Database

The Mars Climate Database (MCD) is a collection of atmospheric statistics compiled from General Circulation Model (GCM) simulations of the Martian atmosphere [Lewis et al., 1999, Forget et al., 1999]. The profiles comprise information from the surface (0.01 km) up to an approximate altitude of 230 km. The GCM numerical simulations were developed by Laboratoire de Météorologie Dynamique du CNRS, France in collaboration with the University of Oxford, UK, the Instituto de Astrofísica de Andalucía, Spain, SA, France with support from the European Space Agency (ESA) and Centre National d’Études Spatiales (CNES). The Mars GCMs have been extensively validated using available observational data. The MCD contains simulated data for the planet stored on a 5.675° x 3.75° longitude-latitude grid and covers all seasons of Mars Year 24 (MY24). This includes information on atmospheric temperature, pressure, radiative fluxes and volume mixing ratios of gases. The Mars Year calendar started on April 11th, 1955 at Martian solar longitude L$_s$ = 0° [Clancy et al., 2000].
Correction: 5.2.2 Comparing the LHR with other Instruments

Figure 5.4: Simulated Mars spectra calculated at a spectral resolution of 0.005 cm\(^{-1}\) with 14 ppb methane measured in the nadir, 230 km from the surface at the Nili Fossae region. The methane features (in red) are highlighted from the rest of the spectrum. 0.005 cm\(^{-1}\) corresponds to the resolution of the LHR employing the use of an acousto optical spectrometer to directly analyse the intermediate frequency (IF).

Figure 5.5: Simulated Mars spectra calculated at a spectral resolution of 0.1 cm\(^{-1}\) with 14 ppb methane measured in the nadir, 230 km from the surface at the Nili Fossae region. The methane features (in red) are highlighted from the rest of the spectrum.
Figure 5.6: Simulated Mars spectra calculated at a spectral resolution of 1.3 cm$^{-1}$ with 14 ppb methane measured in the nadir, 230 km from the surface at the Nili Fossae region. The methane features (in red) are highlighted from the rest of the spectrum.

Figure 5.7: Simulated Mars spectra calculated at a spectral resolution of 6.25 cm$^{-1}$ with 14 ppb methane measured in the nadir, 230 km from the surface at the Nili Fossae region. The methane features (in red) are highlighted from the rest of the spectrum.