UNIVERSITY OF CAPE COAST

WAVELENGTH MODULATION ABSORPTION SPECTROSCOPY WITH $2f$ SIGNAL DETECTION: APPLICATION TO MOLECULAR OXYGEN DETECTION

BY

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THESIS SUBMITTED TO THE DEPARTMENT OF PHYSICS OF THE SCHOOL OF PHYSICAL SCIENCES, UNIVERSITY OF CAPE COAST, IN PARTIAL FULFILMENT OF THE REQUIREMNTS FOR AWARD OF MASTER OF PHILOSOPHY DEGREE IN PHYSICS

JUNE 2011

DECLARATION

Candidate's Declaration

I hereby declare that this thesis is the result of my own original work and that no part of it has been presented for another degree in this University or elsewhere.

………………………………… Date: …………………

Peter Osei-Wusu Adueming

(Candidate)

Supervisors' Declaration

We hereby declare that the preparation and presentation of the thesis were supervised in accordance with the guidelines on supervision of thesis laid down by the University of Cape Coast.

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ABSTRACT

Wavelength modulation spectroscopy using second harmonic (*2f*) signals is one of the modulation techniques in absorption spectroscopy used to improve the absorption signal by noise reduction. This second harmonic (*2f*) signal has been simulated using MATLAB, a new approach based on numerical integration, to investigate the influence of normalized modulation amplitude, m and the optimal $2f$ signal was found to occur at $m = 2.1$. Experimentally, free molecular oxygen gas was measured at three different temperatures and at different optical pathlength using the $2f$ signal of the wavelength modulation absorption spectroscopy technique. The technique made it possible to verify the fact that, the longer the pathlength, the greater the intensity of the absorption signal. However the intensities of the $2f$ signal, which depict the absorption of molecular oxygen gas, were found to decrease with increasing temperatures. Using gas in scattering medium absorption spectroscopy (GASMAS) technique which is a modification of the wavelength modulation absorption spectroscopy set-up, molecular oxygen gas was probed in highly scattering media of locally branded polyurethane foams; Latex foam and Ash foam and polystyrene foam. The experiment revealed that for maximum $2f$ signal detection in the scattering media, the width of the scattering sample should be at least equal to the detection area of the detector. The thicknesses of the scattering samples were found to be inversely related to the intensities of their signals.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Dr Alfred Owusu and Dr. Moses Jojo Eghan who are my principal and co-supervisor respectively and not forgotten Dr. Benjamin Anderson for their supervision, advice and guidance from the very early stage of this research as well as giving me extraordinary experience throughout the work. Above all, they provided me with unflinching encouragement and support in various ways. I cannot imagine a more professional and knowledgeable advisors and I am grateful for the opportunity to develop as a researcher under their direction. I am indebted to them more than they know.

My sincere appreciation also goes to the Office of the External Activity (OEA) of the Abdus Salam International Centre for Theoretical Physics (ICTP) Italy, for financially supporting my work and the opportunity given to me to attend conferences. The support from the International Programme in the Physical Sciences (IPPS) of the International Science Programme (ISP) of Uppsala University, Sweden in donating the equipment for gas analysis is gratefully acknowledged.

I am also thankful to all lecturers and staff, both teaching and non-teaching of the Department of Physics especially the Head, Prof P. K. Buah-Bassuah and Prof S. Y Mensah who is the Coodinator of Laser and Fibre Optics Centre (LAFOC) for their support.

I learned a lot from the senior members of the LAFOC research group especially Dr. S. S. Sackey and Mr. E. T. Tatchie. I wish to express my profound gratitude to you for your support and encouragement. A special thanks to all my friends and colleagues in our group especially Charles L. Y. Amuah, Jerry

Opoku-Ansah, Angela G. Akyea and Clement A. Yadem. I am also grateful to the entire administrative staff of LAFOC for all the wonderful discussions that we had about religion, politics, sports and life. A special thank you to Randy Wanye for your support. I really appreciate all the things you did for me.

My parents deserve special mention for their inseparable support and prayers. My Father, Mr Francis Osei-Wusu Adueming, in the first place is the one who showed me the joy of intellectual pursuit ever since I was a child. My Mother, Mrs. Agnes O. Osei-Wusu Adueming, is the one who sincerely raised me with her caring and gently love. Frank, Joe, George, Mary and Emmanuel, thanks a lot for being supportive and caring siblings. The strong backing given by all my friends and loved ones especially Veronica Opoku Afriyie is sincerely appreciated.

Finally, my sincere thanks go to all other people who were behind my progress throughout my studies. Forgive me if your name is not mentioned.

DEDICATION

This work is dedicated to all members of the OSEI-WUSU ADUEMING family- the present and the generation to come.

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CHAPTER ONE

INTRODUCTION

Direct absorption spectroscopy is a simple, noninvasive, in situ technique for obtaining information about different species. From an absorption spectrum, quantitative absolute concentrations can be extracted (Nowakowski et al., 2009). Direct absorption spectroscopy of atoms and molecules in the gas phase, yielding both quantitative absolute concentrations as well as absolute frequency-dependent cross-sections, is a very powerful tool in analytical and physical chemistry. This absoluteness is the reason why sensitive absorption spectroscopic techniques have gained renewed interest, even in research fields where more sophisticated laser based diagnostic techniques are commonly applied. However, direct absorption spectroscopy suffers from a low sensitivity that limits its extension into several research fields. This low sensitivity results from the fact that small light attenuations are measured. However several experimental techniques have evolved to improve the sensitivity. Increasing the absorption pathlength and combining direct absorption spectroscopy with a modulation technique are some of the remedies. (Nowakowski et al., 2009).

Modulation techniques make use of the fact that technical noise usually decreases with increasing frequency and improve the signal to noise ratio by encoding and detecting the absorption signal at a high frequency, where the noise level is low. In this modulation scheme the wavelength of the light source is modulated at a specific frequency and the beam that is transmitted through the sample is detected at this modulation frequency with a phase-sensitive detector (O’Keefe & Deacon, 1988; Engeln et al., 1996; Romanini et al., 1997; Busch & Busch, 1999). The most common modulation techniques are wavelength modulation spectroscopy (WMS) and frequency modulation spectroscopy (FMS). When weak signals are to be monitored with high measurement sensitivity, two techniques which have found wide spread applications in gas sensing are the WMS and FMS. Although WMS and FMS are based on the same fundamental principle, they can be distinguished in terms of modulation parameters and detection technique. (Kraetschmer et al., 2009).

FMS is a powerful technique that can achieve a high signal-to- noise ratio with a relatively simple experimental setup. In a typical FMS experiment, the wavelength of a continuous-wave laser is modulated at a particular frequency. As the center wavelength is scanned across the atomic transition, the wavelength modulation is converted into amplitude modulation, giving rise to a modulation in the optical absorption of a sample at the same frequency. FMS avoids the typical limitations of absorption measurements such as laser-intensity fluctuations, which peaks at DC and fall off roughly as $1/f$, hence the name $1/f$ noise. Using this technique, absorption sensitivities can reach the part per million (ppm) level. For example, H_2S has been detected at the ppm level in air, (Modugno et al., 1998) and methane has been detected at the level of 12 ppb (Petrov et al., 1997). In FMS, the modulation depth is small but the frequency is very high (>100 MHz). FMS has been demonstrated to be capable of measuring both the absorption and dispersion associated with weak

spectral features (Bjorklund, 1980). Despite the inherently higher detection power of FMS technique, WMS technique is still often used, especially for the detection of species under atmospheric pressure conditions in which large modulation amplitudes (as high as a few gigahertz) are required
(Kluczynski & Axner, 1999).

Wavelength modulation spectroscopy (WMS) is an extensively used technique for sensitive detection of absorption signals, as it can significantly reduce the low-frequency noise by shifting the detection band to higher frequencies (Kluczynski et al., 2001; Schilt et al., 2003). WMS can provide substantial sensitivity enhancement and noise immunity compared to direct absorption methods (Zhou et al., 2005). The technique has been successfully demonstrated in gas-sensing applications (Liu et al., 2004: Reid & Labrie, 1981; Silver & Kane, 1999; Dharamsi & Bullock, 1996; Bullock & Dharamsi, 1997). In wavelength modulation, the modulation depth is very large, generating a large number of sidebands, but the modulation frequency is low (<1 MHz). It has been found that various types of background signals often limit the detectability of the technique. The most frequent types of background signal in WMS are those from multiple reflections from pairs of surfaces in the optical system, so called etalon effect, and those from the associated amplitude modulation often referred to as the residual amplitude modulation (RAM) (Kluczynski et al., 2001). Various means of reducing etalon effect have been presented in literature over the years (Liger et al., 1997). With regards to RAM effect, no severe background signals appear for second harmonic (2*f*) detection in WMS under ordinary condition. (Zhu & Cassidy, 1997; Kluczynski et al., 2001). WMS also refers to the case where the modulation frequency (f_m) is much smaller than the absorption linewidth HWHM (typically, f_m is the range 10 to 100 kHz). WMS technique is sensitive to line shape curvature rather than absorption magnitude (Liu et al., 2004) which is helpful for measurements with low absorption levels. WMS with diode lasers has been used by many researchers to perform sensitive measurements in gaseous media. There are several advantages in using diode lasers for such measurements including its tunability and the relative ease with which modulation can be performed with a modulated injected current, its relatively modest capital cost and its small weight (Dharamsi, 1996).

In WMS, the interaction of the modulated light with the absorption line leads to the generation of signal at different harmonics nf (n = 1, 2, 3 …) of the modulation frequency f_m. The signal at a given harmonic can be measured with lock-in detection and is directly proportional to the direct absorption line. Detection of the WMS signal at the second harmonic is the most frequently used since the signal at the second harmonics eliminates the necessity of measuring small differences between two large intensities, I and I_o as in the case of direct absorption. Further advantages of WMS-2*f* signals over direct absorption are also realized: signal processing at twice the modulation frequency eliminates a strongly sloping background often present in direct absorption. The WMS-2*f* signal also reduces low frequency noise due to the KHz detection regime and plays a large discrimination against signals that do not have strong wavelength dependence. The WMS-2*f* signal peaks at line centre and is symmetric (Schilt et al., 2003). All of these factors result in the increasing detection sensitivity as against that of the direct absorption.

The line shape of the WMS-2*f* signal depends heavily on the modulation amplitude and thus normalized modulation amplitude. A small modulation amplitude will result in a weak and noisy signal while a large modulation amplitude will just make the signal broader. The optimal modulation amplitude which gives rise to the best and for that matter the optimal signal is somewhere in between the smallest and the largest modulation amplitudes. In order to obtain the optimal signals, it is expedient to study the influence of the modulation amplitude and thus the normalized modulation amplitude through simulation. One can then maximise the WMS-2*f* signal and optimise the signal to noise ratio in wavelength modulation absorption spectroscopy tectniques knowing the behaviour of the WMS-*2f* signal from the simulation.

A lot of spectroscopic techniques have been applied in the detection of free molecular oxygen in free space, including multi-path cells (35 ppm) and cavity ring down spectroscopy, with less than 1 ppm detection limit. The absorption band of free molecular oxygen which is around 760 nm is often used for absorption based optical sensing as it is the strongest optical transition of oxygen in the visible and infrared range.

The WMS-2*f* technique has been used for the detection of free molecular oxygen gas in a scattering media. This technique of studying free gas embedded in scattering materials has been denoted GASMAS, an acronym for gas in scattering media absorption spectroscopy (Sjöholm et al., 2001). The gas contents in the scattering medium give rise to signals of certain strength, which is determined by the gas concentration as well as the average path length travelled by the light in the scattering medium. The GASMAS technique relies on the fact that the absorption features for free gas are about 10^3 times narrower than the spectral features of the surrounding liquid and solid. This makes it possible to discern the gas. A proper diode laser with single mode output can be tuned on a particular molecular transition by just changing the injection current and/or the temperature. Schemes based on wavelength modulation of the source through application of an oscillatory component to a driving current allow for effective noise reduction detection techniques.

Solids and liquids normally have broad absorption features with peaks seldom sharper than 10 nm. Therefore, spectroscopic equipment with modest resolution is normally employed. However, frequently there exist 10,000 times sharper signals due to free gas enclosures. The signature of this gas can be detected and characterized using diode laser spectroscopy. Gas enclosures constitute inhomogeneities, leading to light scattering. The GASMAS technique opens up new possibilities for characterization and diagnostics of scattering solids and turbid liquids. The GASMAS project emerged from the interaction of diode-laser gas spectroscopy (Kauranen et al., 1994; Gustafsson et al., 2000) with optical mammography (Andersson-Engels et al., 1990; Berg et al., 1993) and differential absorption lidar (Svanberg, 1993; Weibring et al., 2003), which all contain elements of the technique.

Many substances of organic origin and also many construction materials, are porous and contain free gas distributed throughout the material. For instance, wood, plants, fruits, food, powders, sintered materials, and foams can be considered. Oxygen exhibits its characteristic A band around 760 nm, a region which is easily covered by diode lasers (Sjöholm et al., 2001).

Scope of work

One objective of the study focuses on simulation of the wavelength modulation spectroscopy (WMS) second harmonic (2*f*) signal using developed MATLAB code. The simulation seeks to investigate the actual normalized modulation amplitude that gives the largest and for that matter the optimal signal. Knowing the behaviour of the WMS-2*f* signal from the simulation, one can maximise WMS-2*f* signal and optimise the signal to noise ratio in wavelength modulation absorption spectroscopy tectniques.

The other objective is to use wavelength modulation absorption spectroscopy technique to first measure free molecular oxygen gas at three different temperatures and at different optical pathlengths to determine the effect of the optical pathlength and temperature on the WMS-2*f* signal. The second part will look at the use of gas in scattering medium absorption spectroscopy (GASMAS) technique to probe oxygen gas in highly scattering medium of locally branded polyurethane foams (latex foam and ash foam) and polystyrene foam in order to determine the effect of the samples' width and thickness on the WMS-2*f* signal.

Organization of Thesis

The thesis consists of five main chapters. Chapter one gives an introduction to laser absorption spectroscopy techniques and their related concepts and applications to measure free molecular oxygen gas. The scope of the work and the organization of the thesis are also included in the first chapter. Chapter two reviews literature on absorption spectroscopy techniques and the principle underlying the experimental techniques used in this work.

Chapter three offers the methodology used for the simulation as well as the experimental methods for the research work. The results, analyses and discussion from the simulation and the experiments are presented in Chapter four. In the fifth chapter, conclusions are drawn and pertinent recommendations are given to aid further research in this area.

CHAPTER TWO

LITERATURE REVIEW

Light-matter interaction

The fundamental interaction of light with matter depends on the wavelength of the light and the dimensions of the particles involved in the interaction. The properties of the light source and the characteristics of the matter affect the interaction of light with matter. When light enters a medium, the photons may be annihilated, redirected, or converted into lower energy photons. This translates into absorption or scattering events or both in the material. In general, light can either be reflected, refracted, absorbed and/or scattered. See figure 1. Depending on the specific material one or two of these dominate over the other.

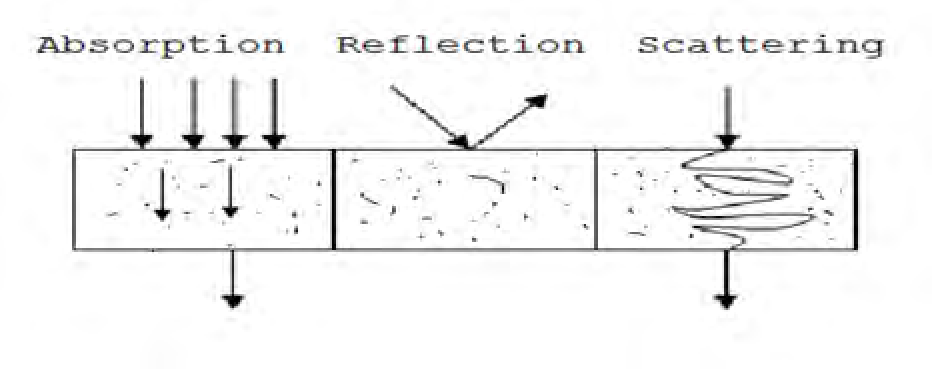

Figure1: Some possible interactions between light and matter; reflection, absorption and scattering.

Reflection is the change in direction of a light at an interface between two different media so that the light returns into the medium from which it originated. Reflection of light is either specular (mirror-like) or diffuse (retaining the energy, but losing the image) depending on the nature of the interface.

One of the three distinct processes that attenuate light incident on a material is absorption. It is the transformation of light energy into some other forms of energy as it moves through matter. Atoms and molecules of matter absorb energy at certain frequencies or wavelengths. Every atom or molecule has a unique set of absorption line and this makes identification of a gas possible through it using absorption analysis.(Svanberg, 1992; Somesfalean, 2004).

Scattering is another process that attenuates light incident on a given material. It is said to occur when a ray of light does not continue in its original straight path. Scattering may be due to rough surfaces which can be described as troughs and valleys that are slightly larger than the incident wavelength. Bubbles, impurities and inhomogeneities in a medium can also cause scattering (Katzir, 1993). Scattering can take the form of reflection or refraction as the photon encounters the interface of the two different refractive indices.

In general, variables involved in the light – matter interaction process is limited when the light source is monochromatic in nature, example is a diode laser. When laser irradiation reaches the matter surface under an angle, a progressively higher percentage of photons will be reflected off the surface at an increasing angle of oblique incidence. The fundamental interaction of laser radiation with matter depends in part on the wavelength of the light and the dimensions of the particles involved in the interaction.

Absorption Spectroscopy

Every atom or molecule of a matter has an absorption finger print that can be described by quantum mechanical theories in absorption spectroscopy. Absorption spectroscopy is a well established technique that can be used to investigate qualitatively and quantitatively, the content of a matter, free or trapped within a scattering medium (Riris *et al.,* 1994; Lytkine, 2006; Arroyo & Hanson, 1993). The fundamental equation for absorption spectroscopy is from Beer–Lambert Law, which states that the intensity of the incident light, I_o attenuates exponentially as the light travels through an absorbing material as illustrated in figure 2.

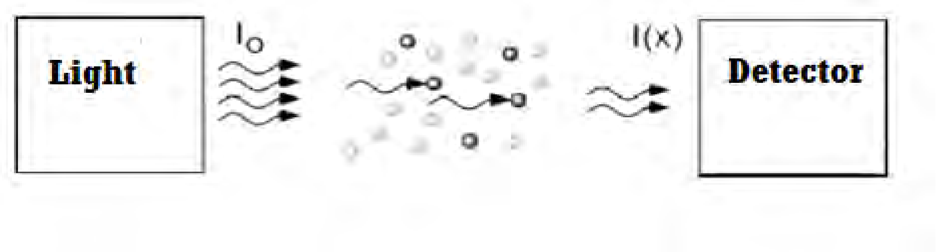

Figure 2: The absorption of a light with intensity I_o according to Beer-Lambert law.

That is

$$I(x) = I_o \exp(-\sigma c x) \tag{1}$$

where I_o is the irradiance at $x = 0$, in other words, the surface of the absorbing material, $I(x)$ is the irradiance after the light has travelled an optical path length of x units. σ and c are the absorption cross section concentration of the sample respectively.

The absorption cross section (σ) is the probability of absorption per unit area per molecule or atom. It depends on frequency or the wavelength of the light having a units of cm^2 per molecule at the line center. It is basically a quantum mechanical property. For gases, σ also depends on other physical parameters such as temperature, velocity and pressure of the sample. All these factors influence the strength and the shape of the absorption spectrum. The absorption cross section, and thus the transmitted intensity, are both highly frequency dependent, matching the energy level structure (Svanberg, 1992; Somesfalean, 2004). Absorption of light by molecules is determined by the number of atoms/molecules encountered, making it obvious that concentration (c) and effective pathlength (x) of the light through a medium influence the absorption in a way.

Absorption cross-section is commonly expressed in terms of absorption coefficient $\alpha\ (v)$ given as

$$\alpha(v) = \sigma(v)N \tag{2}$$

where N represents the number density of the species present which relates to the concentration, c as

$$N = N_A c \tag{3}$$

where N_A is the Avogadro constant. Absorption coefficient measures how quickly a beam of light would lose intensity due to the absorption alone. Mathematically absorption coefficient is expressed as a function of a line-strength $S(T)$ and line-shape function $f(v\text{-}v_0)$ according to

$$\alpha(v) = S(T)\, f\left(v - v_0\right) \tag{4}$$

where v_0 is the frequency at the line centre and v is the mean frequency. Absorption coefficient has been found to decrease as temperature increases. Figure 3 shows a relationship between absorption coefficient and temperature at different wave number.

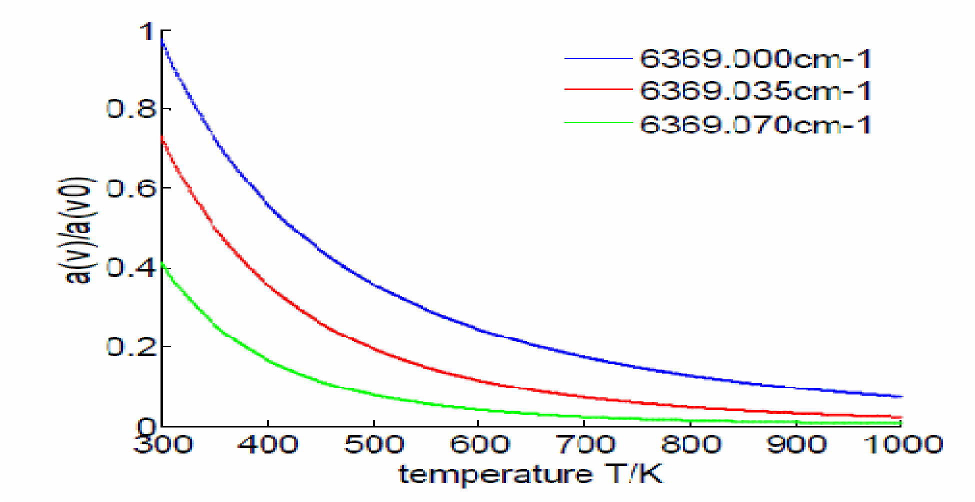

Figure 3: The relationship between the absorption coefficient and temperature at different laser wave number (Guo et al, 2011).

Molecules can exist in a variety of energy states as determined by the Boltzmann population statistics (Allen, 1998). For a molecule to move between energy states, it must absorb exactly the right amount of energy and each molecule or atom has a unique set of energy states and available transitions (Diem, 1993). Absorption spectroscopy takes advantage of this information to interrogate or identify a specific molecule. According to quantum mechanics, a frequency of light carries a certain amount of energy (E) equal to the frequency (v) multiplied by Planck's constant (h) given as

$$E = hv \tag{5}$$

Knowing this, electromagnetic radiation of frequency can be used as an energy source for absorption spectroscopy (Thorne, 1974). By passing a spectrum of frequency through a sample and analyzing the result, the species present in the sample as well as the number density can be determined. Knowing that a molecule (at a specific energy state) can only absorb a discrete amount of energy and also that a frequency of light carries only a certain discrete amount of energy, it is assumed that a scan over a transition would produce an infinitely narrow absorption line at the absorbed frequency. Instead, the absorption line has a definite shape and width as seen in an example of an absorption line in Figure 4.

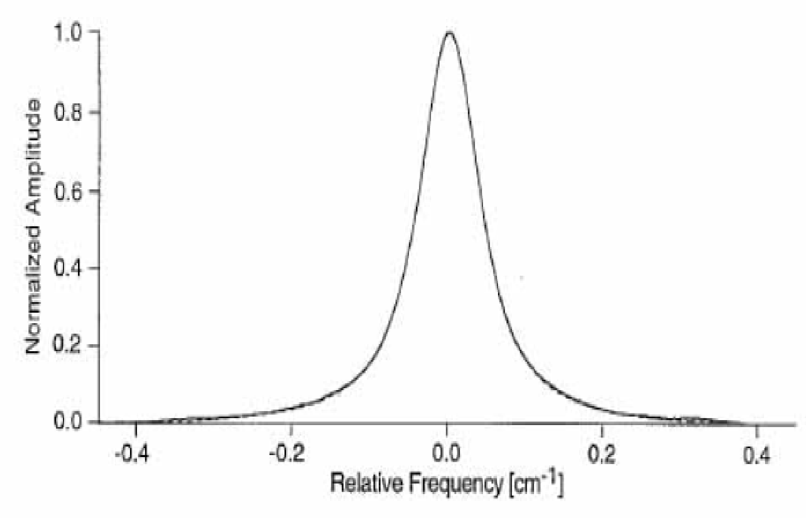

Figure 4: An example of an absorption transition line (Miller et al., 1996).

The broadening of the line is explained by two factors; first, the molecules in the sample are not stationary and even if the sample is not moving relative to the light it will experience a Doppler shift from each of the molecules, whose value is determined by the Doppler shift from that particular molecule at that particular instant. The molecule, if moving towards the light will perceive the light as having a shorter wavelength and will absorb at a longer wavelength than a stationary molecule at the same energy level. The opposite will be true of a molecule moving away from the light source. The velocity distribution with respect to the oncoming light, of molecules at the correct state, is described by a temperature dependant Gaussian curve (Thorne, 1974). The temperature dependence is due to the direct relationship between the temperature and average velocity of the molecules. This effect on the absorption lineshape is termed Doppler broadening.

The second broadening mechanism is termed pressure broadening. It occurs as an extension of natural broadening, a third broadening mechanism that is small compared to the other types of broadening and often deemed negligible. Natural broadening is as a result of Heisenberg's uncertainty principle which states that the uncertainty in the energy level (ΔE) multiplied by its lifetime (Δt) is greater than a constant ($h/4\pi$), where h is Planck's constant) expressed as

$$\Delta E \Delta t > \frac{h}{4\pi} \tag{6}$$

As pressure increases, collisions occur more frequently and the lifetime of an uncertain state decreases. To maintain the above condition the uncertainty in the energy level must increase, resulting in an increase in the range of starting energy states and therefore the range of wavelengths at which absorption will occur (Hohmann, 2007). While pressure and Doppler broadening determine the shape and spread of an absorption spectrum, it is the temperature and concentration of the sample that determines the linestrength, or peak value of the curve. The intensity of all transitions is related to the total number of molecules of the target species, while, at a given concentration, the intensity of any one transition is related to temperature through the Boltzmann population statistics (Allen, 1998).

The peak absorption cross-section at line center (v_0) is related to the integrated line strength through a lineshape function $\Gamma(v)$. This function $\Gamma(v)$

has the same analytical form for all transitions, and in spectroscopy, the broadening of an individual transition due to finite upper-level lifetime is insignificant compared to broadening by the other two important mechanisms – thermal motion and molecular collisions. Their individual and combined effects on a molecular transition at a frequency *v* are expressed as follows: (Tittel et al., 2003).

Thermal motion (Gaussian):

$$\Gamma_D(v) = \frac{1}{\Delta v_D}\left(\frac{Ln2}{\pi}\right)^{1/2} exp - \left[\left(\frac{v-v_o}{\Delta v}\right)^2 Ln2\right] \tag{7}$$

Where $\Delta v_o = 3.58\, x\, 10^{-7}\, v_o \left(\frac{T}{M}\right)^{1/2}$ (8)

Molecular collisions (Lorentzian):

$$\Gamma_L(v) = \frac{1}{\pi}\frac{\Delta v_L}{(v_o - v)^2 + (\Delta v_L)^2} \tag{9}$$

where $\Delta v_L = \Delta v_L^o P \left(\frac{T}{T_O}\right)^{1/2}$ (10)

Combined broadening (Voigt):

$$\Gamma_v(v) = k(v_o)_D \frac{y}{\pi}\int_{-\infty}^{\infty} \frac{e^{-t^2}}{y^2 + (x-t)^2} dt \tag{11}$$

where $k(v_o)_D = \frac{\int \sigma(v) dv}{\Delta v_D}\left(\frac{Ln2}{\pi}\right)^{1/2}$ (12)

with $x = \left(\frac{v - v_o}{\Delta v_D}\right)(Ln2)^{1/2}$; $y = \frac{\Delta v_L}{\Delta v_D}(Ln2)^{1/2}$;

$t = \left(\frac{\delta}{\Delta v_D}\right)(Ln2)^{1/2}$

Here *T* is the gas temperature (K), *M is* the molecular weight, *P is* the gas pressure (atm), and Δv_L^o the coefficient of pressure broadening ($cm^{-1}atm^{-1}$).

$k(v_0)_D$ is the peak Doppler cross-section, δ is the parameter of integration and is used to express the Doppler and Lorentz frequency differences during the convolution process in terms of a single variable. The quantities Δv_D and Δv_L are referred to as the Doppler and pressure-broadened half width at half maximum (HWHM) linewidths. The line shape that results from the combined effect of Doppler- and pressure-broadening is a convolution of the two respective line shapes, and it is known as the Voigt profile. The physical significance of the convolution is that the Voigt profile has different asymptotic shapes for very low and very high gas pressure. At low pressure, molecular collisions are less frequent, leaving thermal motion the dominant broadening mechanism – the corresponding line shape is near-Gaussian. As the gas pressure increases the collisions take over, and the resulting line shape is near-Lorentzian (Tittel et al., 2003).

Direct Absorption spectroscopy

For many years, direct absorption spectroscopy has been the technique of choice for absorption-based measurements of gas parameters because of its simplicity, accuracy, and ability to make absolute measurements. Direct absorption spectroscopy technique is often used for the study of absorption by small molecules at low to moderate pressures. One measures the amount of light that is transmitted through a sample in direct absorption spectroscopy experiment. If the light source is tunable and monochromatic (e.g. a laser), one can record an absorption spectrum of the sample by recording the transmitted intensity as a function of frequency. Alternatively, a broad light source can be used when the incident light or the transmitted light is spectrally dispersed (e.g., in Fourier Transform spectroscopy).

A drawback of direct absorption spectroscopy might be its limited sensitivity. A small attenuation of the light intensity has to be measured on top of a large background of the incident light. Additionally, intensity fluctuations of laser can be rather large (up to 50%), thereby obscuring the absorption signal. And although one can in principle correct for these pulse-to-pulse fluctuations, significantly better results are obtained when more stable light sources, such as continuous wave (cw) instead of pulsed, are used.

From Beer-Lambert law it can be seen that an increase in the absorption path length results in a stronger absorption signal. The absorption path length can be increased in a sophisticated way using a ‘multipass’-cell configuration e.g. White cell (White, 1942) or a Herriott cell (Herriott et al., 1964). A ‘multipass’-cell consists of two or more highly reflective mirrors between which the light is reflected many times, thereby traversing a different optical path upon each reflection. The sample of interest is placed between the mirrors and absorption path lengths of a few hundred meters can be achieved.

Another way to increase the sensitivity is combining direct absorption spectroscopy with a modulation scheme. The sensitivity in these modulation schemes is high since the phase-sensitive detection of the signal takes place at frequencies where the technical noise is weak. Furthermore, the baseline slope that typically is present in an absorption spectrum and intensity fluctuations of the light source are removed, whereas features that are strongly dependent on wavelength, such as molecular absorptions, will be enhanced. Minimum detectable absorption coefficients in the order of $10^{-6}\text{cm}^{-1}\text{Hz}^{-1/2}$ to

$10^{-8}cm^{-1}Hz^{-1/2}$ have been claimed for the various schemes (Paldus & Zare, 1999). Modulation schemes can easily be used with diode lasers, which allows for the application in the field of trace gas detection. Diode lasers are operated with a narrow, single-mode profile to be able to detect the absorption lines. The diode lasers are small, simple to handle, reliable and, relatively cheap. An example of a single double heterostructure diode laser is shown in figure 5.

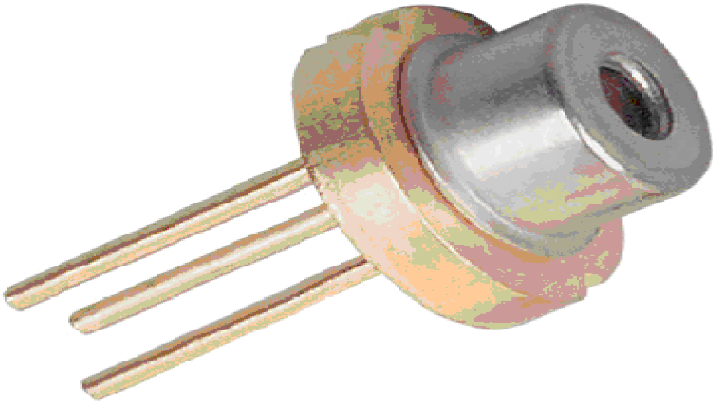

Figure 5: An example of single double heterostructure diode laser.

Modulation in absorption spectroscopy

Modulation means that a high-frequency sinusoidal signal is added to a carrier signal, e.g. the ramp that scans over an absorption line, see figure 6. Modulation of the laser emission wavelength is a commonly used method for improving the detection sensitivity of spectroscopy measurements. (Gehrtz et al., 1985; Whittaker et al., 1983). In such applications, the interaction between the sample and the spectrally modulated radiation field leads to the generation of a signal that varies at the modulation frequency. Thus the signal can be detected coherently with frequency and phase-sensitive detection electronics. Any noise contributions that do not fall into the detection frequency band centered around the modulation frequency are eliminated. The modulation frequency is also sent as a reference to a frequency and phase sensitive lock-in amplifier. The output signal from the detector is filtered by the lock-in amplifier using the reference frequency and analyzed. Through modulation, the signal is moved to a detection band at higher frequencies, where the noise level is lower according to noise theory. Modulation in absorption spectroscopy is also referred to as derivative spectroscopy, because the modulation signal gets the form of the derivative if the modulation is small (Björkwall et al., 2005).

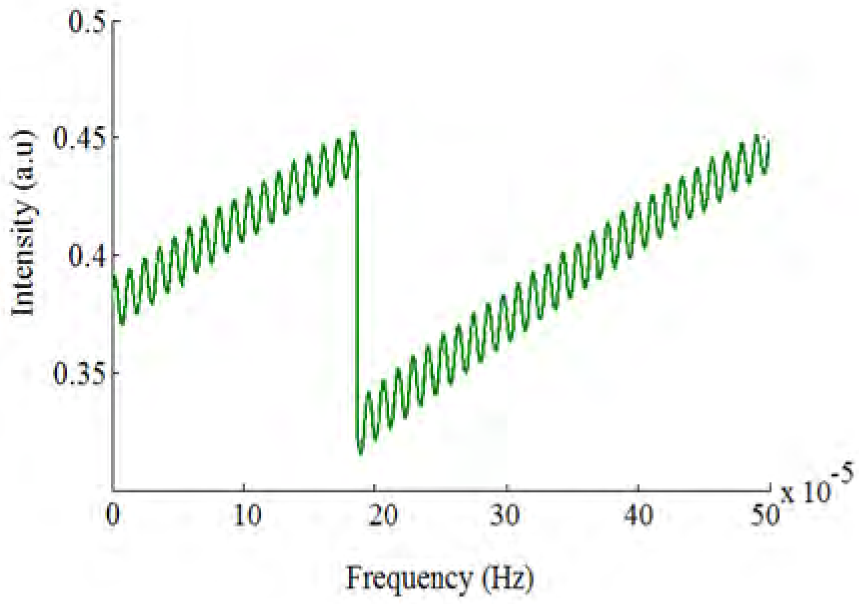

Figure 6: A direct signal, with an arbitrary superpositioned modulation frequency.

In some applications, the absorption signal is smaller than the surrounding noise. To find these small signals, modulation techniques together with a lock-in amplifier can be used. When a diode laser scans the wavelength over an absorption line with a ramped signal, a direct signal, from the detector is obtained by reading directly the output of the detector. In some cases, if the absorption is strong enough, it is possible to see the absorption signal in the direct signal. In other cases the absorption is small and modulation techniques need to be used. The modulation techniques enable measurement of a signal which is only at an order of $10^{-4} – 10^{-5}$ of the direct signal.

Modulation spectroscopy

Modulation spectroscopy is a widely used technique for sensitive trace-species detection and can be used to significantly reduce 1/*f* noise by shifting detection to higher frequencies. Modulation spectroscopy is also classified into two categories: wavelength-modulation spectroscopy (WMS) and frequency-modulation spectroscopy (FMS), according to the relative magnitude of modulation frequency and transition half-width frequency.

Theoretical descriptions of these methods are also based on strongly different formalisms. FM techniques are characterized by a modulation frequency *f* that is much higher than the half-width of the absorption feature Δv_{line} ($f >> \Delta v_{line}$) and a small FM amplitude Δv ($\Delta v << \Delta v_{line}$). These techniques have been described theoretically in detail by several authors (Schilt et al., 2003; Kluczynski & Axner, 1999; Bomse et al., 1992). These theoretical models describe the first and sometimes also the second harmonic signal by considering the interaction of the modulated electric field of the laser with an absorption line. The absorption line is described by a transfer function taking into account both the absorption of the sample and its associated dispersion (a dispersion is always associated with an absorption through the Kramers – Kronig relations). Owing to the low number of sidebands present in the electric field spectrum, the signals at the first two harmonics can be determined by summation of the contributions of all sidebands after their interaction with the absorbant - dispersive sample.

On the other hand, WMS techniques are characterized by a modulation frequency that is much smaller than the half-width of the absorption profile ($f >> \Delta v_{\text{line}}$). Near atmospheric pressure, the absorption lines usually extend over several gigahertz. Although WMS techniques can be described in principle by the same formalism as FM techniques, the calculation of the various harmonic signals is extremely tedious owing to the high number of sidebands in the laser spectrum over which the summation has to be performed.

Modulation frequencies generally used in WMS are in some kilohertz or some tens of kilohertz and for gases at atmospheric pressure, this number is of the order of 10^5–10^6. Thus WMS descriptions are preferably based on an intensity representation of the optical wave, so that no phase information is taken into account. Only the absorption of the sample is considered, and the effect of the associated dispersion is neglected (Schilt et al., 2003).

Harmonic signals are produced using tunable diode lasers (TDL) when a sinusoidal modulation of angular frequency ω is superimposed upon the diode current, resulting in a time variation of the diode frequency given by the expression

$$v(t) = v + a\cos\omega t \tag{13}$$

where ν is the mean frequency of the time, t varying diode frequency and *a*, the sinusoidal modulation amplitude. The mean frequency ν is slowly tuned by low frequency, ω ramping of the diode current. For moderate amplitudes of modulation, it can be assumed that the incident laser intensity is independent of frequency *v* over the narrow range of frequency required to modulate and tune over an isolated line in TDL experiments (Olson et al., 1980; Reid and Labrie, 1981). In harmonic detection, the concern is with weak absorption lines, and analysis is confined to values $\alpha(v)l$, such that $\alpha(v)l \leq 0.05$

The time dependent term of I(*v*(t)), $\alpha(\bar{v} + a\cos\omega t)$, is an even function of time and can be expanded in a cosine Fourier series as

$$\alpha(v + a\cos\omega t) = \sum_{n=0}^{\infty} F_n(v)\cos n\omega t \qquad (14)$$

where $F_n(\bar{v})$ is the nth Fourier component of the modulated absorption coefficient and v is considered to be constant over a modulation period.

If the modulation amplitude *a* is sufficiently small the Fourier components can be expressed as

$$F_n(\bar{v}) = \frac{2^{1-n}}{n!} a^n \frac{d^n\alpha(v)}{dv^n}\bigg|_{v=v}, \qquad n \geq 1 \qquad (15)$$

This small amplitude limit is often referred to as derivative spectroscopy as the output signals are proportional to the derivatives of the absorption line. The absolute values of $F_n(v)$ lie far below their maxima for such small values of *a*.

In wavelength modulation spectroscopy the concern is with values of *a* which maximize the harmonic signal and consequently optimize the signal to noise ratio (SNR) while detecting weak absorption coefficient. Individual lineshapes are considered since the simplified expression in equation (15) is inappropriate for these optimum modulation amplitudes.

Considering the case where the gas pressure broadening dominates the absorption line, α(v), described by a Lorentzian function is given by

$$\alpha(x,m)_L = \frac{1}{1+(x+m\cos\omega t)^2} \tag{16}$$

where x is the normalized frequency and m is a normalized modulation amplitude. x and m are expressed as:

$$x = \frac{v-v_o}{\Delta v} \tag{17}$$

and

$$m = \frac{\mathrm{a}}{\Delta v} \tag{18}$$

respectively following Arndt's conversion (Arndt, 1965). Here v_0 is the central frequency, Δν the half width at half maximum (HWHM) of the absorption line, and the normalized modulation amplitude, m is called the modulation index.

Examples of a first harmonic (1*f*), second harmonic (2*f*) and third harmonic (3*f*) of α (ν) described by a Lorentzian function are shown in Figure 7.

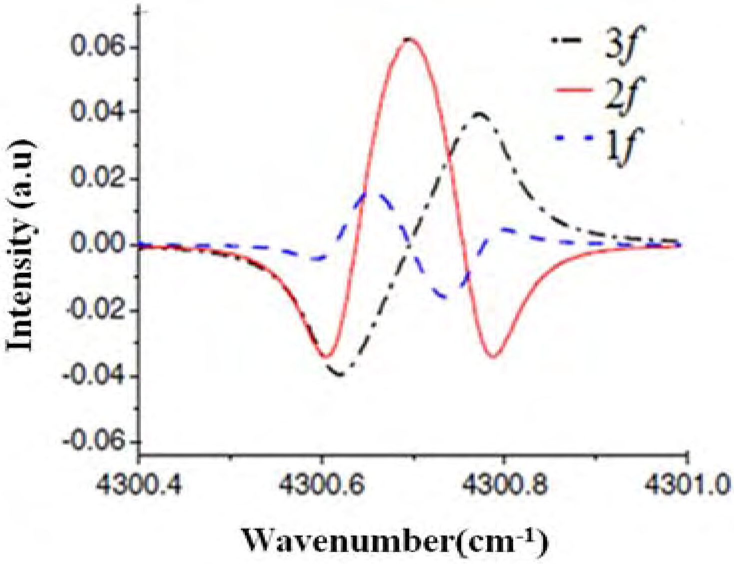

Figure 7: Examples of first, second and third harmonics of a Lorentzian absorption line.

When Doppler broadening is dominant, the absorption line, α(*ν*), described by a Gaussian function, is given by

$$\alpha(x,m)_G = \exp\left[-In2(x+m\cos\omega t)^2\right] \tag{19}$$

Calculation of the second Fourier component for the Gaussian profile was done by Wilson (Wilson, 1963). The same approach was used to calculate two properties of the second harmonic signal employing the following equation.

$$H_2^G(x,m) = \frac{2}{\pi}\int_0^{\pi} exp\left[-ln2(x+mcos\theta)^2\right]cos2\theta d\theta \tag{20}$$

where θ is the integrand. The maximum positive value of the second harmonic 2*f* signal is defined as **P** and the peak negative excursion is defined as **N**. Figure 8 shows a typical 2*f* lineshape exhibiting the two properties.

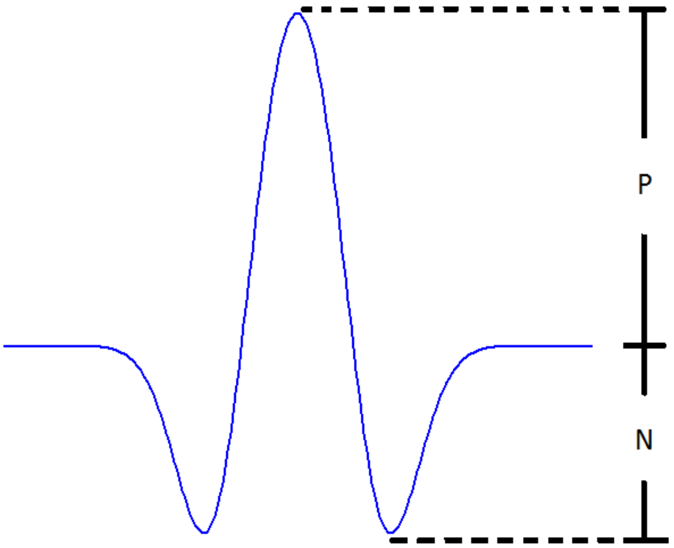

Figure 8: A typical sketch of a 2*f* lineshape showing the maximum positive part P and the peak negative excursion N.

The differences between Gaussian and Lorentzian line shapes are seen at small and large values of *m* but the general behaviour is similar, in particular at a specific value of *m*, the two line shapes have common maximum second derivative signal. (Reid & Labrie, 1981).

The WMS-2*f* signal depends not only on the transition parameters such as line strength, etc, but also on the modulation amplitude *a* (Reid & Labrie, 1981). The WMS-2*f* signal can be maximized and eventually optimize the signal to noise ratio (SNR) by choosing the optimum modulation index, *m.*

Diode laser spectroscopy

Semiconductor lasers were first introduced in the mid-1960s and found immediate application as much needed tunable sources for high-resolution laser absorption spectroscopy. The principal setup of an optical absorption spectroscopy is shown in Figure 9a. All designs contain a radiation source, a detector and the species under investigation is in a closed absorption cell for the determination of gas concentrations according to Beer’s law. Most systems also provide a modulation unit to generate an AC signal. As a prerequisite to obtain the required specific wavelength, selective elements have to be inserted into the optical path. Gasfilter - Correlator systems require a reference cell with a high concentration of the gas under investigation. While for DOAS systems a monochromator is used, FTIR instruments apply a Michelson interferometer as the selective element. Non-dispersive infrared systems (NDIR) are based on gas selective devices. All instruments based on these technologies meanwhile reached a high degree of complexity and sophistication. An alternative approach is to insert the selective element directly into the radiation source-the laser. In principle, laser spectrometers allow less complex optomechanical designs than the current analytical instrumentation and with semiconductor lasers even the

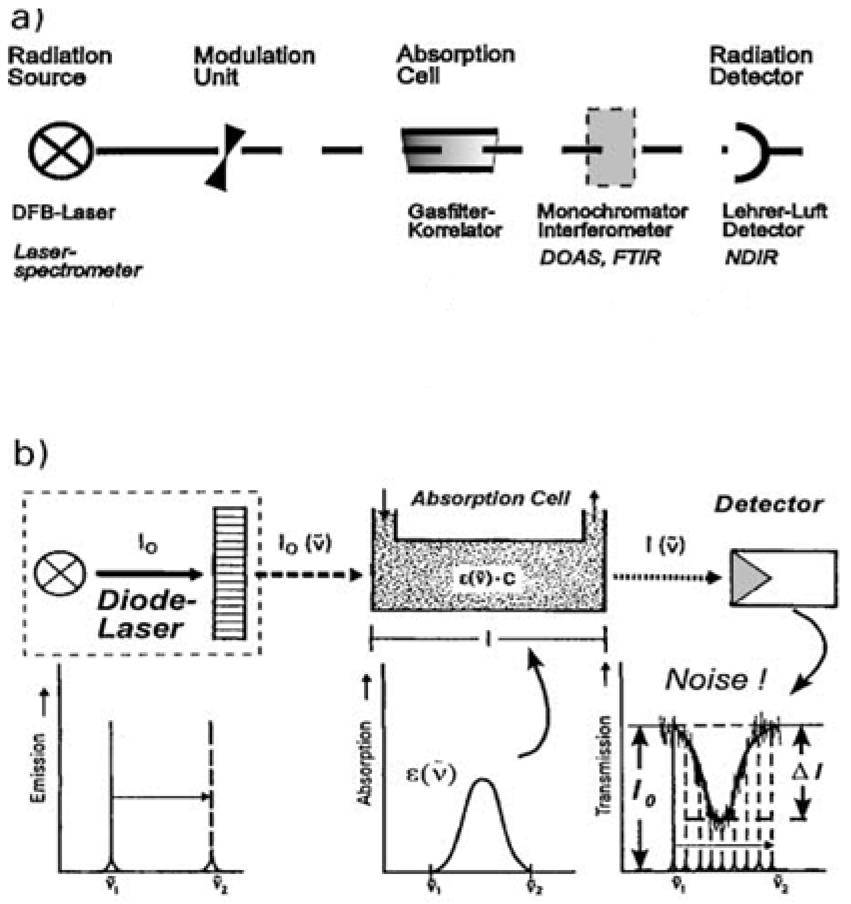

Figure 9: (a) Setup of optical absorption spectroscopy, (b) direct absorption spectroscopy using a tunable diode laser (Werle et al., 2002).

required modulation can be implemented electronically. Therefore, diode laser spectroscopy is an attractive and promising technique for analytical instrumentation. The most important research applications of TDLs in atmospheric field measurements required long-path absorption cells to provide high-sensitivity local measurements. In spectroscopy a single narrow laser line usually scans over an isolated absorption line of the species under investigation (see Figure 9b). To achieve the highest selectivity, analysis is made at low pressure, where the absorption lines are not substantially broadened by pressure. This type of measurements has developed into a very sensitive and general technique for monitoring most atmospheric trace species (Werle, 1998). The main requirement is that the molecule should have an infrared linespectrum which is resolvable at the Doppler limit, which in practice includes most molecules with up to five atoms together with some larger molecules. Since Tunable Diode Laser Absorption Spectroscopy (TDLAS) operates at reduced pressure it is not restricted in wavelength to the atmospheric windows such as 3.4 - 5 and 8 - 13 μm.

Direct absorption measurements have to resolve small changes in a large signal. In comparison with direct spectroscopy, the benefits of modulation spectroscopy in TDLAS are twofold. Firstly, it produces a difference signal which is directly proportional to the species concentration and, secondly, it allows the signal to be detected at a frequency at which the laser noise is significantly reduced. Wavelength modulation spectroscopy (WMS) has been used with tunable diode laser sources since the early 1970s. The earliest TDL systems used a modulation frequency in the lower kHz regime and second harmonic detection. Today 50 kHz modulation with 100 kHz detection is quite usual and, consequently, it is convenient to regard 100 kHz as a limit of conventional wavelength-modulated TDLAS. Modulation spectroscopy is based on the ease with which diode lasers can be modulated. In WMS with diode lasers, the injection current is modulated as the laser wavelength is tuned repeatedly at about 100 Hz over the selected absorption line and a computer-controlled signal-averager is used to accumulate the signal from a lock-in amplifier (see figure 10). This produces a harmonic spectrum of the line, with an amplitude proportional to the species concentration. Scanning over the line gives increased confidence in the measurement because the characteristic feature of the measured species is clearly seen and unwanted spectral features due to interfering species or etalon fringes can easily be identified.

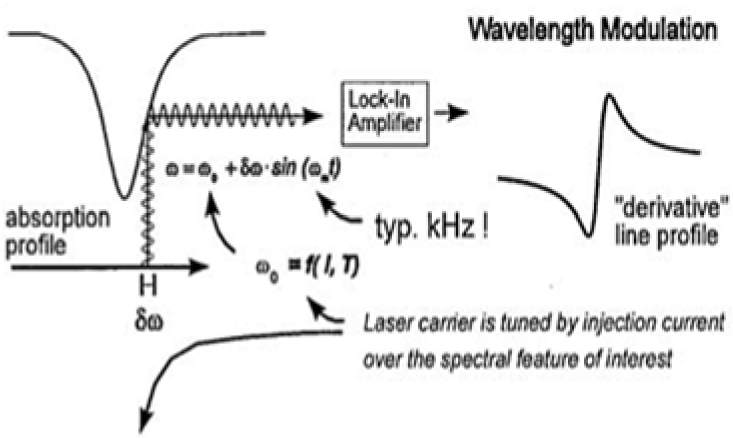

Figure 10: Conventional wavelength modulation (kHz) spectroscopy (Werle et al., 2002).

While mid-infrared lasers operated at cryogenic temperatures cover the fundamental absorption bands required for ultra-sensitive gas analysis, near-infrared room-temperature diode lasers give access mainly to significantly weaker overtone and combination bands. Therefore, the selection of the optimum operating conditions for a gas analyzer is always a tradeoff between the required sensitivity and an operational system. By averaging over periods longer than 1s or by using longer path length the detection limits can be improved. While the predicted sensitivities are based on known line strengths and the performance of a typical TDLAS system, it is in the nature of field measurements that optimum performance is not always achieved due to drift effects and other interfering disturbances (Werle et al., 1993). To cope with these problems different approaches based upon signal processing (Werle et al., 1994) and double modulation techniques (Werle et al., 1999) have been proposed and successfully applied.

Wavelength modulation absorption spectroscopy

Wavelength modulation absorption spectroscopy (WMAS) together with diode lasers or sometimes referred to as tunable diode laser absorption spectroscopy, TDLAS, is a useful technique for sensitive detection of atomic and molecular species under a variety of conditions. The technique is mostly used for environmental monitoring, remote sensing, spectrochemical applications, as well as for combustion analysis.

In the early days of laser spectroscopy the absorption technique was not seen as a viable alternative to other types of laser-based spectroscopic techniques for sensitive detection of atoms and molecules (primarily fluorescence and ionization techniques). One reason was that very few tunable laser sources could, at that time, provide the stable intensity that is required for absorption measurements. Another was that absorption instrumentation was often limited by fluctuations in the transmission of the optical systems (e.g. from the atmosphere or atomizers). This gave fluorescence and ionization techniques (which measure a signal from a ‘low’ light level) an edge over absorption techniques (which measure the signal from a ‘high’ light level).

The first step towards the realization of a powerful laser-based absorption technique was the development of single-mode diode lasers in a variety of wavelength regions. Diode lasers combine good stable intensity with rapid tunability, although only over a limited wavelength region at a time, restricted by mode-hops. It was later realized that the full power of laser-based absorption techniques could be obtained only when the absorption technique was combined with some kind of modulation technique. A variety of modulation techniques have therefore been scrutinized throughout the years. In addition, modulation of the wavelength was preferred to modulation of the power, and smooth and sinusoidal-like modulation was more powerful than an on-off type of modulation (as had been used hitherto in applications encompassing pulsed lasers). This was the basis from which diode laser-based wavelength (or frequency) -modulated absorption techniques were developed during the last decades.

There are two basic reasons why a laser based absorption technique can benefit from the WM technique. One is that an assessment of the concentration of an analyte by direct absorption technique needs to be based upon the difference between two large signals: the detector signal in the presence and absence of the analyte, which, for spectroscopists, is often synonymous with detecting the signal on and off resonance, respectively. This is accomplished by either jumping on/off resonance or by continuously tuning the wavelength over the resonance, which can both be readily performed by modern diode lasers. The other reason, which is gives the WMAS technique its high detectability, is that a smooth modulation of the wavelength at a certain frequency f, often in the kHz_MHz-range, followed by detection of the signal at a certain harmonic of this, nf, where $n = 2, 3, 4...$, shifts the detection to higher frequency, where the $1/f$ noise, which dominates at low frequency, is significantly smaller.

The wavelength of the light is modulated around a given center wavelength at a frequency f with a certain wavelength modulation amplitude. The light is passed through a reservoir whose constituents are to be determined due to a certain fraction of the light being absorbed and the transmitted light is detected by a suitable detector, e.g. a photodiode. The detector signal is fed to a lock-in amplifier in order to extract a certain *n*th harmonic of the detector signal at a detection frequency nf (where $n = 1, 2$, etc) with a bandwidth given by the inverse of the integration time. The most common light source used with wavelength modulation absorption spectroscopy is the diode laser, due to its narrow bandwidth and rapid frequency tunability. The output of a diode laser can be conveniently modulated through its injection current. Applying a small sinusoidal modulation (with a modulation frequency f) to the injection current, $I_{ic}(t)$ of the form:

$$I_{ic} = I_c + I_a \cos(2\pi f t) \tag{21}$$

where I_c represents the center injection current and I_a the injection current modulation amplitude, giving rise to a corresponding modulation of the wavelength of the diode laser light (Kluczynski et al., 2001).

In detecting WMS-2f experimentally, a sinusoidal frequency modulation is applied to a probe laser, which is then scanned across a sharp absorption peak. If the laser is modulated about the center of the peak, the laser samples lower absorption regions on either side of the peak two times for every full frequency modulation. This results in an amplitude modulation that is at twice the frequency as the laser modulation.

In comparison, modulating the laser frequency on the side of the peak produces an amplitude modulation at the same frequency as the laser, and modulating the frequency while probing the flat baseline produces no amplitude modulation at all. The amplitude modulations are analyzed with phase sensitive demodulation, or lock-in, techniques. If the laser is scanned over the peak while being frequency modulated, and the resulting amplitude-modulated signal is demodulated at the frequency that the laser is being modulated, then the first derivative of the absorption feature is recovered. Because the demodulation frequency is the same as the laser modulation frequency, the demodulated signal is known as the WMS-1*f* signal. Similarly, if the amplitude modulations are demodulated at twice the laser frequency modulation, then the second derivative of the peak is obtained. This is known as the WMS-*2f* signal. The different demodulated and true signals are shown in figure 11. The demodulated signals are sensitive to the overall absorption feature for the WMS-1*f* and WMS-2*f* signals, respectively. The WMS-2*f* detection technique involves parking a frequency modulated laser at the center of a target absorption peak and then monitoring the resulting signal that has been demodulated at twice the modulation frequency of the laser.

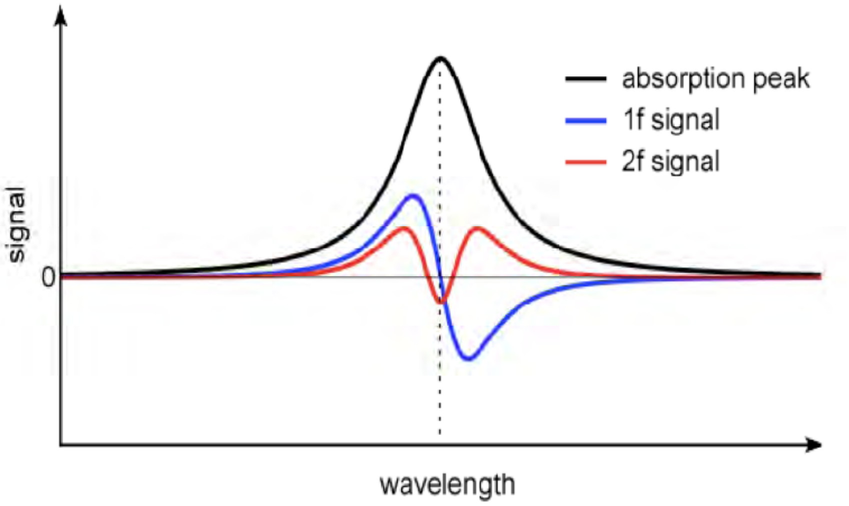

Figure 11: Illustration of the direct, first, and second harmonic absorption lineshapes.

The fundamental detection frequency can be set far above DC. Since most detection systems have a noise profile, the noise increases exponentially at lower frequencies towards DC. Many types of lasers can be modulated at frequencies well over 1 MHz. Lock-in detection techniques can provide arbitrarily narrow detection bandwidths. Depending on the time constant selected, lock-in techniques can easily provide detection bandwidths of less than 1 KHz, further reducing the noise contribution from the detection system, and hence increasing overall sensitivity. The WMS-2*f* signal discriminates against net offsets and broad absorption features in the background. Because the WMS-2*f* signal is proportional to the curvature of the absorption feature, the WMS-2*f* technique is sensitive to “sharp” spectral features only, that is features that have a FWHM comparable to the degree of the frequency modulation (Daylight solutions Inc., 2007).

Experimental equipment of wavelength modulation absorption spectroscopy

The core components of a wavelength modulation absorption spectroscopy set-up are the diode laser, temperature and current controller, sample compartment, photodiode, function generators and the lock-in amplifier. Figure 12 shows the core components in an experimental set-up for WMAS.

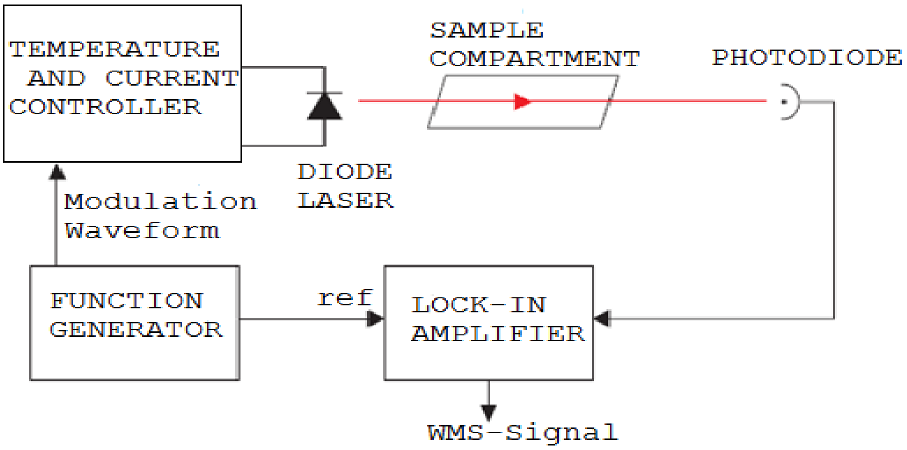

Figure 12: Typical experimental set-up of wavelength modulation absorption spectroscopy.

The usage of diode laser has increased rapidly during the last years. The main reason for this are that their performance has become more stable, their output powers have increased and more wavelength has become available while their price has concurrently dropped. They are today being used with great success in optical communication, CD players, Line code readers, spectroscopy etc. The diode laser was developed from the simplest of semiconductor light sources. Diode lasers, or semiconductor lasers, are produced as a compound of different materials. The materials used depend on which wavelength the laser is manufactured to produce. It is today possible to reach wavelengths between 0.4 to 29 μm with different types of diode lasers. The majority of the diode lasers are made of doped materials from group III (e.g. Al, Ga, In) and group V (e.g. N, P, As, Sb) in the periodic system. The first types of lasers produced were the homojunction lasers but they are obsolete today in favor to heterojunction lasers. Homojunction lasers have a more simple construction than heterojunction laser.

A homojunction diode laser is created by joining semiconducting materials. One of the materials is n doped, has an excess of electrons, and the other one is *p* doped which means it has an excess of positive carriers, called holes. When a voltage is applied over the semiconducting material the electrons from the conduction band and holes from the valence band will diffuse through the interface and be able to recombine. As a result, photons will be emitted with the energy corresponding to the band gap. The homojunction lasers have a major drawback; they cannot work at room temperature. This is partially due to losses from absorption in the junction.

Losses from absorption of the photons in the cavity for example, can be reduced in heterostructure diode lasers. Heterojunction lasers are much more used nowadays than homojunction lasers because they can operate at room temperature and do not need to be cooled. The heterojunction lasers have an active layer, which is a semiconductor, sandwiched between the two semiconductor layers with higher band gap energies.

The key characteristics of a diode laser when being used in absorption spectroscopy is the ability to tune its wavelength. This can be accomplished either by changing the temperature of the laser or its injection current. As the current can be altered swiftly, the wavelength will also be scanned very rapidly. The maximum modulation frequency for a standard diode laser is in the GHz range although being significantly lower (KHz-MHz) under normal wavelength modulation conditions. Typical modulation amplitudes for WMAS are a few times larger than the spectral width of the signal to be detected. The spectral width of the diode laser varies from a few MHz to tenths of MHz, depending on the type of laser.

The current controller is used to provide the diode laser with an injection current. One important property of the current controller is the current limit set. The current limit is important because it is very easy to exceed a certain current which may damage the laser. The temperature controller keeps the diode laser at a very specific temperature since a small sift in temperature will change the wavelength of the diode laser.

The function generator is used to sweep the injection current with a saw tooth signal into the diode laser. The ramp amplitude and the frequency settings are normally altered to achieve the optimal signal since they affect the signal. It is also used to produce high frequency signal that is to be detected by the lock-in amplifier and provides the reference signal for the lock-in amplifier. The upper frequency limit is set by the frequency range of the reference channel in the lock-in amplifier. The modulation frequency cannot be higher than half the reference frequency limit when second harmonic (2*f*) of the modulation signal is being studied.

The element or sample to be detected in WMAS must obviously reside somewhere. The three most commonly used sample compartments are a cell, the atmosphere and an atomizer. A cell is usually a low-pressure, room-temperature environment in which the element of interest has been deposited. It gives a continuous signal relatively free of disturbance and with a very small collision broadening because of the low-pressure condition. The atmosphere is the surrounding present when the technique is used for environmental monitoring and remote sensing. The pressure is most often atmospheric while the temperature depends on the exact location. The atomizer is an atmospheric-pressure, high-temperature surrounding. The atomizer is a sample compartment used for spectrochemical analysis. Atomization is needed in order to convert a sample (solid, liquid, or gaseous) into free atoms, since such are necessary prerequisite for spectrometric techniques used for elemental analysis.

The photodiode is just like the laser diode, made up of a p-n junction with a voltage applied across it. Light impinging on the photodiode will be absorbed if its energy is equal or larger than the bandgap energy. This absorption produces electron-hole pairs that will, under the influence of electric field, drift in opposite directions across the depletion region (electron towards the cathode and holes towards the anode).

A lock-in amplifier is used in wavelength modulation absorption set-up to extract signals at a specific frequency and phase from an environment containing noise that is several orders of magnitude larger than the small analytical signal. The lock-in amplifier, in common with most AC indicating instruments, provides a DC output proportional to the AC signal under investigation. The special rectifier, called a phase-sensitive detector (PSD), which performs this AC to DC conversion forms the heart of the instrument. It is special in that it rectifies only the signal of interest while suppressing the effect of noise or interfering components which may accompany that signal. The noise at the input to a lock-in amplifier is not rectified but appears at the output as an AC fluctuation. This means that the desired signal response, a DC level, can be separated from the noise accompanying it in the output by means of a simple low-pass filter.

In order to function correctly the detector must be programmed to recognize the signal of interest. This is achieved by supplying it with a reference voltage of the same frequency and with a fixed phase relationship to that of the signal. This is commonly done by ensuring that they are derived from the same source. The use of such a reference signal ensures that the instrument will track any changes in the frequency of the signal of interest. This inherent tracking ability allows extremely small bandwidths to be defined for the purpose of signal-to-noise ratio improvement.

Scattering spectroscopy

Light is considered to be scattered when a light beam, passing through a sample does not continue in its original straight path but it is deflected to other directions by undergoing multiple reflections in the sample, until they are either absorbed or converted to other form of energy, or escape from the medium.

Different types of scattering processes do occur and each one of them depends on the material and the wavelength of the incident beam. If the particles causing the effect are small compared to the wavelength, it is called the Rayleigh or Raman scattering. An exception to this is when it is resonant process. Resonant process is obtained if an atomic or molecular system irradiated by light with an energy corresponding to the energy separation between two of its energy state. On the other hand if the particles are large in comparison with the wavelength, then it is called Mie scattering. The more complex Mie theory is used to describe scattering event when the scatterer is too large to be considered as a Rayleigh scatterer. Mie scattering is not strongly wavelength dependent. For natural particle distribution in the atmosphere, the oscillations are smeared out and the scattering intensity varies only slowly with the wavelength. The intensity increases towards shorter wavelength with an approximate λ^{-2} dependence. In the atmosphere Mie scattering from particles is normally more important than Rayleigh scattering from molecules. The visibility is determined by Mie scattering which can be understood from the fact that visibility would be hundreds of kilometers in the absence of particles in the atmosphere.

The Rayleigh and Mie scattering are elastic effects and the energy is conserved in the processes. Inelastic type of scattering where there is energy change in the process, leads to a shift in the wavelength of the radiation source and is referred to as Raman scattering.

A scattering material is normally described using an average scattering coefficient, μ_s (cm^{-1}), that states the probability of scattering per unit length, together with an average angular distribution function (the scattering phase function). On large spatial scales scattering properties can be summarized by stating the equivalent isotropic scattering process. The so called reduced scattering coefficient, μ'_s (cm^{-1}), can alone describe light scattering, and is related to the scattering coefficient and phase function g as stated in Eq. (22), where g is the average of the cosine of the scattering angle.

$$\mu'_s = (1 - g)\mu_s \tag{22}$$

The scattering phase function is describe as the average scattering angle distribution weighted over the probability of each scattering angle and is expressed by

$$g = \int P(\theta)\cos\theta d\omega = \int_{4\pi} P(s, s^{/}).(s, s^{/})d\omega , \tag{23}$$

where $P(\theta)$ equals the probability of a photon being scattered in the direction θ, and $P(\boldsymbol{s},\boldsymbol{s}^{/})$ equals the probability of a photon coming in from direction $\boldsymbol{s}$ is redirected into direction $\boldsymbol{s}^{/}$. The reduced scattering coefficient approximately exhibits a λ^{-n} dependence, where n is mainly dependent on scatterer size. The scattering coefficient and the angular distribution are more sensitive to variations in size and refractive index, and exhibit a more complex wavelength dependence (Mourant et al., 1997).

The scattering process normally maintains the original frequency or the wavelength of the light, but it may also change, due to Doppler and Raman effects. Light scattering also attenuates the transmitted light depending on how dense or thick the medium may be. The attenuation of the light beam due to scattering may often be approximated by the formula

$$I(x) = I(o)\exp(-\beta x) \tag{24}$$

where the coefficient β being the scattering coefficient, also depends on wavelength, and the number of scatterers.

Gas in scattering media absorption spectroscopy (GASMAS)

GASMAS is a new technique within the field of high-resolution laser absorption spectroscopy. The technique shows the possibility of detecting molecular oxygen within materials such as polystyrene foam, wood, fruit, sugar, wheat flour and granulated salt. Using modulation techniques, even in the presence of a large noisy background, the implanted gas gives rise to tiny but narrow signal that can be picked and this gave a name to a measuring technique known as gas in scattering media absorption spectroscopy (GASMAS) (Sj holm et al., 2001).

The GASMAS technique provides new opportunities for studying gas enclosures in natural and synthetic materials. So far the only gas that has been studied under this technique is molecular oxygen and the narrow absorption lines studied belongs to the A- band. Figure 13 shows the narrow absorption lines belonging to the A-band of molecular oxygen. This new technique can be used for characterization and diagnostics of free gas in scattering solids and turbid liquids. Initial demonstrations included proof of-principle measurements of the embedded oxygen concentration relative to an equivalent column of air and of the internal gas pressure as well as assessment of the gas exchange.

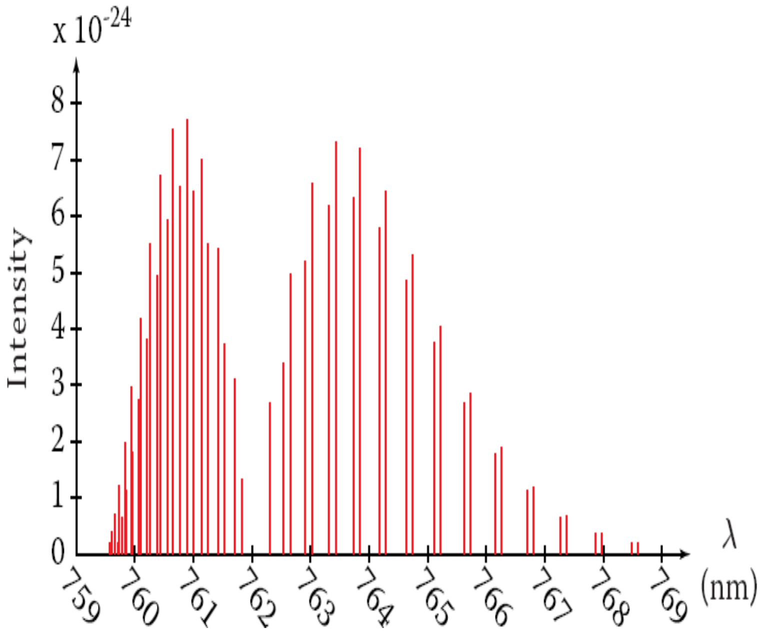

Figure 13: The narrow absorption lines belonging to the A-band of molecular oxygen. (HITRAN database, Sept. 2005).

There are some basic but very important requirements that the technique must fulfill for any ambient gas absorption measurement technique to be useful. It must be sufficiently sensitive to detect the gas under consideration and be specific, which means that the result of the measurement of a particular gas must be neither positively nor negatively influenced by any other trace gas species simultaneously present in the probed volume of air.

The slow wavelength dependence of absorption and scattering of solids stands in great contrast to the sharp absorption features exhibited by free gases. While sub-nanometer resolution is seldom needed to resolve absorption or scattering spectra of solids, the spectral width of the oxygen absorption lines around 760 nm is about 3GHz FWHM (atmospheric conditions), corresponding to about 0.006 nm. It is this contrast that allows detection of gases contained within porous materials to be much stronger processes even when there is bulk scattering and/or absorption.

After having injected light into a highly scattering and porous material, a gas absorption imprint is generated as the light passes through gas-filled pores. Thus, a spectrum carrying high-resolution gas absorption imprints may be detected. GASMAS is based on Tunable Diode Laser Absorption Spectroscopy (TDLAS) technique, which is the use of diode lasers in absorption measurement, and spectra is acquired sequentially by scanning a narrow-band light-source across an absorption feature. The obtained signal, often a WMS-2*f* signal, is referred to as a GASMAS signal.

The pores may be anything from a single large cavity to the innumerable microscopic cavities of a compressed powder. In the case of a more or less homogenous porosity, the magnitude of absorption imprint will increase with an increasing source-detector separation. High scattering and accompanying elongation of pathlengths may result in surprisingly large gas absorption imprint. However, at the same time as scattering may enhance the signal in the above described manner, GASMAS is inherently limited by optical interference originating from the highly scattering samples themselves (Svensson, 2008). By letting the injection current have a saw-tooth shape, the wavelength will be repetitively swept. The diode laser is operated with a narrow, single-mode profile to be able to detect the absorption lines.

Scattering process in GASMAS results in the path length being greater than the thickness of the sample. There will be a larger probability to find more gaseous molecules in a highly scattering material, since the light will travel a longer distance along more complicated pathways. Therefore, the effective gas absorption in the scattering medium can be related to the concentrations in a column of free air. Figure 14 illustrates the parts the light travels in a scattering sample, which is highly dependent on the scattering of the sample.

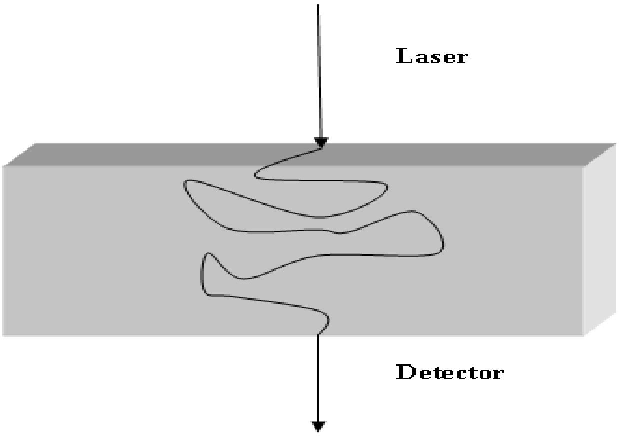

Figure 14: The distance the light travels in a scattering sample is highly dependent on the scattering of the sample.

This scattering process complicates the use of Beer-Lambert law, since the actual trajectory is more difficult to correlate with the sample thickness. When dealing with absorption spectroscopy it is of great importance to normalize the signals, in order to be able to compare results. The measured intensity can vary depending on the sample geometry, the alignment and some other things. In GASMAS, the *2f* signal is normalized using the direct signal, S_{Dir}. This normalized signal is referred to as the GASMAS signal and is denoted GMS, i.e.

$$GMS = \frac{S_{2f}}{S_{Dir}} \tag{25}$$

Figure 15 shows the second harmonic component (*2f*) of WMS signal and its corresponding pure absorptive imprint. Thus, the GMS is also proportional to the absorbance as long as the absorbance is small. The S_{2f} is calculated from the peak-to-peak value of the *2f* signal (Bjorkwall and Cassel-Engquist, 2005).

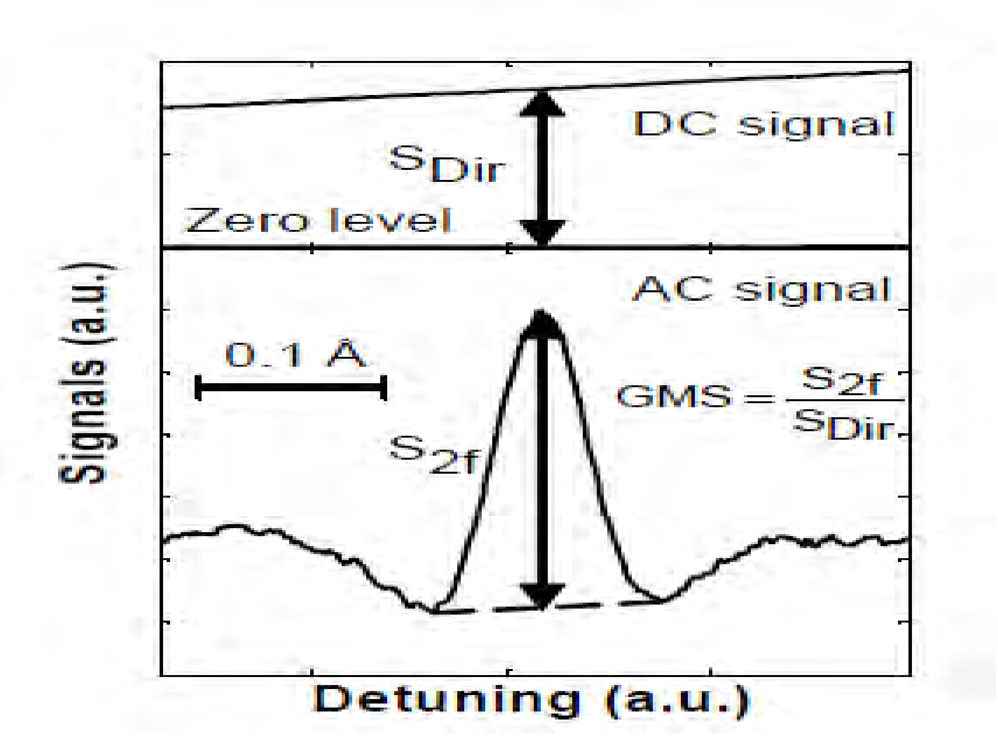

Figure 15: Second harmonic component (*2f*) of WMS signal and its corresponding pure absorptive imprint (Persson et al., 2005).

CHAPTER THREE

SIMULATION AND EXPERIMENTAL METHODS

The first section of this chapter describes the simulation of a second harmonic (2*f*) signal of wavelength modulation spectroscopy (WMS) with written MATLAB codes. The second section describes two experimental set-ups employing different techniques. One of the techniques, wavelength modulation absorption spectroscopy, is used to study the effect of room temperature on the WMS-2f signal and the other to investigate the effect of width and thickness of a scattering medium on the WMS-2f signal. This technique of sensing free gas in a highly scattering and porous media is termed as gas in scattering media absorption spectroscopy (GASMAS).

Simulation of the WMS-2f from wavelength modulation

An algorithm was developed to simulate a second harmonic signal using a model, which is a second Fourier component for a Gaussian profile (H_2^G (x,m)). This is the case where gas pressure is reduced such that pressure broadening is negligible and Doppler broadening is dominant. The simulation of the second harmonic signal was done employing equation 20.

The simulation of the second harmonic signal was done using MATLAB application software [R2010a Matlab 7.10.0, Mathworks Inc]. Figure 16 and 17 respectively shows a structure chart and a flow chart of the simulation program. The algorithm makes use of two matlab codes, one as a function file and the other as the main program, written and saved as m-files that run to simulate the WMS-$2f$ signal.

Matlab codes using numerical integration tools were written and saved as a function file, in a main programme. The function file contains the model to be numerically integrated and the main program uses the function file as part of its execution. The function file uses the extrapolated simpson's rule in an adaptive recursive algorithm. The input parameters for the simulation are the modulation amplitude a, the mean frequencies v, the centre frequency v_{o} and the Half width at Half maximum (HWHM) Δv. The normalized modulation amplitude, m given in the form of the modulation amplitude of the modulation signal was evaluated using equation 18 and the normalized frequencies, x presented in the form of modulation frequencies were also calculated from equation 17. The model was simulated to get the second harmonic signal of wavelength modulation.

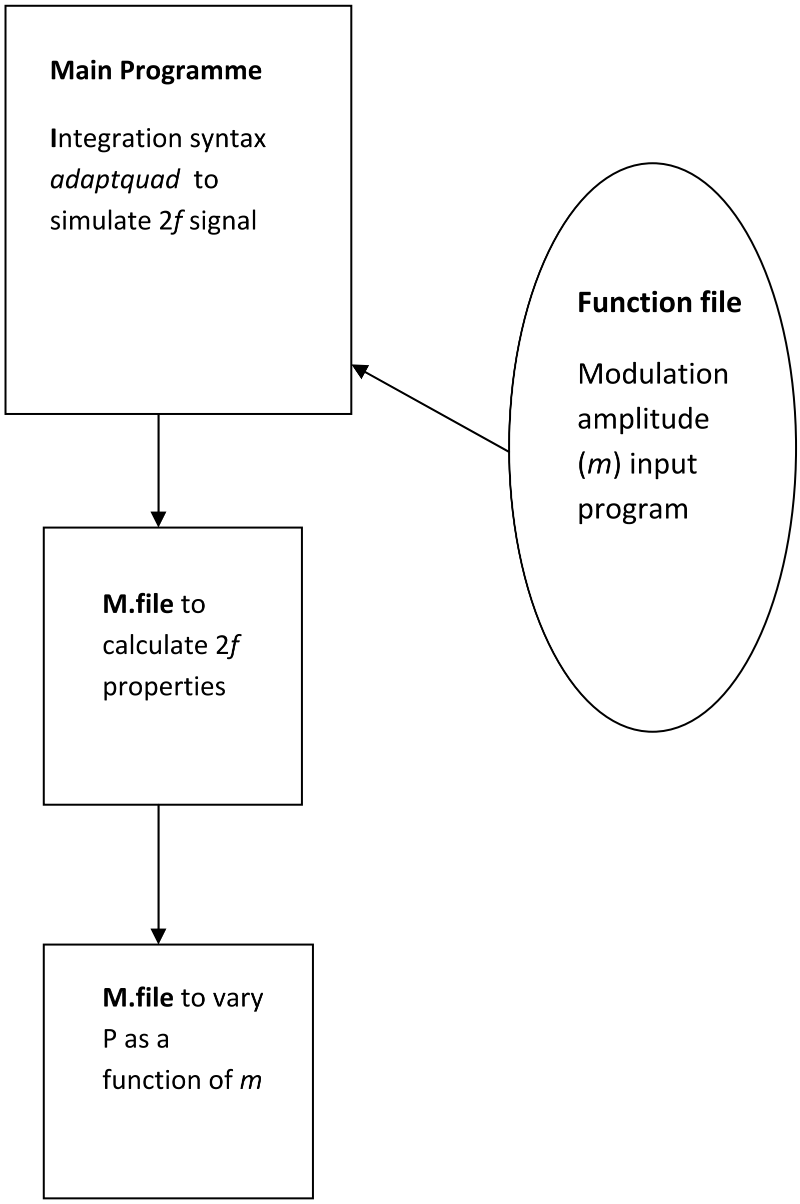

Figure 16: Structure chart of the simulation programme.

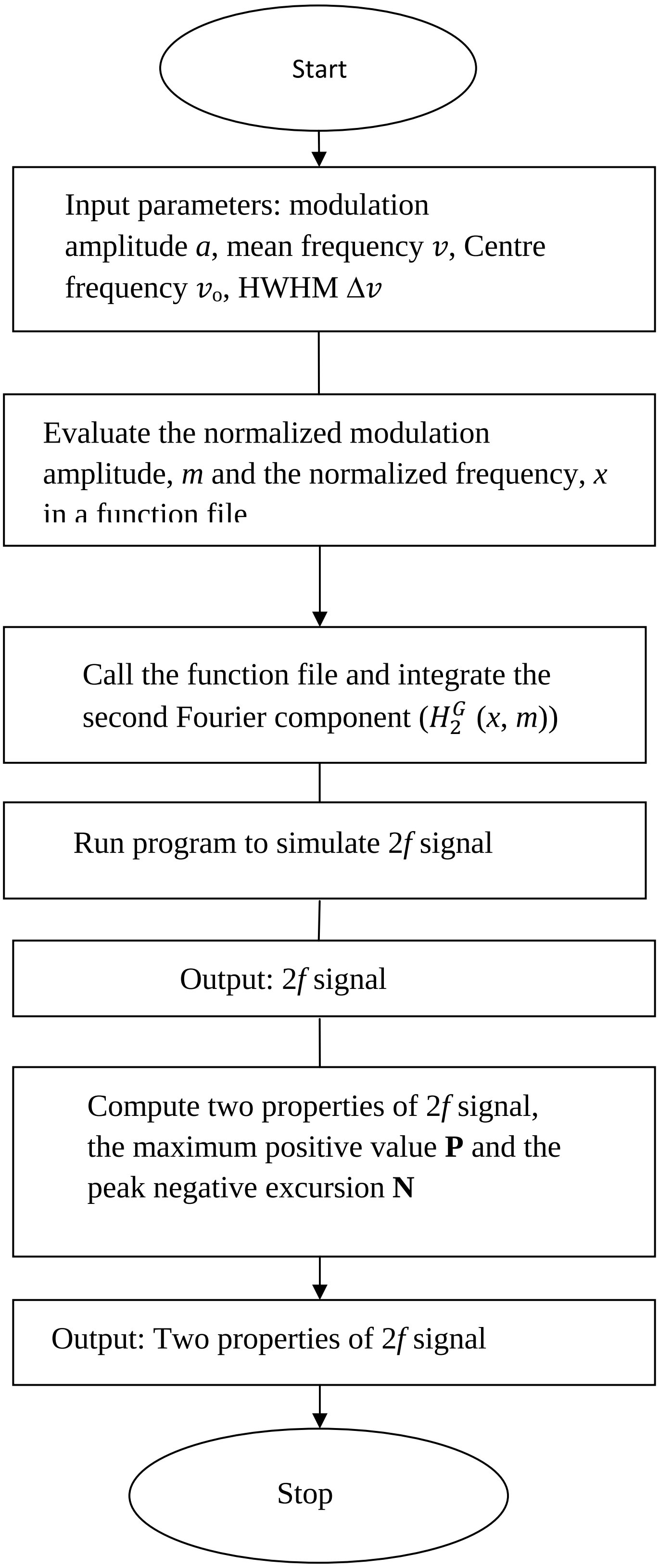

Figure 17: Flow chart of the simulation programme.

The main programme uses the input parameters to evaluate the normalized modulation amplitude *m*. The *m* values after calculation from equation 18 ranges from 0 to 4 at intervals of 0.1.The interval was achieved by carefully choosing the modulation amplitude *a* which ranges from 0 to 12 at an interval of 0.3 as input values. The main programme runs for each value of *m* and corresponding frequencies to obtain the second harmonic, 2*f* signal.

The maximum positive value, **P** and the peak negative excursion, **N** of the simulated second harmonic signal are two properties of the signal computed using the developed MATLAB algorithms. The main programme determines for each plot the maximum intensity of the WMS-2*f* signal as P and also the minimum value as N.

Experimental set-up for wavelength modulation absorption spectroscopy

Wavelength modulation absorption spectroscopy set-up used for this work is illustrated schematically in figure 18. The experimental set-up consists of a distributed feedback semiconductor laser diode (LD-0763-0030-DFB-2), with 5.0 mW maximum power, as a light source. This has been designed for molecular oxygen gas absorption and operates in transverse and longitudinal single mode.

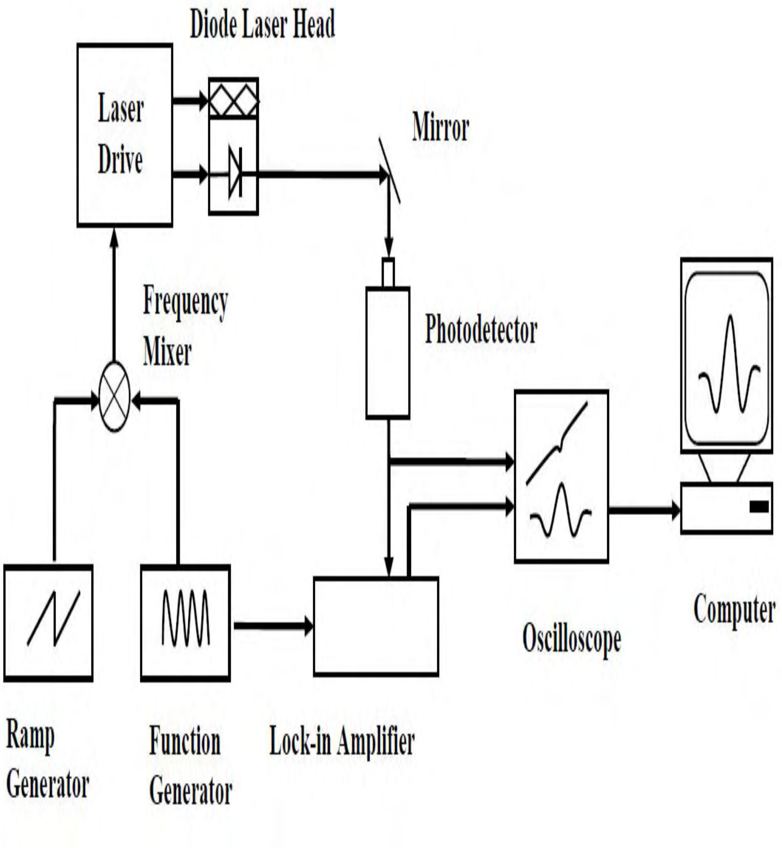

Figure 18: Complete schematic wavelength modulation absorption spectroscopy set-up for WMS.

The diode laser was controlled by a laser diode Combi Controller (THORLABS ITC 502-) system that has dual capabilities; a diode laser driver and a temperature controller. The laser driver provides the current needed to drive the diode laser while the temperature controller controls the operational temperature of the diode. The diode laser is fixed in a diode-laser-head that has a thermoelectrical cooling system. Other uses of the combi controller are for tuning of the current or the temperature of the laser diode. The temperature controller was set to 22.38 ^{o}C while the current limit was set to 100.06 mA. The operational current or temperature depends on the type of absorption line selected for the studies. For this experiment the laser was modulated with functional generators.

Two function generators, one as a ramp generator (TTI 1010A) and the other a function generator (TTI TG 315), were used in the set-up. The ramp generator (RG1) was used to ramp the laser light with a ramp signal of an appropriate amplitude and frequency. A sinusoidal signal of an appropriate amplitude and frequency from the function generator (FG1) was used to modulate the laser light. The ramp and the sinusoidal signal were mixed with a frequency mixer (ZFRSC-2050) and passed unto to the laser via the current of the diode laser via laser diode Combi Controller. The frequency of the sinusoidal signal from the FG1 was also used as the reference signal for the lock-in amplifier.

The light from the diode laser was directed, with the help of plane mirror(s) (PF10-03-P01), onto a custom-made photodetector. The number of mirrors can be increased based on the optical path length required. The light signal was detected with a custom-made photodetector and amplified by an AC source amplifier. The amplified signal was sent to a 100 MHz digital phosphor oscilloscope (Tektronix TDS3014B), referred to as the direct absorption signal, and simultaneously sent to a digital lock-in amplifier (SRS 830 DSP), a key instrument in modulation techniques.

The digital lock-in amplifier instrument uses a technique called phase-sensitive detection to detect the AC signals, in orders of nanovolt, with a very good signal to noise ratio and it has a reference channel frequency that ranges between 1 mHz and 102 kHz. The signal sent to the digital oscilloscope was extracted as wavelength modulated harmonic signal. Thus the direct absorption signal and the second harmonic signal data were then transferred from the oscilloscope using a General Purpose Interface Bus (GPIB) port via USB plug-and-play cable from National Instrument (GPIB-USB-HS) using a developed code in the test and measurement tool box in the MATLAB. The data was stored as matlab file.

Experimental set-up for gas in scattering media absorption spectroscopy

The wavelength modulation absorption spectroscopy set-up described above was modified in order to sense free molecular oxygen gas dispersed within highly scattering media. In the set- up the modulated light is coupled through an optical fibre to the sample. Coupling the laser light into the optical fibre led to weak detection of the light due to coupling loses. The use of the fibre as a transmitting medium was to avoid light absorption of ambient oxygen before the sample. The sample scatters and transmits the light to a detector (PMT) (EMI 9558 QA).

As described previously in wavelength modulation spectroscopy, signals (direct absorption signal) are sent to the digital phosphor oscilloscope, and the phase-sensitive lock-in amplifier. The direct absorption signals as well as the WMS-2*f* signals were recorded as described previously in wavelength modulation absorption spectroscopy experiment.

Plate 1 shows the complete set-up for gas in scattering media absorption spectroscopy (GASMAS) for trans-illumination measurements at the laser and Fibre Optics Centre (LAFOC) in Cape Coast, Ghana with A as the ramp generator, B as the function generator, C as the laser diode controller, D as the photomultiplier tube, E as the sample plate, F as the digital phosphor oscilloscope, G as the lock-in amplifier and H as the frequency mixer.

The set- up described can be modified depending on the type of sample and laser being used, as well as the objective of the research work.

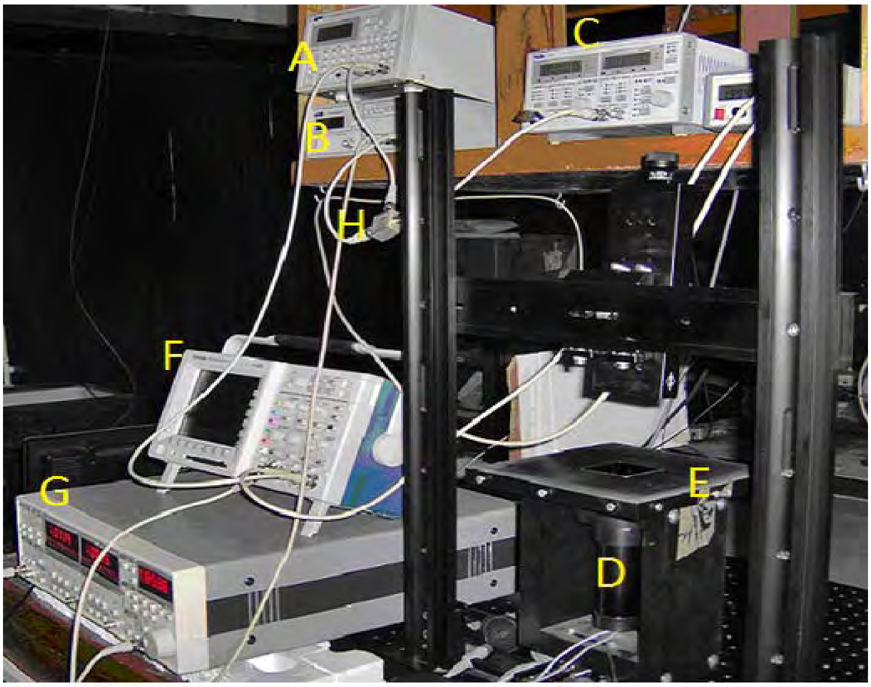

Plate 1: Complete set-up for gas in scattering media absorption spectroscopy (GASMAS) for trans-illumination measurements.

Wavelength modulation absorption spectroscopic measurement of free molecular oxygen gas in free space

Wavelength modulation absorption spectroscopy experiment was performed to measure free molecular oxygen gas and to study the effect of room temperature on WMS-2*f* signal using the set-up in figure 3. Some of the equipments used for the measurement are shown in plate 2.

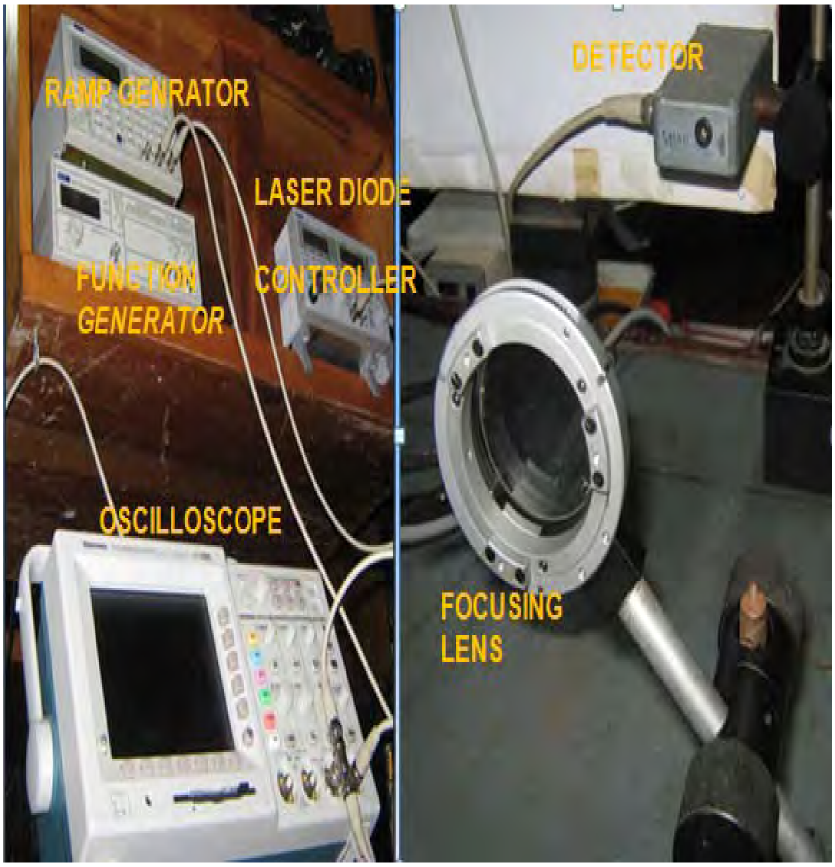

Plate 2: Some of the equipment used for the wavelength modulation spectroscopy set-up.

Using the wavelength modulation absorption spectroscopy experimental set-up described previously, an ideal second harmonic (2*f*) wavelength modulation spectroscopy (WMS) signal was obtained with a good signal to noise ratio by current tuning the diode laser to the molecular oxygen gas absorption line at an operational current of 81.54 mA and setting the time constant and the sensitivity on the lock-in amplifier to 1 ms and 20 mV respectively after ramping the signal with a 2 V peak to peak voltage and a 4.00 Hz frequency superimposed on a sine wave generated from a modulation frequency of 10.00 KHz and amplitude which was set in such a way to obtain the optimal signal. The wavelength of the diode laser was monitored with a spectrometer (USB4000 US-VIS spectrometer) from ocean optics.

Measurements were taken by varying the optical pathlength of the modulated light from the diode laser from 200 cm to 1000 cm at an interval of 100 cm at room temperature of 27^oC. The signals were acquired as previously described in the wavelength modulation absorption spectroscopy set-up. The procedure was repeated for room temperatures of 25^oC and 24^oC. The ambient temperature was achieved by the use of a White-Westinghouse spilt type air conditioner (WSA245T5MB, 2.5 HP) in the laboratory.

Wavelength modulation absorption spectroscopic measurement of free molecular oxygen gas in highly scattering medium

Trans-illumination measurements were made on different set of highly light scattering samples, namely polystyrene foam and memory (polyurethanes) foams. Two types of locally branded polyurethane foams (latex foam and ash foam) were used in this work. In this experiment an ideal second harmonic (2*f*) signal was obtained with a good signal to noise ratio by current tuning the diode laser to the molecular oxygen gas absorption line as done in the wavelength modulation absorption spectroscopy experiment using the GASMAS set-up described previously after placing a polystyrene foam of dimensions 5x1x1 cm^3 directly on the sample table, attached to the PMT. Here the time constant and the sensitivity on the lock-in amplifier were set to 300 ms and 200 mV respectively after ramping the signal with a 2.00 V peak to peak voltage and a 10.00 Hz frequency superimposed on a sine wave generated from a modulated frequency of 10.00KHz and amplitude which was set in such a way to obtain the optimal signal. The second harmonic (2*f*) was then acquired from the digital phosphor oscilloscope the same way it was done in the wavelength modulation absorption spectroscopy experiment. The width of the polystyrene foams was then varied from 1.0 cm to 5.0 cm and data was recorded for each sample of the polystyrene foam. The whole experimental procedure was repeated for the two types of locally branded (polyurethane) foams.

Second set of measurements were performed, by varying the thickness of the polystyrene foams. This was done to study how the thickness of a scattering sample affects the second harmonic (2*f*) signal. The thickness of the polystyrene foam was varied from 1 cm to 5 cm. The modulated laser light was allowed to go through the sample and the second harmonic signal was acquired. The whole experimental procedure was repeated for the two types of locally branded (polyurethane) foams.

CHAPTER FOUR

RESULTS, ANALYSIS AND DISCUSSION

Results obtained from the simulation of the wavelength modulation spectroscopy second harmonic (2*f*) signal are presented and discussed in the first section of this chapter. The second section deals with the results, analysis and discussion of the wavelength modulation absorption spectroscopic measurement of free molecular oxygen gas in free space as well as oxygen gas in highly scattering media.

Simulation

Some of the simulated wavelength modulation spectroscopy second harmonic (2*f*) signals obtained from the simulation are shown in figure 19. It can be seen from the simulated signals that the intensity and the bandwidth of the simulated WMS-2*f* signal were increasing as the normalized modulation amplitude *m*, obtained from the modualtion amplitude *a*, was increasing. The simulated WMS-2*f* signal with *m* value of 2.1 has the highest intensity and the intensities of the signals decrease as the *m* values exceed 2.1. This shows the effect of *m*, which depends on the modulation amplitude *a*, on the intensity as well as the bandwidth of the WMS-2*f* signal.

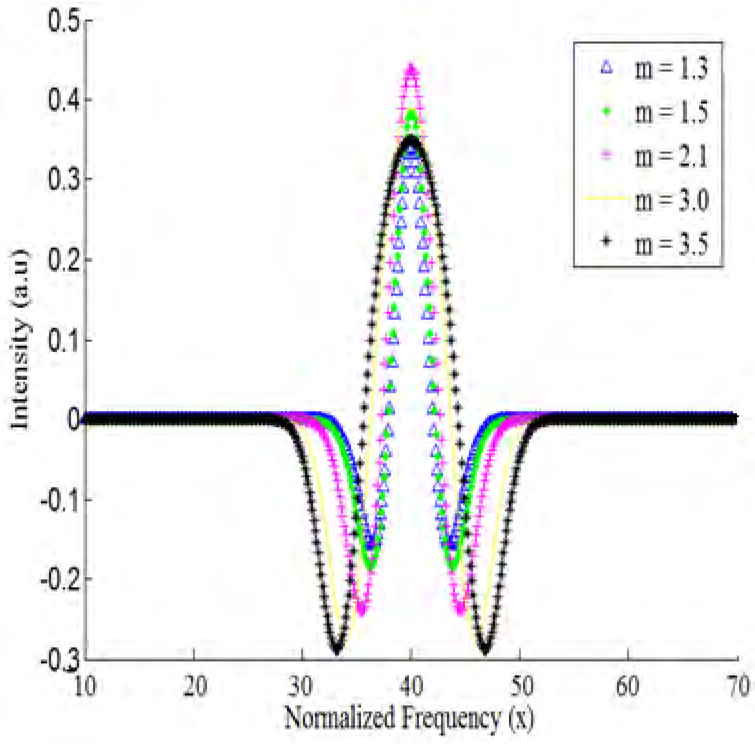

Figure 19: Some simulated second harmonic signals at various normalized modulation amplitudes, *m*.

Figure 19 again shows that the maximum intensity of some of the simulated WMS-2*f* signals coincide, implying that certain *m* values gave similar intensities. This is due to the fact that the intensity of the simulated WMS-2*f* signals increases to a certain point and start to decrease even though the *m* values were being increased. The *m* values were limited to 4.0 because it was observed from the simulation that the intensities of the WMS-2*f* signals decrease after *m* value of 2.1. A plot of the maximum positive values, **P** of the simulated WMS-2*f* signals as a function of the *m* is shown in figure 20. Values of *m* that maximise the second harmonic signal and eventually optimise the signal to noise ratio were of much concern.

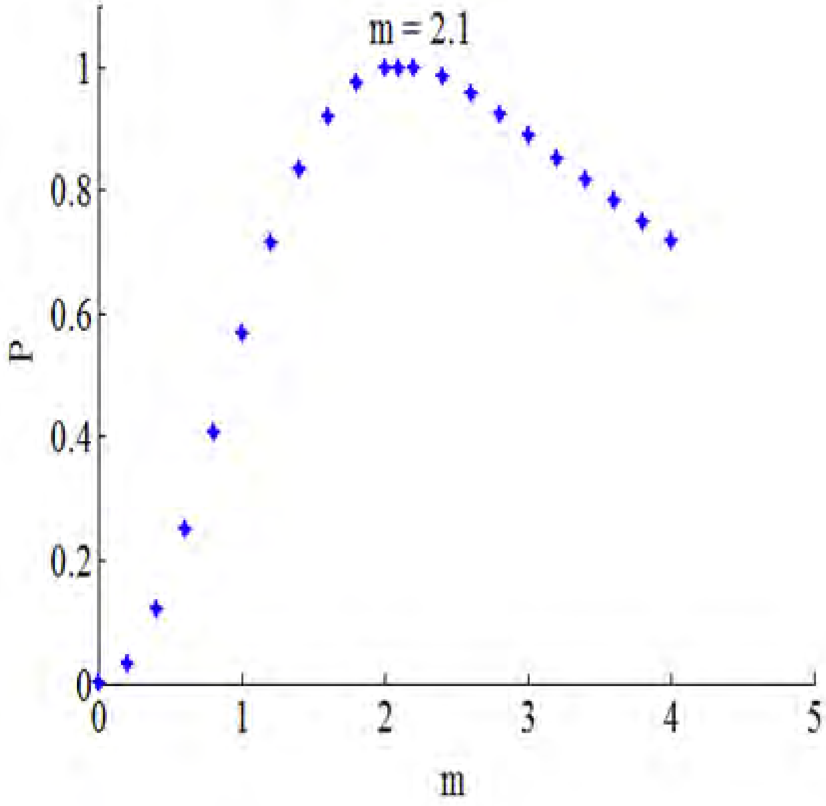

Figure 20: The positive part, P of the lineshape as a function of normalized modulation amplitude, m for an absorption line with Gaussian profile. The peak value of P occur at m = 2.1.

The use of the Matlab approach for the simulation was a simple and fast means of demonstrating the influence of *m* on WMS-*2f* signal. The entire duration for executing one simulation was found to be less than 2.0 s using the tic and toc commands in Matlab. Knowing the behaviour of the WMS-*2f* signal from the simulation, one can maximise second harmonic signal and optimise the signal to noise ratio in wavelength modulation spectroscopy techniques. Again, the simulated result will assist one to gain better understanding of the behavior of the second harmonic signal in wavelength modulation absorption spectroscopy and the effect of modulation amplitude *a*, and thus normalized modulation amplitude, *m* has on it.

Wavelength modulation absorption spectroscopic measurement of free molecular oxygen gas in free space.

Wavelength-modulation absorption spectroscopy technique was used to measure free molecular oxygen gas in free space at different optical pathlength and at three different room temperatures. The spectrum of the diode laser used in this experiment is as shown in figure 21. The wavelength of the diode laser, monitored with a spectrometer (USB4000 US-VIS spectrometer from ocean optics), was found to be 761.9 nm. This line belongs to molecular oxygen A-band and has a narrow bandwidth.

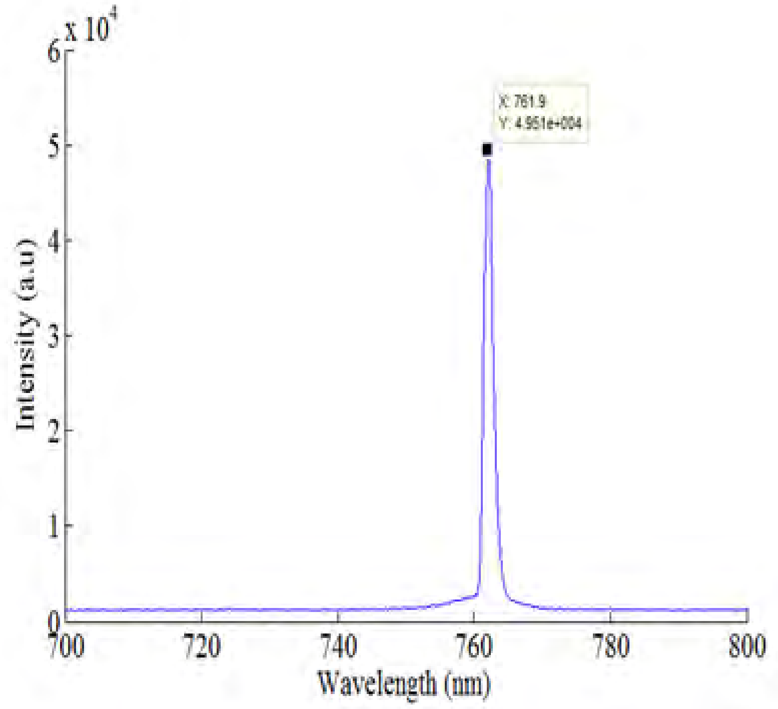

Figure 21: Spectrum of the diode laser lasing at 761.9 nm measured with a USB4000 UV-VIS spectrometer from Ocean Optics.

A graph of an unprocessed direct absorption signal and WMS-2*f* absorption signal acquired from the digital oscilloscope during the experiment as a result of the absorption of free molecular oxygen gas is shown in Figure 22.

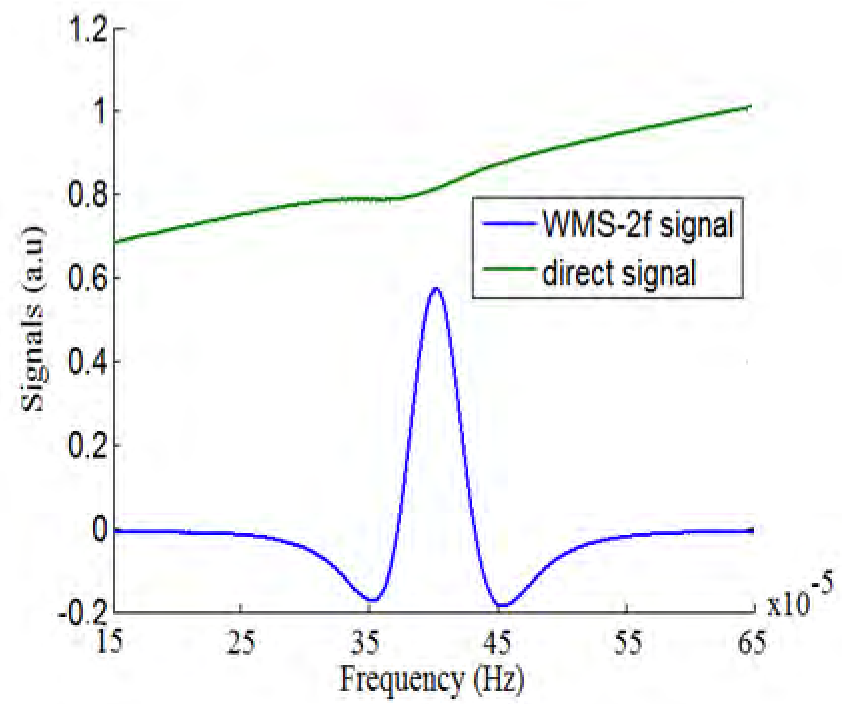

Figure 22: Sample of an unprocessed direct absorption signal and WMS-2*f* signal obtained from an oscilloscope.

It could be seen from the figure that the direct absorption signal has a small absorption dip compared to the WMS-2*f* signal. The small absorption dip in the direct absorption signal, which is detected at low frequency where noise is very high, is as a result of increased background noise. This decreases the signal to noise ratio in the direct absorption measurement. The background noise in the absorption signal makes it difficult for accurate information to be obtained. Thus a higher frequency would improve the signal to noise ratio (S/N) of the signal. The WMS-2*f* signal was detected at twice the modulation frequency using lock-in detection method. This technique not only improves the S/N ratio but also reduces strongly the sloping of the direct absorption signal. The WMS-2*f* signal is better when it comes to data analysis due to it substantial sensitivity enhancement and noise immunity.

The WMS-2*f* signal was then processed to aid evaluation of the signals' intensity by putting it at the zero baseline. This was done by retrieving the data from the WMS-2*f* signal and processed using a Matlab programme. Figure 23 shows a processed plot of the WMS-2*f* absorption signal. The program then determined the maximum point, which corresponds to the intensity of the WMS-2*f* signal.

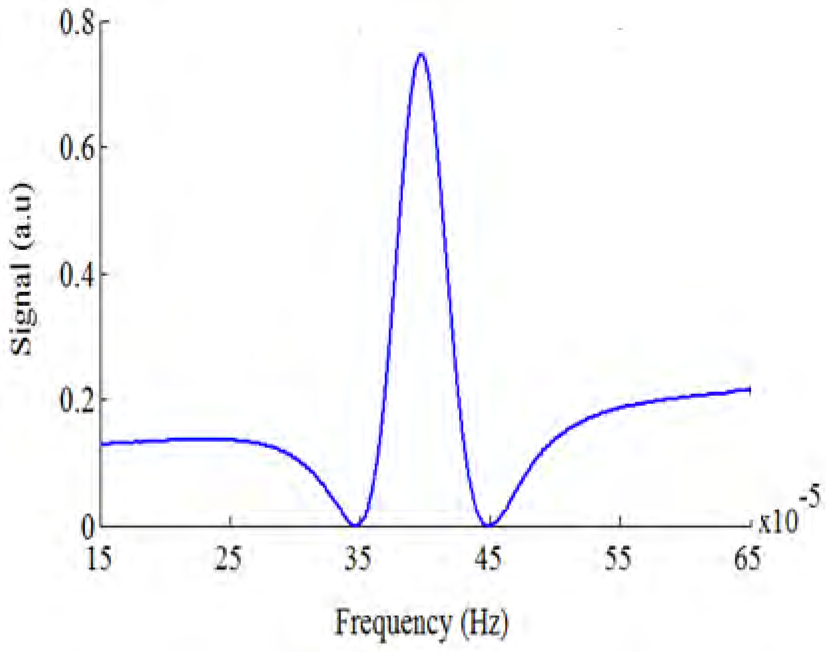

Figure 23: Sample of a processed WMS-2*f* signal.

A graph of the intensities of the WMS-2*f* signals as a function of the optical pathlength at different room temperatures is shown in Figure 24.

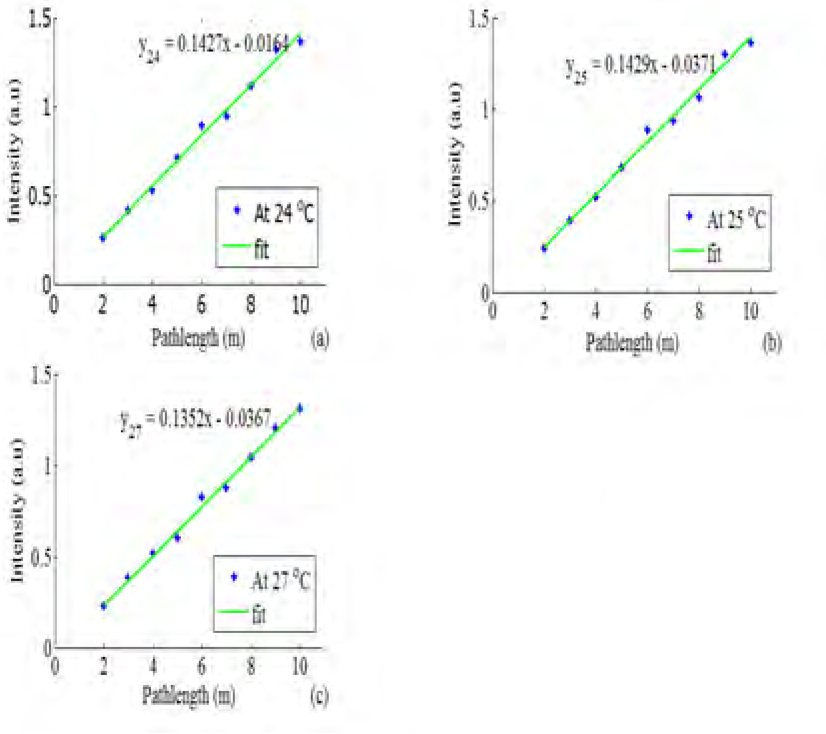

Figure 24: Graphs showing the intensities of WMS -2*f* signals as a function of optical pathlength at different temperatures. (a) at a temperature of 24^{0}C, (b) at a temperature of 25^{0}C, (c) at a temperature of 27^{0}C.

From the graphs in figure 24 it can be seen that there are increases in the intensities of the WMS-2*f* signals as the optical pathlength increases. This implies that the longer the pathlength, the greater the intensity of the absorption signal. This could be attributed to the fact that as the pathlengths were increased more of the oxygen molecules were encounted.

Different slopes and intercepts were obtained from the graphs in figure 24 when the points were linearly fitted. The differences in the slopes is an indication that the intensities of the WMS-2*f* signals were affected by the temperature variation. The intercepts from the fits could be attributed to scattering by some foreign materials. This is because in the absence of scattering, the beer lambert law should not have an intercept. The Beer Lambert law is commonly used in spectroscopy to derive the absorption coefficient of non-scattering medium from continuous wave (CW) measurement (Sassaroli & Fantini, 2004).

The intensities of WMS-2*f* signal as a function of optical pathlength at different temperatures are all shown in Figure 25. It can be seen from the graph in figure 25 that the intensity of the WMS-2*f* signal increase as the temperature decreases at a particular optical pathlength. That is the intensity of the WMS-2*f* signal increase slightly as the room temperature drops from 27°C

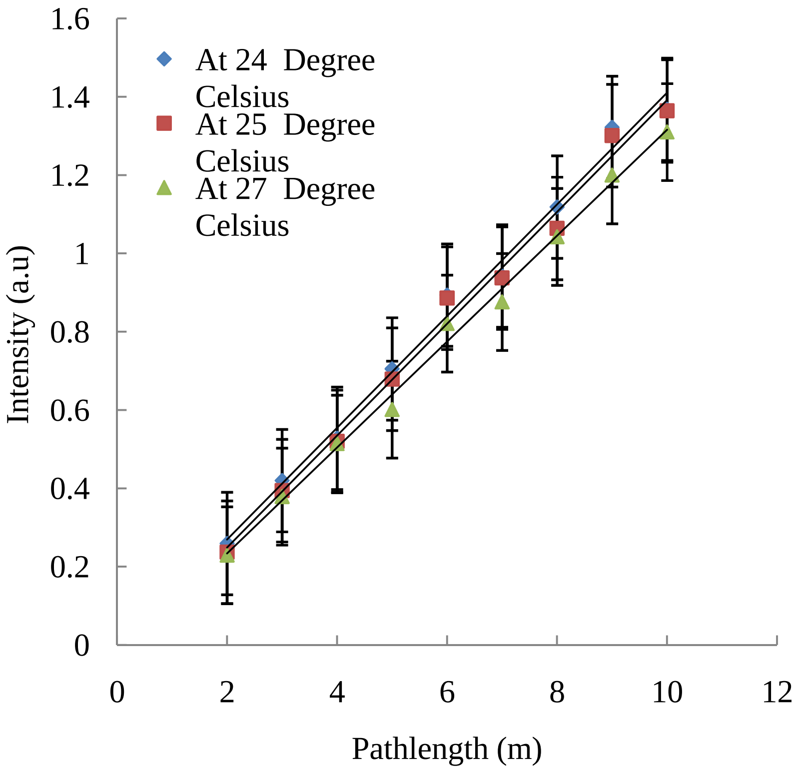

Figure 25: The intensities of WMS-2*f* signal as a function of optical pathlength in metres at different temperatures.

through 25^{o}C to 24^{o}C. This particular trend was observed for all the other optical pathlengths. The free molecular oxygen concentration changes a few percent with changes in temperature (Bugbee & Blonquist, 2005). As temperature increases air expands and the number of free oxygen molecules per unit volume decreases leading to less free oxygen molecules being encounted. The opposite occurs as temperature decreases. It can be deduced from figure 25 that there was a minimum but significant effect of the room temperature on the intensity of the WMS-2*f* signal at smaller optical pathlengths 2 - 4 m as the intensities of the WMS-2*f* signals recorded at three different room temperatures in the region of 2 - 4 m are very close whiles at longer optical pathlength 5 - 10 m the graph show a dispersed nature. The variation brought about by the temperature change is not much but significant as indicated by the error bars. This could be attributed to the fact that the amount of free oxygen molecules encounted as the optical pathlength increases is affected by temperature change.

Wavelength modulation absorption spectroscopic measurement of free molecular oxygen gas in highly scattering medium

Gas in scattering media absorption spectroscopy (GASMAS) technique was used to measure free molecular oxygen gas in some highly scattering media; locally branded polyurethane foams; latex foam and ash foam, and polystyrene foam. Measurements on different slabs of the foams with varying width and thickness were performed. Figure 26 shows a typical plot of the intensities of WMS-2*f* signal as a function of width of the three types of foams.

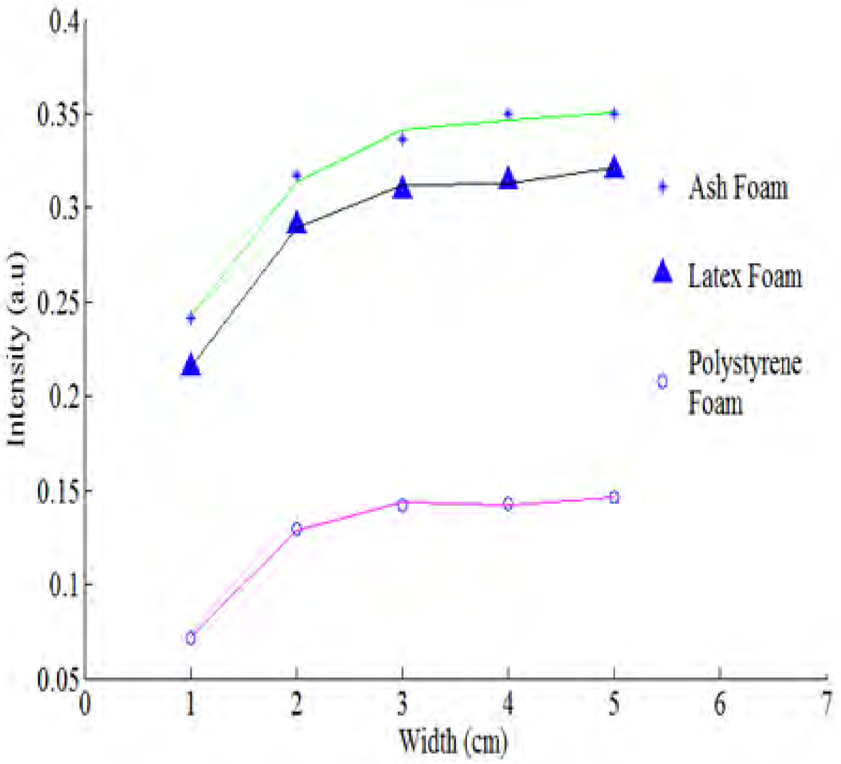

Figure 26: Intensity of WMS-2*f* signals as a function of width of ash foam, latex foam and polystyrene foam.

As can be seen from the graph in figure 26 the intensity of the WMS-2*f* signals increased with increasing width of the scattering media. As the width of the scattering media increases, it increases the pathlength of the scattering light leading to an increase in the intensity of the WMS-2*f* signal. The intensity of the WMS-2*f* signal increase as the width of the scattering media kept increasing till the width of the scattering media got to the full size of the detector. The increases in the intensities of the WMS-2*f* signals were limited by the size of the detector. This suggests that for maximum 2*f* signal detection in the scattering media, the width of the scattering sample should be at least equal to the detection area of the detector. It was further realized from the graph in figure 26 that the smaller foams in terms of width had smaller intensities compared to the wider foams. These trends were observed in all the three scattering media and that suggest that the scattered light leaks out of the foams from the sides leading to less intense WMS-2*f* signals in smaller foams in terms of width. This again suggest that scattering in a 1cm thick polyurethane foam (both ash foam and latex foam) and polystyrene foam stretches approximately to a point to each side perpendicular to the laser beam based on the width size and that of the detector. The graph in figure 26 shows differences in the intensities of the three foams at a different width. Comparing the intensities of the WMS-2*f* signal in all the three foams it was realized that the intensities in the ash foam were higher than that of the latex foam. Polystyrene foam had the least intensities in comparison with the other two foams. This could be due to compactness of the polystyrene foam.

Figure 27 shows a plot of the intensities of the WMS-2*f* signals against the thickness of ash foam, latex foam and that of the polystyrene foam. It can be seen from the graphs that the intensities of the WMS-2*f* signal decreases as

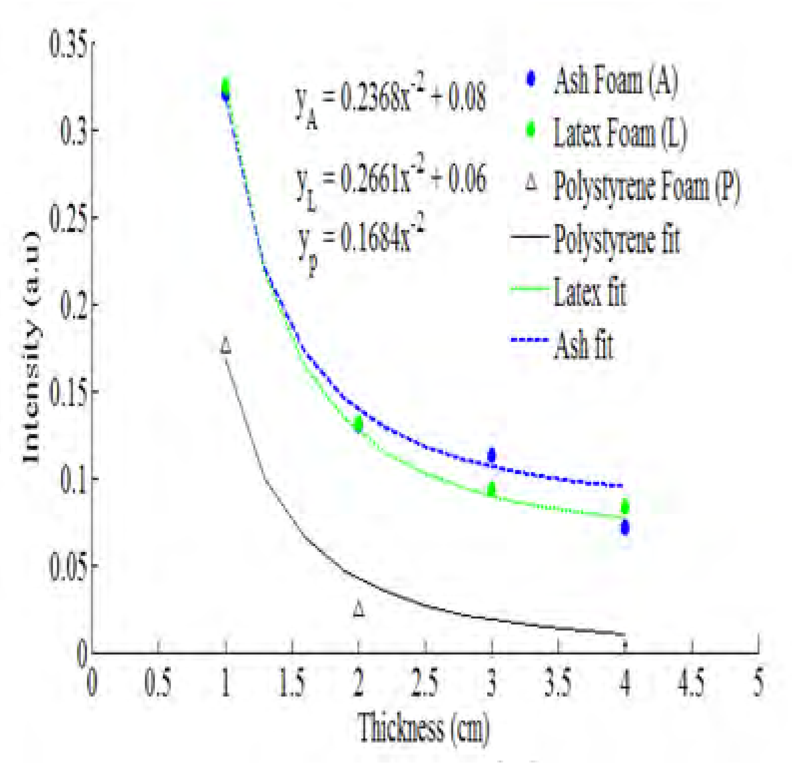

Figure 27: Intensity of WMS-2*f* signals as a function of thickness of Ash foam, Latex foam and Polystyrene foam.

the thickness of the foams increases. The intensity of the WMS-2*f* signal of the two locally branded polyurethane foams kept decreasing till it got to a thickness of 4 cm. Beyond the samples' thickness of 4 cm the detector could not measure any signal. In the case of the polystyrene foam, the detector could not measure any signal beyond the samples' thickness of 2 cm. This could be attributed to the fact that polystyrene foam and the locally branded polyurethane foams of the same size and thickness have different compactness. The result from the graph could also be attributed to the gas content trapped in the pores of the foams. The pores cause multiple scattering (Svanberg, 2009). This goes on to suggest that more of the light was scattered in other direction rather than in the forward direction in polystyrene foam than in the other two foams (latex and ash) resulting in weak WMS-2*f* signals as the thickness of the sample increases. The graph also reveals that the two locally branded polyurethane foams have similar properties but the difference began to show as the thickness of their sample increases from 2 cm through to 4 cm. The data points were fitted with power-law and the constant of proportionality were found to be 0.2368, 0.2661 and 0.1684 for ash foam, latex foam and the polystyrene foam respectively. The constant of proportionality for the three foams could be attributed to the number of pores in the foams. The two locally branded polyurethane foams have greater constants of proportionality from the fit compared to the polystyrene foam which goes on to suggest that the two locally branded polyurethane foams are more porous than the polystyrene foam. Physically, polystyrene foam is very hard, compact and has little flexibility making it difficult for light to travel through to the detector as the thickness increases compared to the locally branded polyurethane foams.

The thickness of the sample has an effect on the WMS-2*f* signal and that the more compact the sample the weaker the WMS-2*f* signal and vice versa. That is to say that the intensities of the 2*f* signals fall with increasing thickness of the sample. The results again show that the intensity of the WMS-2*f* signal in a sample is determined by the compactability of the scattering sample. Furthermore it can be seen from the graph in figure 27 that for stronger WMS-2*f* signal in a sample, the thickness should be 1cm or less.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

Conclusion

Using MATLAB codes it has been possible to simulate second harmonic (2*f*) signal of wavelength modulation spectroscopy (WMS) and to demonstrate the influence of normalized modulation amplitude, *m* on the signals. The simulation programme was based on numerical integration. The simulation has shown that the intensity and the bandwidth of the WMS-2*f* signal increases as *m* increases but the intensity of the signal started decreases after certain values of increasing *m*. The optimal 2*f* signal was found to occur at $m = 2.1$. This result agrees perfectly with the results published by silver (Silver, 1992).

Using molecular oxygen gas in free space as a sample, wavelength modulation absorption spectroscopy of 2*f* signal was experimentally demonstrated. At three different temperatures of 24^{o}C, 25^{o}C and 27^{o}C it has been possible to verify the fact that the longer the pathlength, the greater the absorption signal. However the intensities of the 2*f* signal, which depicts the absorption of molecular oxygen gas, were found to decrease with increasing room temperatures.

Gas in scattering medium absorption spectroscopy has been demonstrated with highly scattering samples. The experiment revealed that for maximum 2*f* signal detection in the scattering media, the width of the scattering sample should be at least equal to the detection area of the detector.

The technique also revealed that the more compact the sample the weaker the WMS-2*f* signal and vice versa. Thus the intensity of the 2*f* signals falls with increasing thickness of the sample.

Recommendations

It is recommended that future work can look at transforming the developed Matlab codes for the simulation of the wavelength modulation spectroscopy second harmonic (2*f*) signal into a graphical user interface (GUI). Demonstrating the behavior of the WMS-2*f* signal to students in a GUI form will be quite easy.

Porosity estimation of the foams can also be looked at as further studies using the gas in scattering media absorption spectroscopy (GASMAS) technique. Wavelength modulation absorption spectroscopic technique can be used to monitor other gases such as ammonia and methane.

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