

**INVESTIGATION OF O₂ LINE BROADENING IN NANOPOROUS
ALUMINA USING GAS IN SCATTERING MEDIA ABSORPTION
SPECTROSCOPY**

BY

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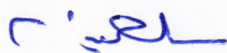
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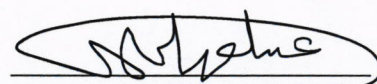


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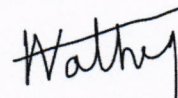


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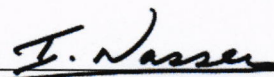
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DEDICATION

I dedicate this work:

To my parents Sadiqa and Younes Al-Saudi who always encourage me with passion and endless support.

To my wife and my children who have been a constant source of support and encouragement during the challenges of graduate.

To my brothers and my sisters for their whole-hearted support.

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LIST OF ABBREVIATIONS

GASMAS	:	GAs in Scattering Media Absorption Spectroscopy
MIP	:	Mercury Intrusion Porosimetry
SEM	:	Scanning Electron Microscopy
XRD	:	X-Ray powder Diffraction
ICDD	:	International Center for Diffraction Data
IUPAC	:	International Union of Pure and Applied Chemistry
FWHM	:	Full Width at Half Maximum
VCSEL	:	Vertical-Cavity Surface-Emitting Laser
DAQ	:	Data Acquisition Device
LabVIEW	:	Laboratory Virtual Instrumentation Engineering Workbench
M	:	Molecular mass
T	:	Temperature measure in Kelvin
k_B	:	Boltzmann's constant.
Γ_{wall}	:	Wall collision broadening
λ	:	Light wavelength
$\bar{w}$	:	Average pore diameter
γ	:	Surface tension
$D(w)$	:	Pore size distribution function measured by MIP
$f(w)$	:	Pore size distribution function measured by gas adsorption
θ	:	Contact angle
P	:	Pressure
P_s	:	Saturated vapor pressure

$\sigma(\nu)$	:	Absorption cross-section per molecule
N	:	Molecule number density
L	:	Light pathlength.
$\Delta\nu_N$	:	Full width at half maximum due to the natural broadening
$\Delta\nu_D$	:	Full width at half maximum due to the Doppler broadening
$\Delta\nu_c$	:	Full width at half maximum due to the collisional broadening
$\Delta\nu_{wall}$	:	Full width at half maximum due to the wall collisional broadening
E_{el}	:	Electronic energy
E_{vib}	:	Vibrational energy
E_{rot}	:	Rotational energy
i	:	Current
Pix	:	Pixel position
R	:	Resistance
ϕ	:	Porosity

Abstract

Full Name : Ahmed Younes Moh'd Al-Saudi
Dissertation Title : Investigation of O₂ Line Broadening in Nanoporous Alumina Using Gas in Scattering Media Absorption Spectroscopy
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There are several techniques for quantifying pore sizes of porous materials. These techniques have few drawbacks. Therefore, there is a need for developing new alternative techniques for pore size assessment. GAs in Scattering Media Absorption Spectroscopy (GASMAS) is a relatively new spectroscopy technique that has the potential to overcome some of these drawbacks.

GASMAS technique can be used to assess the pore size by monitoring the broadening of the absorption line of the confined gas within the pores. The width of the gas absorption line may be influenced by the pore size in which the gas is confined. When the pore size is of comparable size to or smaller than the mean free path due to intermolecular collisions, extra broadening occurs due to collisions of the confined gas molecules with the walls of the pore.

In this study, GASMAS technique is used to study the width of an absorption line around 763 nm of gaseous oxygen entrapped within the pores of alumina solid disc samples and alumina powder samples. The pore size of the alumina solid disc samples is measured by Mercury Intrusion Porosimetry (MIP) with average pore size ranging from 70 nm to 150

nm. Also, the pore size of alumina powder samples is measured by gas adsorption technique with average pore size ranging from 10 nm to 40.

A theoretical model based on the kinetic theory of gas is developed to describe a relation between the contribution of wall collision broadening to the width of absorption line and the pore size measured by MIP and gas adsorption techniques. For both disc and powder samples of two different average pore size ranges, the wall collision broadening is found to be inversely proportional to the average pore diameter measured by MIP and gas adsorption techniques. Furthermore, the shape of the pores of solid disc samples is found to be more consistent with a model of pores of cylindrical shapes of heights much larger than their diameters.

ملخص الرسالة

الاسم الكامل: أحمد يونس محمد السعودي

عنوان الرسالة: التحقق من اتساع خط امتصاص الأكسجين في الألومينا ذات المسامية النانوية باستخدام طيف امتصاص الغاز في وسط مشتمت

التخصص: الفيزياء

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يوجد العديد من التقنيات لقياس أحجام المسام في المواد المسامية و لكن هذه التقنيات لها بعض العيوب. لذلك هناك حاجة لتطوير تقنيات بديلة جديدة لتقييم حجم المسام. أن تقنية طيف امتصاص الغاز في وسط مشتمت تقنية طيفية جديدة نسبياً لها القدرة على التغلب على بعض هذه العيوب.

يتم استخدام تقنية طيف امتصاص الغاز في وسط مشتمت لتقييم حجم المسام من خلال مراقبه توسع خط الامتصاص للغاز المحصور داخل المسام. عندما يكون حجم المسام بحجم مماثل أو اصغر من متوسط المسار الحر بين التصادمات بين الجزيئات حيث يحدث اساع اضافي بسبب تصادم جزيئات الغاز المحصور مع جدران المسام.

في هذه الدراسة تم استخدام تقنية طيف امتصاص الغاز في وسط مشتمت لدراسة عرض خط الامتصاص عند 760 نانومتر لجزيئات الأكسجين المحصوره داخل مسام عينات من أقراص الألومينا الصلبة و عينات من مسحوق الألومينا. أيضاً تم قياس حجم المسام لعينات الاقراص الصلبة من الألومينا باستخدام تقنية الحقن بالزئبق ووجد أن متوسط حجم مساماتها تتراوح بين 70 الى 150 نانومتر. و استخدمت تقنية ادمصاص الغاز لتحديد متوسط حجم المسام لعينات من مسحوق الألومينا ، ووجد أن متوسط حجم مساماتها تتراوح بين 10 الى 40 نانومتر.

تم تطوير نموذج نظري يعتمد على النظرية الحركية للغازات لوصف العلاقة بين التوسع الناتج من تصادم الغاز المحصور مع جدران المسام ومتوسط حجم المسام المقاس باستخدام تقنية الحقن بالزئبق و تقنية ادمصاص الغازات. لقد وجد ان التوسع في عرض خط امتصاص جزيئات الأكسجين المحصورة داخل المسام والناتج عن تصادم هذه الجزيئات مع جدران المسام يتناسب عكسياً مع حجم المسام. وقد وجد ايضا انه من الافضل ان يكون شكل مسام عينات الاقراص الصلبة أسطوانية ذات ارتفاع اكبر بكثير من اقطارها لكي تكون النتائج أكثر تناسقا مع النموذج المطروح.

CHAPTER 1

INTRODUCTION

The interest in porous materials is steadily increasing due to their special chemical, physical and mechanical properties [1-7]. Porous materials have many applications covering wide range of fields and industries such as gas capture[1,2], gas and liquid separation processes [3,4], catalysis [5] and biomedical applications [6-7].

According to the International Union of Pure and Applied Chemistry (IUPAC), porous materials are classified into three categories according to their pore sizes, namely, microporous with pore sizes below 2 nm, mesoporous with pore sizes in the range from 2 nm to 50 nm and macroporous with pore sizes above 50 nm [8]. The determination of the pore size distribution and shape in porous materials is very important to assess their suitability to be used in a particular application. There are several methods for quantifying pore sizes of porous materials. The most common methods are Mercury Intrusion Porosimetry (MIP) [9], gas adsorption [8], Scanning Electron Microscopy (SEM) [10], and nuclear magnetic resonance [11]. These methods, which are based on different physical principles, have limitations and may give different pore size assessment for the same sample [12]. Moreover, these methods have few drawbacks as they are relatively time consuming, destructive, and expensive. In addition, they require complex equipment or using potentially hazardous substances. Therefore, there is always a need for developing new innovative methods for pore size assessment. Gas in Scattering Media Absorption Spectroscopy (GASMAS) is a relatively new spectroscopy technique that has the potential to assess the pore size of materials at the nanometer scale. GASMAS has the potential to

evaluate the average pore size of porous materials by monitoring the broadening of the absorption line of the confined gas within the pores. The width of the gas absorption line may be influenced by the pore size in which the gas is confined. When the pore size is of comparable size to or smaller than the mean free path due to intermolecular collisions, extra broadening occurs due to collisions of the confined gas molecules with the walls of the pore. This extra broadening is commonly known as wall collision broadening, which can be utilized to assess the average size of the pores [13].

In this work, we attempt to find a correlation between wall collision broadening measured by GASMAS and the pore sizes measured by MIP and gas adsorption. Two sets of nanoporous alumina are studied: nanoporous alumina solid disc samples of average pore diameters between 70 and 150 nm, and nanoporous alumina powder samples of average pore diameters between 10 to 40 nm. The average pore diameter of nanoporous alumina solid discs is measured by MIP, while the average pore diameters of nanoporous alumina powders is measured by gas adsorption. Also, a model based on the kinetic theory of gasses is used to find a relation between the wall collision broadening and the average pore diameter measured by MIP and gas adsorption.

1.1 GAs in Scattering Media Absorption Spectroscopy (GASMAS)

GASMAS was first introduced in 2001 by Svanberg group at Lund University as a new technique to monitor the oxygen gas embedded in different materials such as wood, apple, lump sugar and polystyrene foam [14]. Since then, this technique has been used in many applications such as studying the human sinus cavities and sinus inflammation status by comparing the concentrations of oxygen and water in sinuses [15]. Also, GASMAS has been used in many contexts such as studying gas diffusion [16], characterizing

pharmaceutical tablet [17], ceramics industry [18], monitoring food packages [19], and determining the optical porosity [20].

GASMAS is used to study the imprint of gas confined in strong scattering bulk material. It has the capability of differentiating between the absorption from the bulk material and that from the gas confined in it. It is well-known that the confined gases have very narrow absorption peaks compared to the broad absorption bands of the bulk material [21]. Typically, a gas absorption peak is about 10,000 times narrower than a bulk material band [16]. Despite the fact that the gas absorption dip is small, it has a clear and sharp appearance on an almost flat and broad absorption band of the bulk material, so the gas absorption dip can be easily distinguished and extracted [18,22-23], as shown in figure 1-1. The width of the absorption gas dip is due to many contributions such as, limited lifetime of excited state, Doppler effect, intermolecular collisions, and wall collisions.

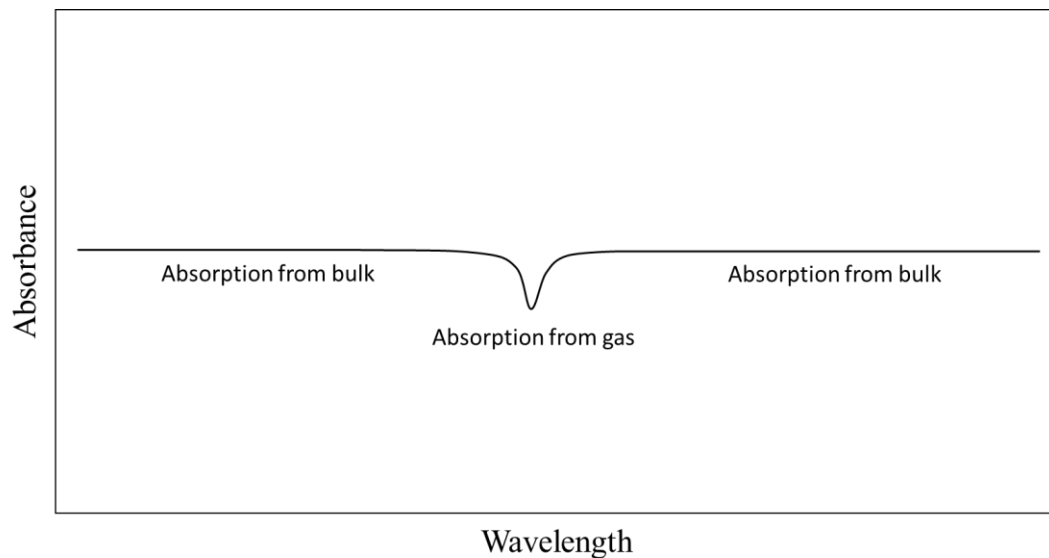


Figure 1-1: Illustration of a narrow absorption peak from a gas in comparison to a broad absorption band from a solid.

1.2 Statement of research problem

Generally, there is no “golden standard” techniques for pore size measurement. All techniques used to quantify the pore size of porous materials have their own advantages and disadvantages. For example, MIP technique has a potential to measure the pore size distribution from few nanometers to hundreds of micron meters. In addition, gas adsorption technique can be used to measure the pore size distribution and the surface area of powder materials of pore sizes less than 70 nm [9].

These techniques used in quantifying the pore size have the disadvantages of being bulky, destructive, hazardous, costly, and even difficult to maintain. Furthermore, these techniques require a special training to operate them. The health risks associated with using these techniques is from direct exposure to radiation and other hazardous fluids and gases that can leak while taking a measurement [8-11].

Therefore, there is a need for developing new alternative methods for pore size assessment that are economic, fast, safe, nonintrusive, and accurate. GASMAS has a potential to overcome some of these drawbacks. In this study, GASMAS will be used to assess the pore size of nanoporous alumina discs and powder and the performance of GASMAS will be compared with MIP and gas adsorption.

1.3 Statement of research aim and objectives

The aim of this work is to use GASMAS technique to study the width of an absorption line around 763 nm of gaseous oxygen entrapped within the pores of alumina solid disc samples and alumina powder samples. The increase in the width of the absorption line due to collision of oxygen molecules with the wall of the pore is then correlated to the pore size.

The pore size of the alumina solid disc samples is measured by MIP technique, while the pore size of the alumina powder samples is measured by gas adsorption technique.

A theoretical model based on the kinetic theory of gas is developed to describe a relation between the contribution of wall collision broadening to the width of absorption line and the pore size of nanoporous materials.

The main objectives of this study are the following:

- Design and develop a GASMAS setup.
- Use the GASMAS setup to study the width of an absorption line around 763 nm of gaseous oxygen entrapped in nanoporous alumina solid discs.
- Use the GASMAS setup to study the width of an absorption line around 763 nm of gaseous oxygen entrapped in nanoporous alumina powder discs.
- Synthesize nanoporous alumina solid discs and nanoporous alumina powders.
- Use MIP to measure the average pore size and pore size distribution of the nanoporous alumina solid discs.
- Use gas adsorption to measure the average pore size and pore size distribution of the nanoporous alumina powder.
- Correlate the wall collision broadening obtained by the GASMAS technique with the pore size obtained by the MIP technique.
- Correlate the wall collision broadening obtained by the GASMAS technique with the pore size obtained by gas adsorption technique.
- Develop a theoretical model to describe the relation between the broadening in the width of the absorption line due to wall collision and the pore size measured by MIP and gas adsorption techniques size.

- Find a relation between the absorbance and the effective porosity of the samples.

1.4 Structure of the dissertation

This dissertation contains five chapters and two appendixes.

Chapter 2 presents literature review and theoretical background related to the subjects under study. It reviews the most common techniques used to determine the pore size. Also, it discusses the absorption lines of oxygen and their broadening mechanisms. Moreover, it presents the basic principle, some application of GASMAS technique. At the end, it discusses some preparation methods of alumina, its phases and some of its application.

Chapter 3 presents the experimental details of this work. At the beginning, it discusses the experimental setup to measure the absorption line of molecular oxygen at 763.84 nm. Then it discusses the procedures needed to develop and optimize the setup.

Chapter 4 presents the results and discussions part of the dissertation. It shows the results of pore size measurements for alumina solid disc samples using the MIP and alumina powder samples using gas adsorption techniques. Also, it presents the measurements of line broadening of gaseous oxygen entrapped within the pores of alumina solid disc samples and alumina powder samples using GASMAS. Moreover, it discusses a relation between the wall collision broadening obtained by the GASMAS technique with the pore size obtained by the MIP and gas adsorption techniques.

Chapter 5 gives a summary of this study.

Appendix A shows labview block diagrams and front panel used for experimental measurement.

Appendix B shows mathematica codes used for data analysis.

CHAPTER 2

LITERATURE REVIEW AND THEORITICAL BACKGROUND

This chapter discusses the following subjects: pore size characterization methods, Beer-Lambert law, broadening mechanisms, GASMAS technique, and absorption lines of oxygen molecules around 760 nm, alumina, and porosity.

2.1 Pore size characterization methods

The international Union of Pure and Applied Chemistry (IUPAC) classifies Porous materials according to their pore sizes into microporous materials with pore sizes below 2 nm, mesoporous materials with pore sizes in the range from 2 nm to 50 nm, and macroporous materials with pore sizes above 50 nm.

Pores may also be classified according to their communication with the external surface of a material. Pores have communication with the external surface are named open pore, while pores having no communication with the external surface are named closed pore. Figure 2-1 region (a) represents a closed pore, regions (b), (c), (d) and (e) represent open pores. If open pores communicate with the external surface by only one open end, then they are called blind pores, like region (e). Open pores communicating with the external surface by two open ends are called through pores, like regions (c) and (d). When the connection between two neighboring pores is very narrow, the open pore is called ink-bottle pore, like region (b) [24].

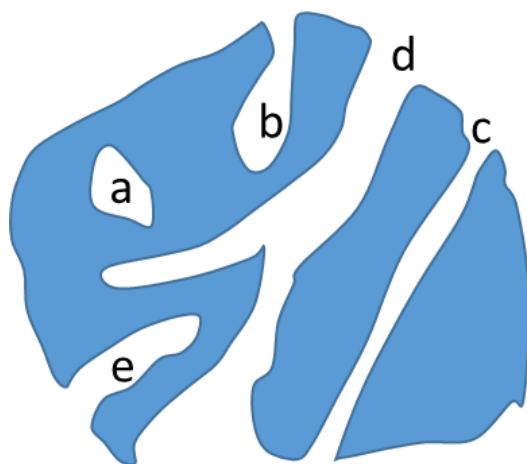


Figure 2-1: A schematic of different pores classification, according to their communication with the external surface of material.

The determination of the pore sizes distribution and shapes in the porous materials is very important to determine their suitability to a particular application. The most common techniques to determine pore sizes are mercury intrusion porosimetry and gas adsorption techniques.

2.1.1 Mercury Intrusion Porosimetry (MIP)

Mercury intrusion is a powerful technique used to investigate pore diameter from few nanometers to hundreds of micrometers. This technique is based on the behavior of non-wetting mercury liquid. The mercury liquid cannot spontaneously penetrate the pore due to the high surface tension of mercury and the size of penetrated pore. Therefore, mercury penetrates the pore with the help of an external pressure [9]. By increasing the pressure, the volume of mercury penetrating into the pores is also increased. A pore of large size is filled by mercury at low pressure, while a small pore is filled by mercury at high pressure. Figure 2-2 shows raw data of MIP collected for an alumina sample.

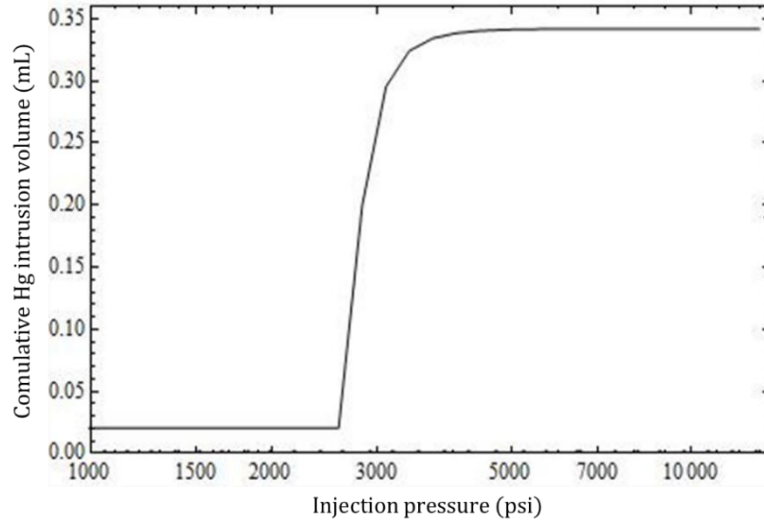


Figure 2-2: An example of raw data of MIP collected for an alumina sample

The relation between the pore diameter w and the applied pressure P is described by the Washburn equation:

$$P = \frac{-4\gamma\cos\theta}{w} \quad (1)$$

where θ is the contact angle between mercury and the pore wall, and γ is the mercury surface tension. The contact angles for mercury with a large variety of materials is between 135° to 142° , so a typical value of 140° can be taken, and the typical value for mercury surface tension is 0.48 N/m [25].

A relation between the applied pressure and the penetrating mercury volume can be used to determine the pore size distribution function $D(w)$ using the following equation [25].

$$D(w) = \frac{P}{w} \frac{dV}{dP} \quad (2)$$

where V is the cumulative volume of the penetrating mercury into the pores.

The pore size distribution curve is obtained by plotting the pore size distribution function and the pore diameter. A typical example is shown in figure 2-3.

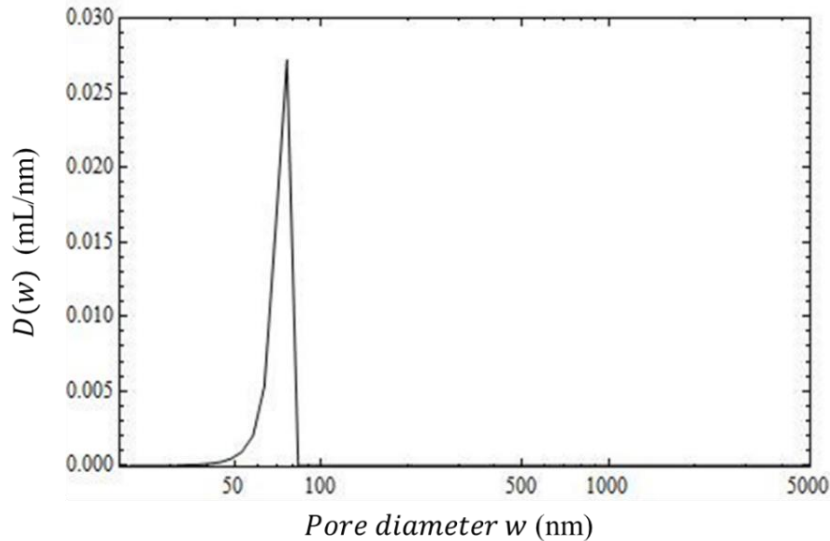


Figure 2-3: An example of pore size distribution function $D(w)$ as a function of pore diameter w for an alumina sample

Although MIP is highly recommended for accurate and precise measurements of pore diameter, some errors still generated during measurement. The most important sources of errors associated with MIP are the following [26]:

- The volume of mercury is slightly changed under high pressure, which lead to record a larger volume than the actual volume.
- The contact angle between mercury and a solid sample varies depending on the type of samples.
- The surface tension of mercury is slightly changed depending on the pressure, temperature, and purity of mercury.

- Calculation associated with MIP assumes that the shape of pore is cylinder, and only the pores that are connected to the surface can be measured. For ink-bottle pore, a large pressure is required to penetrate the small pore neck, but once this pressure is reached, mercury will be able to penetrate into the large pore, giving a large pore size reading for the size of pore neck.
- A deformation of the sample and damaging the pores under high pressure also generate errors.

2.1.2 Gas adsorption technique

Adsorption is defined as the adhesion of molecules, atoms and ions, either on or close to a solid surface. Adsorption can be physisorption or chemisorption. Physisorption occurs when the gas is in contact with the surface of a solid by Van der Waals forces, while chemical bonds are formed in chemisorption. In gas adsorption technique, physisorption is commonly used to measure the surface area, pore size distribution, and pore volume of porous materials [8]. In the following, the experimental procedure for gas adsorption technique will be described. Heat and vacuum are applied to clean the sample. Then, the sample is held within a glass tube opened from one end. The glass tube is then immersed in a liquid nitrogen at 77 *K* for temperature control. The open end of the glass tube is connected to a cylinder of nitrogen gas. A gradual increase in the nitrogen gas pressure causes more adsorption of nitrogen molecules within the pores of the sample. At constant temperature 77 *K*, the adsorption molecules condensates within the pores. The amount of adsorbed gas as a function of pressure at constant temperature is known as adsorption isotherm curve. Figure 2-4 shows a typical adsorption isotherm curve. Usually, the pressure is expressed as a ratio of the equilibrium vapor pressure P to the saturated vapor pressure

over the condensed liquid P_s . The preferred unit for adsorbate amount is millimoles or micromoles adsorbate per gram of adsorbent. The maximum value of relative pressure is 1 [27].

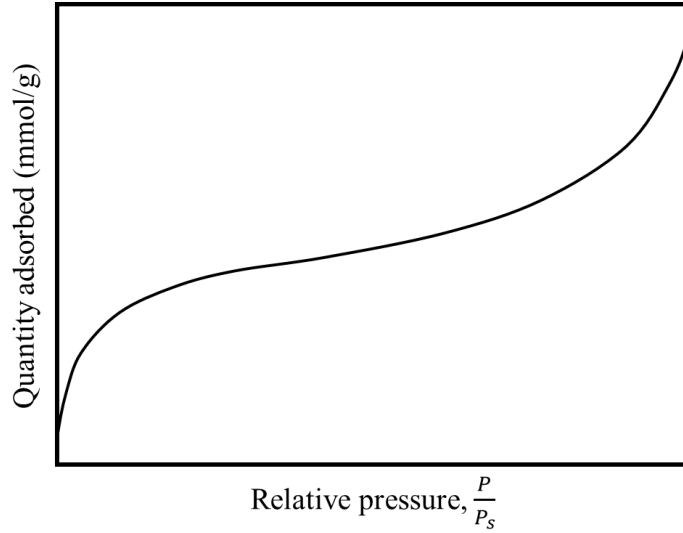


Figure 2-4: Typical adsorption isotherm curve.

There are different methods to calculate the pore size from the isotherm curve. The most common method used is the Barrett, Joyner and Helenda (BJH) method. The BJH method is based on the assumption that the pores have a cylindrical shape. For cylindrical pores assumption, the pore diameter is given by the Kelvin equation:

$$w = -\frac{4\gamma V_m}{RT \ln(P/P_s)} \quad (3)$$

where γ is the surface tension of the liquid nitrogen, V_m is molar volume of liquid nitrogen, R is the gas constant and T is absolute temperature [28]. According BJH method, the pore

size distribution function $f(w)$ is measured by taking a ratio between the changing in volume of adsorbed nitrogen gas ΔV and the corresponding change in pore diameter Δw .

$$f(w) = \frac{\Delta V}{\Delta w} \quad (4)$$

Figure 2-5 shows a typical pore size distribution curve obtained by plotting the pore size distribution function and the pore diameter.

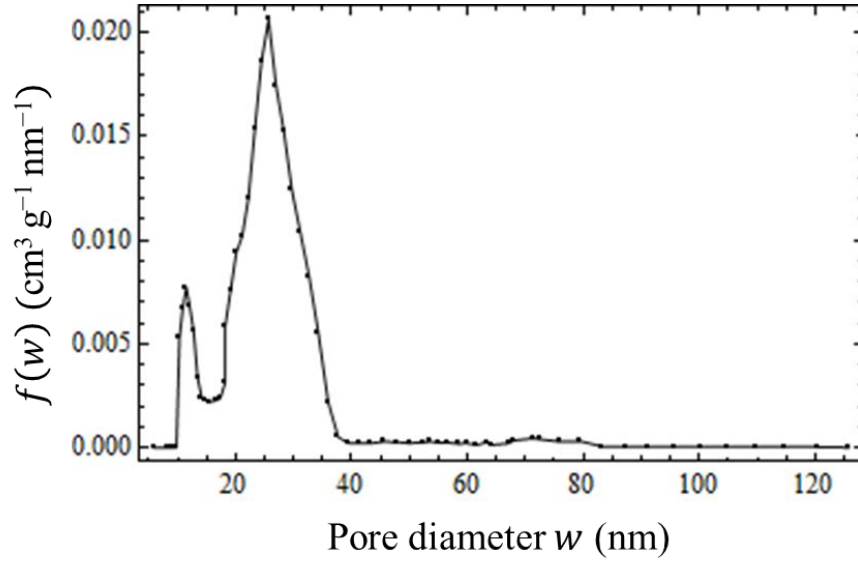


Figure 2-5: Typical pore size distribution curve obtained by using the gas adsorption technique.

The MIP and the gas adsorption techniques are based on different physical principles and may give different pore size assessment for the same sample. The MIP technique gives much larger pore size compared to the gas adsorption technique for the same sample [12]. Also, the gas adsorption technique is used to measure pore sizes of less than 70 nm, while the MIP technique is used to measure pore sizes from few nanometers to hundreds of micrometers [9,26].

2.2 Beer-Lambert Law

When an incident light of intensity $I_o(\nu)$ is transmitted through a molecular gas sample, the gas molecules partially absorb the light and the intensity of the transmitted light $I(\nu)$ is given by the Beer-Lambert law [29]:

$$I(\nu) = I_o(\nu)e^{-\sigma(\nu)NL}, \quad (5)$$

where $\sigma(\nu)$ is the absorption cross-section per molecule, N is the molecules number density and L is the light pathlength.

Often, the absorbance $A = \sigma(\nu)NL = \ln \frac{I_o}{I}$, is used to quantify the absorption by the molecules. For weak absorbance $\sigma(\nu)NL \ll 1$, the Beer Lambert law can be written as:

$$\frac{I_o - I}{I_o} \approx \sigma(\nu)NL \quad (6)$$

Applying the Beer-Lambert law in porous media is more challenging since the actual or physical path length L is hard to determine due to multiple scatterings, as illustrated in figure 2-6. To quantify the effective path length within a porous medium, a mean equivalent path length L_{eq} is introduced. The mean equivalent path length L_{eq} is defined as the distance the light travels in open-air that gives the same absorption signal as that from the gas confined in a porous medium, which can be calculated from [30]

$$L_{eq} = \frac{\text{Amplitude of the absorption signal from the sample}}{\text{Amplitude of the absorption signal from air per meter}} \quad (7)$$

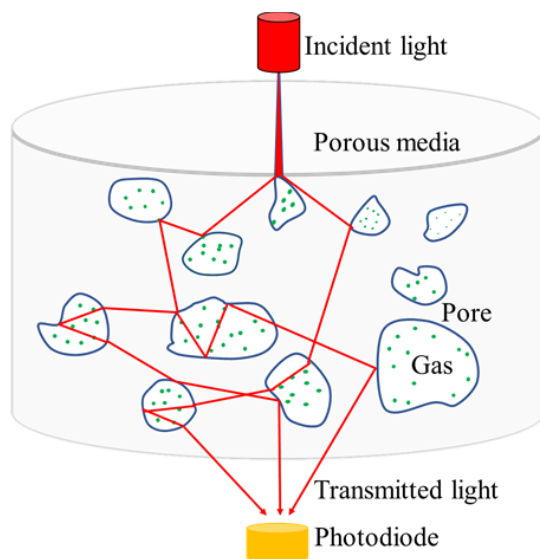


Figure 2-6: A sketch of the light paths in porous media.

2.3 Broadening mechanisms and shape of spectral lines

Three common mechanisms cause the broadening of a molecular absorption line. These are the natural broadening, collisional broadening, and Doppler broadening. In addition, when gas molecules are confined within a container of a comparable size or smaller than the mean free path of intermolecular collisions, the collisions of the gas molecules with the walls of the container can also cause additional broadening, called wall collision broadening. The natural broadening, the collisional broadening, and wall collision broadening are homogeneous broadening, since the probability of absorption causing a transition between energy levels is equal for all molecules.

Doppler broadening is an inhomogeneous broadening, since the probability of the absorption is not equal for all molecules [31,32].

2.3.1 Natural Broadening

The natural broadening is the most fundamental line broadening, which depends on the lifetime of the energy states and not on the surrounding environment. According to

Heisenberg uncertainty principle $\Delta E\tau = h/2\pi$, the uncertainty in the energy state ($\Delta E = h\Delta\nu$) is due to the state lifetime τ . As a result, a transition between two states i and k will not absorb or emit light at a single frequency but in a range of frequencies, as shown in figure 2-7. This causes a broadening to the absorption line, which is called the natural linewidth broadening. The full width at half maximum (FWHM) due to the natural broadening is given by [31]:

$$\Delta\nu_N = \frac{1}{2\pi\tau} \quad (8)$$

For oxygen at atmospheric pressure, this broadening has a small magnitude, which can be neglected compared with the other types of broadenings. For the oxygen absorption line P9P9 at 763.84 nm, the natural broadening is about 4.1 mHz.

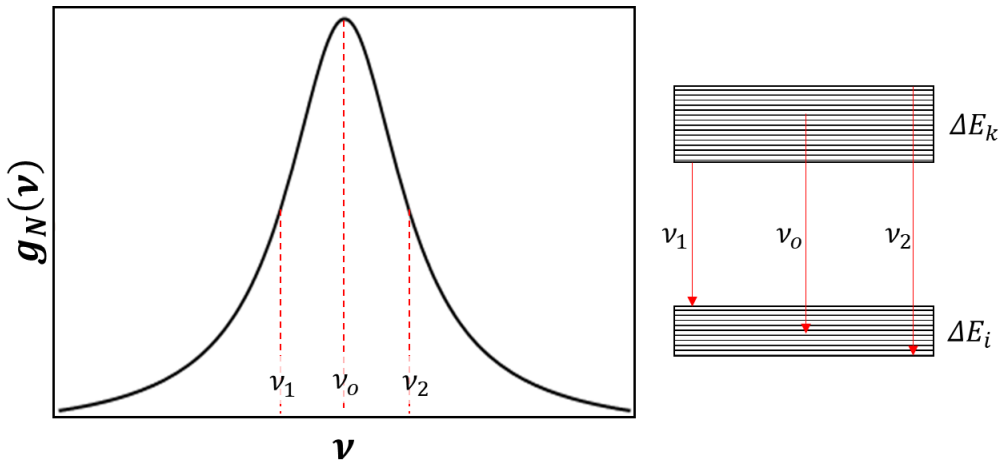


Figure 2-7: Natural linewidth caused by the energies uncertainties ΔE_i , ΔE_k of the transition $E_k \rightarrow E_i$.

This absorption line with the natural broadening only has a Lorentzian shape line, which can be derived using a classical model. In this model, the excited molecular electron is

modeled by a damped harmonic oscillator with frequency ν , mass m , and restoring force constant k . The excited molecule emits its excited energy with rate given by a damping constant γ , and the amplitude of the oscillation $x(t)$ is given by:

$$x(t) = x_o e^{-(\gamma/2)t} \cos(2\pi\nu_0 t) \quad (9)$$

where x_o is the amplitude at $t = 0$, and ν_0 is the central frequency.

The frequency distribution of the amplitudes $x(t)$ is found by taking the Fourier transform of $x(t)$, as:

$$A(\nu) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} x(t) e^{-i2\pi\nu t} dt \quad (10)$$

Solving Eq. 10 gives:

$$A(\nu) = \frac{x_o}{\sqrt{8\pi}} \left(\frac{1}{2\pi i(\nu - \nu_0) + \gamma/2} + \frac{1}{2\pi i(\nu + \nu_0) + \gamma/2} \right) \quad (11)$$

The unnormalized line shape function is proportional to the power spectrum $I(\nu) \propto A(\nu)A(\nu)^*$. The term $\nu + \nu_0$ can be neglected because it is large compared with the central frequency ν_0 :

$$I(\nu) = \frac{C}{(2\pi)^2(\nu - \nu_0)^2 + (\frac{\gamma}{2})^2} \quad (12)$$

where C is a constant. The line shape function is the normalized power spectrum, here C can be found from:

$$g_N(v) = \int_{-\infty}^{+\infty} I(v) dw = 1 \quad (13)$$

The integration of Eq. 13 yields $C = \gamma$, and the normalized line shape function of natural broadening is given by:

$$g_N(v) = \frac{\gamma}{(2\pi)^2(v - v_o)^2 + (\gamma/2)^2} \quad (14)$$

At the central frequency ($v = v_o$), the normalized line shape function $g_N(v_o) = 4/\gamma$. Also, at the half width at half maximum ($v = v'$), the normalized line shape function is $g_N(v') = g_N(v_o)/2$. This can be achieved when $v' - v_o = \gamma/4\pi$. Thus, the FWHM (Δv_N) is given by:

$$\Delta v_N = 2(v' - v_o) = \frac{\gamma}{2\pi} = \frac{1}{2\pi\tau} \quad (15)$$

since $\gamma = 1/\tau$. Both the classical model and the Heisenberg uncertainty principle give the same equation of FWHM for the natural broadening [31,34].

2.3.2 Doppler Broadening

Molecules move freely with speed v in gas phases due to the thermal motion. When they interact with an electromagnetic wave of frequency ν_o , the apparent frequency of the wave is different from that seen by the molecules. The apparent frequency ν seen by a molecule moving with speed v in the opposite direction of the wave propagation is given by:

$$\nu = \nu_o + \left(\frac{\nu_o v}{c}\right) \quad (16)$$

where c is the speed of the wave in the medium. Therefore, the molecular absorption frequency is shifted due to the thermal motion of molecules [31,35]. As in the absorption case, the emission frequency of a moving molecule is also shifted relative to an observer at rest. Doppler broadening has a Gaussian line profile, which can be derived from the Maxwellian-Boltzmann velocity distribution $g(v)$:

$$g(v)dv = \sqrt{\frac{m}{2\pi k_B T}} e^{-v^2(\frac{m}{2k_B T})} dv \quad (17)$$

where m is the molecular mass, T is the gas temperature measured in kelvins, and k_B is the Boltzmann constant.

Using Eq. 16, the velocity v can be written as $v = c(v - \nu_o)/\nu_o$ and $dv = (c/\nu_o)dv$.

Insertion of v and dv into Eq. 17 gives the Gaussian line profile of the Doppler broadening:

$$g_D(v) = \frac{c}{\nu_o} \sqrt{\frac{M}{2\pi k_B T}} e^{-\frac{mc^2}{2k_B T}(\frac{v-\nu_o}{\nu_o})^2} \quad (18)$$

Thus, the FWHM ($\Delta\nu_D$) is given by:

$$\Delta\nu_D = \nu_o \sqrt{\frac{2k_B T \ln 2}{mc^2}} \quad (19)$$

Figure 2-8 shows a normalized Gaussian and normalized Lorentzian profiles. The peak in the Gaussian profile is sharper than the Lorentzian profile, while the wings of the Lorentzian profile are wider than the Gaussian profile. At standard condition for

temperature and pressure, the contribution of the Doppler broadening to the width of oxygen absorption line P9P9 at 763.84 nm is 0.86 GHz.

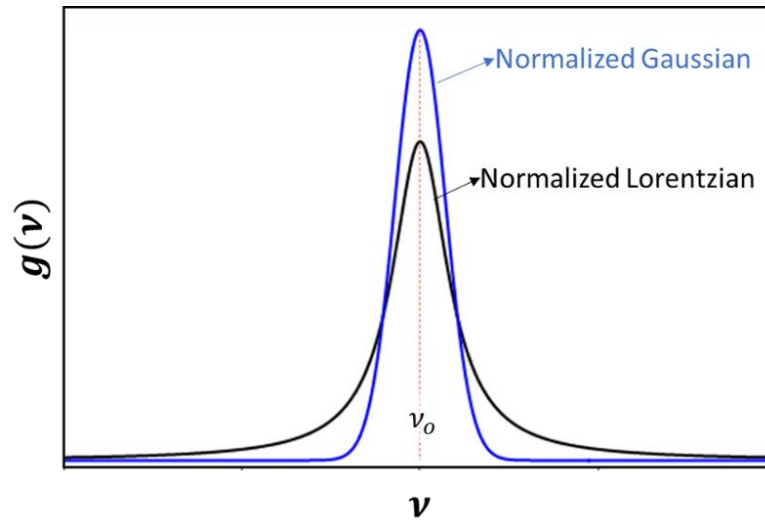


Figure 2-8: Comparison between a normalized Gaussian line profile and a normalized Lorentzian line.

2.3.3 Collisional Broadening

Collisional broadening is the most prominent source of broadening results from collisions of molecules with each other. These collisions will perturb the energy states of the emitting or absorbing molecule, and hence interrupting the emission of the photon, or at least changing the emission phase. The perturbation due to the interaction between a molecule and an electric field causes a broadening called Stark broadening. Also, the perturbation due to the Van der Waals force between neutral molecules causes a broadening called Van der Waals broadening [32].

To find FWHM due to the collisions between molecules, assume that the electric field of the emitted photon between two consecutive collisions vary as [36]:

$$E(t) = E_0 e^{-i2\pi v_o t} , \quad -\frac{T}{2} \leq t \leq \frac{T}{2} \quad (20)$$

where E_0 is the electric field at $t = 0$, v_o is the central frequency, and T is the time between collisions. Using Fourier transform and the power spectrum relation $I(v) \propto A(v)A(v)^*$, the following equations are obtained:

$$A(v) = \frac{1}{\sqrt{2\pi}} \int_{-\frac{T}{2}}^{+\frac{T}{2}} E(t) e^{-i2\pi vt} dt = \frac{E_0}{\sqrt{2\pi}} \frac{2 \sin[\pi T(v + v_o)]}{2\pi(v + v_o)} \quad (21)$$

$$I(v) = C \frac{\sin^2[\pi T(v + v_o)]}{(v + v_o)^2} \quad (22)$$

The probability of collisions occurring in time t is given by a Poisson distribution $P(t)$:

$$P(t) = \frac{1}{T_0} e^{-t/T_0} \quad (23)$$

where T_0 is the average time between collisions. The integration of the power spectrum of individual collisions multiplied by Poisson distribution gives the total power spectrum in the form:

$$I_t(w) = \frac{C}{T_0} \int_0^\infty \frac{\sin^2[\pi T(v + v_o)]}{(v + v_o)^2} e^{-t/T_0} dt = C \frac{1/T_0}{(v + v_o)^2 + (1/T_0)^2} \quad (24)$$

Using the normalization Eq. 13, we find the value of constant C and the normalized line shape function of collision broadening is written as:

$$g_c(\nu) = \frac{1/T_0}{(2\pi)^2(\nu - \nu_o)^2 + (1/T_0)^2} \quad (25)$$

At the central frequency we have $g_N(\nu_o) = T_0$, and at the half with at half maximum we have $g_N(\nu') = g_N(\nu_o)/2$, this achieved when $\nu' - \nu_o = 1/2\pi T_0$. The Lorentzian function is asymmetrical function. Thus, the FWHM ($\Delta\nu_c$) is given by:

$$\Delta\nu_c = 2(\nu' - \nu_o) = \frac{1}{\pi T_0} \quad (26)$$

Thus, the line shape of collision broadening is Lorentzian, and the FWHM is inversely proportional to the average time between intermolecular collisions T_0 . At standard condition for temperature and pressure, the FWHM of oxygen line at 763.8 nm due to the collisional broadening is about 2.94 GHz [37].

2.3.4 Wall Collisional Broadening

When a gas is confined within a pore, the gas molecule collides with other molecules as well as with the walls of the pore. The collisions with the wall influence the width of absorption line, if the mean free path between intermolecular collisions is comparable to the average pore size. At standard conditions for temperature and pressure, the mean free path of the intermolecular collisions is typically of the order of 100 nm. Hence, if the average pore size is of the order of 100 nm or smaller, then the collisions with the pore walls will lead to an extra broadening in the absorption line [13].

The effect of wall collisional broadening was observed in microwave region at very low pressures, and it was found that the broadening Γ_{wall} is dependent on the average time between the consecutive collisions of confined molecules with the walls pore τ_{wall} , as [38]:

$$\Delta v_{wall} = \frac{1}{\pi \tau_{wall}} \quad (27)$$

Many studies on collision broadening in the microwave region [39], as well as in the near infrared region [13,23], assume that contributions from the wall collisions has a Lorentzian line shape.

2.3.5 Saturation Broadening

When the intensity of the laser is sufficiently strong, the optical pumping rate becomes larger than the relaxation rate. This results in saturating the population densities which causes an additional broadening called saturation broadening, which is given by:

$$\Delta v_s = \Delta v \sqrt{1 + \frac{2\sigma I}{h\nu_o A}} \quad (28)$$

where Δv is the full width at half maximum of homogeneous broadening, σ is the absorption cross section, h is the Planck constant, I is the laser intensity, and A is the Einstein coefficient [31]. In our case, the additional broadening to collisional linewidth by saturation is about 1.1×10^{-5} Hz. Therefore, the effect of saturation can be neglected compared with collisional linewidth of about 2.94 GHz.

2.3.6 Voigt line shape

In general, the resultant line shape is contributions from a Gaussian and a Lorentzian line shape. If the two types of broadening are independent, the resultant line shape is obtained by convoluting the Gaussian and the Lorentzian line shape, which is called a Voigt line shape $g_V(\nu)$.

$$g_\nu(\nu) = \int_{-\infty}^{+\infty} \frac{2}{\Delta\nu_G} \sqrt{\frac{\ln 2}{\pi}} e^{-4\ln(2)\left(\frac{\nu-\nu_o}{\Delta\nu_G}\right)^2} \frac{\Delta\nu_L/2}{\pi(\nu - \nu_o)^2 + (\Delta\nu_L/2)^2} d\nu \quad (29)$$

where $\Delta\nu_G$, $\Delta\nu_L$ are FWHM of the Gaussian and Lorentzian line shapes, respectively.

$\Delta\nu_G$ and $\Delta\nu_L$ can be found from the line shape by finding the best fit to Eq. 29.

It is well known that the FWHM of the convolution of two or more Lorentzian line shapes is given by [32]:

$$\Delta\nu_L = \Delta\nu_{L1} + \Delta\nu_{L2} + \dots \quad (30)$$

Also, the FWHM of the convolution of two or more Gaussian line shapes is given by:

$$\Delta\nu_G^2 = \Delta\nu_{G1}^2 + \Delta\nu_{G2}^2 + \dots \quad (31)$$

For oxygen at standard condition, the convolution of the Doppler line shape and the natural line shape has approximately a Gaussian line shape, because the contribution from the Doppler broadening is much larger than that of the natural broadening. The shape of the laser line is Lorentzian with a linewidth of 0.1 GHz which is much smaller than the width of the Doppler lineshape. Also, the convolution of the collisional line shape and the Doppler line shape has approximately a Lorentzian line shape, because the contribution from the collisional broadening is larger than that of the Doppler broadening.

2.4 Absorption line of oxygen molecules around 760 nm

Molecular oxygen (O_2) is a diatomic molecule that is composed of two oxygen atoms held together by a covalent bond. The energy of any molecule can be divided into three types of energy: (1) electronic energy E_{el} , due to the charge and spin interactions of molecule's electrons and nuclei; (2) vibrational energy E_{vib} , due to the vibration of the atoms within the molecule; (3) rotational energy E_{rot} , due to the rotation of the molecule about its center of mass. Thus, the total energy E_{tot} of a molecule can be written in the form [40]:

$$E_{tot} = E_{el} + E_{vib} + E_{rot} . \quad (32)$$

A molecule can make a transition between different energy states by absorbing or emitting a photon with energy equal to the difference between the energy of the transition states.

Figure 2-6 shows that each electronic state E_{ele} contains many vibrational states E_{vib} , and each vibrational state contains many rotational states. Transitions between electronic states take place in the visible and ultraviolet regions of the spectrum. Transitions between vibrational states within the same electronic states take place in the infrared region of the spectrum, while transitions between rotational states within the same vibrational states take place in the microwave region of the spectrum [41]. The vibrational and rotational energy for diatomic molecules can be described by [41,42]:

$$E_{vib} = hv \left(v + \frac{1}{2} \right) - \sigma hv \left(v + \frac{1}{2} \right)^2 \quad v = 0, 1, 2, \dots , \quad (33)$$

$$E_{rot} = BJ_{rot}(J_{rot} + 1) - DJ_{rot}^2(J_{rot} + 1)^2 \quad J_{rot} = 0, 1, 2, \dots , \quad (34)$$

where v and J_{rot} are the vibrational and rotational quantum number, respectively, σ is the anharmonicity constant, D is the centrifugal distortion constant, μ is the reduced mass and r is the atomic separation.

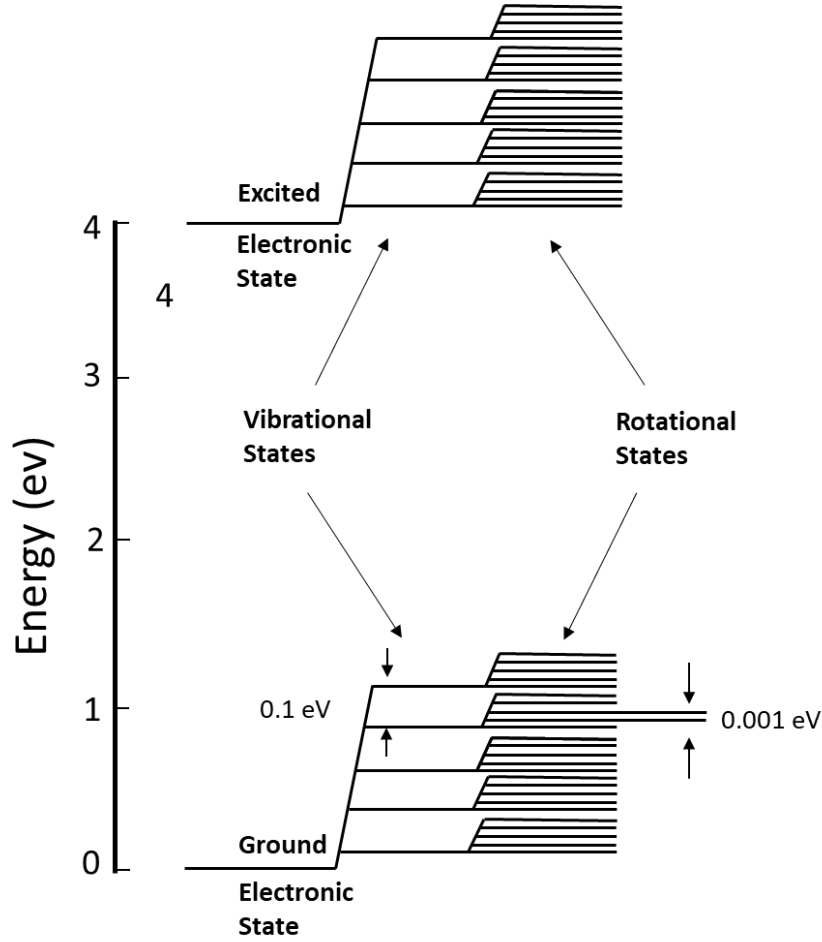


Figure 2-9: Schematic of a molecular energy level diagram with electronic levels, vibrational levels and rotational levels [40].

Figure 2-10 shows a schematic of an energy diagram of $X^3\Sigma_g^-$ and $X^3\Sigma_g^-$ electronic states of O_2 . The transition from the ground electronic state $X^3\Sigma_g^-$ to the excited electronic state $b^1\Sigma_g^+$ contains a number of bands such as A band and B band. The

transition from ground vibrational state ($v' = 0$) of $X^3\sum_g^-$ to the ground vibrational state ($v'' = 0$) of $b^1\sum_g^+$ is the oxygen A band, while the transition from ($v' = 0$) of $X^3\sum_g^-$ to state ($v'' = 1$) of $b^1\sum_g^+$ is the oxygen B band [43]. Within the A band, there are many absorption lines due to the transition between rotational states. The rotational states are described by the total angular momentum J , which is equal the sum of the rotational angular momentum N and the spin angular momentum S . The ground electronic state $X^3\sum_g^-$ is a triply degenerate state contains a states designated by $J' = N' - 1, N', N' + 1$, with only odd values of N' . The $b^1\sum_g^+$ upper state is a singlet state and the available states are designated by $N'' = J''$, with only even values of N'' . The transition between states is determined by the following selection rules $\Delta J = 0, \pm 1$ and $\Delta N = 0 \pm 1$. The oxygen A band is then comprised of four branches, PP, PQ, RQ, and RR. The selection rules $\Delta N = -1$ and $\Delta J = -1$ give the PP branch, $\Delta N = -1$ and $\Delta J = 0$ give the PQ branch, $\Delta N = +1$ and $\Delta J = 0$ give the RQ branch, and $\Delta N = +1$ and $\Delta J = +1$ give the RR branch [44,45]. Also, the transition between states is denoted by $\Delta N N' \Delta J J'$. For example, the transition from $N' = 9$ to $N'' = 8$, and from $J' = 9$ to $J'' = 8$ give the P9P9 transition line.

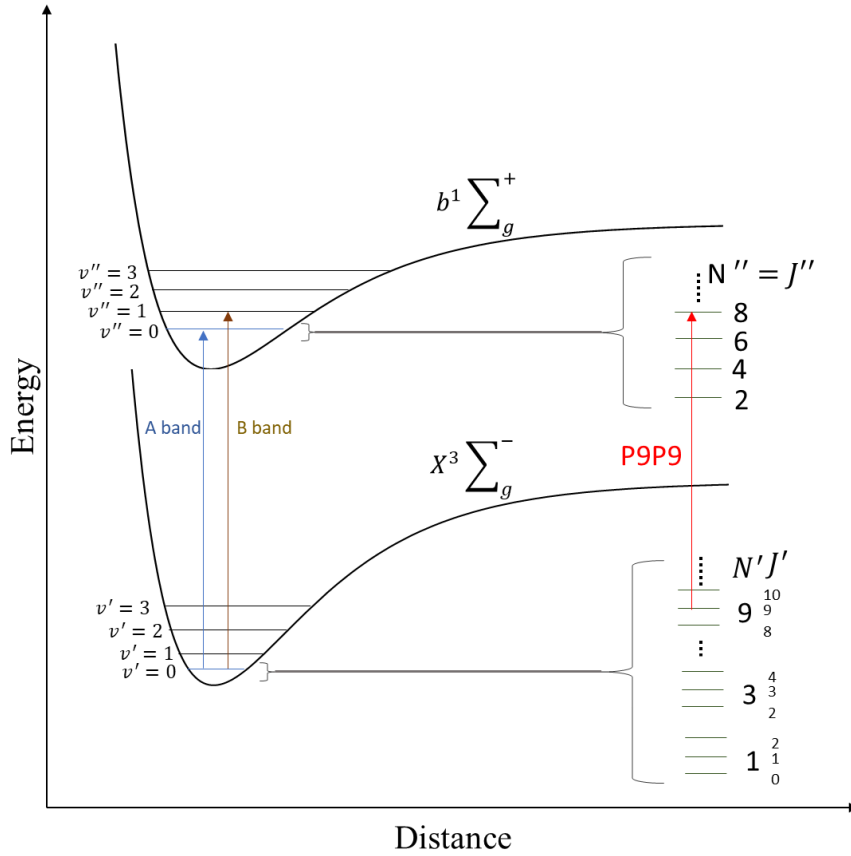


Figure 2-10: Schematic of the energy diagram of oxygen A band.

The wavelength range of the O_2 A band is from 759.3 nm to 773.3 nm [45]. Figure 2-7 shows a part of the O_2 A band absorption spectrum generated from data obtained from HITRAN database (High-resolution TRANsmission molecular absorption database). In this work, we use the P9P9 absorption line of the O_2 A band which has a wavelength of 763.84 nm and is indicated in red line in figure 2-11. Under temperature and pressure standard conditions, the P9P9 absorption line has a width of about 3 GHz and has an absorption cross section at the peak of about $4.4 \times 10^{-23} \text{ cm}^2/\text{molecule}$. This corresponds to an absorbance of about 0.023 per meter in ambient air.

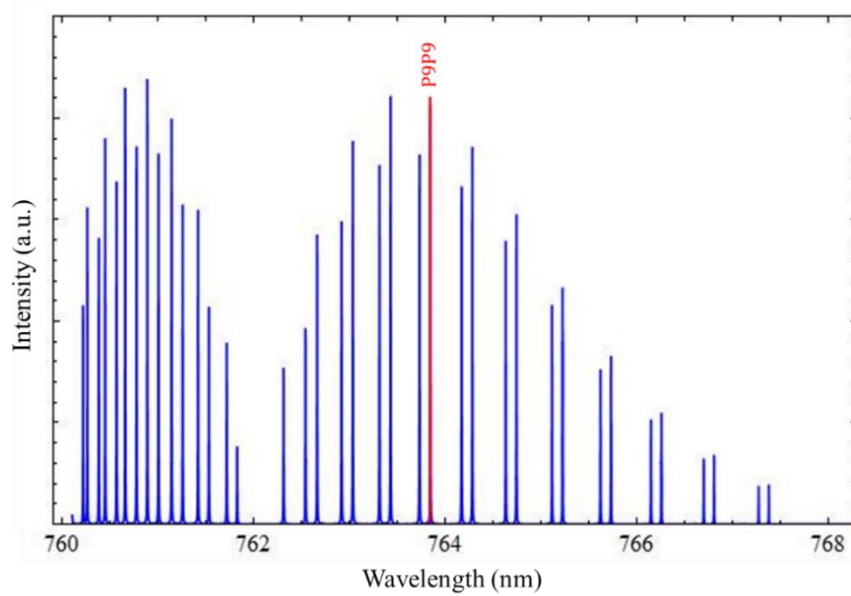


Figure 2-11: A part of absorption spectrum of the molecular oxygen (A-band).

2.5 GASMAS principle and applications

GASMAS has the capability to differentiate between the absorption from a bulk material and that from a gas embedded in it. The embedded gas has very narrow absorption dip compared to the broad absorption bands of the bulk material.

The first report of GASMAS technique was on monitoring the oxygen gas absorption line within wood, apple, and polystyrene foam [14]. In succeeding publications, the experimental setup of GASMAS was developed to study the oxygen line and water vapor [46-49].

Later, the GASMAS technique was used to study diffusion processes. For example, samples of materials can be flushed for long time by nitrogen gas. Then, these samples were exposed to open-air and diffusion of gases such as oxygen gas and water vapor were studied [30,50-51]. In addition, GASMAS technique was used in food packages by

monitoring the absorption signal of oxygen gas and water vapor in the food stuff or in a surrounding headspace. The oxygen gas contents can be assessed non-intrusively by normalizing the oxygen signal to water vapor. Variations in oxygen gas concentration is observed between the tested samples of different expiration-date [19,52].

GASMAS technique is also used in sensing gas inside a human body such as sinus cavities. A simple device containing two laser sources at different frequencies is used to measure the signals from oxygen gas and water vapor within the sinus cavity. The ratio between these signals is related to oxygen gas concentration. It was obvious that there was a good agreement between the results obtained by the GASMAS technique and X-ray computed tomography for many volunteers [15,53-54].

GASMAS technique is used to assess a pore size of nanoporous materials by studying a width of gas absorption line confined within the pores of nanoporous materials. There are four papers, by the same group, that reported on wall-collision broadening obtained by the GASMAS technique and pore size measured by MIP. In the first paper [18], alpha alumina of pore diameter of 70 nm and gamma alumina of pore diameter of 18 nm were studied. The contribution of wall collision broadening on the width of R9Q10 oxygen absorption line was 1.4 GHz in alpha alumina, while the contribution of wall collision broadening in gamma alumina was 6.8 GHz. No model was presented in this paper to study a relation between wall collision broaden and pore diameter. In the second paper [13], only two zirconia samples were investigated under different pressures, and without modeling. The contribution of wall collision broadening on the width of R9Q10 oxygen absorption line was 2.22 GHz in zirconia of pore diameter 43 nm, while the contribution of wall collision broadening in zirconia of pore diameter 115 nm was 1.24 GHz. In the third paper [22], two more samples, titania and alumina, in addition to three previously reported samples, were

studied without modeling. The contribution of wall collision broadening on the width of R9Q10 oxygen absorption line was 1.18 GHz in titania of pore diameter 79 nm, while the contribution of wall collision broadening in alumina of pore diameter 3700 nm was 0.03 GHz. In the fourth paper [23], four more zirconia samples, in addition to the five samples previously reported, were studied and a model assuming pores of a spherical shape was used, but the average pore diameter extracted from this model was almost double that measured by MIP. Table 2-1 lists the samples that used in the references [13,18,22,23] along with their corresponding pore diameter, and wall collision broadening Γ_{wall} .

Table 2-1: Values of the pore diameter and the wall collision broadening Γ_{wall} for samples used in the references [13,18,22,23].

Samples	Pore diameter (nm)	Γ_{wall} (GHz)	Reference
Alpha alumina	70	1.4	[18]
Gamma alumina	18	6.8	[18]
Zirconia	43	2.22	[13]
Zirconia	115	1.24	[13]
Titania	79	1.18	[22]
Alumina	3700	0.03	[22]
Zirconia	54	1.67	[23]
Zirconia	80	1.39	[23]
Zirconia	104	1.10	[23]
Zirconia	131	1.01	[23]

2.6 Alumina (Al_2O_3)

Aluminum oxide Al_2O_3 or alumina is a solid chemical compound occurs naturally as corundum, which has a crystalline form of alpha alumina. If corundum contains magnetite (Fe_3O_4) or hematite (Fe_2O_3), they are called emery. If the corundum contains some elements in their structure, gemstones are formed, with specific names for their colors: (a) sapphire-blue (Fe, Ti); (b) ruby-red (Cr); (c) topaz yellow (Fe^{2+} , Fe^{3+}); (d) emerald-green (Fe^{2+}) [55]. Also, alumina is mainly obtained from bauxite, aluminum hydroxide, which can be found in nature in five different crystalline structures: gibbsite, diaspor, boehmite, bayerite and nordstrandite [56]. Commercially, alumina is obtained by the Bayer process. In the Bayer process, bauxite ore is crushed and mixed with a solution of sodium hydroxide, then heated up to 150-160 °C in a pressure vessel to form a liquid. The formed liquid is aluminum hydroxide with a precipitation impurity. Finally, the aluminum hydroxide is heated to drive off the water to produce alumina [57].

Furthermore, nano alumina particle can be easily synthesized in laboratory by a number of methods, such as, sol-gel method, hydrothermal method, template method, precipitation method, and electrolysis method [58]. In reference [59], a solution of aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (> 98%) and anhydrous ethanol $\text{C}_2\text{H}_5\text{OH}$ mixed with propylene oxide $\text{C}_3\text{H}_6\text{O}$ (> 99%) to form a gel. The gel is then calcined to produce a nano porous alumina. Furthermore, nanoporous alumina can be prepared by anodization process. Anodization is done by applying an electric current to an aluminum substrate in the presence of an acid electrolyte to obtain highly ordered nanoporous alumina [60].

Figure 2-12 shows the phase transition of alumina during the calcination process [61]. Alumina changes their structure until all the material is converted into thermodynamically

stable α -alumina. Several transitions of alumina are produced during this process where the phase transition between them is irreversible and occurs only by increasing the temperature. Alumina phases are described by Greek letters to identify them such as: gamma (γ) alumina, delta (δ) alumina, theta (θ) alumina, kappa (κ) alumina, chi (χ) alumina, eta (η) alumina and rho (ρ) alumina [62].

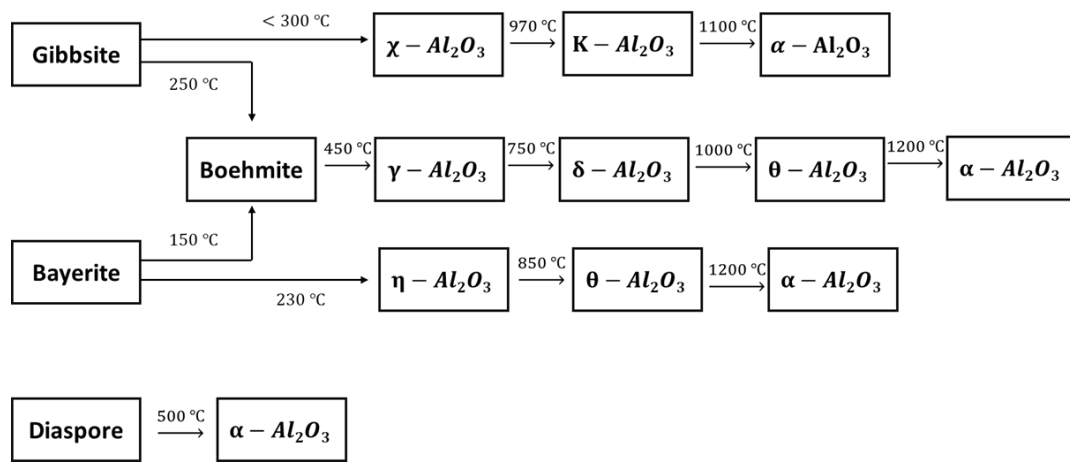


Figure 2-12: A sketch of the phase transition of alumina.

The difference between these phases is mainly in their crystal structures. The X-Ray powder Diffraction (XRD) is a common way to identify the crystal structures of these phases. Figure 2-13 shows the XRD of alpha, kappa, gamma, eta, theta, and chi alumina. These spectra are obtained from the International Center for Diffraction Data (ICDD) and they have the following ICDD code numbers: the alpha is 01-071-6478, for gamma is 00-029-0063, for theta is 00-056-0456, for kappa is 00-026-0031, for chi alumina is 00-004-0880, for eta is 01-080-0955.

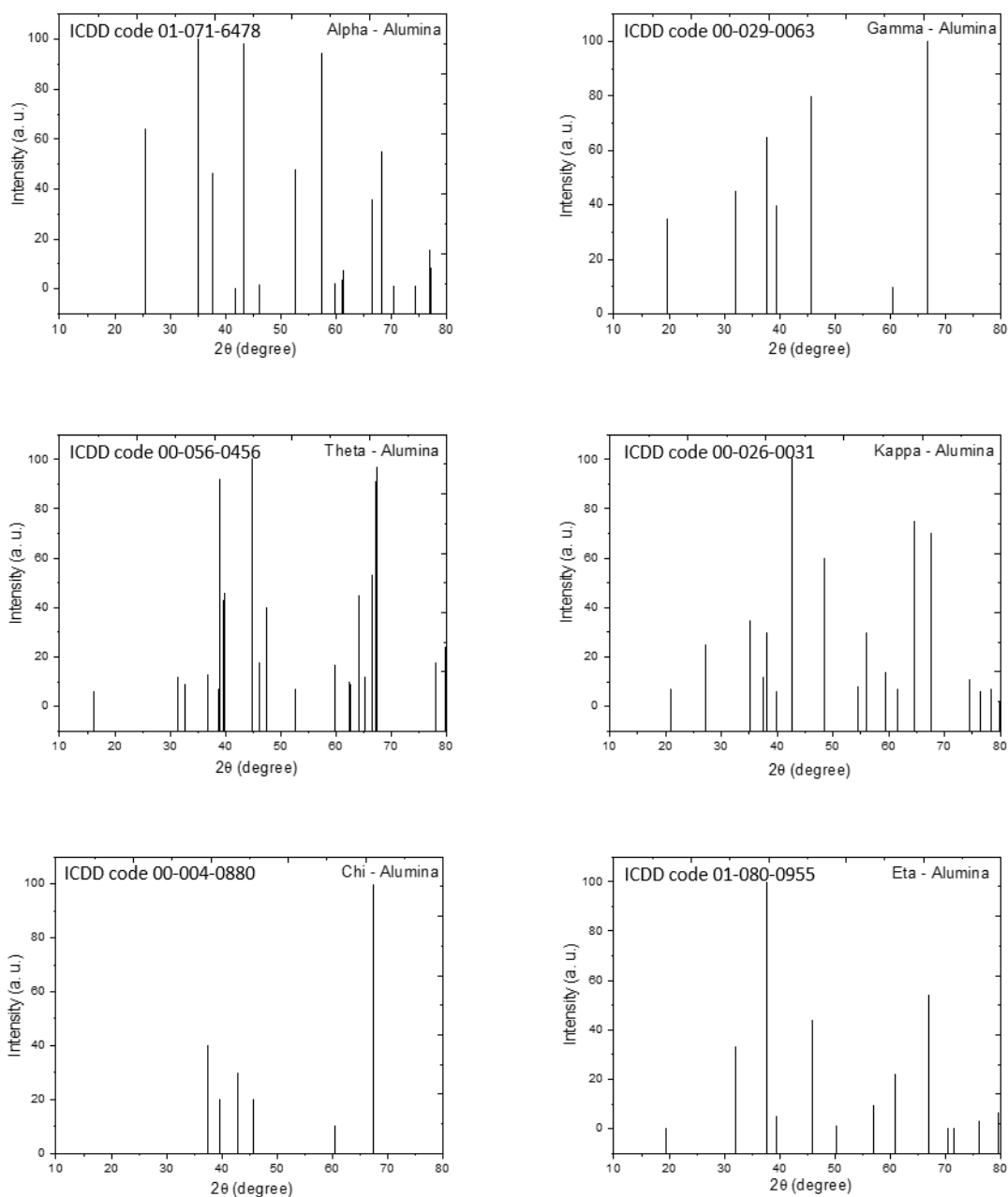


Figure 2-13: XRD spectra for the most common alumina phases.

Alumina has many favorable properties such as high hardness, high thermal stability, excellent wear resistance, and high melting temperature over 2000 °C. These properties make alumina used in various industries and applications such as abrasive industries, pharmaceutical industries for gastric treatment, refractory industries as a shielding

materials, coating industries as wear resistant paints, electronic industries as a substrate for certain electronic circuits and thermal shock resistance industries as spark plug bodies [63]. Porous alumina is also used in many fields and applications such as, water purification [4], gas capture [64], biomedical materials for bone spacer and teeth implants [6], and in catalytic applications [65].

Alumina has suitable optical properties for GASMAS. Alumina has high refractive index of about 1.76 at wavelength 760 nm and low absorption coefficient less than 0.01 cm^{-1} . Thus, the light is heavily scattered within alumina samples and a strong absorption signal can be detected from gaseous oxygen entrapped within the pores of alumina.

2.7 Porosity

Porosity may be classified as total porosity or effective porosity. The total porosity is a ratio of the volume of space within the bulk to the total volume of the bulk. The space includes isolated pores, interconnected pores, and cracks. The effective porosity is a fraction of the volume of the interconnected pores to the total volume of the bulk. The porosity can be expressed as a percentage varying between 0% to 100%.

Porosity can be found theoretically for an object made of identical solid spherical grains packed in an order way such as in cubic, hexagonal, and rhombohedral packing. For example, for cubic packing of spherical grains of diameter d , the bulk volume is $V_b = d^3$ while the grain volume is $V_s = \pi d^3/6$. Thus, the porosity is $\phi = [(V_b - V_s)/V_b] \times 100\% = 47.6\%$ [66]. There are several factors that may changes the value of porosity such as, grain shapes, grain sizes, and random packing of grains.

Practically, the effective porosity can be measured using different methods such as, buoyancy method, and saturation method. In saturation method, the sample is dried and

weighed w_{dry} , and the volume of dried sample is determined V_{bulk} . Then, the sample is saturated with water of density ρ_{water} , and weighed after removing any excess water from its surface w_{sat} . The effective porosity is given by [67]:

$$\phi = \frac{(w_{sat} - w_{dry})}{\rho_{water} \times V_{bulk}} \quad (35)$$

CHAPTER 3

EXPERIMENTAL DETAILS

This chapter discusses the experimental details of this work. Section 3.1 gives details about the employed laser diode; section 3.2 presents the experimental setup for measuring the P9P9 absorption line of molecular oxygen in open-air and in porous material; section 3.3 addresses samples and their characterization.

3.1 The laser

The laser used is a Vertical-Cavity Surface-Emitting Laser (VCSEL) (FU-763-0.3-TO5-01, Frankfurt Laser Company). It is a single-mode laser with linewidth of about 0.1 nm. The spectral mode of this laser is checked by a spectrometer (SPEX 1403). Also, it has a built-in temperature sensor of a Negative Temperature Coefficient (NTC) thermistor type. The resistance of the thermistor R is fixed by a temperature controller (TED200C, Thorlabs), and the laser temperature T is determined using the following relation:

$$R = 10 / \exp[3892 \left(\frac{1}{298} - \frac{1}{T} \right)] \quad (36)$$

where R in $k\Omega$ and T in kelvins.

Figure 3-1 shows a picture of the used VCSEL laser, and table 3.1 presents its specifications.

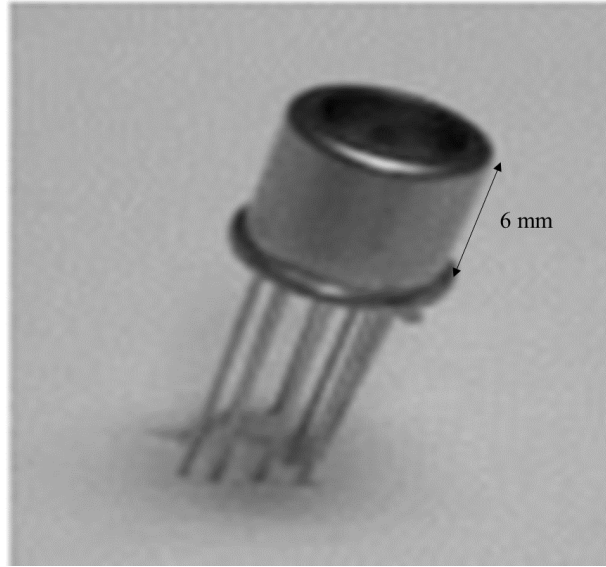


Figure 3-1: A picture of the employed VCSEL laser.

Table 3-1: FU-763-0.3-TO5-01 VECSEL laser diode specifications.

Specifications	Units	Min	Typical	Max
Emission wavelength	nm	762	763	764
Threshold current	mA		0.5	
Laser current	mA			2
Output Power	mW	0.25	0.3	
Threshold voltage	V		1.8	
Laser voltage	V		2	
Spectral bandwidth	MHz		100	
Operation temperature	°C	-20		80
Thermistor resistance	kΩ		10	
Beam divergence	°	10		25

The operating temperature of the laser is fixed by TED200C at 25 °C. A national instruments data acquisition device DAQ (NI USB-6366, National Instruments) is used to control the voltage of current source. Its sampling rate 2.00 MS/s sample rate with 16 bits

Analog to Digital Conversion (ADC) resolution over a range of -10 to 10 V. The operating current of the laser is in the range between 0.5 mA to 2 mA, which is small compared to the operating range of -500 to 500 mA of the current controller LDC 205C from Thorlabs available in the lab. The current controller is driven by the 16-bit DAQ card which gives a resolution of 0.015 mA or 4 GHz per the smallest step voltage of the card. This is not enough to measure the linewidth of O₂ which has a linewidth of 3 GHz. To have more resolution, a homemade voltage-controlled current source is built to operate the laser. Figure 3-2 shows a diagram of the circuit of the voltage-controlled current source. The current is kept fixed through the laser by maintaining a fixed potential difference across R₅:

$$I_c \approx I_e = \frac{V_1 - V_5}{R_5} \quad (37)$$

V₁ is fixed by the voltage regulator LM317 while V₅ is controlled by V_{in}. V₁ = V_{ref}(1 + R_L/R_H) = 1.25(1 + 3.9 kΩ / 1kΩ). V_{ref} = 1.25 V is a stable reference voltage maintained by LM317 between its OUT and ADJ terminals. From the fact that no current flows into the inputs of operational amplifier 1, V₂ = V₁R₂/(R₁+R₂) = V₁/2 . Since the inputs of operational amplifier 1 have the same electric potential, V₂ = V₃, and since no current flows in the inputs of operational amplifier 2, (V₄ - V₃)/R₄ = (V₃ - V_{in})/R₃) or V₄ = R₄/R₃(V₃ - V_{in}) + V₃ = 2V₃ - V_{in} = V₁ - V_{in}. Since V₄ = V₅, the voltage drops across the resistor R₅ is V₁ - V₅ = V_{in}. Thus, I_c = 0.55 × 10⁻³ V_{in}.

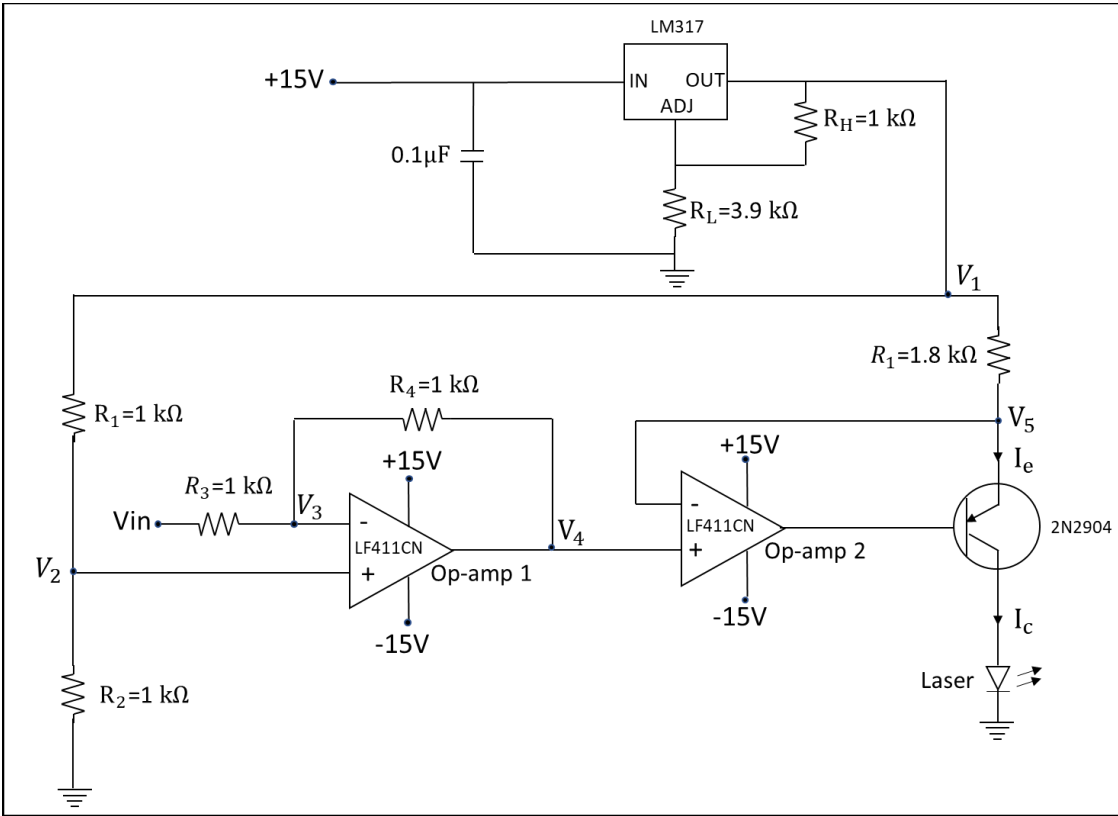


Figure 3-2: Diagram of the circuit of the voltage-controlled current source.

The voltage-controlled current source is checked with a red-Light Emitting Diode (LED) before using with the laser diode. Figure 3-3 shows current produced by the source versus the input voltage. The current source can generate a maximum current of 2 mA with a driving voltage of 3.5 V. With the current source, the minimum voltage change in V_{in} that can be produced by the DAQ card corresponds to a current change of 0.00017 mA or 0.04 GHz in the laser frequency.

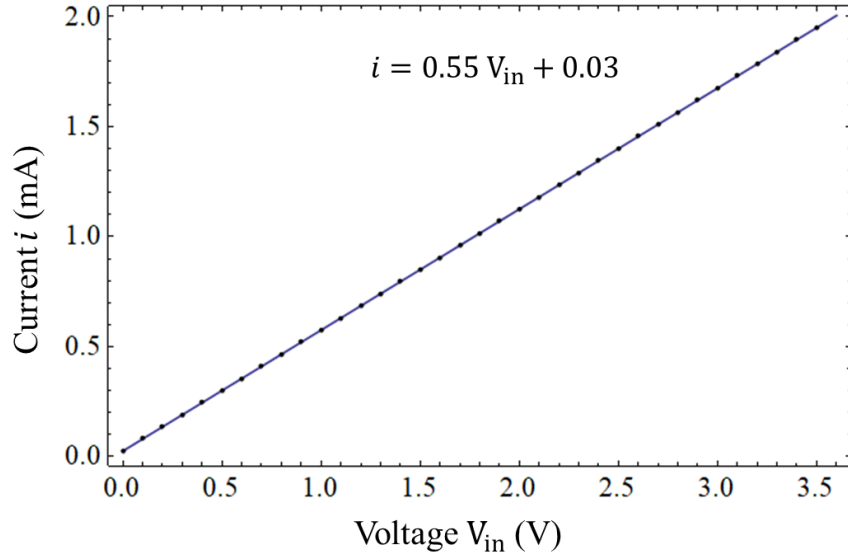


Figure 3-3: Voltage-current characteristic of the voltage-controlled current source.

The wavelength of the laser is calibrated using a high-resolution spectrometer (SPEX 1403) coupled with an Aphalas CCDS3600-D(-UV) CCD camera, and using a wavemeter (HighFinesse, WS6/200). The spectrometer itself is calibrated using a krypton spectroscopic lamp at vacuum wavelength 760.36 nm and argon lamp at vacuum wavelength 763.72 nm. The emission lines of the krypton and argon lamps are observed at pixel 3129 and 1027.5 of the CCD line camera, respectively. The following is the calibration function for the spectrometer:

$$\lambda(Pix) = 765.363 - 0.0015989 Pix \quad (38)$$

Figure 3-5 shows a schematic diagram of the experimental setup used to calibrate the laser wavelength. The voltage-controlled current source is connected to DAQ to change the injection current i . An aspheric coated lens (C230TMD-B, Thorlabs) of focal length of

4.51 mm with low reflectance at wavelength rang 600-1050 nm is used to collimate the laser beam.

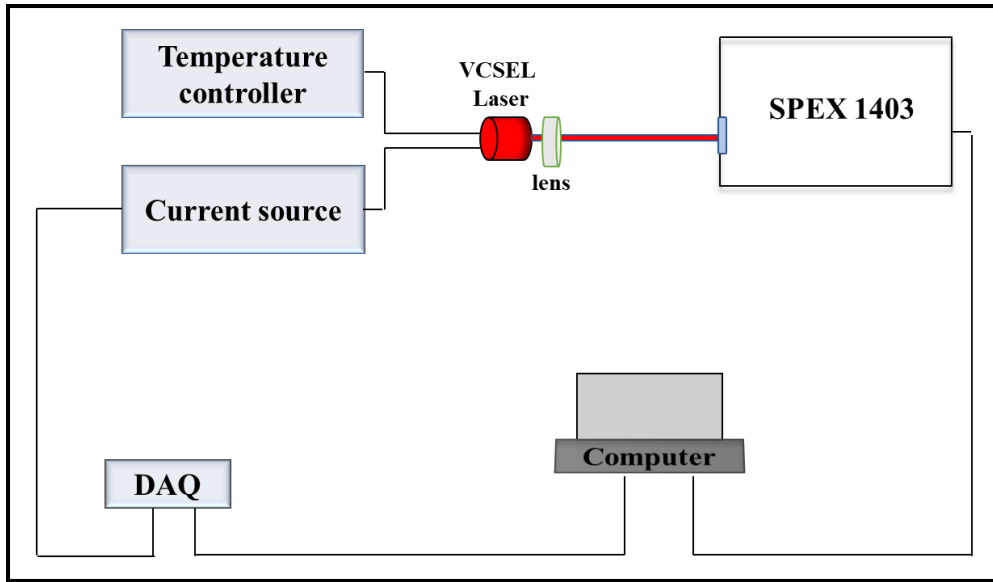


Figure 3-4: An overview of the experimental setup to operate and calibrate the laser diode using the spectrometer (SPEX1403)

Figure 3-6 shows the calibration curve of the pixel position of the spectrometer and the current i of the laser, and a quadratic relation is obtained:

$$Pix(i) = 1463.03 - 217.923i - 36.0108i^2 \quad (39)$$

The wavelength of laser in nanometer as a function of injection current is given by substitution the Eq. 39 in Eq. 38:

$$\lambda(i) = 765.363 - 0.0015989 (1463.03 - 217.923i - 36.0108i^2) \quad (40)$$

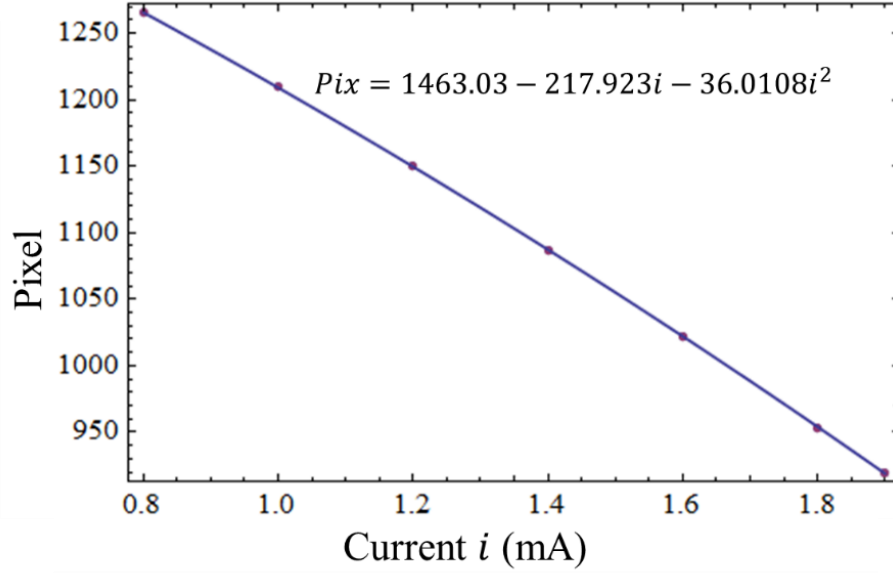


Figure 3-5: Calibration curve of the laser wavelength as a function of injection current is obtained using the spectrometer (SPEX1403)

Also, the wavelength of the laser is calibrated using a wavemeter (HighFinesse, WS6/200) which has an absolute accuracy of 0.0005 nm. The wavemeter itself is calibrated using a stabilized helium-neon laser.

Figure 3-7 shows the vacuum wavelength of laser λ in nm measured by the wavemeter as function of the injection current i in mA. The wavelength of the laser is found to fit very well the following quadratic equation:

$$\lambda(\text{nm}) = 763.011 + 0.378899 i + 0.0451823 i^2 \quad (41)$$

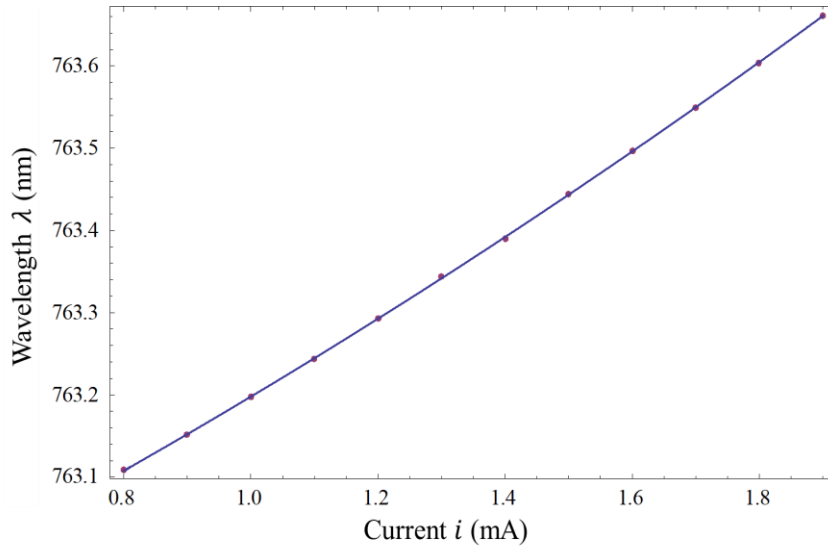


Figure 3-6: laser wavelength as a function of the injection current.

Both calibrations of laser wavelength, using the spectrometer and the wavemeter, give the same result of wavelength with a small difference in measurements of about 10^{-3} nm. For example, the wavelength of laser measured using the spectrometer is 763.837 nm at $i = 1.8$ mA, while the measured wavelength at the same current using a wavemeter is 763.839.

3.2 Absorption from molecular oxygen

Figure 3-8 shows a schematic diagram of the experimental setup to observe the absorption line of molecular oxygen around 763 nm in open-air.

The DAQ board and a LabVIEW code are used to control the injection current as well as to collect the output signal from the photodetector. The LabVIEW code generates a triangular signal to vary the laser wavelength by varying the injection current in a step manner, the injection current was varied from 0 to 2 mA with an increment of 0.001 mA, (see Appendix A). At each step, the LabVIEW code reads 100 samples and averages them to reduce the noise. The noise is further reduced by averaging over 25 signals.

The laser is mounted into a homemade heatsink to dissipate heat into the ambient air.

The aspheric lens is mounted into a lens cell adapter (S1TM10, Thorlabs). Then, the laser and the aspheric lens is mounted into a lens tube (SM1.5L10, Thorlabs). The transmitted beam through 5 m of open-air is collected by a silicon PIN photodiode (DET36A/M, Thorlabs) with an active area of 13 mm² and a responsivity of about 0.45 A/W at a wavelength of 763 nm.

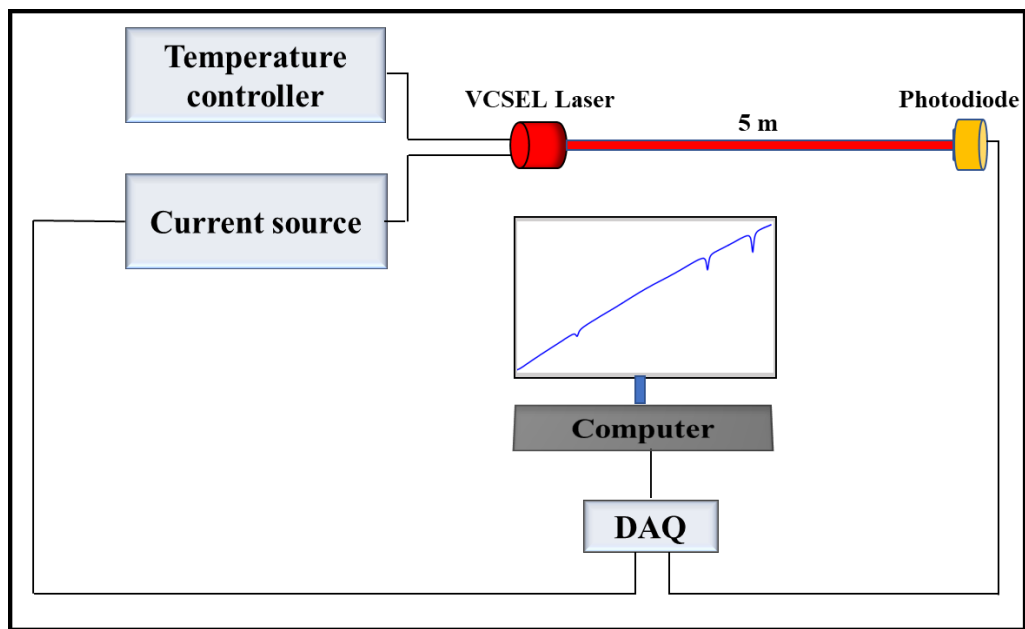


Figure 3-7: Schematic diagram of the experimental setup to observe the absorption lines of molecular oxygen in open-air.

Figure 3-9 shows the measured signal from the detector as a function of the laser injection current. This range covers three strong oxygen absorption lines of the oxygen A-band, namely, P9P9 line at 763.84 nm, P9Q8 line at 763.73 nm, and P7P7 line at 763.43 nm. The measured wavelengths agree with that obtained from HITRAN data base [37].

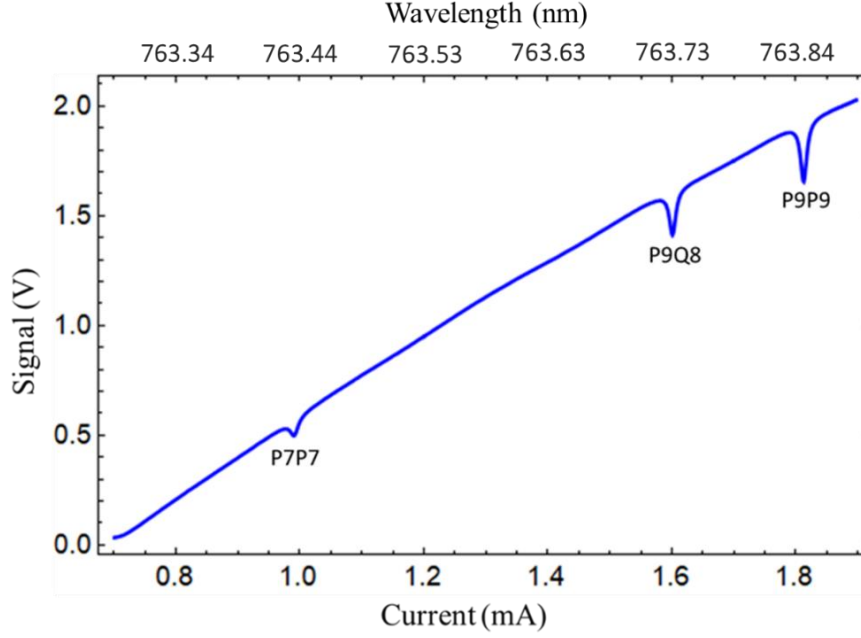


Figure 3-8 : Molecular oxygen absorption lines P7P7 at 763.43 nm, P9Q8 at 763.73 nm and P9P9 at 763.84 nm measured through 5 m path length of open-air.

Figure 3-10 shows a schematic diagram of the experimental setup to study the absorption of molecular oxygen in alumina samples. The laser beam passes through sample without using the collimating lens. The open-air distance between the laser and sample is about 1 cm. This distance is much smaller than the effective pathlength within the sample, which is around 1 m. Hence, the absorption from oxygen in the open-air path is negligible compared with the absorption of oxygen entrapped in the sample.

Optical interference fringes often limit the sensitivity of laser absorption measurement [68]. The speckle patterns caused by interference can be reduced either by rotating the sample or by dithering the laser beam [48]. Thus, a moving lens in horizontal way is employed to dither the laser beam, hence, the speckle patterns are converted to noise and then are reduced by averaging. The dithering lens system, which consists of a lens and two tracking coils, is extracted from a CD player. A sine wave generator feeds the tracking coils

with a low frequency signal of 200 Hz. Figure 3-11 shows the effect of dithering process on the absorbance measurements for the same sample. The laser, the dithering lens, and the detector are vertically arranged. This arrangement allows for powder samples to be placed directly on the detector without the need of a glass window, which may cause unwanted optical interference that may arises from the surfaces of the glass window.

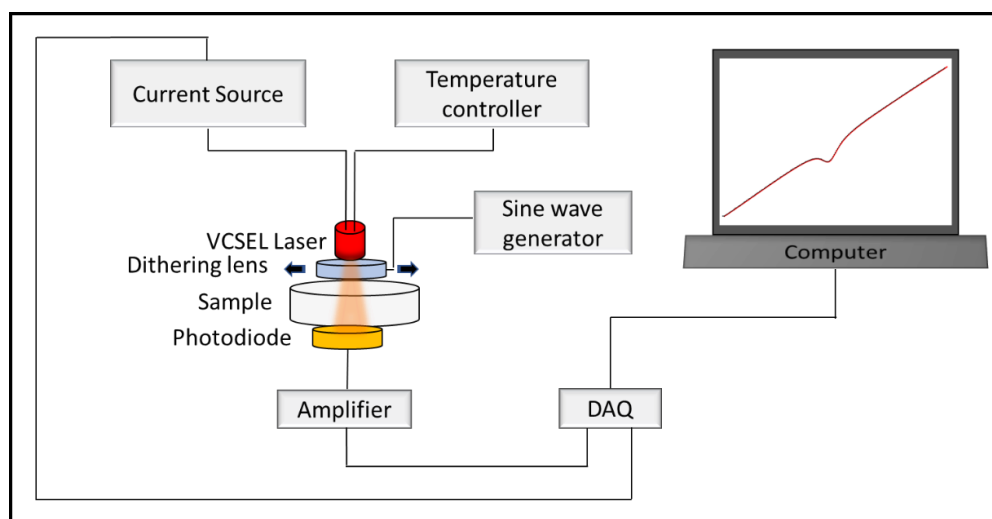


Figure 3-9: Schematic diagram of the experimental setup to observe the absorption line of molecular oxygen in alumina samples.

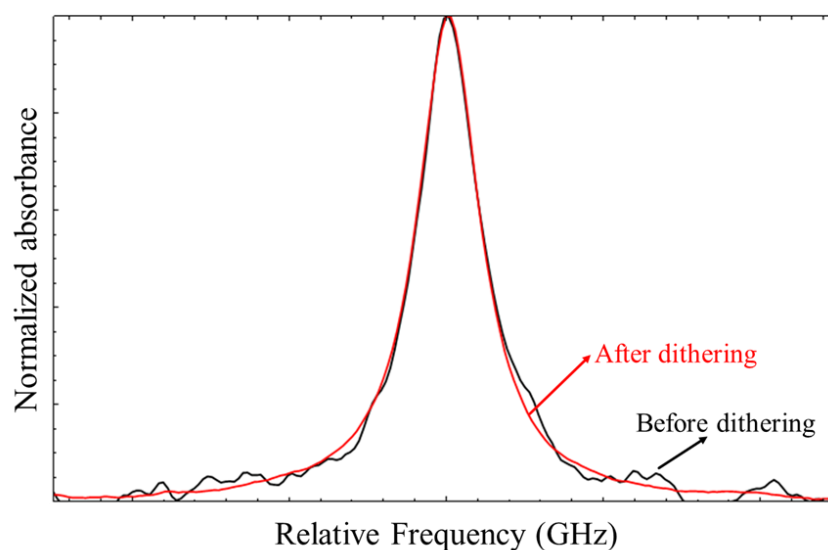


Figure 3-10: An example of optical fringes removed by using dithering lens for the same sample.

Figure 3-12 depicts a picture of the part of the experiment where the laser, the dithering lens, and the detector are vertically arranged. A metal cover is used to eliminate the unwanted light from the surrounding. The metal cover and the base form a vacuum chamber which can be used to control the environment in which the experiment is conducted.

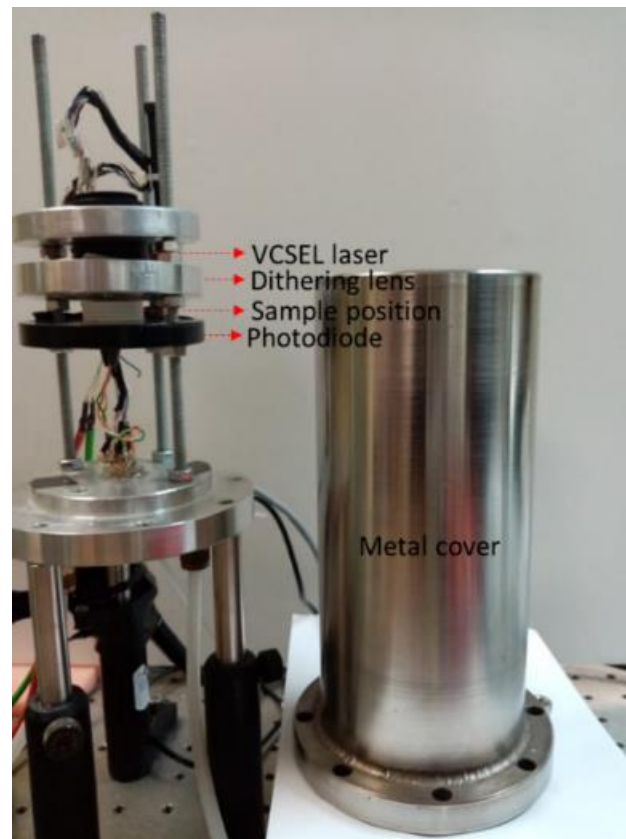


Figure 3-11: A picture of the laser, dithering lens, and detector.

3.3 Samples and their characterization

This section discusses the procedures to prepare two different sets of samples: solid disc and powder samples of alumina. The section also discusses the techniques used to characterize these samples.

Three homemade solid discs are prepared by mixing 80 g of aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (> 98%) and 350 mL of anhydrous ethanol $\text{C}_2\text{H}_5\text{OH}$ at room temperature. After the aluminum nitrate is fully dissolved, propylene oxide $\text{C}_3\text{H}_6\text{O}$ (> 99%) is added drop wise while stirring until the mixture is converted into a transparent gel. The gel is then sealed with a piece of polyethylene film and kept under static conditions for one week for aging. After that, the wet gel is cut into pieces and dried at 100 °C for two days. The pieces' color become transparent yellowish and their size is shrunk to about half of the original size. Then the samples are treated at 400 °C for ten hours till their color become white yellowish. After that, the samples are further treated at 1100 °C for another 10 hours until their color become white. Finally, each sample is compressed under a different high pressure and shaped into a disc of a diameter of 15 mm. Three different samples are produced using compression pressures of 2-ton, 3-ton and 4-ton with thicknesses of 6.2 mm, 5.8 mm and 5.2 mm, respectively. The discs are made solid and cohesive by heat treatment at 1100 °C for 10 h.

Powder samples are prepared from alumina powder 100-200 mesh obtained from Bio-Rad laboratories (catalogue # 132-1340). To obtain samples with different pore sizes, the alumina powder is treated at different temperatures. One sample is not treated with heat, while the other samples are treated at specific temperatures of 700, 850, 950, 1000, 1150 and 1270 °C. In the heat treatment process, the temperature of samples is gradually raised

with a rate of 2.00 °C/min to the desired temperature and kept at the desired temperature for 10 hours before it is gradually cooled to the room temperature.

The pore size of the alumina solid disc samples is measured by the MIP technique, while the pore size of the alumina powder samples is measured by the gas adsorption technique.

The MIP data were collected by Gabas Omni Petroleum Services Company using a micrometrics autopore 9600 mercury porosimeter with a pressure ranging from approximately 1 psi (pound-force per square inch) to 60000 psi.

The pore size of the alumina powder samples is measured by gas adsorption technique.

The gas adsorption data were collected using a Quantachrome instruments quadrasorb automated surface area & pore size analyzer.

X-Ray diffractometer from Bruker, model D2 phaser, are used to identify the samples and determine their phases.

CHAPTER 4

Results and discussions

Two different sets of alumina samples are investigated: the first set consists of alumina discs while the second set consists of alumina powder.

In the first section of this chapter, α -alumina disc samples are investigated by GASMAS and MIP. The GASMAS is used to measure the broadening of the absorption line at 763.84 nm of oxygen entrapped in the samples, while the MIP technique is used to measure the pore size of these samples. The range of the measured average pore size of the samples is between 70 and 150 nm. A theoretical model based on kinetic theory of gases is developed to find a correlation between the wall collisional broadening of the P9P9 molecular oxygen absorption line and the average pore size of the samples. For the investigated samples, it is found that the line broadening due to wall collisions is inversely proportional to the average pore size.

In the second section, powder alumina samples are investigated by GASMAS and the gas adsorption technique. The GASMAS is used to measure the broadening of the P9P9 absorption line of oxygen entrapped in the samples, while the gas adsorption technique is used to measure the pore size of these samples. The average pore size of the powder samples lies within the range 10 nm to 40 nm. In this range, the contribution of the wall collision broadening is found to be approximately inversely related to the average pore diameter. Furthermore, the confined oxygen gas absorbance measured by GASMAS is found to be linearly correlated to the effective porosity evaluated by the saturation method.

4.1 Pore size assessment of alumina discs by GASMAS and MIP

Seven alumina solid discs are investigated, four of which are purchased and three are homemade. A picture of these discs is shown in figure 4-1.

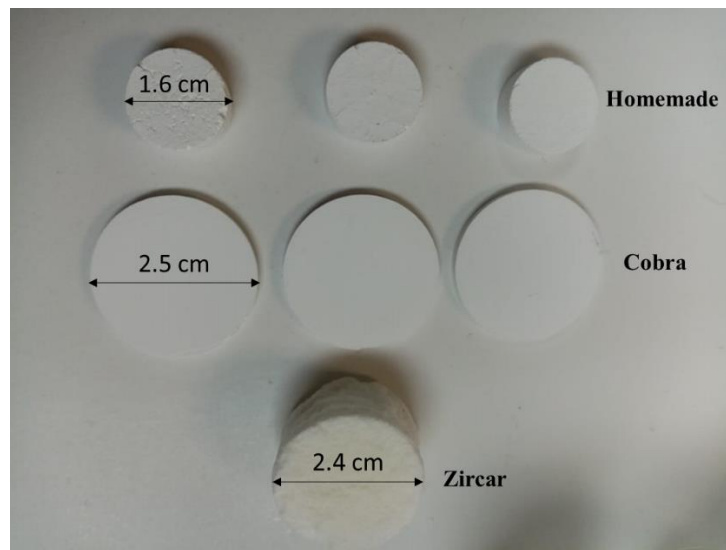


Figure 4-1: Photograph of alumina solid discs.

Three of the purchased discs are from Cobra Technologies B.V., while the fourth disc is from Zircar Ceramics, Inc. The Cobra discs are of high-purity alpha alumina ($\alpha\text{-Al}_2\text{O}_3$) (> 99.9%) with identical dimensions of 25.4 mm in diameter and 2 mm in thickness. The Zircar disc is a multiphase alumina of micrometer pore size distribution with the same diameter as that of Cobra discs but with a thickness of 10 mm.

The samples are characterized using MIP, XRD and Scanning Electron Microscopy (SEM). Figure 4-2 shows the raw data of the MIP for the Cobra discs (*a*), and the homemade discs (*b*).

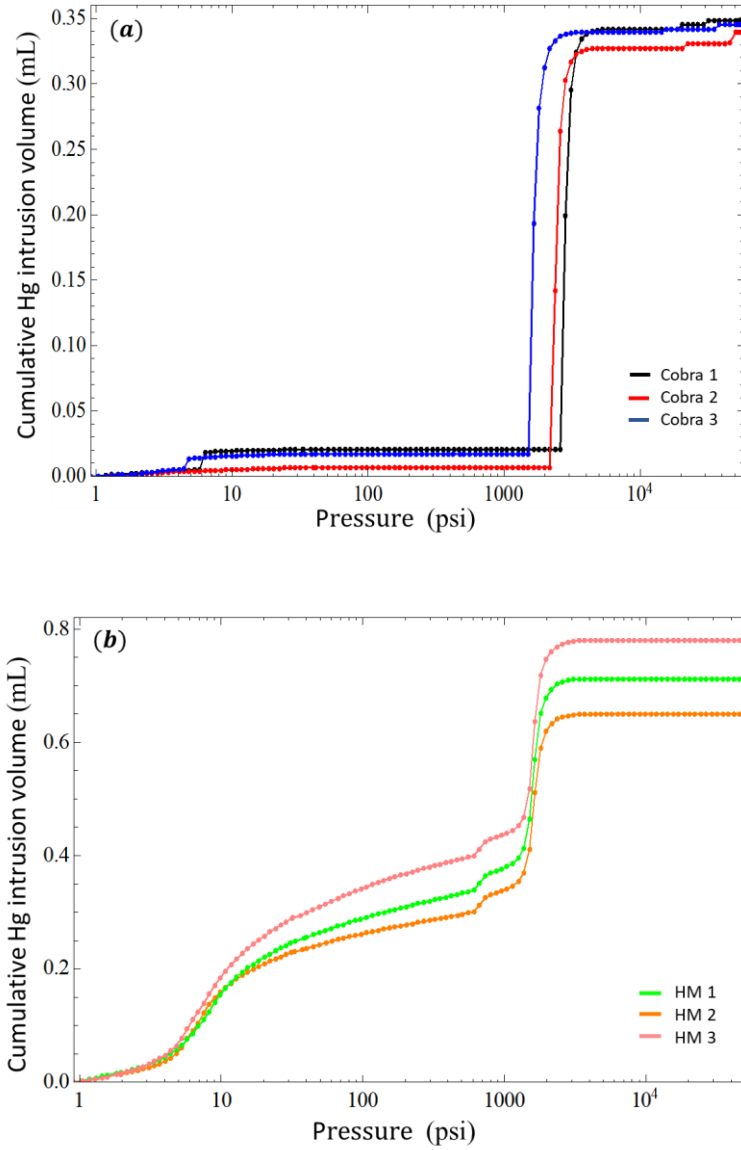


Figure 4-2: Raw data of the MIP, (a) for the Cobra discs, and (b) for the homemade discs .

Figure 4-3 shows the distribution function of pore diameter $D(w)$ as a function of pore diameter w obtained from the raw data of the MIP for the Cobra discs (a), and the homemade discs (b). It is found that the samples have narrow pore distributions with average pore diameters of 72 nm (Cobra 1), 84 nm (Cobra 2) and 123 nm (Cobra 3) for the Cobra discs, and average pore diameters of 145 nm (HM 1), 146 nm (HM 2) and 144 nm (HM 3) for the homemade discs.

nm (HM 3) for the homemade discs. MIP was not performed for the Zircar disc because it is so fragile. Its pore size of about 10^3 nm is estimated roughly from its SEM image.

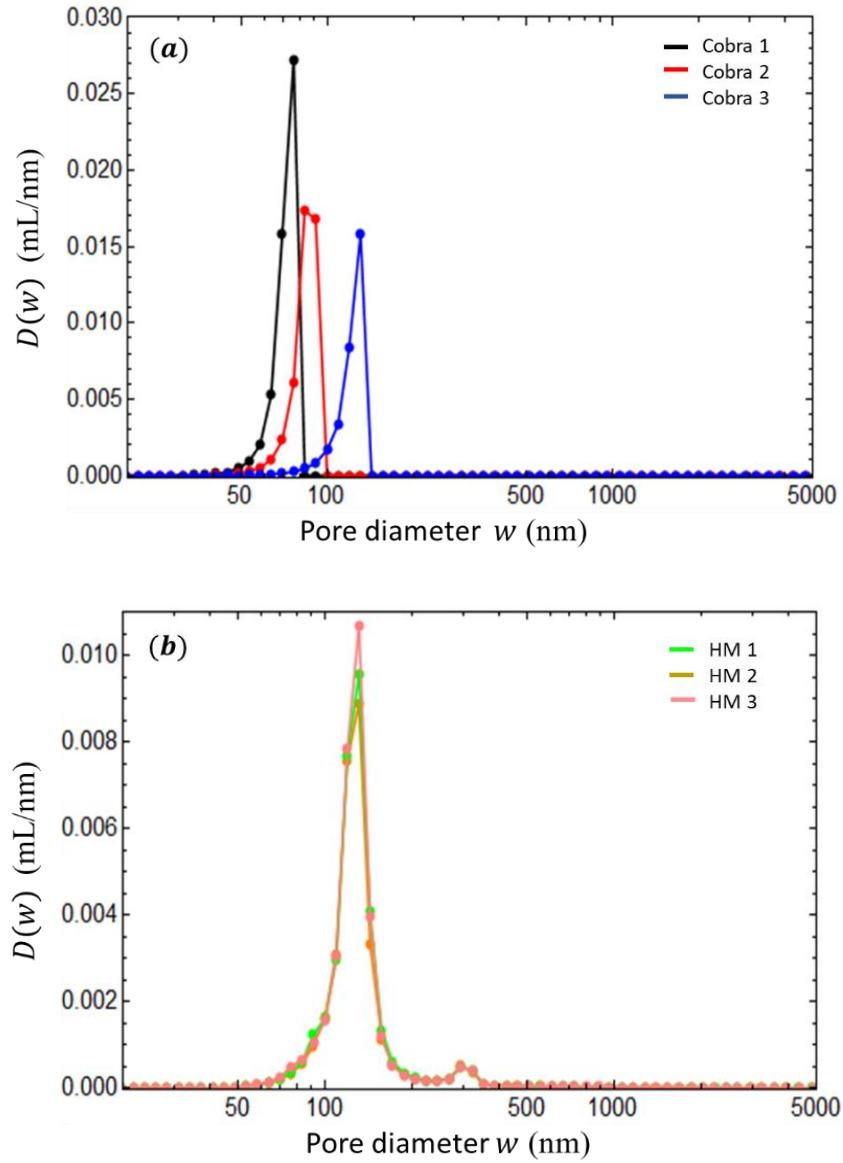


Figure 4-3: Distribution function of pore diameter $D(w)$ as a function of pore diameter w , (a) for the Cobra discs, and (b) for the homemade discs.

The average pore diameter $\bar{w}$ of the samples is evaluated by using the following equation:

$$\bar{w} = \frac{1}{\sum_{i=1}^n (D(w))_i} \sum_{i=1}^n w_i \times (D(w))_i \quad (42)$$

SEM images of the samples are shown in figure 4-4. The images of Cobra 1, Cobra 2 and Cobra 3 are shown in figure 4-4 (a), (b), and (c), respectively while the image of the Zircar disc is shown in figure 4-4 (d). The homemade discs have similar SEM images and here only the image of HM 1 disc is shown in figure 4-4 (e). Although the SEM images cannot give an accurate estimate of the average pore size, they can give a qualitative assessment. It should be noted that the pores in the SEM images have sizes of the same order of magnitude as those measured by the MIP technique.

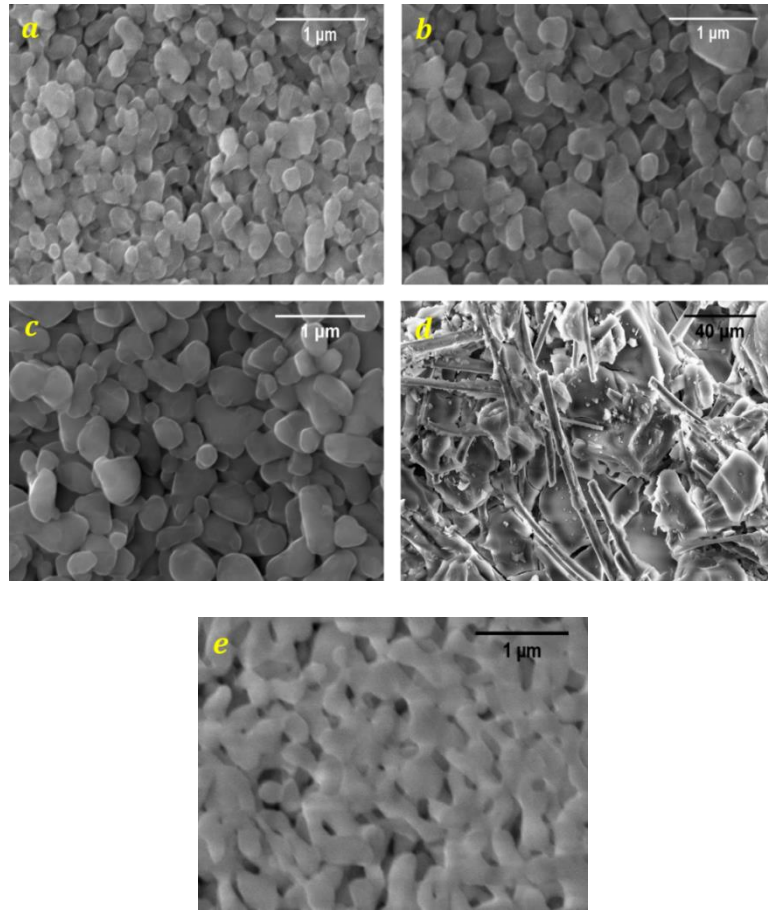


Figure 4-4: SEM images of (a) Cobra 1, (b) Cobra 2, (c) Cobra 3, and (d) Zircar alumina (e) HM 1.

The Cobra and homemade discs have XRD spectra like that of a pure α -alumina. Figure 4-5 shows an excellent agreement between the XRD spectrum of a reference α -alumina (black) and that of the Cobra 1 (red), and the homemade HM1 (blue). However, the XRD spectrum of the Zircar sample (pink) shows that it is not a pure α -alumina but rather a mixture of α -alumina with other alumina phases.

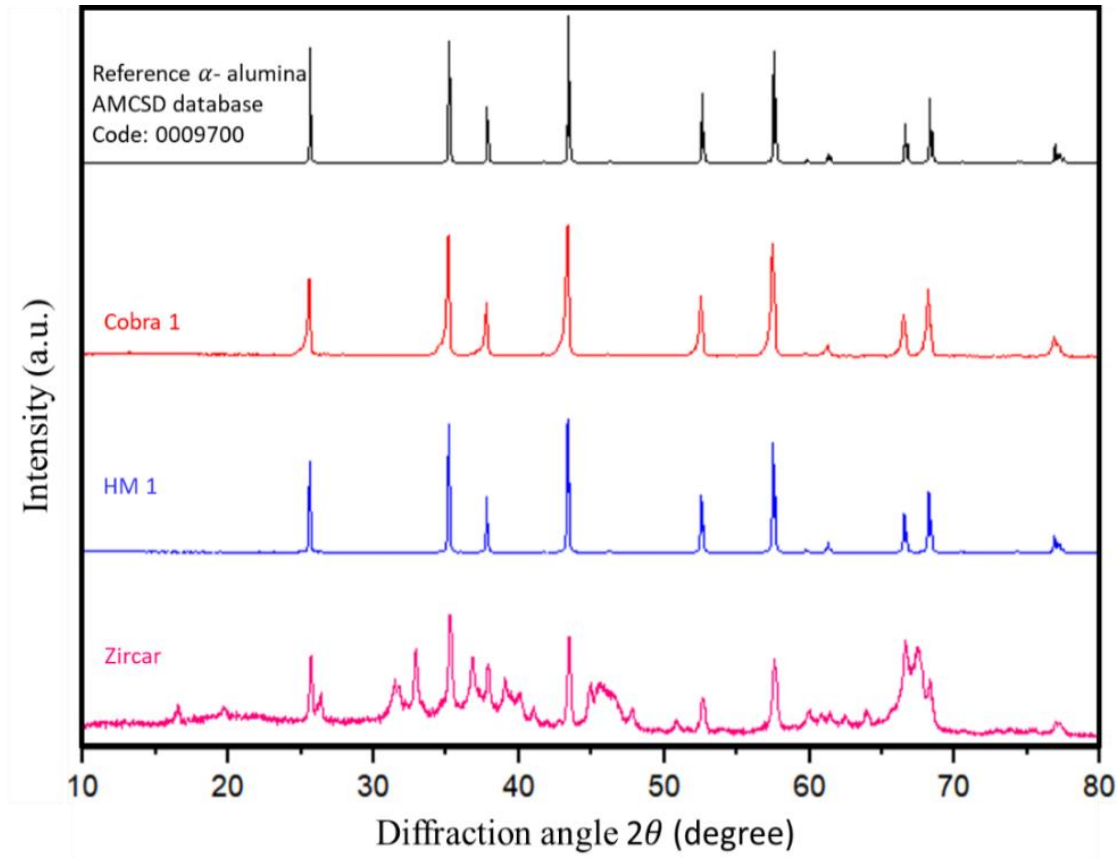


Figure 4-5: XRD spectra for the reference α -alumina, Cobra 1, HM 1 and the Zircar disc.

Although, the samples have thicknesses of few millimeters, multiple scatterings within the samples make the effective path length long enough to observe a clear oxygen absorption signal by direct absorption spectroscopy. For example, the absorbance from oxygen in 5 mm open-air is about 10^{-4} while the observed absorbance in the samples is typically 10^{-2} .

Figure 4-6 shows the detected transmitted signal $s(i)$ as a function of the laser injection current i from Cobra 1 disc. The signal increases almost linearly due to the variation of the laser intensity with the laser injection current, which can be fitted to a polynomial function. The dip at the middle is due to the absorption by the oxygen gas, which is expected to have an approximately Lorentzian shape. Therefore, in order to obtain the absorbance from the oxygen gas alone, the transmitted signal $s(i)$ is fitted to a Lorentzian function summed with a polynomial function of order m (see appendix B):

$$s(i) = a \frac{(\gamma/2)^2}{(i - i_o)^2 + (\gamma/2)^2} + \sum_{n=0}^m c_n (i - i_o)^n \quad (43)$$

where the fitting parameters are a, i_o, γ , and c_n . Here a represents the height of the Lorentzian function, i_o represents the current at which the Lorentzian function peaks, γ represents the full width at half maximum FWHM of the Lorentzian function measured in mA, c_n 's represent the coefficients of the polynomial function, and $m = 6$ is the order of the polynomial function. The oxygen absorbance at the peak of the Lorentzian function can be obtained from $-a/c_0$.

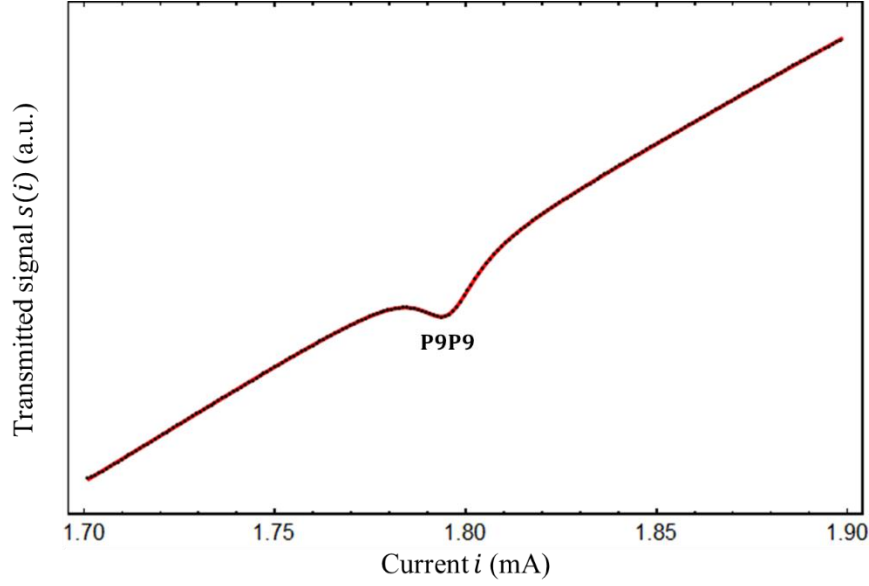


Figure 4-6: Raw data of the oxygen absorption line P9P9 (black points) along with a fitting curve (red line) for the Cobra 1 disc.

The FWHM γ measured in mA can be converted to FWHM Γ in GHz by using Eq. 42, and the frequency can be obtained from $\nu = c/\lambda$, where c is the speed of light.

Figure 4-7 shows the normalized absorbance as a function of relative frequency $\nu - \nu_0$ obtained from the signal of figure 4-6. The maximum absorbance is 1.66×10^{-2} , which corresponds to an effective oxygen absorption path length of 69 cm in open-air. The absorbance peak has a FWHM Γ_{total} of 5.12 GHz. As can be observed, the absorbance fits well to a Lorentzian function.

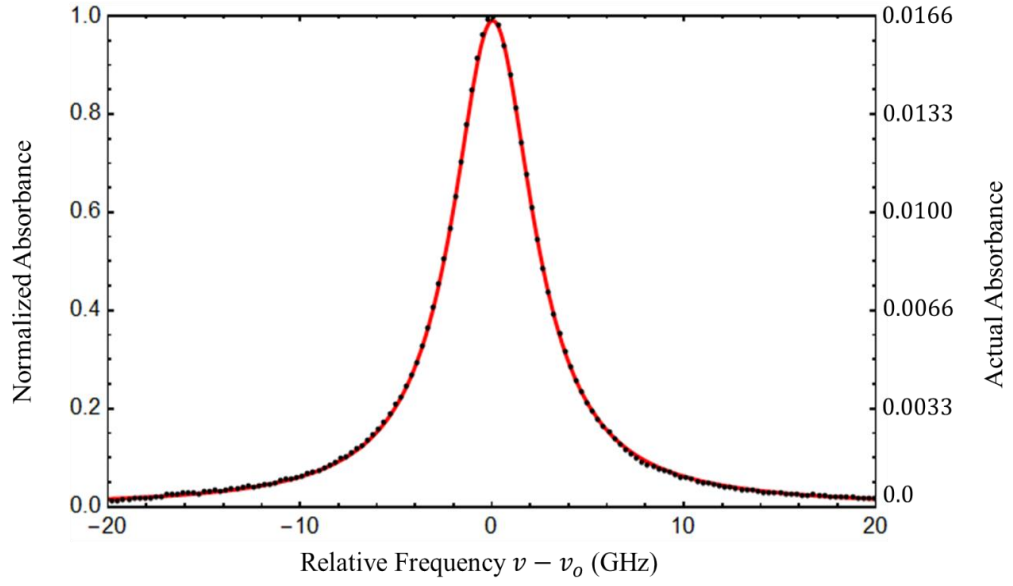


Figure 4-7: Normalized absorbance for the P9P9 molecular oxygen line (black points) along with a fitting curve (red line) for the Cobra 1 disc.

Table 4-1 lists the alumina solid disc samples along with their corresponding FWHM of P9P9 line Γ_{tot} , and the absorbance.

Table 4-1: Measured values of the FWHM of P9P9 line Γ_{tot} , and the absorbance for samples.

Samples	Γ_{tot} (GHz)	Absorbance
1-m ambient air	3.3	0.0239 ± 0.0001
Cobra 1	5.12	0.0166 ± 0.0001
Cobra 2	4.85	0.0236 ± 0.0001
Cobra3	4.41	0.0345 ± 0.0001
HM 1	4.14	0.0236 ± 0.0003
HM 2	4.2	0.0238 ± 0.0005
HM 3	4.23	0.0243 ± 0.0008
Zircar	3.37	0.0150 ± 0.0001

Figure 4-8 shows the normalized absorbance spectra for the P9P9 oxygen molecular line for open-air as well as for Cobra 1 and HM 1 discs. The spectrum in open-air has a FWHM of 3.30 GHz while the FWHM of the Cobra 1 is 5.12 GHz and that of HM 1 is 4.17 GHz. The uncertainty in the FWHM measurements is estimated to be 0.05 GHz, which is the standard deviation of ten different linewidth measurements for each sample. For all samples, the uncertainty is found to be approximately the same.

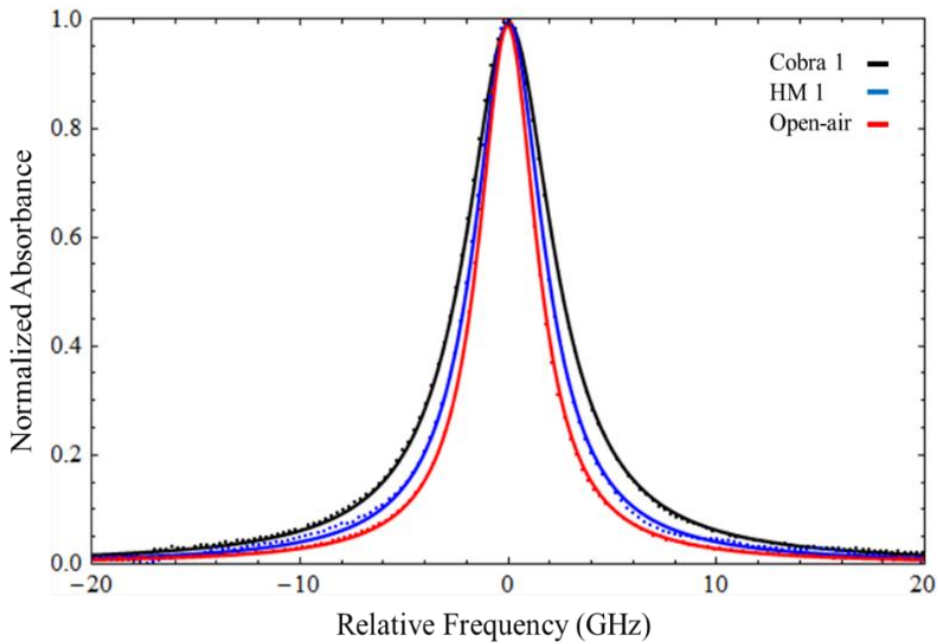


Figure 4-8: Normalized absorbance of the P9P9 molecular oxygen line from open-air as well as from Cobra 1 and HM 1 discs.

The open-air oxygen absorption linewidth $\Gamma_{open-air} = 3.30$ GHz is a result of convoluting the collisional broadened P9P9 line, the Doppler-broadened P9P9 line, and the laser line. The linewidth of the laser alone is 0.1 GHz, the linewidth due to intermolecular collisions alone is 2.94 GHz according to HITRAN database, while the linewidth due to Doppler broadening alone is 0.86 GHz, which is calculated from Eq. 19 for O_2 ($m = 32$ amu) at $\lambda =$

763 nm and $T = 289$ K. Since the line shapes due to collision broadening and due to the laser have Lorentzian profiles, their linewidths add up to 3.04 GHz. The line shape due to Doppler broadening has a Gaussian profile and its convolution with a Lorentzian of a linewidth of 3.04 GHz results in a linewidth of 3.28 GHz, using Eq. 29.

When oxygen molecules are confined in pores with sizes comparable or smaller to the intermolecular mean-free path, extra broadening occurs due to the collisions of oxygen molecules with the pore walls. This broadening is commonly known as wall collision broadening and its contribution to the total linewidth Γ_{total} will be called Γ_{wall} . In our study, the shape of total absorption line from the sample Γ_{total} and from open-air $\Gamma_{open-air}$ are approximately Lorentzian, as in figure 4-8. Since the convolution of two Lorentzian function is a Lorentzian with a linewidth equal to the sum of the linewidth of convoluted functions, it can be assumed that the contribution from the wall collision broadening is also Lorentzian. It should be noted that many studies on collision broadening in the microwave region [39], as well as in the near infrared region [13,23], assume that the broadening contributions from the wall and intermolecular collisions are approximately additive. Thus,

$$\Gamma_{total} = \Gamma_{open-air} + \Gamma_{wall} \quad (44)$$

The broadening from the wall collisions alone can be estimated using a model based on the kinetic theory of gases [38]. According to the kinetic theory of gases, the average time τ_{wall} between two consecutive collisions with the pore walls is:

$$\frac{1}{\tau_{wall}} = \frac{A \bar{v}}{V 4} \quad (45)$$

where A is the pore surface area, V is the pore volume, and $\bar{v} = \sqrt{8k_B T / \pi m}$ is the average speed of confined molecules. For O_2 , $m = 5.31 \times 10^{-26}$ kg at $T = 298$ K, the average speed $\bar{v} = 444$ m/s.

Using Eq. 27, the broadening due to wall collisions alone can be written as:

$$\Gamma_{wall} = \frac{1}{\pi \tau_{wall}} = \frac{A}{\pi V} \frac{\bar{v}}{4} \quad (46)$$

Although, the shapes of the pores in our samples are irregular and hence their volumes and areas cannot be determined exactly, the ratio of the pore volume to the pore surface area should scale with the average diameter of the pore $\bar{w}$, if the shapes of the pores in different samples have almost the same morphology, as in the case of our samples. Therefore, the broadening due to wall collisions alone in the samples should scale with the inverse of the average pore size $\bar{w}$

$$\Gamma_{wall} \propto \frac{1}{\bar{w}} \quad (47)$$

Figure 4-9 shows the measured line broadening due to wall collisions Γ_{wall} as a function of the average pore diameter $\bar{w}$ measured by MIP. It is clear, that the linewidth of P9P9 absorption line increases with decreasing average pore diameter. This trend can be explained by the fact that with smaller average pore diameter, oxygen molecules collide more frequently with the walls of the pores. In the same context, for the case of the Zircar disc, there is almost no broadening due to wall collisions. This is because the Zircar disc has an average pore diameter of about 10^3 nm, which is much bigger than the intermolecular mean free path of oxygen in air which is about 100 nm.

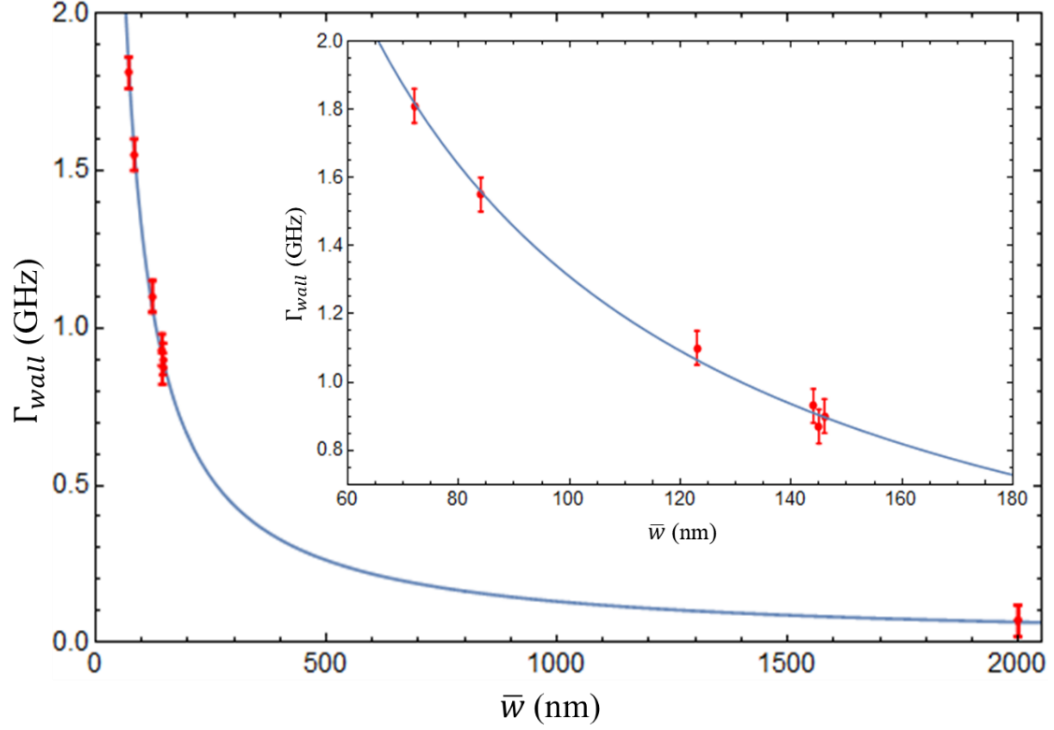


Figure 4-9: The line broadening due to wall collisions Γ_{wall} as a function of the measured average pore diameter $\bar{w}$ by MIP. The solid line is a fit to a function of the form $b/\bar{w}$, where b is a fitting parameter. The insert is a magnification of the region between 60 and 180 nm.

Figure 4-9 also shows that Γ_{wall} fits very well to a function of the form $b/\bar{w}$, as indicated by the solid line in the figure, where b is a fitting parameter and is found to be $131 \text{ GHz} \cdot \text{nm}$. The shape of the pores might be modeled as a simple shape like a sphere [23] or a cylinder [69]. If a spherical pore shape is considered, $A/V = 6/\bar{w}$ and thus the fitting parameter b should be $3\bar{v}/2\pi = 212 \text{ GHz} \cdot \text{nm}$. If a cylindrical pore shape of diameter $\bar{w}$ and height h is considered,

$$\frac{A}{V} = \frac{\pi\bar{w}^2/2 + \pi\bar{w}h}{\pi\bar{w}^2h/4} = 4 \left(\frac{1}{2h} + \frac{1}{\bar{w}} \right) \quad (48)$$

For a cylinder with height much greater than its diameter, $A/V \cong 4/\bar{w}$ and hence the fitting parameter b should be $\bar{v}/\pi = 141 \text{ GHz} \cdot \text{nm}$, which is very close to the experimentally obtained fitting parameter. Consequently, the pores in our sample are better modeled as cylinders with large heights compared to their diameters than spherical pores. However, the fitting parameter might vary if the samples have different morphology.

The model based on pores of long cylindrical shape, introduced in this work, is found to yield much better agreement, not only with the measurements presented in this work, but also with measurements reported in literature [13,18,22,23]. Previously, a model based on pores of spherical shape is used in Ref. [23] and it obtains an average pore size, extracted from the wall-collision broadening, almost double that measured by MIP. Figure 4-10 shows wall-collisional broadening as a function of average pore diameter measured using MIP for this work as well as those presented in Ref. [23]. The figure shows three curves of the form $b/\bar{w}$; one is the fit of figure 4-9, one is using parameter b for long cylindrical pores, and the last one is using parameter b for spherical pores. It is clear that the measurements are better modeled with pores of long cylindrical shape than pores of spherical shape. It should be noted that the MIP measurements usually give smaller average diameter than the real ones [9,23]. If this factor is also taken into consideration, the model may even yield better fitting. Certainly, further investigation is needed to have better understanding of the relationship between the average pore shape and the wall-collision broadening.

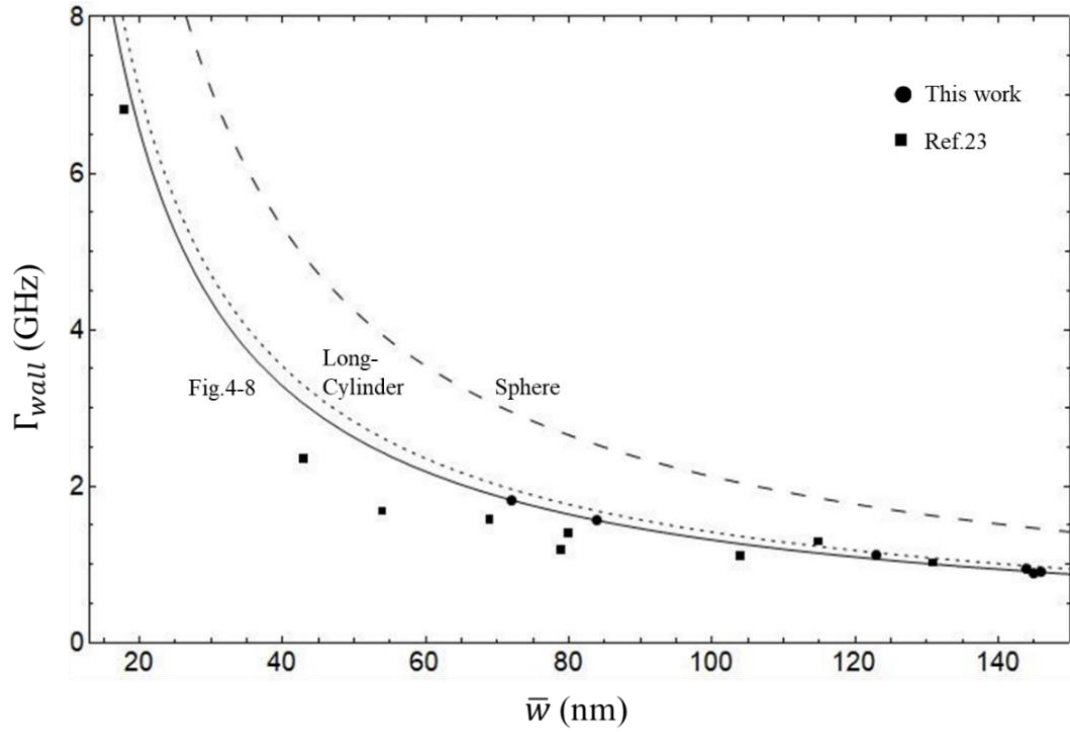


Figure 4-10: Comparison between measurements and models based on kinetic theory of gases. The dashed curve is for broadening due to wall collision using a model with spherical pores, the dotted curve is for broadening due to wall collision using a model with long cylindrical pores, and the solid curve is the fit of Fig. 4-9.

The multiple scattering of the laser beam in porous alumina discs gives rise to longer effective optical path lengths. The equivalent mean path length L_{eq} is defined as the distance of light traveling in open-air that gives the same absorption signal in air as that from the sample which can be calculated from Eq. 7. Table 4-2 shows the equivalent mean path length L_{eq} and the physical thickness of the samples. The equivalent path is almost 100 times as the physical thickness.

Table 4-2: Equivalent mean path length L_{eq} for all alumina discs samples.

Samples	Physical Thickness (mm)	Average pore size (nm)	L_{eq} (cm)
Cobra 1	8	72	69
Cobra 2	8	84	98
Cobra3	8	123	114
HM 1	12	145	99
HM 2	12	146	99
HM 3	12	144	102
Zircar	10	10^3	63

4.2 Pore size assessment of alumina powder samples by GASMAS and gas adsorption

The effect of the size of pores in alumina powder samples on the broadening of the oxygen gas absorption line is investigated. The average pore size is determined using the gas adsorption technique. Furthermore, the confined oxygen gas absorbance measured by GASMAS is correlated to the effective porosity evaluated by the saturation method.

Figure 4-11 shows the results of the gas adsorption technique of the pore size distribution $f(w)$ as a function of pore diameter w for all samples. The average pore diameter $\bar{w}$ of the samples lies within the range 10 to 40 nm, where $\bar{w}$ is evaluated by using Eq. 43.

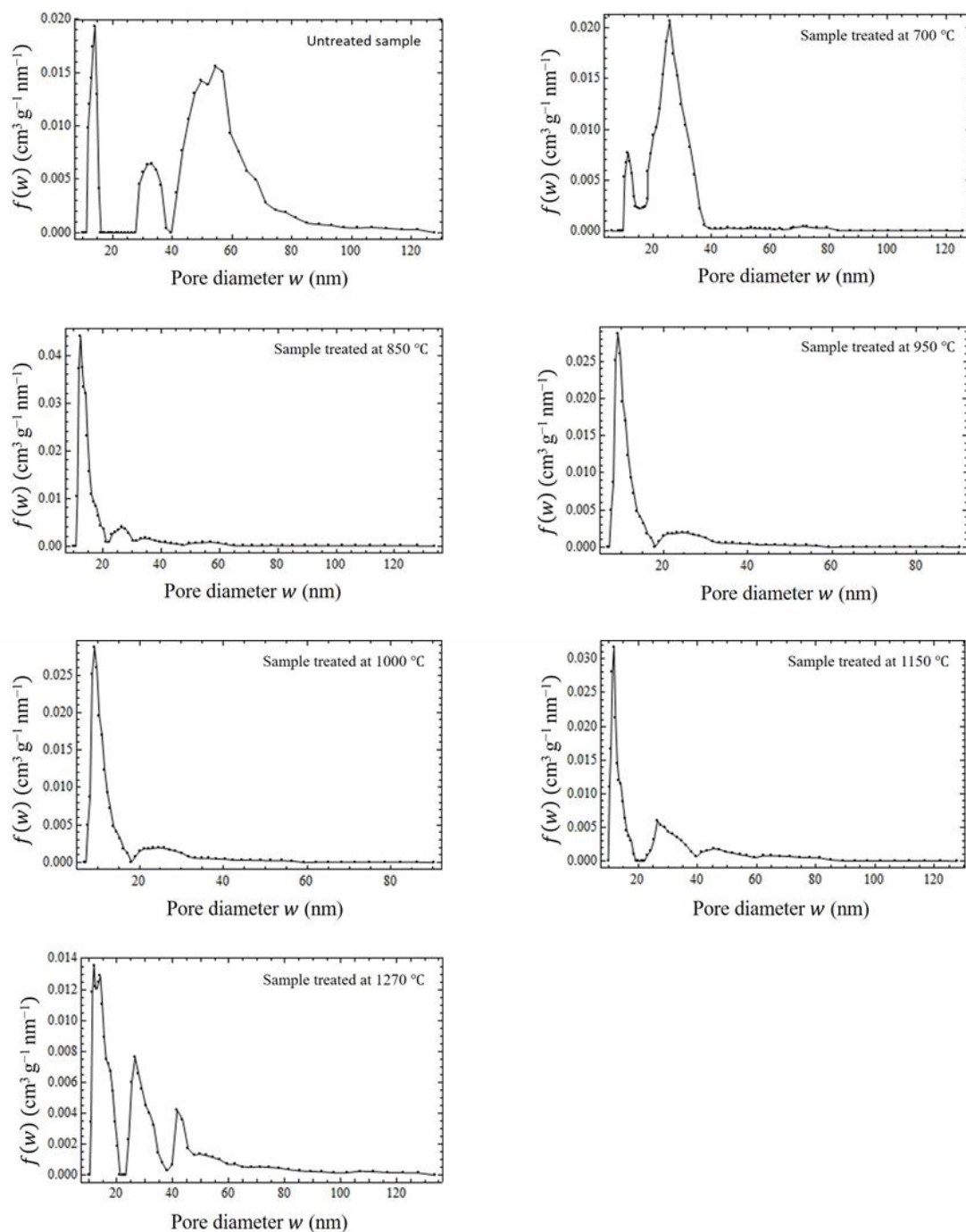


Figure 4-11: Distribution of pore size $f(w)$ as a function of pore diameter w for all samples

Figure 4-12 shows the XRD of the alumina powder samples used in this study. The XRD patterns are compared to reference patterns obtained from the International Center for Diffraction Data (ICDD). It is clear that the alumina samples change their phases during

the heat treatment. The untreated powder sample contains the chi (χ) alumina phase and boehmite while the powder sample treated at 700 °C contains a mixture of the chi (χ) and gamma (γ) alumina phases. The Delta (δ) alumina phase is observed at 850 °C mixed with the γ and χ phases. At 950 °C the kappa (κ) and theta (θ) alumina phases appear mixed with χ , γ and δ phases. The powders treated at 1000 °C, 1150 °C and 1270 °C are mainly of the alpha (α) alumina phase. It is observed that the peaks become sharper with temperature, which indicates that the grain size is getting larger [70].

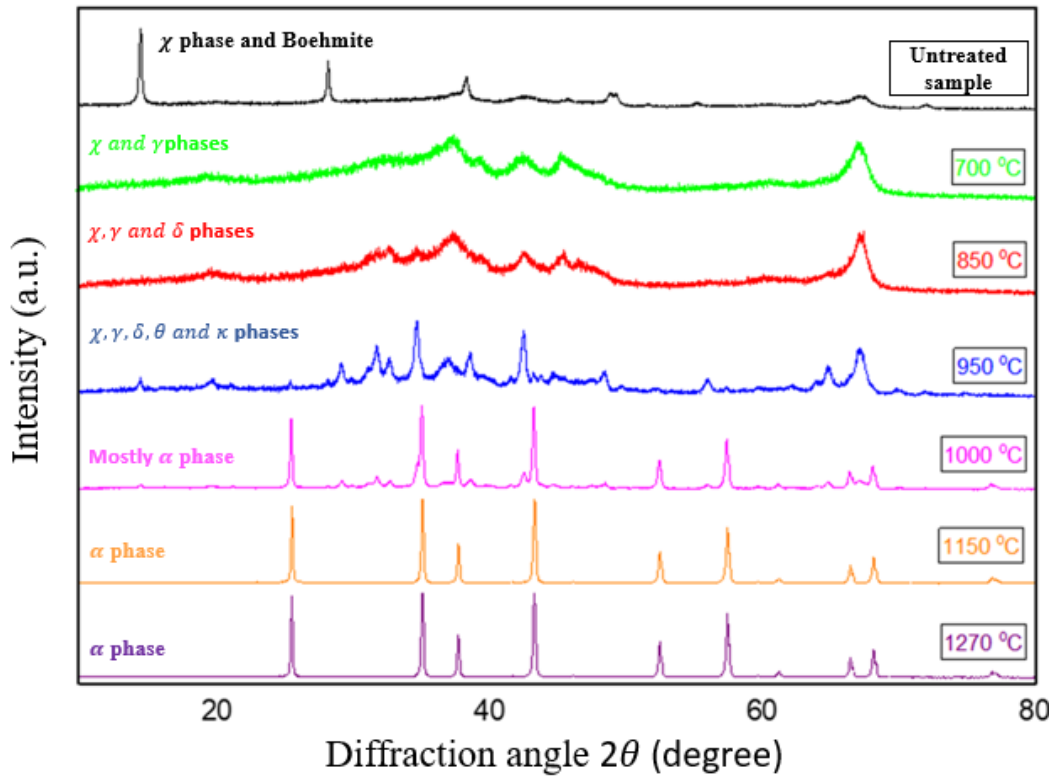


Figure 4-12: The XRD patterns for the alumina samples treated at different temperatures.

Figure 4-13 shows the detected signal $s(i)$ as a function of the laser injection current i for the untreated powder sample. The line broadening and the absorbance are obtained using the same procedure used for solid disc alumina samples in section 4-1.

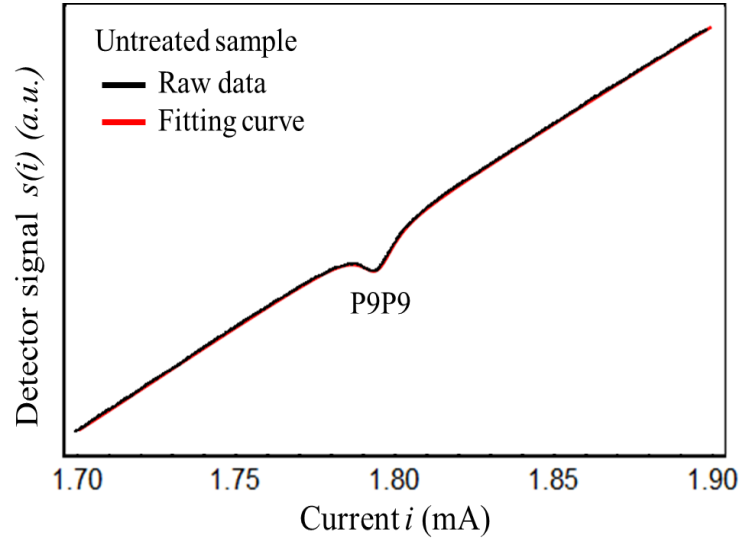


Figure 4-13: Raw data of the oxygen absorption line P9P9 along with a fitting curve for untreated sample and for of 3.75 m pathlength of open air.

Table 4-3 lists the treatment temperature of the alumina powder samples along with the corresponding FWHM Γ_{tot} of the P9P9 line, the average pore diameter $\bar{w}$ obtained from the gas adsorption technique, the wall collision broadening Γ_{wall} , and the absorbance.

Table 4-3: Measured values of the FWHM of P9P9 line Γ_{tot} , average pore diameter $\bar{w}$ obtained from gas adsorption technique, wall collision broadening Γ_{wall} and the absorbance for samples.

Samples	Γ_{tot} (GHz) ± 0.03	$\bar{w}$ (nm)	Γ_{wall} (GHz) ± 0.03	Absorbance ± 0.0001
1-m ambient air	3.3			0.0239
(untreated sample)	3.54	38.19	0.24	0.0131
(treated at 700 °C)	3.6	23.86	0.30	0.0154
(treated at 850 °C)	3.76	16.11	0.46	0.0182
(treated at 950 °C)	3.95	12.59	0.65	0.0244
(treated at 1000 °C)	3.85	14.90	0.55	0.0324
(treated at 1150 °C)	3.71	18.68	0.41	0.0545
(treated at 1270 °C)	3.64	22.11	0.34	0.0581

In figure 4-14, the blue curve represents the contribution from the wall collision broadening Γ_{wall} of the P9P9 line as a function of the treatment temperature of the samples while the red curve represents the average pore diameter $\bar{w}$ obtained by gas adsorption technique. As expected, the average pore diameter and the contribution from the wall collision to the width of the P9P9 line are observed to have opposite trends, the smaller the pore size, the bigger is the wall collision broadening.

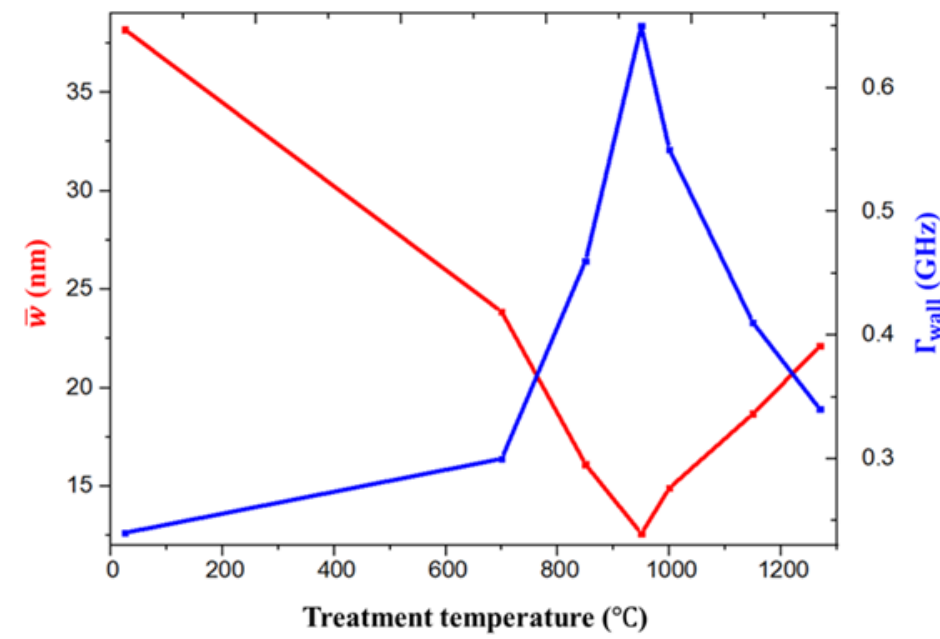


Figure 4-14: The average pore diameter $\bar{w}$ (red curve) and the contribution from the wall collision broadening Γ_{wall} (in blue) as a function of the treatment temperature of the samples.

Using data of figure 3-14, the contribution of the wall collision broadening Γ_{wall} can be plotted as a function of the average pore diameter $\bar{w}$, as shown in figure 4-15. It is clear from the figure that the contribution of wall collision broadening Γ_{wall} decreases with the average pore diameter $\bar{w}$.

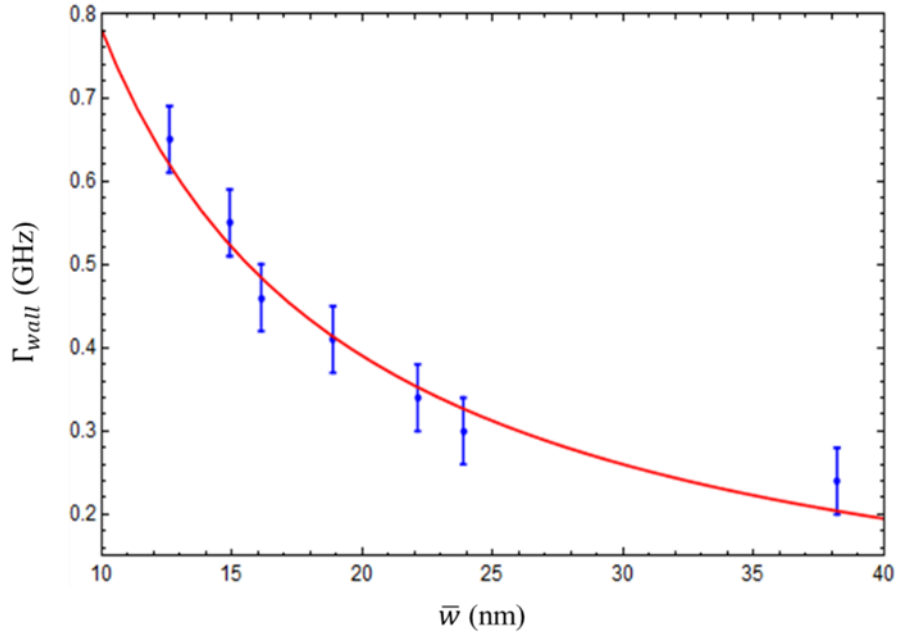


Figure 4-15: The contribution of wall collision broadening Γ_{wall} as a function of the average pore diameter $\bar{w}$. The solid curve represents the theoretical model fit.

The solid curve in figure 4-15 represents a fit curve based on the model that was presented in section 4.1. In this model, the wall collision broadening is assumed to have a Lorentzian line shape and is inversely proportional to the average pore diameter $\bar{w}$. Here, the fitting parameter b is found to be 7.8, while the fitting parameter b in section 4-1 is found to be 131. Also, the average pore diameters of powder samples measured by the gas adsorption technique are much smaller than the average pore diameter of solid discs samples measured by MIP technique. Thus, the smaller average pore diameter is expected to have a larger broadening, but our finding contradicts with this expectation. This apparent contradiction might be probably due to the different nature of the technique used to assess the average pore size as well as the nature of the sample. The MIP and gas adsorption techniques are based on different physical principles and may give different pore size assessment for the same sample. Particularly, in reference [12], the MIP technique gives much larger average

pore size compared to the gas adsorption technique for the same sample, which might explain this apparent contradiction. Indeed, more investigation is needed to better understand this behavior.

Furthermore, the relationship between the pore size and absorbance is also investigated, however, no clear dependence is found. Instead, we find a linear dependence between the absorbance and the effective porosity. Figure 4-16 shows the absorbance as a function of the effective porosity and the solid line represents a linear fit of the data. It should be noted that the samples we investigate have fixed thickness and their porosity is in the range between 18 and 34%, which is relatively low. For very high porosity, the relation between absorbance and effective porosity may not be necessarily linear. Hence, it will be of interest to investigate this relation for samples of high porosities. This finding is consistent with the results reported in [71] where it is found that the absorption is almost linearly proportional to the effective porosity at low porosities but is not linear for high porosities. The increase in absorbance is caused by the availability of more oxygen molecules as well as the occurrence of more light scattering in the sample. As can be seen in figure 4-14, the pore size decreases until the treatment temperature reaches 950 °C then it increases. Nevertheless, the population of pores seems to be increasing with the treatment temperature as it is evident from scanning electron microscopy (SEM) images, shown in figure 4-17 for the samples treated at 850 °C, 950 °C, and 1270 °C. However, the pore population cannot be quantified from the images. It is clear from the images that the geometry of pores changes at about 950 °C, which corresponds to the transition temperature to the α phase.

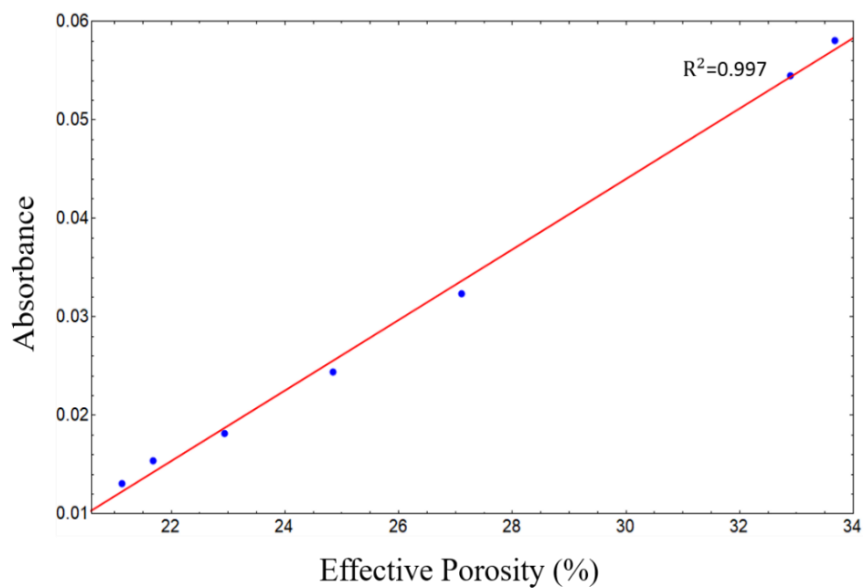


Figure 4-16: Absorbance as a function of the effective porosity.

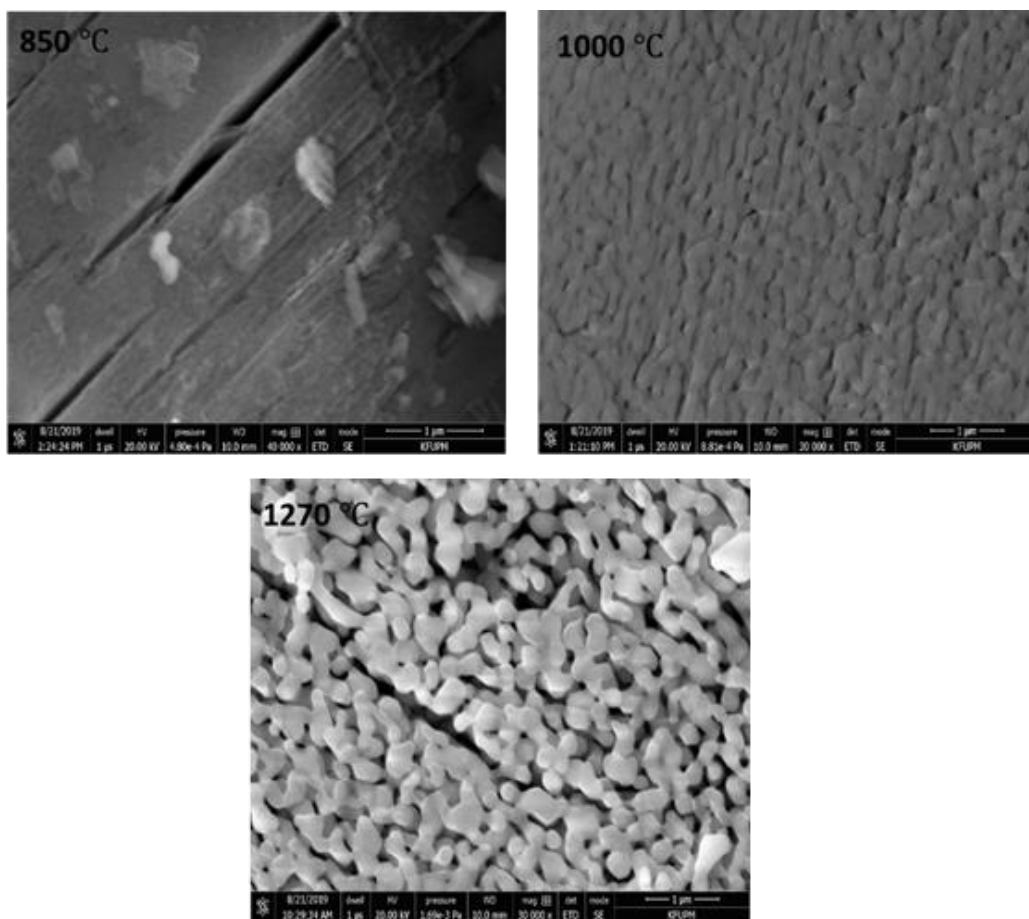


Figure 4-17: SEM images of alumina powder samples treated at 850 °C, 1000 °C and 1270 °C.

CHAPTER 5

Conclusion

The essence of this dissertation is the spectroscopic-based experimental and theoretical assessment of nanopores in disc and powder alumina samples. Throughout this research work, the experimental methods employed are; GASMAS, gas adsorption, XRD, SEM, and MIP. Also, a theoretical model based on the kinetic theory of gasses is used to help assessing pore size. The GASMAS technique is used to study the width of an absorption line around 763.84 nm of oxygen molecules entrapped within the pores of alumina solid disc samples and alumina powder samples. The increase in the width of the absorption line due to collision of oxygen molecules with the wall of the pore is then correlated to the pore size. The pore size of the alumina solid disc samples is measured by the MIP technique, while the pore size of the alumina powder samples is measured by the gas adsorption technique. A theoretical model based on the kinetic theory of gas is developed to describe a relation between the contribution of wall collision broadening to the width of absorption line and the pore size of nanoporous materials.

As predicted for both alumina solid disc samples and alumina powder samples, the wall collision broadening is found to be inversely proportional to the average pore diameter. Also, no significant wall collision broadening is observed for samples of pore diameters much larger than the mean free path of intermolecular collisions in open-air.

The relation between broadening and average pore diameter measured by MIP is found to be more consistent with a model of the samples having pores of long cylindrical shapes than a model of pores of spherical shapes. Also, a linear dependence is found between the

absorbance and the effective porosity measured by the saturation method for powder samples.

Future work is needed to reach definitive conclusion on the relation between the fitting model and pores morphology.

Appendix A

LabVIEW program

Front panel and a block diagram of the virtual instrument used to measure the absorption lines of molecular oxygen are shown below.

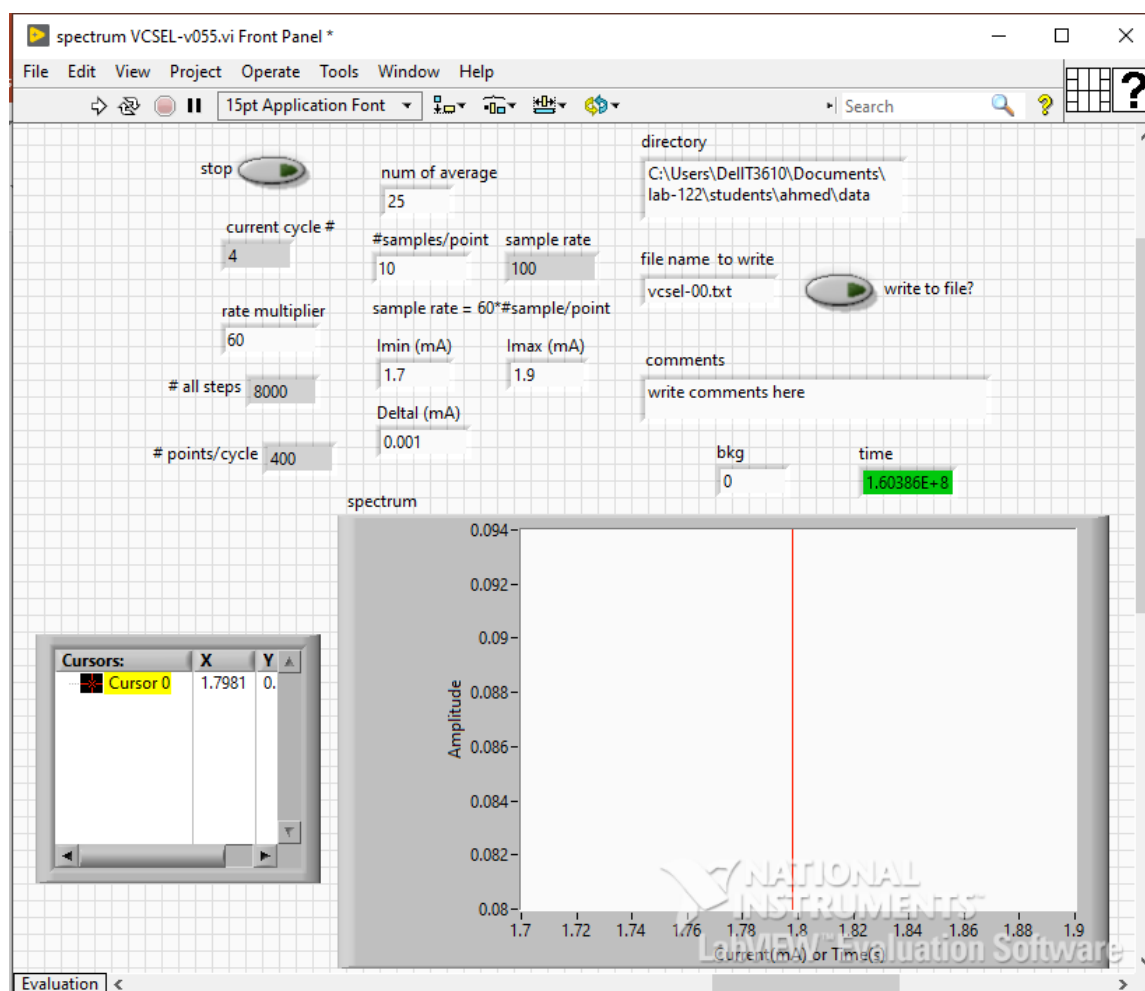


Figure A1: Front panel of the LabVIEW program used to measure the absorption lines of molecular oxygen.

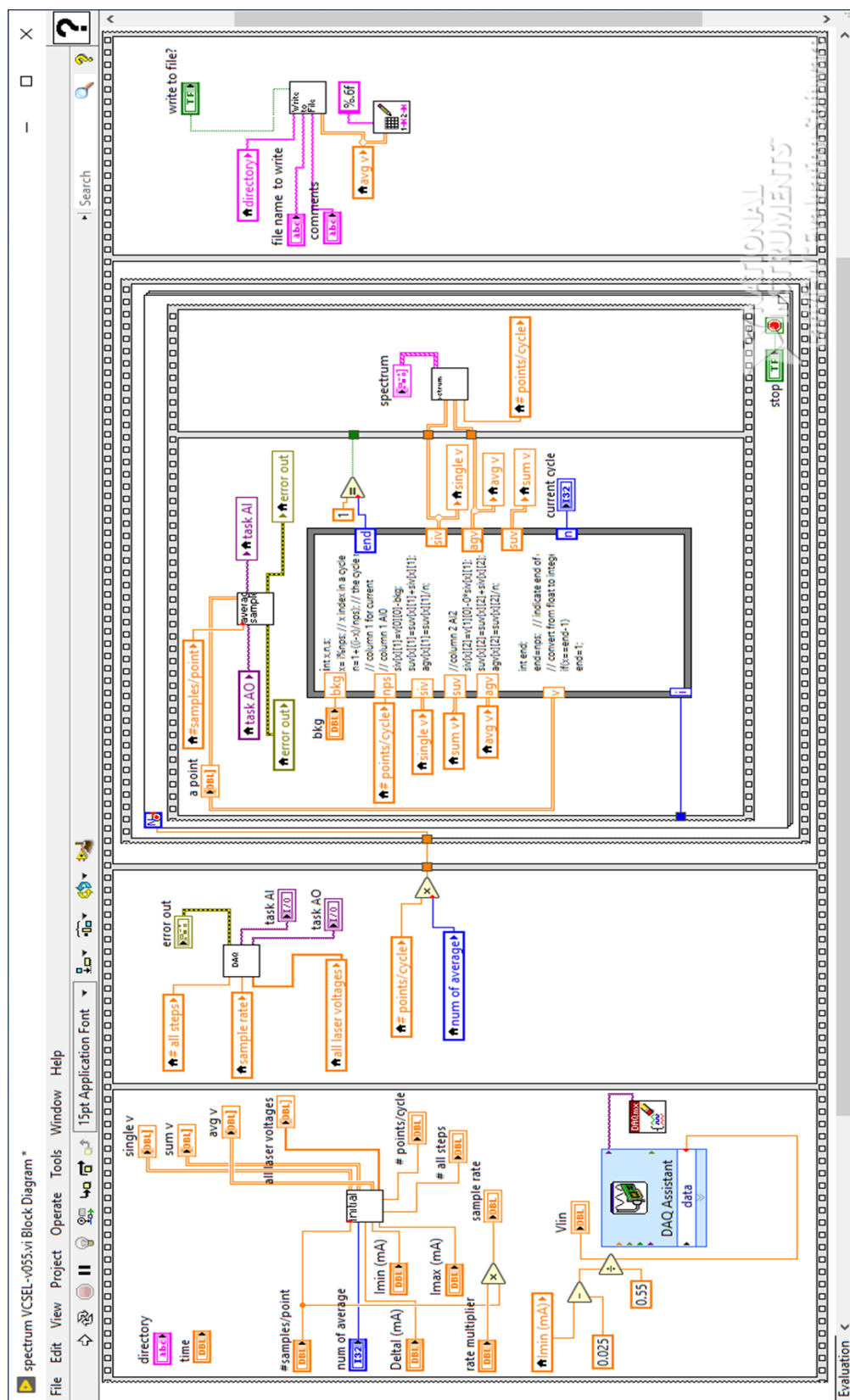


Figure A2: The block diagram associated with the front panel of figure A1. The front panels and block diagrams of the sub VI “initial”, “DAQ”, “spectrum”, and “write to file” are shown in figures A3, A4, A5, A6, A7, A8, A9, and A10, respectively.

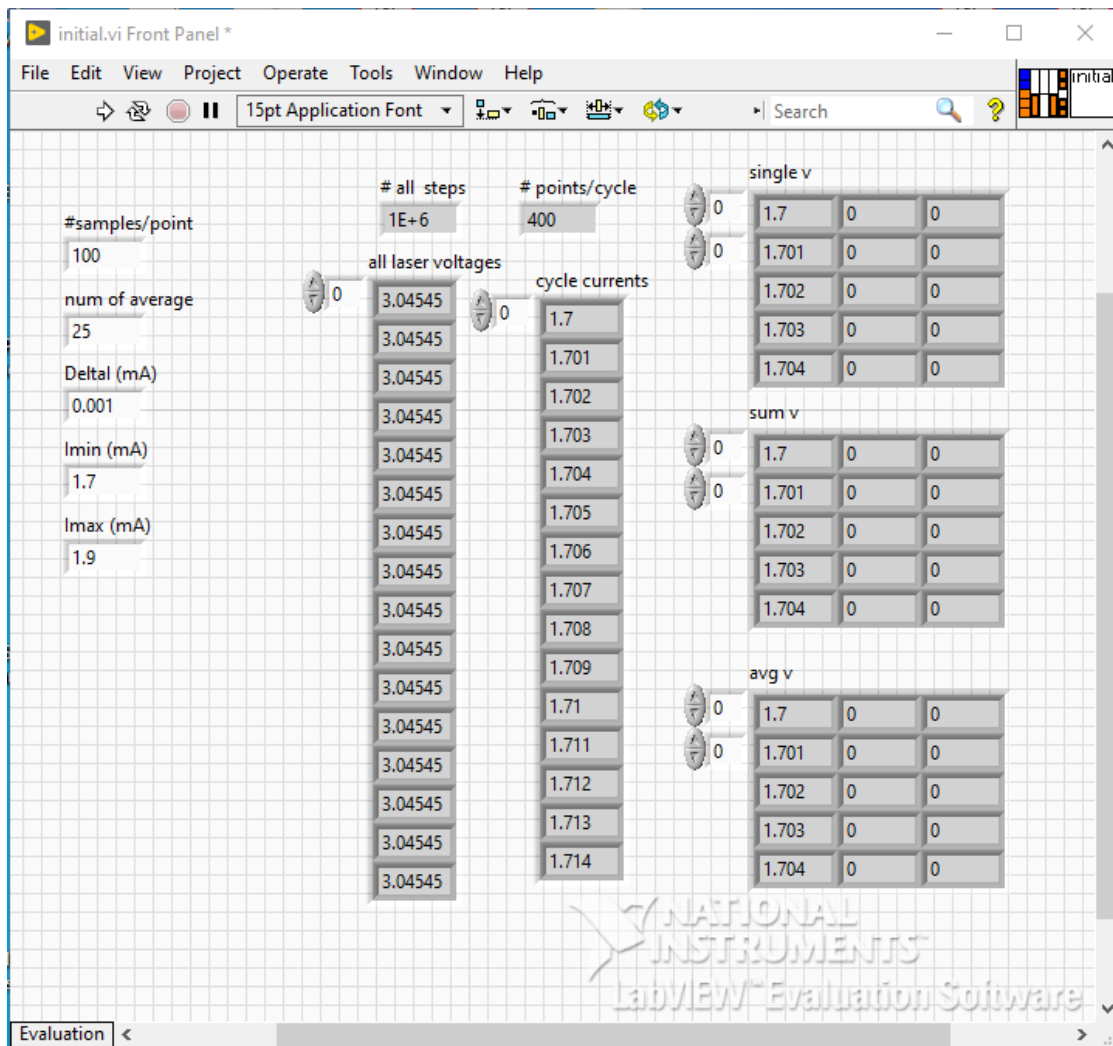


Figure A3: The front panel of the sub VI “initial” used in figure A2.

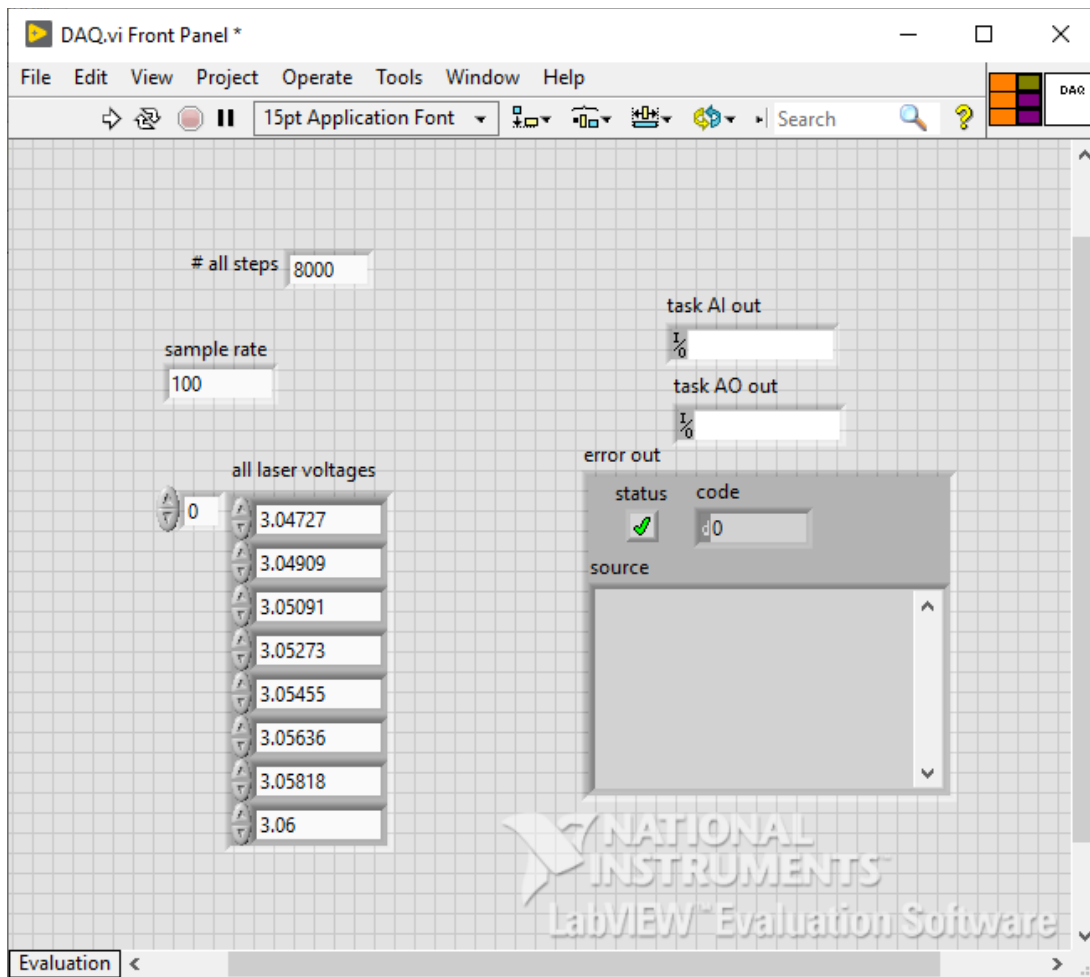


Figure A5: The front panel of the sub VI “DAQ” used in figure A2.

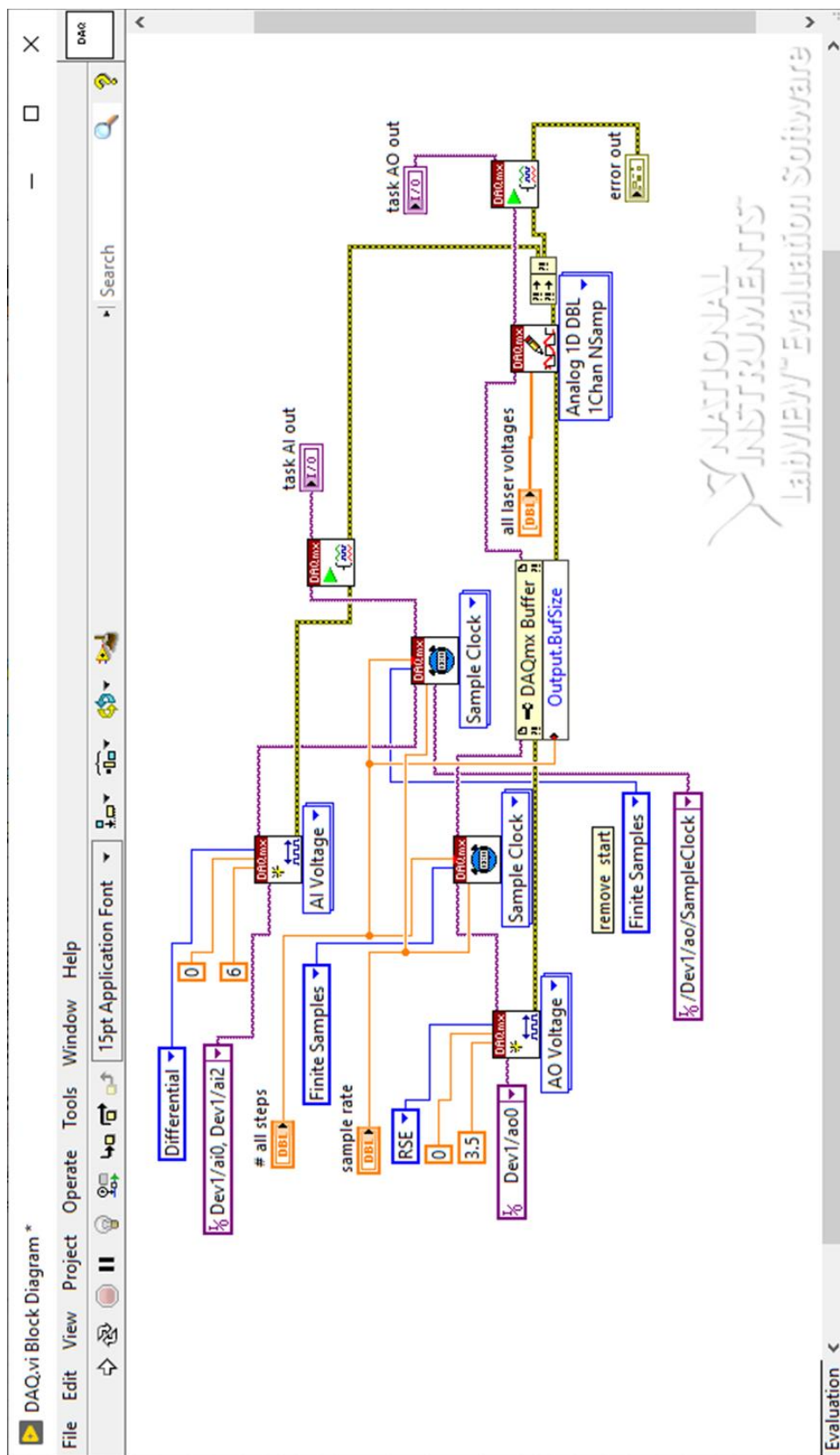


Figure A6: The block diagram of sub VI “DAQ” used in figure A2.

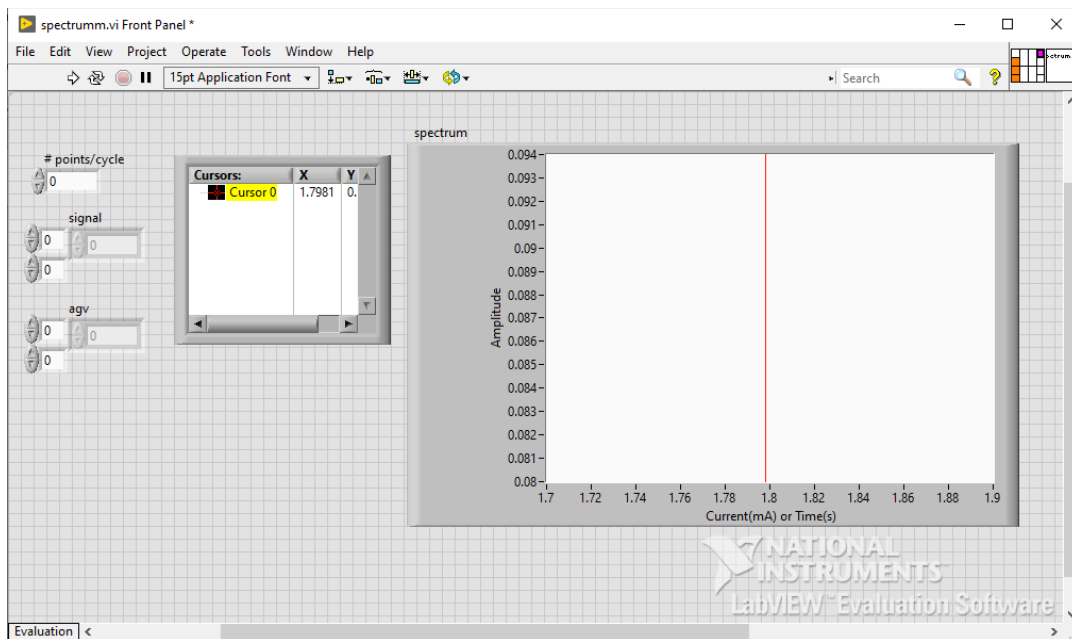


Figure A7: the front panel of the sub VI “spectrum” used in figure A2.

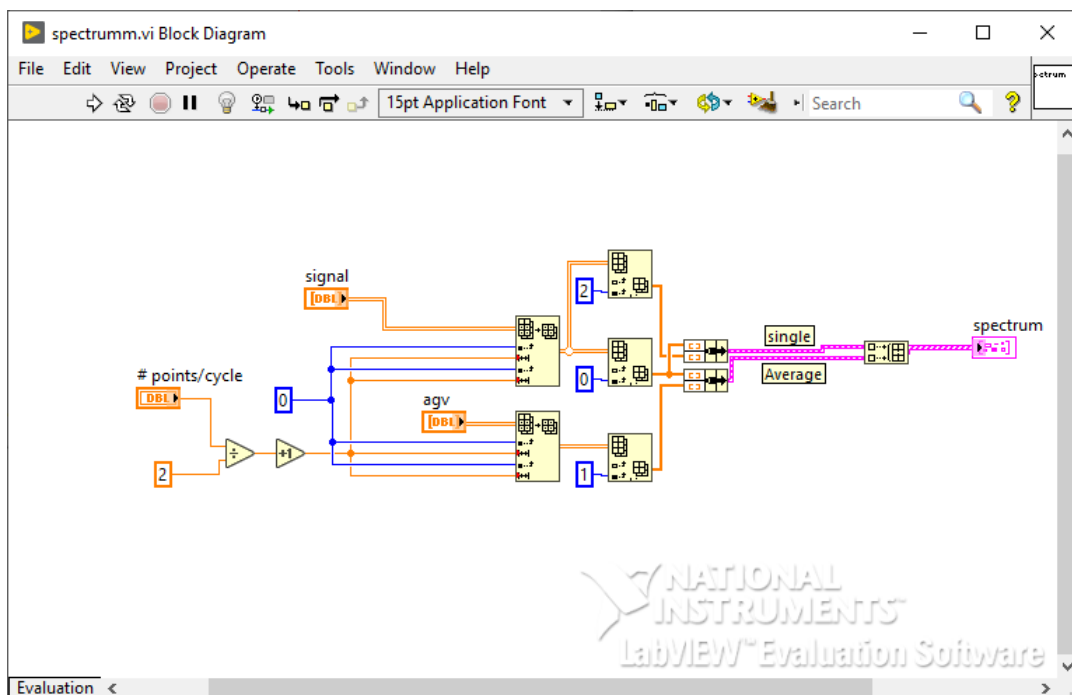


Figure A8: The block diagram of the sub VI “spectrum” used in figure A2.

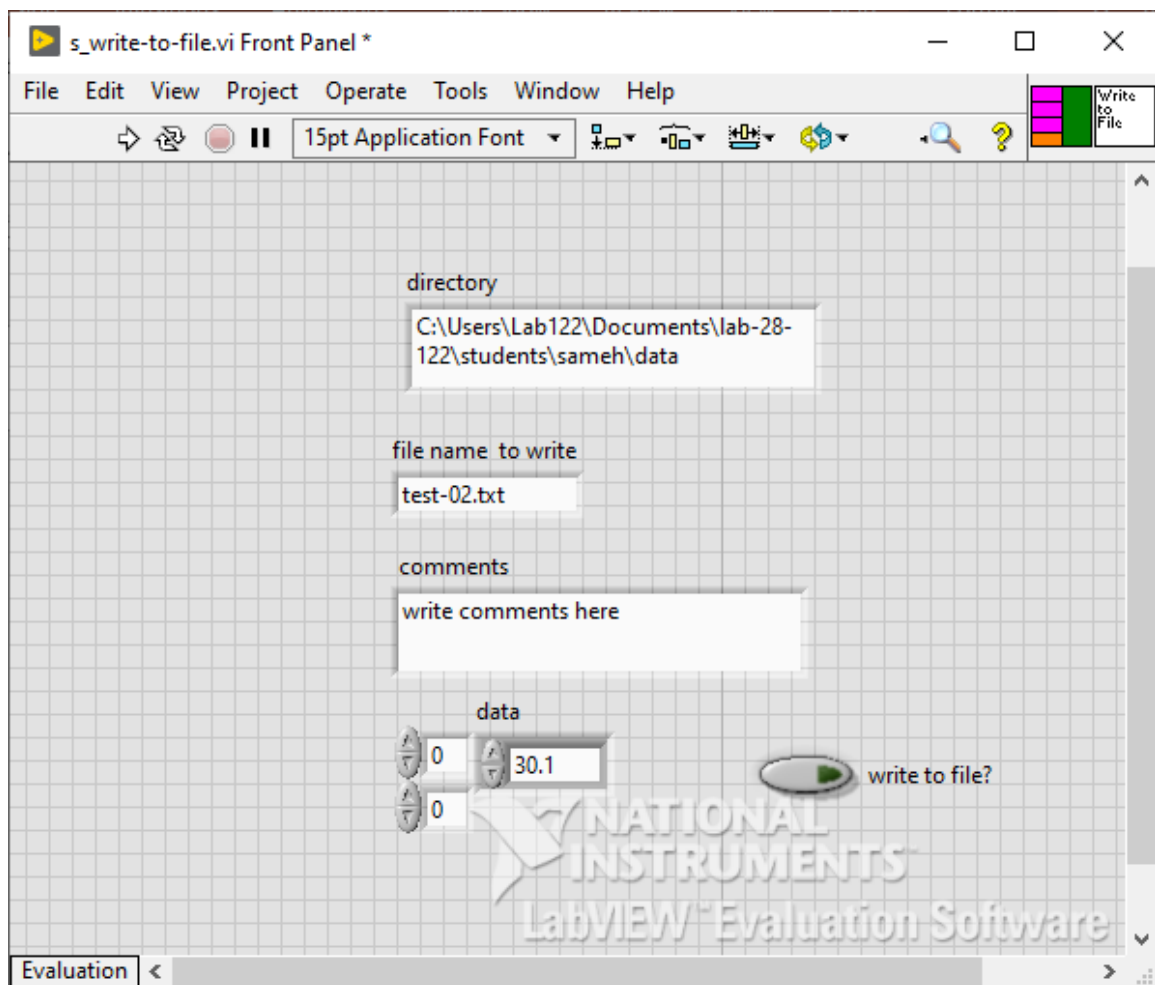


Figure A9: The block diagram of the sub VI “write to file” used in figure A2.

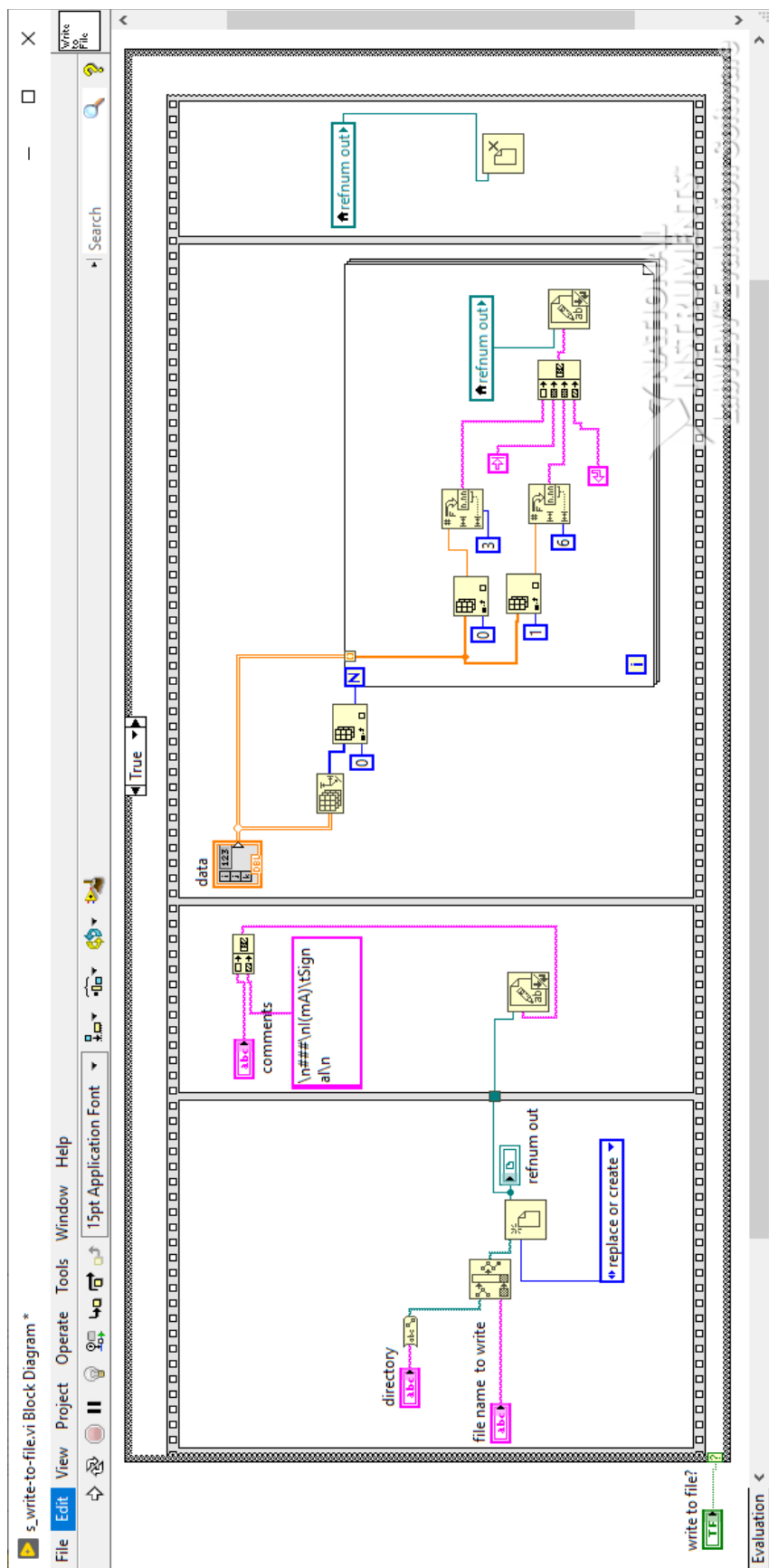


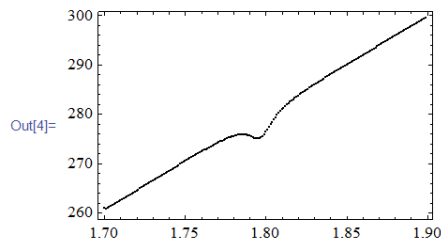
Figure A10: The block diagram of sub VI “write to file” used in figure A2.

Appendix B

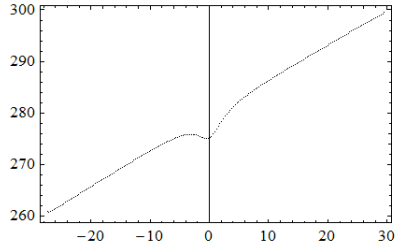
Mathematica codes for data analysis

Mathematica is used for reading file, analyzing, and fitting the experimental data.

```
In[1]= vcsel[file_] := (  
    SetDirectory[NotebookDirectory[]];  
    str = OpenRead[file];  
    lst0 = ReadList[str, {Record, Record, Record}, RecordSeparators -> {"", "\n", "\t"}];  
    lst1 = ToExpression[Table[StringReplace[lst0[[i]], "e" -> "*10^"], {i, 1, Length[lst0]}]];  
    lst2 = lst1[[All, {1, 2}]];  
    Return[lst2];  
    Close[str];)  
  
In[2]= (* finding i0 and v0 *)  
    lstS = vcsel["co50-1.txt"];  
    lstR = Table[{lstS[[i, 1]], 1000 lstS[[i, 2]]}, {i, 1, Length[lstS] / 2}];  
    pltd = ListPlot[lstR, Joined -> False, PlotRange -> {All, All}, Frame -> True,  
        PlotStyle -> {Black, PointSize[.005]}]  
    i0 = 1.7967; (* mA *)
```



```
In[7]= (* covert current in mA to wavelength in nm and find peak frequency in GHz *)  
    c = 3 × 108;  
    λ[i_] :=  
        765.15283 - 0.001598858 (1463.0306084092617 - 217.92349090996467 i - 36.010823324441084 i2);  
    λ0 = λ[i0];  
    f0 = c / λ0;  
    df[i_] := f0 - c / λ[i];  
  
In[12]=  
    (* Data as function of df change in frequency from the peak frequency *)  
    lstR = Table[{df[lstS[[i, 1]]], 1000 lstS[[i, 2]] - v0}, {i, 1, Length[lstS] / 2}];  
    (* votlage is converted to mV *)  
    pltd = ListPlot[lstR, Joined -> False, PlotRange -> {All, All}, Frame -> True, Axes -> True,  
        PlotStyle -> {Black, PointSize[.002]}]
```



```

In[14]:= (* Fitting and absorbance *)

fFit = FindFit[lstR, a  $\frac{(fwhm/2)^2}{(x-b)^2 + (fwhm/2)^2}$  + a0 + a1 x + a2 x^2 + a3 x^3 + a4 x^4 + a5 x^5 + a6 x^6,
  {{a, 50}, {b, 0}, {fwhm, 3}, {a0, 0}, {a1, 5}, {a2, 0}, {a3, 0}, {a4, 0}, {a5, 0}, {a6, 0}}, x]

(* pltf = polt fit *)
pltf = Plot[a  $\frac{(fwhm/2)^2}{(x-b)^2 + (fwhm/2)^2}$  + a0 + a1 x + a2 x^2 + a3 x^3 + a4 x^4 + a5 x^5 + a6 x^6 /. fFit,
  {x, -27, 30}, Axes → False, Frame → True, PlotStyle → {Red, 10}];

(* pltl = polt lorentzian *)
pltl = Plot[a  $\frac{(fwhm/2)^2}{(x-b)^2 + (fwhm/2)^2}$  /. fFit, {x, -27, 30}, PlotRange → All];

(* pltp = polt polynomial *)
pltp = Plot[a0 + a1 x + a2 x^2 + a3 x^3 + a4 x^4 + a5 x^5 + a6 x^6 /. fFit, {x, -.1, .1}];

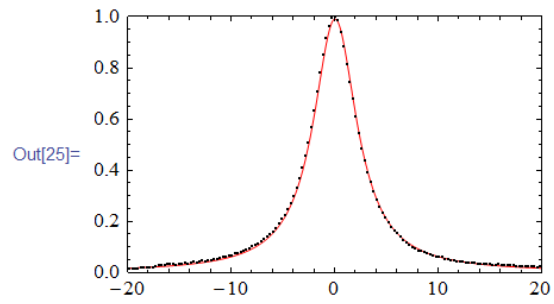
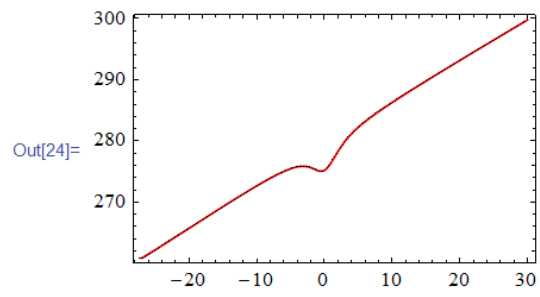
Out[14]= {a → -4.62421, b → 0.0376288, fwhm → 5.1224, a0 → 279.827, a1 → 0.679151, a2 → -0.000644789,
  a3 → 0.0000318903, a4 → -7.59579 × 10-7, a5 → -3.38946 × 10-8, a6 → 1.06281 × 10-9}

In[18]:= poly[x_] := a0 + a1 x + a2 x^2 + a3 x^3 + a4 x^4 + a5 x^5 + a6 x^6 /. fFit;
(* function find polynomial background *)
abs0 =  $\frac{-a}{v0 + a0}$  /. fFit
abs[x_] :=  $\frac{-a}{v0 + a0} \frac{(fwhm/2)^2}{(x-b)^2 + (fwhm/2)^2}$  /. fFit;

lstAbs0 = Table[{lstR[[i, 1]], -Log[ $\frac{lstR[[i, 2]]}{poly[lstR[[i, 1]]}$ ]}], {i, 1, Length[lstR]};
m = Max[lstAbs0[[All, 2]]];
lstAbs = Table[{lstR[[i, 1]], -Log[ $\frac{lstR[[i, 2]]}{poly[lstR[[i, 1]]}$ ]] / m}, {i, 1, Length[lstR]};
pltAbsData = ListPlot[lstAbs, Joined → False, PlotRange → {{-20, 20}, {0, 1}},
  Frame → True, Axes → False, FrameStyle → Directive[Red, 10],
  PlotStyle → {Black, PointSize[.003]}];
pltAbsFit = Plot[abs[x] / m, {x, -27, 30}, PlotRange → {{-20, 20}, {0, 1}}, Frame → True,
  FrameStyle → Directive[Black, 10], Axes → False, PlotStyle → {Red, Thickness[0.004]}];
Show[pltf, pltd]
s1 = Show[pltAbsFit, pltAbsData]

```

Out[18]= 0.0165252



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List of publications:

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