# LASER ABSORPTION SPECTROSCOPY OF GAS IN SCATTERING MEDIA

Märta Lewander

Doctoral Thesis 2010



LUND UNIVERSITY

LASER ABSORPTION SPECTROSCOPY OF GAS IN SCATTERING MEDIA

© 2010 Märta Lewander All rights reserved Printed in Sweden by Media-Tryck, Lund, 2010

Division of Atomic Physics Department of Physics Faculty of Engineering, LTH Lund University P.O. Box 118 SE-221 00 Lund Sweden http://www.atomic.physics.lu.se

ISSN 0281-2762 Lund Reports on Atomic Physics, LRAP-424

ISBN: 978-91-7473-061-6

What the mind can conceive and believe, it can achieve.  $$_{\mbox{\scriptsize NaPOLEON HILL}}$$ 

# Abstract

Absorption spectroscopy constitutes a chemical analysis tool which can be applied to various samples and application fields. This thesis focuses on gas absorption spectroscopy with the means of diode lasers - tunable diode laser absorption spectroscopy, TDLAS. In particular, the absorption of gases inside porous scattering solids and liquids, referred to as GASMAS - gas in scattering media absorption spectroscopy, has been studied. The spectrally sharp wavelength from a diode laser is scanned over the absorption fingerprint of the studied gas, and the transmitted intensity is detected. Although the light is heavily absorbed and scattered by the bulk material, the gas absorption imprint can still be distinguished. The free gas, in contrast to the bulk material which is made out of perturbed molecules, exhibits narrow absorption lines and its absorption can thus be isolated although the light has been heavily absorbed by the solids and liquids. The diffuse light propagation demands alternative solutions to extract gas concentration, which otherwise is obtained through the Beer-Lambert law using the interaction distance. Water vapor sensing in samples with liquid water present has shown to be a feasible way to achieve information about the effective distance through gas inside the sample even though the light is heavily scattered.

Applications studied in this thesis work include gas sensing within the human body for medical diagnostics, gas monitoring inside food packages for quality assurance, and fundamental studied of gas in nanoporous ceramics.

Investigations of GASMAS as a diagnostic tool for the paranasal sinuses, subject to the common rhinosinusitis have been carried out. Correlation between obstruction and ventilation of the sinuses diagnosed by computer tomography and GASMAS data has been demonstrated. Diagnostic useful data from the air cell system in the mastoid bone, located behind the ears, have also been obtained. Furthermore, possibilities of gas sensing in the lungs of premature born babies have been demonstrated in a feasibility study on a realistic model made out of animal lung tissue and gelatin based phantoms. Sensing of the gas non-intrusively by GASMAS has been demonstrated on packages of minced meat, bread as well as on the headspace of translucent containers with milk or orange juice. Food packages are to an increasing extent filled with a modified atmosphere where the  $O_2$  concentration is suppressed. Traditional gas detectors for food packages are intrusive or demand direct optical access. GASMAS constitutes an alternative interesting approach with high potential.

Gas detection in nano-porous samples allows fundamental studies of the gas molecules. Broadening of absorption lines of  $O_2$  and  $H_2O$  due to tight confinement in nano pores in ceramics has been studied, as well as diffusion of the gases. In addition to fundamental physical interest the study of broadening and diffusion allows for assessment of material parameters.

# Populärvetenskaplig sammanfattning

Ljus växelverkar med materia på ett mycket specifikt sätt och är anledningen till att saker har färger, himlen är blå, vår spegelbild reflekteras i en spegel och att solljus kan delas upp i en regnbåge genom vattendroppar. Läran om hur ljus växelverkar med material - spektroskopi - används inom astronomi, kemi, fysik och medicin. Absorptionsspektroskopi studerar just hur olika material absorberar elektromagnetisk strålning, och gör det möjligt att avbilda genom röntgenstrålning och kvantitativt bestämma gaser i atmosfären. Inom kemisk analys är absorption av ljus (UV, synliga och IR området) ofta använt. Varje atom och molekyl absorberar ljus på ett unikt sätt, vilket är ett resultat av dess inre struktur. Overgångar mellan de diskreta energinivåerna, ett resultat av kvantmekaniken, leder till absorptionslinjer. Då ljus absorberas av en molekyl exciteras denna, vilket innebär att den ändrar sin elektronkonfiguration, d.v.s. elektronorbital, vibration och/eller rotation.

Denna avhandling avser absorptionspektroskopi genom att studera absorptionen av ljus emitterat från diodlasrar - diodlaserspektroskopi. Laserljus är en ytterst lämplig ljuskälla för absorptionsspektroskopistudier då ljuset från en laser är har alldeles specifika egenskaper. Särskilt intressant är diodlasern för absorptions-spektroskopi, då den är svepbar. Diodlasern består av ett halvledarmaterial som man skickar en ström igenom. Genom att ändra diodlaserns temperatur eller drivström så ändras den utsända våglängden - man kallar detta att diodlasern är svepbar i våglängd. Typiskt sveps våglängden över en absorptionslinje av den studerade gasen genom att strömmen till diodlasern snabbt Diodlasrar är kompakta små enheter, som är enkla rampas. att styra och reglera, vilket ytterliggare bidragit till deras stora användning inom absorptionsspektroskopi.

Avhandlingen syftar till utveckling av diodlaserspektroskopitekniken och ett särskilt fokus har varit att studera gaser inuti fasta prover som sprider och absorberar ljus kraftigt. Sprid-

ning innebär att ljusets utbredningsriktning ändras, jämför t.ex. laserljus som passerar genom ett glas med vatten (det går rakt igenom) och laserljus som går genom ett mjölkglas (det blir diffust). Möjligheten att mäta gas fastän den är lokaliserad inuti ett fast absorberande och spridande material är en relativt ny diodlaserspektroskopiteknik (har funnits i 10 år) och har givits namnet GASMAS - gas in scattering media absorption spectroscopy. Den fundamentala skillnaden mellan GASMAS och traditionell diodlaserspektrosopi är att ljuset inte går rakt igenom provet och växelverkar med gasen, utan istället studsar runt inuti provet och växelverkar med gas när det stöter på denna. Den diffusa ljusutbredningen som spridningen orsakar leder till att vägsträckan genom gas är okänd och att endast mycket små mängder ljus kan detekteras. Klassiskt används vägsträckan för att bestämma koncentrationen på gasen genom Beer-Lamberts lag. Den okända gas-väglängden i GASMAS-fallet leder till en mer komplex koncentrationsanalys. För att detektera det spridda ljuset används en detektor med stor känslig yta,  $25 - 400 \text{ mm}^2$ . Typiskt detekteras 1 nW – 1  $\mu$ W då laserljus med effekten 0.5 – 1 mW sänds in i provet. Tranmissionen av provet är en avgörande begränsning för GASMAS-tekniken.

Möjligheten att detektera absorptionen från gasen (typiskt absorberas 1 av 10 000 fotoner) fastän provet kraftigt absorberat och spritt ljuset beror på att gasen spektralt sett absorberar mycket skarpare än bulkmaterialet. Till skillnad från fria molekyler - gas upplever molekyler i flytande och fast fas störningar av närliggande molekyler vilket gör att deras absorption blir mer bredbandig.

I detta avhandlingsarbete har GASMAS-tekniken undersökts för medicinsk diagnostisering, livsmedelsförpackningsanalys samt fundamentala gas- och material-studier.

Gasmonitorering i människokroppen är begränsad till vävnadens transmission av ljus och tillgängliga absorptionslinjer. Vävnad absorberar ljus kraftigt, men i området från 600 nm till 1400 nm (optiskt vävnadsfönster) är det möjligt för ljus att passera igenom. Inom det optiska vävnadsfönstret har syre, O<sub>2</sub>, och vattenånga, H<sub>2</sub>O, absorptionslinjer och kan därmed bli detekterade. I detta avhandlingsarbete visas hur detektion av O<sub>2</sub> och H<sub>2</sub>O i mänskliga käk- och pann-bihålor samt gaskaviteter i mastoidbenet, med hjälp av icke-invasiv GASMAS-teknik ger klinisk relevant information. Mastoidbenet, lokaliserat bakom örat, är en gasfylld benstruktur som kan bli igensatt vid sjukdom. Bihålorna som i ett friskt tillstånd är gasfyllda kavitier som ventileras via näskaviteten blir i ett sjukligt tillstånd blockerade och igensatta. Inga enkla tillförlitliga diagnostiseringsmetoder finns vilket leder till stora överförskrivningar av antibiotika. GASMASteknikens icke-invasiva natur och kompakta instrumentering utgör ett intressant alternativ med stor klinisk användbarhet. Genom en klinisk studie, då GASMAS-data och annan klinisk data (utvärdering av datortomogafibilder) jämförts, har god korrelation av diagnostisk överensstämmelse visats. Absorptionen av H<sub>2</sub>O ger hur stor gasmängd som laserljuset gått igenom (koncentrationen av H<sub>2</sub>O är känd eftersom gasen är mättad med vattenånga och kroppstemperaturen är känd) - d.v.s. relaterar till hur stor gasmängd som finns i bihålan. Genom att använda denna kända parameter (vägsträcka genom gas) är det möjligt att extrahera O<sub>2</sub>-koncentrationen i bihålan genom att mäta O<sub>2</sub>- och H<sub>2</sub>O-absorptionen simultant.

Vidare har GASMAS-tekniken undersökts som möjlig metod för att monitorera gas i lungorna hos för tidigt födda barn - ett högst kritiskt fall som skulle nyttjas av en icke-invasiv teknik. GASMAS-mätningar har utförts på en realistisk modell bestående av lungvävnad från djur och gelatinfantomer (med absorbtion och spridning som vävnad), i rimliga dimensioner. Resultaten visar att gasmonitorering av för tidigt födda barns lungor bör vara möjligt både i transmissions- och reflektions-geometri.

Att mäta gasen i livsmedelsförpackningar utan att punktera dem är en annan intressant applikation av GASMAS-tekniken. Behovet att mäta gas i förpackningar är stort då många livsmedel förpackas i en modifierad atmosfär, d.v.s. syrekoncentrationen är reducerad. Med diodlaserspektroskopi är det möjligt att mäta gasen i en förpackning om det finns fri optiskt tillgång, d.v.s. en passage där ljuset kan gå rakt igenom. GASMAS-tekniken expanderar användingsområdet till förpackningar där ljuset kan gå genom spridande förpackningsmaterial och livsmedel. Demonstration av tekniken har gjorts genom köttfärspaket och bröd paketerade i en modifierad atmosför. Ytterliggare har studier av gas inuti mjölkpaket och olika syrgasinnehåll för juice-paket med olika hållbarhetsdatum utförts.

Analys av gas i nanoporösa material är en ny applikation av GASMAS. Ljusabsorptionen av den instängda gasen påverkas av molekylernas kollisioner med väggarna, vilket leder till breddning av absorptionslinjerna. Förutom fundamentala intressanta aspekter, ger denna breddning också möjlighet att studera materialegenskaper, såsom porstorlek.

# LIST OF PUBLICATIONS

This thesis is based on the following papers, which will be referred to by their Roman numerals in the text.

I Quasi zero-background tunable diode laser absorption spectroscopy employing a balanced Michelson interferometer

Z. G. Guan, M. Lewander, and S. Svanberg. *Optics Express* **16**, 21714 – 21720 (2008).

II Fast and sensitive time multiplexed gas sensing of multiple lines using a miniature telecom diode laser between 1529 nm and 1565 nm
M. Lewander, A. Fried, D. Richter, P. Weibring, and L. Rippe. Submitted.

III Disordered strongly scattering porous materials as miniature multipass gas cells
T. Svensson, E. Adolfsson, M. Lewander, C. T. Xu, and S. Svanberg.
arXiv, 1011.0900v1 (2010); to appear.

IV Laser absorption spectroscopy of water vapor confined in nanoporous alumina: wall collision line broadening and gas diffusion dynamics
T. Svensson, M. Lewander, and S. Svanberg. Optics Express 18, 16460 – 16473 (2010).

- V Wall collision line broadening at reduced pressures: towards non-destructive characterization of nanoporous materials
   C. T. Xu, M. Lewander, S. Andersson-Engels, E. Adolfsson,
  - T. Svensson, and S. Svanberg. *Manuscript*.
- VI Gas analysis within remote porous targets using LIDAR multi-scatter techniques
   Z. G. Guan, M. Lewander, R. Grönlund, H. Lundberg, and

S. Svanberg. Applied Physics B **93**, 657 – 663 (2008).

VII Food monitoring based on diode laser gas spectroscopy

M. Lewander, Z. G. Guan, L. Persson, A. Olsson, and S. Svanberg. Applied Physics B 93, 619 – 625 (2008).

VIII Non-intrusive measurements of headspace gas composition in liquid food packages made of translucent materials

M. Lewander, P. Lundin, T. Svensson, S. Svanberg, and A. Olsson.

Accepted to Packaging Technology and Science.

# IX Gas monitoring in human sinuses using tunable diode laser spectroscopy

L. Persson, M. Andersson, M. Lewander, K. Svanberg, and S. Svanberg.

Journal of Biomedical Optics 12, 054001 (2007).

X Simultaneous detection of molecular oxygen and water vapor in the tissue optical window using tunable diode laser spectroscopy

L. Persson, M. Lewander, M. Andersson, K. Svanberg, and S. Svanberg.

Applied Optics 47, 2028 – 2034 (2008).

- XI Clinical system for non-invasive in situ monitoring of gases in the human paranasal sinuses
  M. Lewander, Z.G. Guan, K. Svanberg, S. Svanberg, and T. Svensson.
  Optics Express 17, 10849 – 10863 (2009).
- XII Non-invasive diagnostics of the maxillary and frontal sinuses based on diode laser gas spectroscopy
   M. Lewander, S. Lindberg, T. Svensson, R. Siemund, K. Svanberg, and S. Svanberg. Submitted.

## XIII Method for studying gas composition in the human mastoid using laser spectroscopy

S. Lindberg, M. Lewander, T. Svensson, R. Siemund, K. Svanberg, and S. Svanberg. Submitted.

 XIV Non-intrusive gas monitoring in neonatal lungs using diode laser spectroscopy - Feasibility study M. Lewander, A. Bruzelius, V. Fellman, K. Svanberg, and S. Svanberg. Manuscript.

# ABBREVIATIONS

AO	anharmonic oscillator
BSG	binary superimposed grating
CT	computerized tomography
DBR	distributed Bragg reflector
DFB	distributed feed back
DFG	difference frequency generation
DIAL	differential absorption lidar
dWMS	digital wavelength modulation spectroscopy
FP	Fabry Pérot
GASMAS	gas in scattering media absorption spectroscopy
HO	harmonic oscillator
HWHM	half width at half maximum
HITRAN	high resolution transmission molecular absorption database
IR	infrared
IR LIDAR	infrared light detection and ranging
IR LIDAR MAP	infrared light detection and ranging modified atmosphere packaging
IR LIDAR MAP MEMS	infrared light detection and ranging modified atmosphere packaging microelectromechanical system
IR LIDAR MAP MEMS MIR	infrared light detection and ranging modified atmosphere packaging microelectromechanical system mid infrared
IR LIDAR MAP MEMS MIR MG-Y	infrared light detection and ranging modified atmosphere packaging microelectromechanical system mid infrared modulated grating Y-banch
IR LIDAR MAP MEMS MIR MG-Y NEP	infrared light detection and ranging modified atmosphere packaging microelectromechanical system mid infrared modulated grating Y-banch noise equivalent power
IR LIDAR MAP MEMS MIR MG-Y NEP NIR	infrared light detection and ranging modified atmosphere packaging microelectromechanical system mid infrared modulated grating Y-banch noise equivalent power near infrared
IR LIDAR MAP MEMS MIR MG-Y NEP NIR NR	infrared light detection and ranging modified atmosphere packaging microelectromechanical system mid infrared modulated grating Y-banch noise equivalent power near infrared non-rigid rotor
IR LIDAR MAP MEMS MIR MG-Y NEP NIR NR PD	infrared light detection and ranging modified atmosphere packaging microelectromechanical system mid infrared modulated grating Y-banch noise equivalent power near infrared non-rigid rotor photo diode
IR LIDAR MAP MEMS MIR MG-Y NEP NIR NR PD PMT	infrared light detection and ranging modified atmosphere packaging microelectromechanical system mid infrared modulated grating Y-banch noise equivalent power near infrared non-rigid rotor photo diode photomultiplier tube
IR LIDAR MAP MEMS MIR MG-Y NEP NIR NR PD PMT ppb	infrared light detection and ranging modified atmosphere packaging microelectromechanical system mid infrared modulated grating Y-banch noise equivalent power near infrared non-rigid rotor photo diode photomultiplier tube parts per billion $(1 \times 10^{-9})$
IR LIDAR MAP MEMS MIR MG-Y NEP NIR NR PD PMT ppb ppm	infrared light detection and ranging modified atmosphere packaging microelectromechanical system mid infrared modulated grating Y-banch noise equivalent power near infrared non-rigid rotor photo diode photomultiplier tube parts per billion $(1 \times 10^{-9})$ parts per million $(1 \times 10^{-6})$

QE	quantum efficiency
RAM	residual amplitude modulation
RR	rigid rotor
RTE	radiative transport equation
SG	sampled grating
SMSR	side mode suppression ratio
SNR	signal-to-noise ratio
SSG	super-structured grating
TIA	trans-impedance amplifier
TDLAS	tunable diode laser absorption spectroscopy $% \left( {{{\left( {{{{{{}}}} \right)}}}} \right)$
TOFS	time-of-flight spectroscopy
WMS	wavelength modulation spectroscopy
UV	ultraviolet
VCSEL	vertical cavity surface emitting laser

# CONTENTS

1	Intro	oduction	1
<b>2</b>	Abso	orption spectroscopy	3
	2.1	Atomic and molecular structure	3
	2.2	Spectral lines	5
		2.2.1 Line intensity	5
		2.2.2 Line profiles	6
	2.3	Chemical analysis	8
	2.4	HITRAN	9
		2.4.1 Wavelength regions of interest	10
3	Tuna	able diode laser absorption spectroscopy	11
	3.1	Principle	11
	3.2	Advantages and disadvantages	12
	3.3	Applications	13
	3.4	Instrumentation	14
		3.4.1 Diode lasers	14
		3.4.2 Detectors	16
		3.4.3 Gas cells	17
		3.4.4 Interference reductions	17
	3.5	Modulation techniques	18
		3.5.1 Digital wavelength modulation spectroscopy	23
4	Ligh	t propagation in turbid media	<b>25</b>
	4.1	Scattering	26
	4.2	Diffuse light propagation	26
	4.3	Measuring the optical properties with time-of-flight spectroscopy	28
	4.4	Turbid media	28
5	Gas	in scattering media absorption spectroscopy	31
	5.1	Principle	31
	-	5.1.1 Equivalent mean path length	32
		5.1.2 Concentration extraction	34
	5.2	Limitations	35
	5.3	Review	36
		5.3.1 Similar work	38
6	App	lication of GASMAS	19
U	6 1	Food-packaging applications	43
	0.1	6.1.1 Modified atmosphere packaging - MAP	40
		6.1.2 Current gas-sensing techniques	-1-1 44
		6.1.3 Review	-1-1 11
		6.1.4  Outlook	44
	6 2	Cas sensing in the human body	40
	0.2	6.2.1 Dependent diagnostics	40
		0.2.1 Faranasal sinus diagnostics	4ð

6. 6. 6.	2.2 M 2.3 N 2.4 O	astoid d eonatal utlook	liagno lung ( 	ostics diagno	ostics	· · ·	 		- ·	•				54 55 57
Comments	on the	Paper	5											59
Acknowled	lgement	s												65
References	8													67

## Papers

I	Quasi zero-background tunable diode laser absorption spectroscopy employing a balanced Michelson interfer- ometer	81
II	Fast and sensitive time multiplexed gas sensing of multiple lines using a miniature telecom diode laser between 1529 nm and 1565 nm	91
III	Disordered strongly scattering porous materials as miniature multipass gas cells	101
IV	Laser absorption spectroscopy of water vapor confined in nanoporous alumina: wall collision line broadening and gas diffusion dynamics	107
V	Wall collision line broadening at reduced pressures: to- wards non-destructive characterization of nanoporous materials	123
VI	Gas analysis within remote porous targets using LIDAR multi-scatter techniques	129
VII	Food monitoring based on diode laser gas spectroscopy	139
VIII	Non-intrusive measurements of headspace gas composition in liquid food packages made of translucent materials	149
IX	Gas monitoring in human sinuses using tunable diode laser spectroscopy	165
х	Simultaneous detection of molecular oxygen and water vapor in the tissue optical window using tunable diode laser spectroscopy	175
XI	Clinical system for non-invasive in situ monitoring of gases in the human paranasal sinuses	185
XII	Non-invasive diagnostics of the maxillary and frontal si- nuses based on diode laser gas spectroscopy	203
XIII	Method for studying gas composition in the human mas- toid using laser spectroscopy	213
XIV	Non-intrusive gas monitoring in neonatal lungs using diode laser spectroscopy - Feasibility study	223

## Chapter 1

# INTRODUCTION

Optical spectroscopy, i.e. the study of how light interacts with matter, provides an effective way to obtain information on a sample. Light interacts with matter in a particular way, dependent on the specific molecule or atom and its environment, allowing assessment of various parameters such as abundance, concentration, temperature, phase, pressure etc. Optical spectroscopy is today used in an enormous number of applications within fields such as analytical chemistry, environmental monitoring, medical diagnosis, and process control.

This thesis focuses on absorption spectroscopy of gases located inside scattering condensed matter and the use of diode lasers. By analyzing the absorption of light with a specific wavelength, information on the gas can be obtained even when the light is heavily attenuated by the solids or liquids, both by absorption and scattering. Molecules in gas phase are free and exhibit narrow absorption profiles while perturbed molecules in liquids and solids absorb light in a broad manner. This fundamental difference between molecules in different phases allows gas even inside a bulk medium to be studied, e.g. bubbles of water vapor can be monitored inside a glass of water or an ice cube. The study of gas within scattering media is such a special niche that it has been given the name GASMAS, gas in scattering media absorption spectroscopy. Scattering media, or turbid media are samples where the light does not propagate in a straight forward manner; compare, e.g., the passage of sunlight through a clear sky and through a white cloud. When light passes though a scattering medium, such as a cloud, the light is scattered around and the emerging light is diffuse.

The thesis work has involved gas sensing within the human body for medical diagnosis, monitoring of gas inside food packages for quality assurance, as well as technical and fundamental work within tunable diode laser absorption spectroscopy, TDLAS. The outline of the thesis is as follows. After this introductory chapter the principle of absorption spectroscopy is described. The molecular structure and how they absorb light are covered. The applications and the instrumentation of absorption spectroscopy based on diode lasers - tunable diode laser absorption spectroscopy, TDLAS - is presented in a succeeding chapter. Chapter 4 describes how light propagates through turbid, or scattering matter. Absorption spectroscopy in the regime of diffuse light propagation, referred to as GASMAS, is covered in the succeeding chapters. In Ch. 5 the principle of GASMAS is given and a review of the publications within this field is given. In Ch. 6 the applications of GASMAS in focus for this thesis work are presented and put into a context. The chapter also includes outlooks into future work.

The scientific papers are found at the end of the thesis. The papers are arranged in the order they are treated in the thesis text. Papers ?? – III present improvements to the TDLAS field, and ranges from zero-background spectra, gas sensing with a widely tunable diode laser, and a miniature gas cell based on strongly scattering media. Fundamental studies of gas  $(O_2 \text{ and } H_2O)$  inside porous samples are presented in Papers III - V. The application work towards the food packaging field is presented in Papers VI - VIII, where remote detection, proof-of principle gas monitoring in food packages, and further investigations are reported. GAS-MAS applied for medical applications are presented in the remaining papers; Papers IX – XIV. The first four, Papers IX – XII, cover the work carried out on GASMAS as a tool to diagnose the paranasal sinuses. Laboratory measurements are reported, and in particular the results from a clinical trial are presented. Furthermore, new application areas of gas sensing within the human body using GASMAS are presented in Papers XIII and XIV. Monitoring of gas inside the air cell cavities in the mastoid bone, shows diagnostic relevance in a clinical trial. A feasibility study of gas detection in lungs of premature born children, based on a lab-model, is demonstrated.

## Chapter 2

# Absorption spectroscopy

Atoms and molecules absorb light in a unique manner due to their quantum mechanical nature, providing us with a useful method to analyze them. From the light intensity reductions at specific wavelengths, information on species presence as well as concentration, pressure and temperature can be obtained with high sensitivity and specificity. This chapter describes the fundamentals of absorption spectroscopy and its applicability. The chapter starts out with a description of the atomic and molecular structure, i.e. the energy levels studied with absorption spectroscopy. Further, spectral transitions, i.e. the origin of the change in energy configuration of an atom or a molecule, and specifically the induced transitions due to absorption of light are discussed. The characteristics of the absorption line, i.e. the line intensity and profile, as well as the application of them for chemical analysis are presented. The chapter is concluded with a description of the database HITRAN.

## 2.1 Atomic and molecular structure

Each atom has a unique set of electronic energy levels, springing from the electromagnetic force acting on the electrons. According to quantum mechanics the levels are discretized, a result of the wave nature of the electron. Only standing-waves states described by the wave function,  $\psi$ , are allowed and constitute stationary energy states. The state of an electron in an atom is described by a set of quantum numbers<sup>1</sup> and the atom configuration with all present electrons is given by the term symbol<sup>2</sup> using capital letters. The electron occupation of the states is governed by the Pauli exclusion principle, stating that two electrons cannot have the same set of quantum numbers.

The energy splitting for molecules is more complex than for atoms. Firstly the electron configuration in molecules can be ref-

#### $^{1}$ Atomic quantum number

 $\begin{array}{lll} \mbox{Principal:} & n, & n \geqslant 1 \\ \mbox{Azimuthal:} & l, & 0 \geqslant l \geqslant n-1 \\ \mbox{(angular momentum)} \\ \mbox{Magnetic:} & m_l, & -l \geqslant m_l \geqslant l \\ \mbox{(projection of l)} \\ \mbox{Spin:} & m_s, & m_s = \pm 1/2 \\ \mbox{(projection of s)} \end{array}$ 

<sup>2</sup> Term symbol 
$${}_{2S+1}L_J$$

$$L = \sum_{i} l_{i}, S = \sum_{i} s_{i}, J = \sum_{i} j_{i}$$
$$L = 0, 1, 2, 3, 4$$
$$S, P, D, F, G$$

<sup>3</sup> Molecular	quantu	ım nu	mber
Electronic:	n, l,	$m_l, m$	s
Vibrational:	v,	$v \geqslant 0$	
Rotational:	J,	$J \geqslant 0$	

<sup>4</sup> Term symbol

$$2\Sigma + 1 \Lambda_{\Omega,(\text{parity})}^{\text{symmetry}}$$
$$\Omega = |\Lambda + \Sigma|$$
$$\Lambda = |\sum_{i} m_{li}|, \Sigma = |\sum_{i} m_{si}|$$
$$\Sigma = S, S - 1, S - 2, \dots, -S$$
$$\Lambda = 0, 1, 2, 3,$$

 $\Sigma$ ,  $\Pi$ ,  $\Delta$ ,  $\Phi$ 

 $\begin{aligned} \psi(-x,-y,-z) &= \psi(x,y,z) \\ \text{u: ungerade} \\ \psi(-x,-y,-z) &= -\psi(x,y,z) \end{aligned}$ 

symmetry: (for  $\Sigma$ -states) +: even  $\psi(-x, -y, z) = \psi(x, y, z)$ -: odd  $\psi(-x, -y, z) = -\psi(x, y, z)$ 

<sup>5</sup> The electronic states are labeled in rising energy order with X, A, B, C, ..., where X is the ground state.



erenced to an internal field, e.g. the internuclear axis for a diatomic molecule. This results in the use of other electronic quantum numbers<sup>3</sup> than for the atomic case, and the use of capital Greek lettering in the term symbol.<sup>4</sup> Further, molecules exhibit additional quantized energy levels due to internuclear vibration and rotation, with two individual quantum numbers. These states do not exist in atoms because of their symmetry. The vibration and rotation of the molecule result in splitting of the energy levels originating from the charge of the electron, i.e. the electronic state ( $E_{\rm elec}$ ), into a set of vibrational energy states ( $E_{\rm vib}$ ) with an inner structure of rotational energy states ( $E_{\rm rot}$ ). The Born-Oppenheimer approximation declares that each of these energy constituents can be treated independently, i.e. with individual wave functions.

$$\psi = \psi_{\text{elec}}\psi_{\text{vib}}\psi_{\text{rot}}, \qquad (2.1)$$

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}. \qquad (2.2)$$

The magnitudes of the individual energy components are typically  $E_{\rm elec} \sim 1 - 10$  eV,  $E_{\rm vib} \sim 0.1$  eV, and  $E_{\rm rot} \sim 1 \times 10^{-3}$  eV.

The potential curve in a molecule, or the electronic state, is often described by the Morse potential, a function of internuclear distance, r, which increases infinitely as r approaches zero (Coulomb repulsion) and falls off to the dissociation energy,  $D_{\rm e}$ , as r increases.

$$E(r_{\rm eq} - r) = D_{\rm e} \left(1 - e^{-\beta(r_{\rm eq} - r)}\right)^2,$$
 (2.3)

where  $r_{\rm eq}$  is the internuclear distance at equilibrium, i.e. the minimum of the potential, and  $\beta$  is a molecular specific constant with the unit m<sup>-1</sup>. The Morse potential for the ground state<sup>5</sup> of O<sub>2</sub>, X  ${}^{3}\Sigma_{g}^{-}$  is presented in Fig. 2.1. Around the  $r_{\rm eq}$  the Morse potential can be approximated by a harmonic oscillator (HO), yielding an equidistant vibrational splitting:

$$E_{\rm vib}^{\rm HO} = h\nu_{\rm e}(v+1/2), \quad v = 0, 1, 2, \dots$$
 [SI] (2.4)

$$\varepsilon_{\rm vib}^{\rm HO} = \tilde{\nu}_{\rm e}(v+1/2),$$
 [cm<sup>-1</sup>] (2.5)

where h is the Planck constant  $(6.62606896 \cdot 10^{-34} \text{ kgm}^2/\text{s})$ , and  $\nu$ and  $\tilde{\nu}_{\rm e}$  are the oscillation frequency in Hz and cm<sup>-1</sup>, respectively. Historically, molecular specific constants are given in cm<sup>-1</sup>;  $E = h\nu = hc/\lambda = hc\tilde{\nu} = h\omega/2\pi$ , and  $\varepsilon = E/hc$ . The anharmonicity of the potential can be incorporated - anharmonic oscillator (AO) by including higher-order correction terms,  $x_{\rm e}$  and  $y_{\rm e}$ :

$$\varepsilon_{\rm vib}^{\rm AO} = \tilde{\nu}_{\rm e}(v+1/2) - \tilde{\nu}_{\rm e}x_{\rm e}(v+1/2)^2 + \tilde{\nu}_{\rm e}y_{\rm e}(v+1/2)^4$$

As each electronic level splits up into vibrational levels, each of these states have a finer structure due to rotations. Similarly as the vibrational levels, the rotational energy is usually first derived from a simple model, which for the rotation case is the rigid rotor (RR) model for a diatomic molecule, and is later improved by adding distortion terms.

$$E_{\rm rot}^{\rm RR} = \frac{\hbar^2}{2I}J(J+1), \quad J = 0, 1, 2, \dots$$
 [SI] (2.6)

$$\varepsilon_{\rm rot}^{\rm RR} = \frac{h}{8\pi^2 Ic} J(J+1) = BJ(J+1), \quad [\rm cm^{-1}] \quad (2.7)$$

B is the rotational constant. The non-rigid rotor model (NR) of the rotation includes a distortion factor, the centrifugal distortion constant D;

$$\varepsilon_{\rm rot}^{\rm NR} = BJ(J+1) - DJ^2(J+1)^2.$$
 (2.8)

The distortion constant is connected to the vibration of the molecule, and is given by  $D = 4B^3/\tilde{\nu}^2$ .

For further studies of molecular structure the reader is referred to [1] for a general description and to [2] for extensive material.

### 2.2 Spectral lines

A spectral line<sup>6</sup> arises from a transition between an initial state,  $|1\rangle$ , to a final state,  $|2\rangle$ , by interaction with electromagnetic radiation. Detailed descriptions can be found in Refs [2, 3]. Briefly, the light induces dipole moments which alter the wavefunctions of the states and may cause a transition. The major contribution of the dipole moment originates from the electric field,<sup>7</sup>  $\mathbf{E}(t)$  of the light:

$$\mathbf{E}(t) = E_0 \cos(2\pi\nu t) \mathbf{\hat{e}},\tag{2.9}$$

where  $E_0$  is the amplitude of the field and  $\hat{\mathbf{e}}$  the direction of the oscillating field. The Hamiltonian can be written as  $H' = e\mathbf{r} \cdot \mathbf{E}(t)$ , giving a transition rate (probability of transition per unit time) as:

$$T_{1\to 2} \propto |\langle 2|\mathbf{r} \cdot \hat{\mathbf{e}}|1 \rangle|^2$$
 (2.10)

When the frequency of the light is in resonance with the energy separation between the levels a transition can take place. For gases this transition is sharply defined whereas in solids and liquids the perturbation causes the formation of energy bands instead of sharp energy levels, resulting in broader absorption profiles.<sup>8</sup>

#### 2.2.1 Line intensity

The intensity of the spectral line is both dependent of the transition probability and the population of the state. At thermal <sup>6</sup> The name spectral line originates from the use of spectrographs with a slit entrance.

<sup>7</sup> Magnetic dipole and higher order electric dipole moments also induce transitions, but these are generally much weaker.

<sup>8</sup> Rare-earth atoms within a solid matrix also exhibit sharp absorption lines, due to shielding by outer electrons.

equilibrium the states are occupied according to the Boltzmann distribution function:

$$\frac{N_2}{N_1} = e^{-\Delta E/kT},$$
 (2.11)

where  $N_i$  is population number at energy level i,  $\Delta E$  is the energy between the states, T is the thermodynamic temperature in K, and k is the Boltzmann constant. For rotational energy levels Eq. (2.11) is modified to include the degeneracy:

$$N_J \propto (2J+1)e^{\Delta E/kT} = (2J+1)e^{-BJ(J+1)/kT}.$$
 (2.12)

The J(J + 1)-degeneracy of rotational states results in an occupation of the states, where the lowest energy state does not have the largest occupation, see Fig. 2.2. The relation between different transitions can be used to determine the temperature.

### 2.2.2 Line profiles

An absorption line always has a finite width, the half width at half maximum, HWHM. How wide it is and the shape of the line profile depend on the sample temperature, pressure, and the surrounding materials.

#### Natural broadening

Every absorption line has a natural line width,  $\Delta \nu_{\rm N}$ , related to the lifetime of the upper state. As indicated by the Heisenberg uncertainty principle

$$\Delta E \cdot \Delta t \ge \frac{\hbar}{2},\tag{2.13}$$

states have an uncertainty in time,  $\Delta t$ , and in energy,  $\Delta E$ , and thus frequency.

The natural line width is given by:<sup>9</sup>

$$2\Delta\nu_{\rm N} = \frac{1}{2\pi\tau} \tag{2.14}$$

The natural broadening gives rise to a Lorentzian lineshape and has a width which is - under standard conditions - only of the order of 0.1 - 100 MHz.

#### Doppler broadening

The broadening due to thermal motion of the atoms or molecules, the Doppler broadening, usually dominates over the natural line broadening. In the visible region the Doppler broadening is about







Figure 2.2. Rotational population

distribution for different J quan-

tum numbers.

0.5 GHz. The Doppler broadening,  $\Delta \nu_{\rm D}$ , depends on the temperature, T, and molecular mass, M, of the studied gas:

$$\Delta\nu_{\rm D} = \frac{2\sqrt{2R\ln(2)}}{c}\nu_0\sqrt{\frac{T}{M}} \tag{2.15}$$

The broadening has a Gaussian profile, which can be derived from classical gas kinetics, through the Maxwell velocity distribution of the molecules:

$$f(v) = \sqrt{\frac{M}{2\pi RT}} e^{-(M/2RT)v^2}$$
(2.16) v: velocity (2.16)

The Doppler shift is  $\Delta \nu = \nu - \nu_0 = \nu_0 v/c$ , where  $\nu$  is the Doppler shifted frequency that the particles experience and  $\nu_0$  the frequency for a system at rest. The Doppler shift is directly proportional to the velocity and the profile follows a Gaussian lineshape.

The Doppler broadening is an inhomogeneous broadening, meaning that each molecule individually affects the lineshape. The Doppler lineshape function,  $f_{\rm D}$  is

$$f_{\rm D}(\nu) = \frac{\sqrt{\ln 2}}{\sqrt{\pi} \Delta \nu_{\rm D}} e^{-\ln 2(\nu/\Delta \nu_{\rm D})^2}.$$
 (2.17)

#### Pressure broadening

Pressure broadening originates from a random time-dependent perturbation caused by intermolecular collisions. The perturbation induces both a probability of phase shift and transition, resulting in an alternation of the lifetime and thus a broadening.

$$\Delta\nu_{\rm P}(P,T) = \Delta\nu_{\rm P}^0 \frac{P}{P_0} \sqrt{\frac{T_0}{T}}$$
(2.18)

$$\Delta \nu_{\rm P}^0 = 4\sigma_{\rm coll}^2 \sqrt{\frac{\pi}{RMT_0}} P_0 \tag{2.19}$$

Similarly as the natural linewidth the pressure broadening also follows a Lorentzian lineshape. This can be derived by studying the exponential decay of an excited state due to intermolecular collisions. The pressure broadening lineshape function,  $f_{\rm P}(\nu)$  is:

$$f_{\rm P}(\nu) = \frac{\Delta \nu_{\rm P}}{\pi ((\nu - \nu_0)^2 + \Delta \nu_{\rm P}^2)}$$
(2.20)

#### The Voigt lineshape

At atmospheric pressure, the broadening due to intermolecular collisions dominates over the natural and Doppler broadenings.<sup>10</sup> At intermediate pressures, 10 - 500 Torr, the resulting profile is a

 $\begin{array}{l} ^{10} \mbox{Ex: } {\bf O}_2 \mbox{ transition at 760 nm} \\ \Delta \nu_{\rm P} \sim 1.5 \mbox{ GHz} \\ \Delta \nu_{\rm D} \sim 0.4 \mbox{ GHz} \\ \Delta \nu_{\rm N} \sim 0.01 \mbox{ Hz} \mbox{ - This state has} \end{array}$ 

 $\Delta \nu_{\rm N} \sim 0.01$  Hz - This state has an extremely long life time ( $\tau =$ 7.1 s).

R : general gas constant

 $\nu_P^0: \nu_P$  at standard conditions  $P_0$ : standard pressure  $T_0$ : standard temperature  $\sigma_{\text{coll}}$ : collision cross-section

convolution of a Gaussian and a Lorentzian profile, called a Voigt profile:

$$f_{\rm V}(\nu) = f_{\rm P}(\nu) * f_{\rm D}(\nu) = \int_{-\infty}^{\infty} f_{\rm P}(\nu') f_{\rm D}(\nu - \nu') \mathrm{d}\nu' \qquad (2.21)$$

Insertion of Eqs (2.17) and (2.20) into Eq. (2.21) gives:

$$f_{\rm V}(\nu) = \int_{-\infty}^{\infty} \frac{\Delta\nu_{\rm P}}{\pi((\nu'-\nu_0)^2 + \Delta\nu_{\rm P}^2)} \frac{\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_{\rm D}} e^{-\ln 2\left((\nu-\nu')/\Delta\nu_{\rm D}\right)^2} \mathrm{d}\nu'.$$

Change of variable [4]:

$$t = \sqrt{\ln 2} \frac{\nu - \nu'}{\Delta \nu_{\rm D}}$$
$$d\nu' = -\frac{\Delta \nu_{\rm D}}{\sqrt{\ln 2}} dt,$$

gives

$$f_{\rm V}(\nu) = -\frac{\ln 2\Delta\nu_{\rm P}}{\pi^{3/2}\nu_{\rm D}^2} \int_{-\infty}^{\infty} \frac{e^{-t^2}}{(\frac{\nu-\nu_0}{\Delta\nu_{\rm D}/\sqrt{\ln 2}} - t)^2 + \frac{\ln 2}{\Delta\nu_{\rm D}^2}\Delta\nu_{\rm P}^2} dt.$$
 (2.22)

#### Additional broadening effects

Additional broadening effects that may contribute to the absorption lineshape are, e.g. instrumental factors and perturbations causing shortened lifetimes. An instrumental factor which is important to consider is the linewidth of the laser, which otherwise degrades the signal by broadening and reduces the SNR. Perturbations decreasing the lifetime can, e.g. be hard collisions. In Papers III – V, gas confined in nano-cavities has been studied. The tight confinement causes wall collisions, decreasing the lifetime of the states and results in broadened lines.

#### 2.3 Chemical analysis

With absorption spectroscopy it is possible to investigate a sample quantitatively and qualitatively from the fingerprint created by the energy levels in the atom or the molecule. The concentration, temperature, and pressure can be extracted.

The absorption is governed by the Beer-Lambert law stating that the light is attenuated exponentially as it passes through an absorbing sample.

$$I = I_0 e^{-\sigma(\nu)NL} = I_0 e^{-\mu_a L}$$
(2.23)

Often the absorbance,  $a = \sigma(\nu)NL$ ,<sup>11</sup> is used to quantify an absorbing medium. The concentration can be deduced through N by

<sup>11</sup> For liquids the absorbance is defined using base 10 instead of e.

- I: detected intensity
- $I_0$ : incident intensity
- $\sigma(\nu)$ : abs. cross-section [cm<sup>2</sup>/molecule]
- N: number density [molecules/cm<sup>2</sup>]
- L: interaction length [cm]

 $\mu_a$ : absorption coefficient [cm<sup>-1</sup>]

the use of the ideal gas law,<sup>12</sup> and  $c = N/N_0$ , with  $N_0$  being the Loschmidt number.

The frequency dependency of the absorption cross section,  $\sigma(\nu)$  is given by:

$$\sigma(\nu) = S \cdot f(\nu), \qquad (2.24)$$

where  $f(\nu)$  is the lineshape function discussed in Section 2.2.2 and S is the linestrength of the absorption line  $[(\text{cm}^2/\text{molecule})\text{Hz}]$ ,

$$S = \int_0^\infty \sigma(\nu) \mathrm{d}\nu. \tag{2.25}$$

### 2.4 HITRAN

HITRAN (high-resolution transmission molecular absorption database) is a database with molecular constants which are useful for absorption spectroscopy [5-8]. The HITRAN data can be used to simulate, predict and analyze the measured absorption. The majority of the constants are theoretically calculated. The database itself is free (http://www.cfa.harvard.edu/HITRAN/), and one can develop softwares to utilize it. However, a couple of different compilers, using the HITRAN data already exist. Spectralcalc (http://spectralcalc.com/) is a versatile webbased compiler that allows easy visualization of the absorption. Options like pressure, path length, and instrumental function are incorporated. Parts of Spectralcalc are open to public and part only to subscribers (low subscription fee). Another compiler software is HITRAN PC (developed by Prof. D. Killinger and Dr. W. Wilcox at the University of South Florida) which can be purchased through Ontar Corporation (http://www.ontar.com).

The parameters included in HITRAN:

M: Molecular number

I: Isotopologue number

u: Vacuum wavenumber  $[\text{cm}^{-1}]$  S: Intensity  $[(\text{cm}^2/\text{molecule})\text{cm}^{-1}]$  (linestrength) A: Einstein A coefficient  $\gamma_{\text{air}}$ : Air-broadened HWHM (pressure broadening)  $\gamma_{\text{self}}$ : Self-broadened HWHM E'': Lower-state energy  $n_{\text{air}}$ : temperature-dependency exponent for  $\gamma_{\text{air}}$   $\delta_{\text{air}}$ : Air-pressure-induced line shift V', V'', Q', Q'': Vibrational and rotational quantum number

HITRAN refers to the linestrength as intensity and gives it in the unit relevant when using cm<sup>-1</sup> units instead of Hz, as it was defined earlier in this thesis,  $S^{\text{Hz}} = 100c \cdot S^{\text{cm}^{-1}}$ .

<sup>12</sup> Ideal gas law

pV = NkT

p - pressure

- V volume k Boltzmann constant
- T temperature.



Figure 2.3. Absorption lines simulated through Spectralcalc.

### 2.4.1 Wavelength regions of interest

From HITRAN one can see that the MIR, mid-IR (3-15 µm), is a rich spectral region where many interesting trace gases have their fundamental rotational-vibrational modes, yielding strong absorptions, Fig. 2.3. However, the high presence of H<sub>2</sub>O requires good spectral resolution. In the NIR (0.8-3 µm), the first and second overtones of rotational-vibrational modes are located, with room-temperature operated diode lasers available. However, the absorption is one or two magnitudes lower.

# Chapter 3

# TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY

Already two years after the first laser was demonstrated in 1960 [9], the semiconductor laser or diode laser was invented. The diode laser was early recognized as a good light source for absorption spectroscopy due to its easy tunability, compactness and low cost, and was demonstrated for gas sensing in the mid 70's [10, 11]. Today the diode laser is a natural component in an optical gas sensor which are used for an enormous number of applications. In this chapter the now frequently used method for absorption spectroscopy based on diode lasers, namely tunable diode laser absorption spectroscopy, TDLAS, will be presented. The chapter will describe the technique, its applications together with its limitations and advantages. The instrumentation and technical challenges are also given. For further reading on TDLAS, several good review papers exist. Two recent general TDLAS papers are Refs [12, 13]. Application oriented TDLAS review papers are; for industrial applications [14–17], combustion diagnostics [18], environmental monitoring [17, 19, 20], and more general [21]. Furthermore, technique-related review papers are Refs [22–26].

### 3.1 Principle

Absorption spectroscopy with the use of a frequency-tuned diode laser is a common technique for analyzing a gas quantitatively. Besides being inexpensive, small, and available at many interesting wavelength regions, the diode laser has nice spectroscopic characteristics<sup>1</sup> and can be tuned in frequency by changing the temperature or injection current.

The standard procedure for pursuing TDLAS is to scan the sharp frequency of the diode laser over an absorption line of the <sup>1</sup> Single-mode operation: sidemode-suppression-ratio (SMSR), and narrow enough linewidth. Typical values for a diode laser are: SMSR: 30 dB and a linewidth of about 10 MHz.



Figure 3.1. The principle of TD-LAS. The key components are a tuned diode laser, an absorbing gas and a detector system.

studied gas and monitor the intensity reductions in time, Fig. 3.1. From the reductions in transmission the concentration can be extracted if the interaction distance and absorption cross section are known, using the Beer-Lambert law:

$$I(\nu) = I_0(\nu) e^{-\sigma(\nu)g(\nu - \nu_0)NL}$$
(3.1)

This equation is the same as given earlier, Eq. (2.23), with the modification that the intensity is altered as the diode laser wavelength is scanned. Thus,  $I_0(\nu)$  is the transmitted diode laser intensity with no absorption present and  $I(\nu)$  the true transmitted intensity.

Besides species concentration, other measurable properties with TDLAS include temperature (through Boltzmann distribution or line broadening), pressure (through line broadening), velocity (through Doppler shift), and flux (combination of concentration and velocity) [27].

## 3.2 Advantages and disadvantages

Linnerud  $et \ al.$  [16] list the characteristics of an ideal gas sensor for industrial process monitoring:

- (i) measure correctly without influence from other gases or dust
- (ii) automatically compensate for temperature and pressure effects
- (iii) measure continuously with short response time
- (iv) require little maintenance with few or no consumable parts
- (v) have high reliability and availability
- (vi) be insensitive to vibrations and mechanical instabilities
- (vii) use components operating near room temperature

According to these demands TDLAS possesses several favorable characteristics. It has a high sensitivity and selectivity. The instrumentation can be small and robust, and operate in harsh environments. Continuous *in situ* data acquisition in real-time is supported. Furthermore, TDLAS instrumentation is cost-effective. The disadvantages of TDLAS are mainly connected to the diode laser sources. The available spectral ranges and the tuning range of the diode laser are two limitations. As discussed in Section 2.4.1 most gases exhibit their strongest absorption lines (the fundamental lines) in the MIR. Diode lasers and detectors operating in this region, e.g. Pb-based diode lasers, require cooling. Large efforts are now invested in the development of a new type of diode laser, i.e. quantum cascade lasers, which emit in MIR. An alternative approach to reach the MIR is the use of DFG, difference frequency generation [19, 28, 29]. Such systems have shown high sensitivity (an absorption fraction of  $2 \times 10^{-7}$  [30]), but are more complex and costly.

The tuning of the diode laser, typically below one nm for a current-tuned diode laser, limits the instrument to only monitor one or two absorption lines. For many applications this is not a concern, but there are cases where one desires a larger tunability; multi-species detection, temperature sensing etc.

## 3.3 Applications

The TDLAS technique is applied in several fields. Here follows short descriptions of a couple of application fields for TDLAS.

**Environmental** Atmospheric sensing was one early application of TDLAS, and already in 1975 absorption of CO in a long open path (610 m) was measured in the MIR with a Pb-based diode laser [31]. Today, TDLAS is used in a variety of different environmental applications, both for industrial purposes and for atmospheric research with TDLAS instrumentation incorporated into fixed emission sites, balloon platforms, and into aircrafts.

The results from TDLAS spectrometers have made a large impact on the understanding of atmospheric chemistry. Both trace-gas sensing (ppt - parts per trillion) and isotopic ratio measurements have played important roles. Considering environmental applications of TDLAS, one does not only refer to monitoring of trace gases in the atmosphere, but also monitoring of the emission from pollutant sources, such as traffic, industry and agriculture [21].

**Combustion** Detection of combustion gases was also an early application field of TDLAS and is closely related to the environmental field [18]. The applications within the combustion field have expanded and include *in situ* sensing of gases and temperature in combustion engines [32, 33], NO<sub>x</sub> sensing in coal-combustion exhausts [34], and CO sensing in burners [35]. TDLAS for combustion applications is highly suitable due to the possibility to sense gas *in situ* non-invasively. A high interest for widely tunable diode lasers to monitor several properties and species simultaneously is present within the combustion field [36].

Medical Within the medical field the breath analysis application is where the TDLAS has had the largest impact. Diagnosis based on breath analysis carries high potential and a variety of gas sensors have been used, including TDLAS-based ones [37]. Examples of gases that have been monitored with TDLAS Gases of interest

Gases of interest

Gases of interest CO<sub>2</sub>, NO, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, etc.

in exhaled air are ethane ( $C_2H_6$ ) at 3.4 µm for cell damage investigation [38], simultaneous monitoring of nitric oxide (NO) and carbon dioxide (CO<sub>2</sub>) at 5.2 µm for airway inflammation analysis [39], and <sup>13</sup>C and <sup>14</sup>C urea isotope monitoring. Urea test, i.e. analysis of the isotope ratio of carbon in exhaled CO<sub>2</sub> after swallowing a calibrated capsule, is utilized for identification of the bacteria *Heliobacter pyloria* [40, 41].

**Gases of interest**   $O_2$ , CO, NH<sub>3</sub>, HCl, HF, NO, etc. **Industrial** The TDLAS technique possesses several qualities (*in-situ* monitoring, fast response, low maintenance, etc.) for industrial gas sensing, such as emission monitoring, process control, and safety systems. Gases interesting to monitor include  $O_2$  (760 nm), CO (1560 nm), NH<sub>3</sub> (1510 nm), HCl (1740 nm), HF (1280 nm, 1300 nm), and NO (1810 nm) [16]. Examples of applications are  $O_2$  and CO detection for combustion control at chemical and petrochemical plants, and NH<sub>3</sub> detection at power plants to reduce the emissions of NO<sub>x</sub> [16].

## 3.4 Instrumentation

The key components in a TDLAS instrument are the diode laser, the detector and the gas interaction assembly, typically a gas cell. Here short overviews are given together with detection schemes and methods to minimize the optical interferences, often limiting the sensitivity of a TDLAS instrumentation.

#### 3.4.1 Diode lasers

Diode lasers have proven to be good light sources for absorption spectroscopy due to their stable and smooth wavelength tunability, as well as being easy to handle and control. Changing the current or temperature of the laser diode results in an altered wavelength (modification of the band gap, the refractive index, and the gain curve). Review papers on diode lasers are Refs [42, 43].

The diode lasers are produced using advanced material processing techniques, and the materials used depend on the wavelength the laser is intended for. The majority of the diode lasers are made of doped materials from group III (e.g. Al, Ga, In) and group V (e.g. N, P, As, Sb) in the periodic system. Diode lasers fabricated from these materials emit light in the wavelength range of approximately 375 - 2700 nm and are operated at room temperature.<sup>2</sup>

Three common diode laser types are; Fabry Pérot (FP), distributed-feed back (DFB), and vertical cavity surface emitting lasers (VCSEL). The FP diode laser is the most common type and is based on a Fabry-Pérot resonator. The cavity is formed by having a reflectance of about 30-40% on the cleaved faces of the semiconductor material. FP diode lasers exist in the UV, NIR and

<sup>2</sup> The diode laser are typically packaged in metal transistor cans [TO-3, TO-5, TO-8 (9 mm), and TO-72 (5.6 mm)]. IR regions and can be found with high output powers. The main problem with the FP diode lasers is that they suffer from poor continuous tuning range due to mode jumps, originating from the multiple cavity modes. Contrary, the DFB diode laser exhibits a larger continuous tuning and a more narrow linewidth (~ 1 MHz instead of ~ 10 – 100 MHz). The resonator is made out of diffraction or Bragg gratings<sup>3</sup> resulting in narrow feedback to the laser [44]. For a DFB, temperature tuning results in a wavelength shift of 0.1 nm/K or -25 GHz/K, and current tuning results in a shift of 1 – 10 GHz/mA. Practically, this means that the temperature is used for coarse tuning and the injection current for fine tuning of the wavelength. The DFB diode lasers were first presented in 1972 [45] and are today used for several applications [46]. The DFB diode lasers can today be found from 640 nm to 2900 nm.<sup>4</sup>

The VCSEL was invented in 1977 [47] and is becoming more and more popular in TDLAS [36, 48–52]. As the name implies, the laser cavity in VCSELs is oriented perpendicular to the active region, contrary to FP and DFB diode lasers. The resonator is like in the DFB case based on feedback from a grating structure, but in the VCSEL case built above the active medium. The design allows a more convenient manufacturing process resulting in a lower price. The short cavity results in other tuning and operating characteristics as well as a lower optical power ( $\sim 0.5 - 1 \text{ mW}$ ) compared to DFB and FP diode lasers [53]. The injection currents are typically much smaller and the current tuning is larger than for a DFB diode laser (a factor of 10 in difference) [54]. VCSELs can be found in the 670 – 2300 nm spectral region [55, 56].<sup>5</sup> The VCSEL generally exhibits smaller drifts over time compared to DFB and FP diode lasers; see Fig. 3.2 [16].

A concern for the TDLAS community is the tuning range of the diode laser. Normally the tuning range of diode lasers limits the detection to only one absorption line, or a couple of lines that coincide [57]. Multiplexing of several diode lasers, either in time or in frequency, allows multi-species detection, but increases the complexity and the cost of the system. Efforts have been invested into enlarging the tuning range of diode lasers [58, 59]. An example of a widely tunable diode laser solution is the fabrication of an array of parallel diode lasers monolithically [55]. For spectroscopy such an array of quantum cascade DFB diode lasers, each individually driven and with a filter controlling which laser to output, ranging from  $8.7 - 9.4 \,\mu\text{m}$ , has been demonstrated [60]. Another solution to enlarge the tuning range is to use of an external cavity. Mechanically tuned gratings do not allow repeatable diode laser control and is thus often not feasible for absorption spectroscopy. Instead efforts have been invested into incorporating a grating on the laser chip. Examples of such a construction is the use of MEMS, microelectromechanical system, and the tuning of a VCSEL has in such a way been expanded to 60 nm ( $\lambda = 1550$  nm) [61]. Additional

<sup>3</sup> It is also possible to place the diffraction Bragg reflector outside the cavity and operated separately. This is called a DBR diode laser.

 <sup>4</sup> DFB diode laser providers: Nanoplus: 760-2900 nm
 Eagleyard: 760-1080 nm
 Toptica: 640-685 nm, 760-2880 nm
 Roithner: 760-2735 nm

<sup>5</sup> VCSEL providers: ULM photonics: 760-90 nm Roithner: 670-980 nm



Figure 3.2. The drift of a VCSEL, DFB and FP diode laser [16].

approaches to obtained a large tuning range with one single laser is the use of the Vernier effect, i.e. two differently spaced scales that together give a higher precision. Superimposing two reflection spectra with different peak separations and seeding into the diode laser allow large tunability by the combination to align different peaks. Possible reflectors for such cases are Fabry-Pérot cavities or gratings. Sampled gratings, SG, superstructured gratings, SSG, and binary superimposed gratings, BSG, have been demonstrated - first on DBR diode lasers and later on DFB diode lasers [62]. For a DFB diode laser with a BSG reflector, giving a tunability of 21 nm, sensing of H<sub>2</sub>O and HCl has been shown [62].

#### 3.4.2 Detectors

In order not to affect the sensitivity of a TDLAS measurement careful considerations of the photon detector should be taken. A review of this topic can be found in Ref. [63].

Two commonly used detectors in TDLAS are the photomultiplier tube (PMT) and the photodiode (PD), both based on the photoelectric effect. As light is impinging onto the detector material electrons are released and create a current - a photo current. In the PMT the photo current is amplified by letting the electrons pass through a series of dynodes creating an avalanche of electrons. In the PD case the photo current is most often converted to a voltage by the use of a trans-impedance amplifier, TIA (which also demands careful selection with respect to, e.g. noise and bandwidth).

Important properties of the detector are the quantum efficiency, responsivity, signal-to-noise ratio (noise-equivalent power, NEP), spectral response, bandwidth, dynamic range, dark current, etc. The quantum efficiency, QE or  $\eta$ , defines the ratio of the created number of electrons from the incident number of photons. If every photon creates an electron the QE is 1 or 100%.

The responsivity, R, of the detector is the amount of current created for every incident unit power:

$$R = \frac{\eta M e}{h\nu} \quad [A/W], \tag{3.2}$$

where M is the gain factor (one for PD).

The noise of the detector is often described in terms of noiseequivalent power (NEP), and states the amount of optical power required to achieve an SNR of 1 (for the detector bandwidth).<sup>6</sup> The spectral response of a detector is the quantum efficiency or the responsivity for different wavelengths.<sup>7</sup> PMTs usually have a more narrow spectral response than photodiodes.

The dark current of the detector is the current from the detector when no light is detected. With optimal detector selection, shot-noise limited performance can be expected.<sup>8</sup>

<sup>6</sup> The NEP is dependent on the modulation of the laser and is thus typically given in  $[W/\sqrt{Hz}]$  at a specific wavelength and modulation frequency.

<sup>7</sup> Spectral response
 Si: 190 - 1100 nm,
 Ge: 400 - 1700 nm,
 InGaAs: 800-2600 nm,
 PbS: <1000-3500 nm,</li>

<sup>8</sup> Shot-noise arises from the statistical dispersion of the detected photons and is limited by the amount of detected photons:  $\langle i_N \rangle = \sqrt{2ei} [A/\sqrt{Hz}].$
# 3.4.3 Gas cells

In TDLAS the absorption of a gas can be measured in various ways and common approaches include a long-absorption path length of open air by the use of a retro-reflector, a glass cell, or a multi-pass cell with the studied gas. By reflecting the light back and fourth using spherical mirrors, multi-pass cells can achieve path lengths enhancements up to two orders of magnitude. A couple of different configurations of multi-pass cells exist, e.g. Herriott [64, 65] and White [66].

The choice of gas cell is dependent on the application of the TDLAS instrument. Important properties for gas cells include the light transmission, alignment characteristics, fast gas dynamic properties, low gas volume, and the introduction of optical noise (scattering and interferences). Integrating spheres have been proposed as a way to reduce the size of gas cells and also possess good alignment properties. In Paper **III** a highly scattering porous ceramic is demonstrated as a miniature gas cell, with small gas volume, easy alignment and extremely small size.

# 3.4.4 Interference reductions

The sensitivity of a TDLAS instrument is most often limited by interference fringes and feed back to the laser [67, 68]. Optimization approaches include the use of isolators and reduction of optical interferences originating from reflected light, giving etalon effects. The reflections from gas cell windows usually constitutes the largest problem [69]. When the etalon fringes have a similar free spectral range as the studied absorption feature, these can be detrimental to the sensitivity, e.g. a 10 cm spacing will result in a 1 GHz free spectral range, comparable to absorption linewidths at ambient conditions. Standard procedures to overcome the optical interferences include wedged surfaces [70] and anti-reflection coatings, but these actions are often not sufficient to fully eliminate the fringes. Large efforts have been invested into minimizing the optical interferences and the solutions can be divided into three categories [71]:

- (i) Diode laser: Jitter of the laser diode output frequency [72], or optimization of the modulation parameters (discussed in the next section) [73–75].
- (ii) Signal processing: Post-detection filtering [76, 77] and dual beam approaches [78].
- (iii) Optical system: Mechanically modulating the fringe spacing by, e.g. a Brewster plate spoiler [79], or a modulated mirror position [67], or movement of the laser beam [80].

<sup>9</sup> For direct absorption measurements the detection limit is  $10^{-4} - 10^{-3}$  while corresponding numbers for modulation spectroscopy are  $10^{-7} - 10^{-8}$ .

 $^{10}$  It is also possible to move the detection band with a fast direct absorption scheme [36].



Figure 3.3. The principle of WMS [16]. a) As the wavelength is scanned over the absorption profile the higher frequencies are introduced into the detected transmission signal. b) The detected signal (top) is filtered with double modulation frequency yielding the second harmonic component, whose envelope is the WMS 2f signal (bottom).

In addition to these approaches interference reduction can also be achieved by alternating the absorption line with, e.g. pressure [81], external magnetic [82, 83] or electric fields [83, 84].

Different approaches of signal filtering to eliminate the optical interferences can be made. A fitting model of the detected signal,  $y_{det}(t)$ , typically includes a background component,  $y_{bkg}(t)$ , and an absorption component,  $y_{abs}(t)$ :

$$y_{\rm det}(t) = y_{\rm bkg}(t) + y_{\rm abs}(t) \tag{3.3}$$

The background component can consist of, e.g. a polynomial and an interference or background pattern. Such a background signal can be obtained by a dual beam configuration where the background is monitored simultaneously with a second detector, employed in Papers IV, VII – X, and XII – XIV, or by flushing the gas assembly with zero concentration of the sensed gas, employed in Paper II.

## 3.5 Modulation techniques

In TDLAS, modulation techniques are typically used to enhance the detection of small absorption signals.<sup>9</sup> By adding a highfrequency sinusoidal modulation to the carrier signal (scan over the absorption line) and studying the generated harmonics, the detection band is moved to a region where the 1/f-noise from the laser is minimized.<sup>10</sup> Frequently, the phase-sensitive detection and filtering is accomplished by the use of lock-in amplifiers, but digital approaches, e.g. employing coherent sampling and software-based post processing, is becoming more common.

The modulation techniques are divided into two categorizes depending on the modulation frequency used; *frequency modula*tion (larger than the absorption line HWHM, ~ GHz) and wavelength modulation (much smaller than the absorption line HWHM, ~ kHz). The modulation technique applied in this thesis work is wavelength modulation spectroscopy, WMS, also referred to as derivative spectroscopy, and is the one which will be further elaborated here.

The principle of WMS is that the non-linear response, when scanning over the absorption line, induced generation of higher harmonics, see Fig. 3.3. The strength of the absorption signal decreases for higher harmonics, but are less affected by background effects, such as etalon fringes [85–87]. Standard studied WMS harmonic is the second, the 2f signal. The major reason for this is that the first harmonic, 1f is accompanied with an offset due to amplitude modulation. As the frequency of the diode laser is modulated the output intensity is also altered. This is referred to as a residual amplitude modulation, RAM, and is often unwanted. The 2f signal is positioned at a zero background level, and does not demand large dynamic range, which otherwise is the case in 1f and direct absorption measurements. However, there are situations where the RAM can be useful, e.g. intensity normalization of the detected signal. This approach was applied in the developed TDLAS instrument in this thesis work which detects both  $O_2$  and  $H_2O$  simultaneously, Paper XI.

The theory of WMS generation has been deeply investigated throughout the years and relies on a couple of different approaches; Taylor expansion [88, 89], numerical integration [90, 91], Fourier analysis [92–94]], and based on the same formalism as FM spectroscopy, i.e analyzing the modulation of the phase and the electrical field [69, 95–97]. Here a derivation based on the Fourier analysis is given.

According to the Beer-Lambert law, Eq. (2.23), the detected signal,  $S(\nu)$ , can be written as

$$S(\nu) = \beta T(\nu) I_{\rm L}(\nu) e^{-\sigma(\nu)LN}.$$
(3.4)

For a small absorption, Eq. (3.4) can be expanded by Taylor series (truncating after the second term) to

$$S(\nu) = \beta I(\nu)[1 - \sigma(\nu)LN], \qquad (3.5)$$

where  $I(\nu) = T(\nu)I_{\rm L}(\nu)$ . Rewriting Eq. (3.5) yields

$$S(\nu) = \beta I(\nu) - \beta I(\nu) L N \sigma(\nu), \qquad (3.6)$$

$$S(\nu) = S_{\rm bkg}(\nu) + S_{\rm abs}(\nu).$$
 (3.7)

Within modulation spectroscopy,  $\nu = \nu_{\rm c} + \nu_{\rm a} \cos(2\pi f_{\rm m} t)$ , resulting in a modulated signal,

$$S(\nu_{\rm c}, \nu_{\rm a}, t) = S_{\rm bkg}(\nu_{\rm c}, \nu_{\rm a}, t) + S_{\rm abs}(\nu_{\rm c}, \nu_{\rm a}, t), \qquad (3.8)$$

where

$$S_{\rm bkg}(\nu_{\rm c},\nu_{\rm a},t) = \beta I(\nu_{\rm c},\nu_{\rm a},t) = \beta \left(\sum_{n=0}^{\infty} I_n^{\rm e}(\nu_{\rm c},\nu_{\rm a})\cos(2\pi n f_{\rm m}t) + \sum_{n=0}^{\infty} I_n^{\rm o}(\nu_{\rm c},\nu_{\rm a})\sin(2\pi n f_{\rm m}t)\right), (3.9)$$

and

$$S_{\rm abs}(\nu_{\rm c},\nu_{\rm a},t) = -\beta I(\nu_{\rm c},\nu_{\rm a},t)LN\sigma(\nu_{\rm c},\nu_{\rm a},t) = -\beta LN \Big[\sum_{n=0}^{\infty} I_n^{\rm e}(\nu_{\rm c},\nu_{\rm a})\cos(2\pi n f_{\rm m}t) + \sum_{n=0}^{\infty} I_n^{\rm o}(\nu_{\rm c},\nu_{\rm a})\sin(2\pi f_{\rm m}t)\Big] \cdot \sum_{n=0}^{\infty} \sigma_n^{\rm e}(\nu_{\rm c},\nu_{\rm a})\cos(2\pi n f_{\rm m}t), \quad (3.10)$$

 $\begin{array}{l} \nu_{\rm c}: \mbox{ center frequency [Hz]} \\ \nu_{\rm a}: \mbox{ modulation amplitude [Hz]} \\ f_{\rm m}: \mbox{ modulation frequency [Hz]} \end{array}$ 

T: transmission factor  $I_{\rm L}$ : intensity from the diode laser  $\sigma$ : absorption cross section [m<sup>2</sup>] L: path length [m] N: number density [m<sup>-3</sup>]

 $\beta$ : instrumental factor

using Fourier series expansion of  $\sigma$  and I given by,<sup>11</sup>

<sup>11</sup> Since the signal is in phase with the lineshape-dependent  $\sigma$ , no odd terms appear.

$$\sigma(\nu_{\rm c}, \nu_{\rm a}, t) = \sum_{n=0}^{\infty} \sigma_n^{\rm e}(\nu_{\rm c}, \nu_{\rm a}) \cos(2\pi n f_{\rm m} t),$$
  
$$I(\nu_{\rm c}, \nu_{\rm a}, t) = \sum_{n=0}^{\infty} I_n^{\rm e}(\nu_{\rm c}, \nu_{\rm a}) \cos(2\pi f_{\rm m} t) + \sum_{n=0}^{\infty} I_n^{\rm o}(\nu_{\rm c}, \nu_{\rm a}) \sin(2\pi n f_{\rm m} t).$$

This leads to generation of harmonics in the signal of the modulation frequency. In the general case, Eq. (3.8) can also be expanded into a Fourier series,

$$S(\nu_{\rm c}, \nu_{\rm a}, t) = \sum_{k=0}^{\infty} S_k^{\rm even}(\nu_{\rm c}, \nu_{\rm a}) \cos(k2\pi f_{\rm m}t) + \sum_{k=1}^{\infty} S_k^{\rm odd}(\nu_{\rm c}, \nu_{\rm a}) \sin(k2\pi f_{\rm m}t).$$
(3.11)

The k:th Fourier coefficients in Eq. (3.11) can be calculated as,

$$S_{k}^{\text{even}}(\nu_{\rm c},\nu_{\rm a}) = \frac{2-\delta_{k0}}{\tau} \int_{0}^{\tau} S(\nu_{\rm c},\nu_{\rm a},t) \cos(k2\pi f_{\rm m}t) \mathrm{d}t, \quad (3.12)$$

$$S_k^{\text{odd}}(\nu_{\text{c}},\nu_{\text{a}}) = \frac{2}{\tau} \int_0^{\tau} S(\nu_{\text{c}},\nu_{\text{a}},t) \sin(k2\pi f_{\text{m}}t) dt.$$
(3.13)

In the framework cast by Fourier theory, the detected signal can be described by inserting Eqs (3.9) and (3.10) into Eqs (3.12) and (3.13). Each harmonic of the background signal can thus be divided into an even term and an odd term,

$$S_{\text{bkg},k}^{\text{even}} = \beta I_k^{\text{e}}(\nu_c, \nu_a), \qquad (3.14)$$

$$S^{\text{odd}}_{\text{bkg},k} = \beta I^{\text{o}}_k(\nu_c, \nu_a). \tag{3.15}$$

From these expressions it is possible to see that the first background harmonic includes an offset with a linear intensity dependency ( $\nu = \nu_{\rm c} + \nu_{\rm a} \cos(2\pi f_{\rm m} t)$  gives  $I = I_{\rm c} + I_{\rm a} \cos(2\pi f_{\rm m} t)$ ).

 $\tau$ : set to be  $1/f_{\rm m}$  $\delta_{k0}$ : Kronecker's delta The even term in the absorption signal is,

$$S_{abs,k}^{even}(\nu_c,\nu_a) = -\beta LN \frac{2-\delta_{k0}}{\tau}$$

$$\int_0^{\tau} \left[\sum_{m=0}^{\infty} I_m^e(\nu_c,\nu_a) \cos(2\pi m f_m t) + \sum_{m=0}^{\infty} I_m^o(\nu_c,\nu_a) \sin(2\pi m f_m t)\right]$$

$$\sum_{n=0}^{\infty} \sigma_n^e(\nu_c,\nu_a) \cos(2\pi n f_m t) \cos(2\pi k f_m t) dt =$$

$$= -\beta LN \frac{2-\delta_{k0}}{\tau} \left[\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} I_m^e(\nu_c,\nu_a)\sigma_n^e\right]$$

$$\int_0^{\tau} \cos(2\pi m f_m t) \cos(2\pi n f_m t) \cos(2\pi k f_m t) dt +$$

$$\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} I_m^o(\nu_c,\nu_a)\sigma_n^e(\nu_c,\nu_a)$$

$$\int_0^{\tau} \cos(2\pi m f_m t) \sin(2\pi n f_m t) \cos(2\pi k f_m t)\right]. \quad (3.16)$$

The integrals can be rewritten using trigonometric relations  $^{12}$  into

$$\frac{1}{\tau} \int_0^\tau \cos(2\pi m f_{\rm m} t) \cos(2\pi n f_{\rm m} t) \cos(2\pi k f_{\rm m} t) = \frac{1}{4} (\delta_{n-m-k,0} + \delta_{n-m+k,0} + \delta_{n+m-k,0} + \delta_{n+m+k,0}), \quad (3.17)$$

and

$$\frac{1}{\tau} \int_0^\tau \cos(2\pi m f_{\rm m} t) \sin(2\pi n f_{\rm m} t) \cos(2\pi k f_{\rm m} t) = 0, \qquad (3.18)$$

since the integration limit is set to an integer number of periods. The even term of the signal then becomes

$$S_{\text{abs},k}^{\text{even}} = -\beta L N \frac{1}{4} \Big[ \sigma_0^{\text{e}} I_0^{\text{e}} \delta_{k0} + (2 - \delta_{k0}) \sum_{m=0}^k \sigma_{k-m}^{\text{e}} I_m^{\text{e}} + (2 - \delta_{k0}) \sum_{m=0}^\infty \sigma_m^{\text{e}} I_{m+k}^{\text{e}} + (2 - \delta_{k0}) \sum_{m=0}^\infty \sigma_{m+k}^{\text{e}} I_m^{\text{e}} \Big], \qquad (3.19)$$

which can be consolidated into

$$S_{\text{abs},k}^{\text{even}} = -\beta L N \frac{1}{2} \Big[ \sum_{m=0}^{k} \sigma_{k-m}^{\text{e}} I_{m}^{\text{e}} + (1 - \frac{1}{2} \delta_{k0}) \sum_{m=0}^{\infty} \sigma_{m}^{\text{e}} I_{m+k}^{\text{e}} + (1 - \frac{1}{2} \delta_{k0}) \sum_{m=0}^{\infty} \sigma_{m+k}^{\text{e}} I_{m}^{\text{e}} \Big].$$
(3.20)

In a similar fashion, the odd term can be expressed as

$$S_{\text{abs},k}^{\text{odd}} = -\beta LN \Big[ \frac{1}{2} \sum_{m=0}^{k} \sigma_{k-m}^{\text{e}} I_{m}^{\text{o}} - \frac{1}{2} \sum_{m=0}^{\infty} \sigma_{k+m}^{\text{e}} I_{m}^{\text{o}} + \frac{1}{2} \sum_{m=0}^{\infty} \sigma_{m}^{\text{e}} I_{k+m}^{\text{o}} \Big].$$
(3.21)



Figure 3.4. Simulated WMS signals using Fourier based retrieval.

Analyzing the expressions in Eqs (3.20) and (3.21) is a powerful way to understand WMS. By simply glancing at the expression, it is obvious that even while only examining a fixed k, for example, using a lock-in amplifier, the signal will contain harmonics of both higher and lower orders. By expanding the sums, more detailed information can be discerned. The first and second harmonics will be provided below.

For the first harmonic (k = 1),  $S_{\text{abs},1}^{\text{even}}$  and  $S_{\text{abs},1}^{\text{odd}}$  are

$$\begin{split} S^{\text{even}}_{\text{abs},1} &= -\beta LN \frac{1}{2} \Big[ 2\sigma_1^{\text{e}} I_0^{\text{e}} + (2\sigma_0^{\text{e}} + \sigma_2^{\text{e}}) I_1^{\text{e}} + (\sigma_1^{\text{e}} + \sigma_3^{\text{e}}) I_2^{\text{e}} + \dots \Big],\\ S^{\text{odd}}_{\text{abs},1} &= -\beta LN \frac{1}{2} \Big[ 2\sigma_1^{\text{e}} I_o^{\text{o}} + (2\sigma_0^{\text{e}} + \sigma_2^{\text{e}}) I_1^{\text{o}} + (\sigma_1^{\text{e}} + \sigma_3^{\text{e}}) I_2^{\text{o}} + \dots \Big]. \end{split}$$

As seen, the main components in the expressions are the modulated first harmonics of the absorption cross-section, which is a line-shape dependent factor. However, as mentioned above, higher order terms also couple into the expression, with decreasing amplitude with respect to k. The coefficients for the second harmonic are

$$\begin{split} S^{\text{even}}_{\text{abs},2} &= -\beta LN \frac{1}{2} \Big[ 2\sigma_2^{\text{e}} I_0^{\text{e}} + (\sigma_1^{\text{e}} + \sigma_3^{\text{e}}) I_1^{\text{e}} + (2\sigma_0^{\text{e}} + \sigma_4^{\text{e}}) I_2^{\text{e}} + \\ & (\sigma_1^{\text{e}} + \sigma_5^{\text{e}}) I_3^{\text{e}} + (\sigma_2^{\text{e}} + \sigma_6^{\text{e}}) I_4^{\text{e}} + \dots \Big], \\ S^{\text{odd}}_{\text{abs},2} &= -\beta LN \frac{1}{2} \Big[ (\sigma_1^{\text{e}} - \sigma_3^{\text{e}}) I_1^{\text{o}} + \\ & (2\sigma_0^{\text{e}} - \sigma_4^{\text{e}}) I_2^{\text{o}} + (\sigma_1^{\text{e}} - \sigma_5^{\text{e}}) I_3^{\text{o}} + (\sigma_2^{\text{e}} - \sigma_6^{\text{e}}) I_4^{\text{o}} + \dots \Big]. \end{split}$$

By the same token, the second harmonic of the absorption cross section will be the main contributor to the signal.

### 3.5.1 Digital wavelength modulation spectroscopy

Traditionally, WMS was carried out with the use of a lock-in amplifier, but the use of digital alternatives are growing and are referred to as dWMS. Typically, dWMS is performed by digitizing the detected signal and performing post-detection signal processing. Here a description of dWMS based on coherent detection of the detected signal and demodulation by filtering out the wanted harmonic in the Fourier domain is given. This approach was first demonstrated in 2002 [98] and is used in Papers II, IV, VII, VIII, and XII – XIV.<sup>13</sup>

Coherent sampling of the detected signal allows harmonic analysis to be performed post-detection. Coherent sampling refers to careful choice of operating and sampling parameters, enables averaging of several sampled segments without loosing information about certain frequency components.

$$\frac{f_{\text{studied}}}{f_{\text{sampling}}} = \frac{N_{\text{cycles}}}{N_{\text{samples}}} \tag{3.22}$$

The idea is to sample a full amount of cycles of the studied frequencies which means that the next sampled segment does not interfere with the previous one. Coherent sampling is a common tool when analyzing data with means of Fourier analysis. Typically the number of cycles are chosen as a prime number to eliminate errors originating from, e.g. bit errors, but this is not a concern in TDLAS since the laser exhibits RAM. Furthermore, the sampling number is chosen to be  $2^{N}$  to minimize computational resources for the FFT (Fast Fourier Transform).

Demodulation of the detected signal, u(t), is achieved by studying the Fourier components of the filtered and translated positive frequency harmonic from the spectral representation of the detected signal, see Fig. 3.4. The detected signal can be expressed as a Fourier series:

$$u(t) = \sum_{k=0}^{\infty} a_k(t) \cos(k2\pi\nu t) + \sum_{k=0}^{\infty} b_k(t) \sin(k2\pi\nu t)$$
$$= \sum_{k=0}^{\infty} \frac{1}{2} (a_k(t) - b_k(t)i) e^{ik2\pi t} + \sum_{k=0}^{\infty} \frac{1}{2} (a_k(t) + b_k(t)i) e^{-ik2\pi t}$$

The Fourier coefficients  $(a_k \text{ and } b_k)$  can be obtained from the positive k:th harmonic frequency  $(k \cdot \nu)$  component. This component is filtered out with a window function,  $w(\nu)$ , of the spectral representation of the detected signal:

$$U_{k^+}(\nu) = \mathcal{F}(u(t))w(\nu).$$
 (3.23)

The filtered harmonic is translated to zero frequency,  $U_{k+}^{0}(\nu) = U_{k+}(\nu+k\cdot\nu)$ , yielding the envelope of the harmonic. A translation

<sup>13</sup> A version of dWMS was also applied in Paper X based on a lock-in toolkit in LabVIEW.

 $f_{\text{studied}}$ : studied frequency  $f_{\text{sampling}}$ : sampling frequency  $N_{\text{cycles}}$ : number of cycles  $N_{\text{samples}}$ : number of samples



**Figure 3.5.** The complex representation of the WMS signals in phaseamplitude plots together with projected WMS signals. The detected signal (left) includes a background originating from optical interferences. The extracted absorption signal (middle) is used to evaluate the absorption and plot the WMS signal (right).

of the  $(k \cdot \nu)$  in the Fourier domain is equivalent to a division by  $e^{ik\nu t}$  in the time domain.

The inverse Fourier transform gives a complex representation of the k:th WMS signal,  $u_k(t)$ .

$$u_k(t) = 2\mathcal{F}^{-1}(U_{k+}(\nu)) = a_k(t) + b_k(t)i, \quad u_k(t) \in \mathbb{C}$$
(3.24)

The factor of 2 compensates for only the positive frequency being filtered out. A good way to visualize the complex WMS signal is in a phase-amplitude plot. In contrast to the traditional lock-in WMS signals the complex representation provides further useful information. Information of the out-of-phase and in-phase components can be obtained simultaneously. Furthermore, the complex WMS signal allows easy decomposition of the amplitude modulation signal, AMS, and the wavelength modulation signal, WMS. The AMS signal provides a way to study direct absorption signals with the advantages that modulation spectroscopy holds, i.e. moving of the detection to a higher frequency where the 1/f noise is low. The use of AMS signals for calibration-free concentration and pressure assessments has been studied in Refs [99, 100].

# Chapter 4

# LIGHT PROPAGATION IN TURBID MEDIA

As light passes through a medium it becomes attenuated by absorption and scattering. Absorption of light is governed by the Beer-Lambert law, as described in Section 2.3. Scattering is the process when the direction of the light is altered as it travels through the medium. Continuous scattering of light results in a diffuse light propagation.

A strongly scattering medium, or a turbid medium, is a material where the scattering is larger than the absorption. Typical every-day turbid media include white paint, milk, and clouds, all which appear whitish. Figure 4.1 shows scattering of light with varying concentrations of scatterers. In these cases, the fat particles in the milk introduce inhomogeneities causing the light to scatter.

This chapter gives a brief introduction to the scattering process and in particular to Mie and Rayleigh scattering, i.e. elastic scattering processes. Methods to model the resulting diffuse light propagation and a way to measure the optical properties (absorp-



**Figure 4.1.** Pictures of a laser beam passing through media of varying scattering. As the concentration of scatterers increase (left to right), the light becomes more and more diffuse.

tion and scattering) of a material are also introduced. The chapter is concluded with a description of the turbid media of interest for this thesis work, i.e. biological tissue and porous materials.

# 4.1 Scattering

For light propagating through a medium with varying refractive indices, classical theory dictates that it will become refracted at every interface. Within the field of diffuse optics, the optical properties of the material of interest are typically divided into the scattering coefficient,  $\mu_s$ , and the absorption coefficient,  $\mu_a$ , which determine the distance the light travels before it is attenuated. However, many materials exhibit forward (anisotropic) scattering, i.e. the probability for a scattering event to result in a forward direction is the most probable. Thus the anisotropic factor,  $g = \langle \cos \theta \rangle$ , is usually introduced, giving the reduced scattering coefficient  $\mu'_s = g\mu_s$ .

The scattering phenomena are usually divided into two cases, known as the Mie and Rayleigh scattering. For particles with dimensions comparable with the wavelength of the light, Mie scattering occurs. As the dimension of the particles decreases, such that it is much smaller than the wavelength of the light, Rayleigh theory can be used to describe the scattering phenomena. Such scattering typically falls off as a function of the wavelength to the power of four ( $\sim \lambda^{-4}$ ).

# 4.2 Diffuse light propagation

Light propagation inside scattering materials is a highly complex problem to model. In principle, using the Maxwell equations, the problem can be solved, accounting for all the wave properties of the light. However, such a model would involve a very well defined geometry, which is, in most cases very hard or practically impossible to obtain. Thus the problem is often solved without considering the wave nature of the light. Two of the commonly used models are based on the radiative transport equation, RTE, and the diffusion equation.

The RTE relies on the particle nature of light [101]. It can be derived by considering the flux of particles inside a small volume within the medium. Analytical solutions to this equation are at best very scarce, even for the simplest geometries, and numerical methods, such as Monte-Carlo simulations must often be used to obtain an internal photon distribution. The diffusion equation can be derived from the RTE by expanding it into a set of suitable basis functions and truncating the higher order terms. However, this implies that fast transient phenomena and sharp gradients cannot be resolved when using the diffusion equation [102].

#### Simulation of diffuse light propagation

Since the RTE describes a transport problem, it can be expressed and modeled to a high degree of accuracy using, for example, Monte-Carlo simulations.<sup>1</sup> Such simulations have been used in a variety of fields, typically dealing with transport problems [103– 105]. Monte-Carlo simulations within the field of diffuse optics are typically initialized by sending in a large number of photon packets into a predefined geometry. A robust random-number generator is then used to determine the fate of each packet as it propagates inside the material, i.e. if they are to be absorbed, scattered or refracted for every discrete step length. Since the method is based on the statistical results of the launched photon packets, the accuracy is dependent of the number of photons used. The method is thus also highly demanding in terms of computation operations. However, due to the linearity of Monte-Carlo simulations, they are very suitable for multi-threading, and parallelized implementations utilizing parallel graphics processing units (GPU) have been reported [106, 107].

Several open-source software packages exist to perform Monte-Carlo simulations, with multi-layered structure (MCML) and GPUaccelerated MCML being two of the most commonly used ones [106–108]. It is also possible to use commercial ray-tracing softwares to solve the transport problem. Ray-tracing is typically used to model light propagation through optical components in an optical system, for example, a laser oscillator. They can, however, be modified to resemble Monte-Carlo simulations by inserting random scattering and absorption events. Two common softwares are ASAP and FRED. Unfortunately, such softwares are generally not designed for Monte-Carlo simulations, thus the computation time required to perform a simulation using a ray-tracing software, as compared with specialized softwares, such as MCML, is typically magnitudes upon magnitudes longer.

As mentioned above, Monte-Carlo simulations are highly demanding in terms of computation time. Since light propagation within a turbid material is a diffusive-transport problem, the diffusion equation,

$$\left(\frac{1}{c}\frac{\partial}{\partial t} + \mu_{\mathbf{a}} - \nabla \cdot \kappa(\mathbf{r})\nabla\right)\Phi(\mathbf{r},t) = Q(\mathbf{r},t),\tag{4.1}$$

can also be used to describe the light propagation.<sup>2</sup> In Eq. (4.1),  $\kappa = 1/3(\mu'_{\rm s} + \mu_{\rm a})$  denotes the diffusion coefficient;  $\Phi$  denotes the distribution of the fluence rate [W/m<sup>2</sup>]; while Q is the source term.

Equation (4.1) can be solved analytically for some simple homogeneous geometries, such as, semi-infinite media or slabs, using  $Q = \delta(\mathbf{r} - \mathbf{y})\delta(t - s)$ . This leads to the Green's function.<sup>3</sup> Such functions obviously do not describe the true physical problem due to its point-like definition. However, it is possible to convolve the <sup>1</sup> It is worth to notice that Monte-Carlo simulations are actually only a discrete version of the RTE.

<sup>2</sup> It is obvious that this only applies for regimes where the light is propagating diffusively, i.e.  $\mu'_{\rm s} \gg \mu_{\rm a}$ . In addition, transient responses and sharp gradients cannot be accurately described, which means that solutions close to the source with respect to both the time and spatial domains may be invalid.

<sup>&</sup>lt;sup>3</sup> Green's function is a type of function used to solve inhomogeneous differential equations subject to specific initial conditions or boundary conditions.

Green's function to account for a source that has a finite range both in the time and the spatial domain. For more complicated geometries, the diffusion equation can be solved using numerical methods, such as the finite element method, FEM. This method discretizes the domain into small elements and approximates a solution using a polynomial function in each element [109].

# 4.3 Measuring the optical properties with time-of-flight spectroscopy

Since both the scattering and the absorption of a material results in attenuation of light, the separation of them is a nontrivial task. Over the years, large efforts have been invested into the development of methods to separate the scattering and absorption, on the macroscopic scale. It has been shown that the Green's function in the frequency or the time domain can be used to separate  $\mu'_{\rm s}$  and  $\mu_{\rm a}$ , without the need for absolute fluence measurements [110].<sup>4</sup> Using an integrating sphere, it is, in addition, possible to not only separate scattering from absorption, but it is also possible to obtain the *g*-factor.

Time-of-flight spectroscopy has been used to extract  $\mu'_{\rm s}$  and  $\mu_{\rm a}$  from both biological and ceramic materials, which are used in this thesis work. The method relies on fitting the point-spread function of a short pulse to a model. The model used was the time-dependent Green's function. By performing a fit of the experimental data to the predicted data by the Green's function using the Levenberg-Marquardt optimization algorithm, the optical properties from the materials of interest were measured [110].

# 4.4 Turbid media

#### **Biological tissue**

Biological tissue can be considered to be an inhomogeneous medium containing absorbing particles in water. As light propagates within tissue, the mismatch of the refractive indices of these particles relative to their surrounding, causes the light to scatter heavily. In addition, the organelles within the cells also contribute to the scattering of light. However, it should be noted that the origin of the scattering effects is not yet fully understood [117].

Since the composition within tissue is relatively well known, it should, in principle, be possible to model the light scattering using, for example, Mie theory [118, 119]. Such a model mainly investigates the scattering on the cellular level, by modeling the individual cells (scatterers) as spherical or oblate spherical particles. Practically, this method is tricky to realize since it relies on detailed geometrical structure found within tissue. Instead, tissue

<sup>4</sup> By using absolute fluence measurements it is also possible to use spatially resolved methods [111, 112].

Ref.	Material	Wavelength	$\mu_{\rm a} \ [{\rm cm}^{-1}]$	$\mu'_{\rm s}  [{\rm cm}^{-1}]$	Technique
Torricelli [113]	Forehead	760  nm	0.085	10.2	TOFS
	in vivo	820  nm	0.0925	9.3	
		935  nm	0.215	8.0	
Matcher [114]	Skull	760 nm	-	9.6	TOFS
	in vivo	820 nm	-	9.1	
		935  nm	-	8.8	
Bevilacqua [115]	Skull	674 nm	0.208	11.9	FDPM
	in vivo	849  nm	0.215	9.1	
		956  nm	0.355	7.7	
[116]	Polystyrene foam	760  nm	0.002	40	TOFS
Paper III	$TiO_2$ (79 nm)	760  nm	0.12	$1.21\times 10^4$	TOFS
Paper III	$ZrO_2$ (43 nm)	760  nm	< 0.01	$8.28\times 10^3$	TOFS
Paper III	$ZrO_2$ (115 nm)	760  nm	< 0.01	$9.27\times 10^2$	TOFS
Paper III	$Al_2O_3$ (69 nm)	760  nm	< 0.01	$1.80\times 10^3$	TOFS
Paper III	$Al_2O_3$ (3.6 µm)	760  nm	< 0.01	$1.29\times 10^3$	TOFS

Table 4.1: Summary of the optical properties of biological and ceramic materials of interest within this thesis measured using time-of-flight spectroscopy (TOFS) and frequency-domain photon migration (FDPM) methods.

is often modeled as random continuous segments, each with its own designated absorption coefficient, scattering coefficient and gfactor [120]. Typical values of the optical properties for the tissue types of interest within this thesis are given in Tab. 4.1.

#### **Porous** materials

Within the scope of this thesis, porous materials are defined as materials which have an internal geometrical structure that contains gas. The investigated materials are composed of sintered ceramic powders of  $Al_2O_2$ ,  $ZrO_2$ , and  $TiO_2$ . Depending on the sintering parameters, such as, temperature, pressure, time and particles sizes, ceramic tablets with varying internal pore-size distributions can be fabricated. The bulk material within such tablets has a relatively high refractive index, typically in the 1.7 – 2.5 range, causing the light to scatter heavily.<sup>5</sup> The optical properties for the ceramic samples of different pore diameters, which have been investigated within this thesis, are given in Tab. 4.1.

One of the most interesting aspects of the ceramic tablets is that they can be fabricated to create pore structures of the nmscale as shown in Fig. 4.2, which opens up new possibilities to study physical phenomena. The optical properties within the ceramic tablets as well as their potential to be used as gas-sensing



Figure 4.2. SEM image of  $ZrO_2$  sample.

```
<sup>5</sup> Fresnel reflection gives:
```

$$R = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2$$

cells, due to their long gas-interaction path lengths, have been investigated in Paper III. However, in order to use such materials as gas cells, an important aspect to grasp is the gas-diffusion dynamics. For example,  $H_2O$  is usually termed a 'sticky' gas, which easily adheres to surfaces. This leads to a slow exchange of gas with the surrounding as compared with relatively inert gases, in the diffusion sense, such as  $O_2$ . Thus the gas diffusion dynamic properties were investigated in Paper IV.

Recently, it was proposed and shown that gases confined within nanoporous materials exhibit major line broadening effects due to wall collisions [121]. Confined molecules of course experience wall collisions regardless of the dimensions of the confinements. However, within nanoporous materials, the intermolecular collision times and the wall collision times become comparable and thus constitutes a major source of perturbation, e.g. broadening. In order to better understand and model the broadening effect, studies under reduced pressures were performed in Paper  $\mathbf{V}$ .

# Chapter 5

# GAS IN SCATTERING MEDIA ABSORPTION SPECTROSCOPY

Applying absorption spectroscopy to porous or hollow gas-filled samples with large scattering and absorption properties is such a special case that it has been given the name: GASMAS. The technique can be seen as a fusion between the topics dealt with in the previous chapters, i.e. absorption spectroscopy, TDLAS, and light propagation in turbid media. The name GASMAS is an abbreviation of GAs in Scattering Media Absorption Spectroscopy, and as the name implies, it is the sample or the medium that is the fundamental difference. The GASMAS concept was first introduced in 2001 by our group and has since been shown to be applicable for sensing of  $O_2$  and  $H_2O$  in various samples and environments.<sup>1</sup>

Considering the fact that GASMAS is a new domain of spectroscopy where gas for the first time can be sensed within absorbing and scattering solids and liquids, it is easy to realize that the applications are tremendous. This chapter presents the principle of the GASMAS technique with its special demands for concentration extraction. A review of the GASMAS activities, both instrumental and application wise, up to this point is given at the end of the chapter.

# 5.1 Principle

The fundamental principle that GASMAS relies upon is the intrinsic difference between absorption of light by free molecules and atoms and perturbed ones. As the molecules and atoms are held together in a solid or liquid the energy levels form bands, resulting in broad-band absorption. In contrast, molecules and atoms in gas phase exhibit sharp transitions,<sup>2</sup> about a factor of 10 000 in difference. Due to the narrow absorption of gases they can be <sup>1</sup> Since 2009 GASMAS has an entry at Wikipedia: http://en.wikipedia.org/wiki/GASMAS

<sup>2</sup> A free molecule in ambient air typically experience an absorption which is  $\sim 1$  GHz in HWHM. Corresponding number for molecules in a solution is  $\sim 20$  nm ( $\sim 10$  400 GHz at 760 nm).



Figure 5.1. GASMAS principle and three types of GASMAS samples; small gas filled pores surrounded by scattering media, small scatterers surrounded by gas, and a large pore surrounded by turbid material.



Figure 5.2. Standard addition of an unknown  $H_2O$  absorption measured with a pigtailed-DFB GASMAS setup.

monitored even in a surrounding of absorbing solids. The gas absorption in a GASMAS measurement can typically be of the order of  $1 \times 10^{-4}$  (one out of 10 000 photons gets absorbed), while the bulk medium absorbs and scatters such that only one per mille of the injected light reaches the detector. This means that although only a fraction of the light passes through the sample and reaches the detector, the small absorption dip can still be distinguished due to its spectrally sharp absorption nature. The GASMAS principle is illustrated in Fig. 5.1 and shows as light passes through a scattering and absorbing sample the light gets attenuated by the bulk medium to a varying degree, dependent on the wavelength. If the light travels through a gas pore the light exhibits an alternative absorption - this is the spectrally sharp gas absorption.

The gas-embedded samples can be of various forms. It can be a large gas cavity surrounded by a scattering medium, such as a sinus cavity surrounded by tissue. It can also be a sample of many small pores surrounded by a scattering medium, such as alveoli in the lung. Furthermore, it can also be a sample constructed of scatterers with gas in between, e.g. a sintered ceramic material. With the GASMAS technique gas embedded in pores ranging from the nm to cm regime has been studied.

Since the GASMAS technique studies diffuse light both transmission and reflection detection geometries are feasible.

It should be noted that GASMAS does not need to be based on a diode laser such as in TDLAS, but is applicable with any gasabsorption spectrometry. In Paper **VI** the LIDAR (light detection and ranging, laser radar technique) technique DIAL (differential absorption LIDAR - an on-off resonance range-resolved gas sensing method) was employed to perform large-scale remote GASMAS.

#### 5.1.1 Equivalent mean path length

As described in the previous chapter, traditional TDLAS utilizes the Beer-Lambert law, Eq. (2.23), to extract species concentration. Prerequisites then are known path length and a molecular specific absorption coefficient (which can be found through, e.g. the HI-TRAN database). The diffuse light propagation in GASMAS, with a distribution of photons traveling through unknown gas distances, demands an alternative approach. Already in the first presented GASMAS paper, the parameter *equivalent mean path length*,  $L_{eq}$ , was introduced. As the name implies, this parameter is a measure of length, namely the distance the light needs to pass through a reference gas, typically ambient air, to experience an equivalent absorption as when traveling through the sample. This means that if the gas within the sample is under the same conditions as in the referenced ambient air, i.e. same temperature, pressure, and mixing ratio,  $L_{eq}$  corresponds to the true mean distance the pho-

Sample	Thickness	$L_{\rm eq}$	Comment	Ref.
Polystyrene foam	$19 \mathrm{~mm}$	600 mm		[122]
	10  mm	100  mm		[116]
	70  mm	5000  mm		[116]
Epoxy	19  mm	5  mm	Turbid due to air bubbles	[122]
Sintered ceramic	7.2  mm	5410  mm	$ZrO_2 - 115 \text{ nm pores}$	Paper III
	7.0  mm	860  mm	$ZrO_2 - 43 nm pores$	Paper III
	5.5  mm	833  mm	$Al_2O_3$ - 69 nm pores	Paper III
	9.9  mm	595  mm	$Al_2O_3$ - 3700 nm pores	Paper III
	1.4  mm	190  mm	$TiO_2$ - 79 nm pores	Paper III
Pharmaceutical tablet	3.4  mm	17  mm		[123]
	$3-4 \mathrm{mm}$	$5-50 \mathrm{~mm}$	Compression variation	[123]
Wood	10 mm	$123 \mathrm{~mm}$	Dry pine	[122]
	6  mm	80  mm	Balsa	[124]
	6  mm	35  mm	Birch	[124]
	18 mm	65  mm	Bambo stalk	[125]
Apple	26 mm	10  mm		[122]
	70  mm	60  mm	Full apple - transmission	[126]
		10  mm	Full apple - reflection	[126]
Mushroom	-	13  mm	Reflection geometry	[126]
Avocado	-	$3-8 \mathrm{mm}$	Reflection geometry	[126]
Orange	_	4  mm	Reflection geometry	[126]
Aubergine	57  mm	300  mm		[127]
Sugar	12  mm	20  mm	Lumped	[122]
Salt	18  mm	170  mm	Granulated	[122]
Flour	18  mm	380  mm	Wheat	[122]
Bread	—	175  mm	Bake-off bun	Paper VII
Minced meat	_	$20-40\ mm$	Including polystyrene foam tray	Paper $VII$
Headspace	_	220  mm	Milk carton	Paper $\mathbf{VII}$
(liquid container)	-	10-50  mm	Orange juice container (intact)	Paper <b>VIII</b>
	-	$55-85 \mathrm{~mm}$	Orange juice container (perforated)	Paper <b>VIII</b>
Sinus	_	$1 \mathrm{mm}$	Frontal sinus - reflection	[128]
(healthy)	-	$10-23~\mathrm{mm}$	Frontal sinus - (semi) - transmission	Paper IX
	_	$20-30~\mathrm{mm}$	Maxillary sinus - reflection	Papers <b>IX-XII</b>
	-	$8-35\ mm$	Maxillary sinus - transmission	Papers <b>IX-XII</b>

Table 5.1: Typical  $L_{eq}$  of  $O_2$  measured and reported in the GASMAS literature.

tons have passed through the gas in the sample. The  $L_{eq}$  values obtained for various samples are presented in Tab. 5.1.

Determination of the  $L_{\rm eq}$ -parameter can be made in a couple of different ways. The first approach used was based on the principle of standard addition, which is a common technique to determine the concentration in an unknown sample. By sequential addition of known concentrations the start-point can be extracted. Figure 5.2 shows the standard addition for the GASMAS case, where known distances of air are added and the absorption monitored. Extrapolation to the x-axis yields the  $L_{\rm eq}$ , in this case 18 mm. Standard-addition curves are obtained for GASMAS systems both with the intent to estimate the resolution of the systems and for calibration purposes.

 $^4$  An absorption signal from a sample with a gas concentration of 20% and an gas-interaction distance of 25 mm and an absorption signal from a concentration of 10% and an interaction distance of 50 mm gives the same  $L_{\rm eq}$ .

The second  $L_{\rm eq}$ -extraction method relies on fitting the measured absorption signal,  $y_{\rm unknown}$ , to a single large-absorption signal,  $y_{\rm abs.ref.}$ , referred to as the absolute-reference signal.<sup>3</sup> The absolute reference signal is typically a distance of ambient air,  $L_{\rm abs.ref.}$ , with known properties of relative humidity, pressure, and temperature.

It should be noted that the  $L_{eq}$  is dependent on both the mixing ratio of the gas in the sample and the gas-interaction distance of the detected photons.<sup>4</sup> An interpretation of  $L_{eq}$  is thus non-trivial and demands further knowledge of the sample. As already stated, for a sample with equal gas conditions as in the absolute reference (or with known relation) the  $L_{eq}$  correspond to the average distance traveled through gas of the photons. Such information can be valuable in material analysis, such as porosity, and research on this topic has been carried out at our division [116, 129]. The mean traveled gas-interaction distance can also be used as a measure of the amount of gas present in a sample, e.g. if a sinus is obstructed or not (Paper **XII**). Further, it can also be used as a calibration for a second sensed gas with an unknown concentration, assuming they probe the sample similarly. This has been used both for the food packaging (Paper VII) and the sinus diagnosis (Papers IX and **XI**) applications and is described in detail in Section 5.1.2. It is worth mentioning that if both the gas concentration and the gas-interaction distance in the sample are unknown, the  $L_{eq}$  can still be a useful measure. Examples of this are when monitoring relative changes, e.g. diffusion or time courses, or if knowledge of the presence of a gas is sought for.

#### 5.1.2 Concentration extraction

As described in the previous section, straight-forward quantification of the concentration, using the Beer-Lambert law is not applicable in the GASMAS case. Instead, the parameter  $L_{\rm eq}$ , with the unit mm, is used to measure the absorption. Different ways to extract the mixing ratio of a sensed gas (O<sub>2</sub>) from the  $L_{\rm eq}$  parameter have been applied. The first method used relied on measuring the traveled photon distances with time-resolved spectroscopy [116]. The concentration of the sensed oxygen gas,  $c_{\rm O_2}$ , was extracted by the assumption that the oxygen gas-interaction distance,  $L_{\rm g}^{\rm O_2}$ , was the full length traveled by the detected photons in the sample,  $L_{\rm s}$ .<sup>5</sup>

Later an alternative  $O_2$  concentration extraction method, based on the sensing of  $H_2O$ , was applied. As already noted, with known concentration of a detected gas the  $L_{eq}$  corresponds to the mean traveled distance through gas. In samples with closed cavities and liquid water present (such as cavities in the human body, liquids in containers, and wet samples) the water concentration is given by the temperature of the sample. The  $H_2O$  saturation point

 $^{5}$  c<sub>O2</sub>-extraction assumption 1

$$L_{\rm g}^{\rm O_2} = L_{\rm s}$$
$$c_{\rm air} \times L_{\rm eq} = c_{\rm s} \times L_{\rm s}$$

6

is dependent on the temperature and can be described by, e.g. the Arden-Buck equation [130].

$$p = 6.032 \times 10^{-3} \, e^{\frac{17.502 \, T}{240.97 + T}} \tag{5.1}$$

Assuming that the laser light sensing H<sub>2</sub>O and O<sub>2</sub> travels through the sample in a similar manner, and thus probe the same amount of gas, the O<sub>2</sub> concentration can then be extracted by normalization with H<sub>2</sub>O.<sup>6</sup> This assumption corresponds to that the gasinteraction distance of the H<sub>2</sub>O-sensing light,  $L_{\rm g}^{\rm H_2O}$  (which is the same as its  $L_{\rm eq}$ ,  $L_{\rm eq}^{\rm H_2O}$ , since the concentration is known)<sup>7</sup> is the same as the gas-interaction distance for O<sub>2</sub>,  $L_{\rm g}^{\rm O_2}$ . The assumption is valid if the optical properties of the sample,  $\mu_{\rm a}$  and  $\mu_{\rm s}$ , are the same for the two laser wavelengths used. Table 4.1 lists literature values. Up to now 760 nm has been used to detect O<sub>2</sub> and 980 nm and 935 nm to measure H<sub>2</sub>O.

Furthermore, it is also possible to extract a gas concentration with GASMAS by using an internal sample reference measurement. This approach was utilized in Paper **VIII** and is based on a second measurement, where the gas concentration in the same sample is known. In Paper **VIII** the gas composition in headspace of juice containers was studied. By perforating the package, allowing ambient air to enter, a reference for concentration extraction was obtained.

# 5.2 Limitations

The GASMAS technique measures gas embedded in solids and liquids, but for the technique to be applicable the sample needs to be translucent.<sup>8</sup> Opaque materials are not possible to investigate, and thus limit what samples and which wavelength regions that are feasible, e.g. samples with liquid water present can not be studied above 1400 nm. For every GASMAS sample one must consider the absorption of the bulk absorption and the available gas absorption lines in the region where the sample is translucent.

Optical interference is always a concern in TDLAS, and in the special case that GASMAS constitutes one must take the speckle and fringes originating from inside the sample into account. Approaches to minimize the sample-induced optical interferences have been developed and include vibration and rotation of the sample as well as dithering the laser light injection spot [131], see Fig. 5.3.

A further limitation of the GASMAS technique is, as already noted in Section 5.1.1, the unknown gas interacting length. The distance of the light probing the gas in the sample will be a distribution, where some detected photons may not have traveled through any gas. Such photons do not carry any gas imprint, and results in a dilution of the measured absorption. This aspect is of high importance when studying samples in reflectance geometry *p*: H<sub>2</sub>O partial pressureT: temperature

#### $^{6}$ c<sub>O2</sub>-extraction assumption 2

$$\begin{array}{rcl} L_{\rm g}^{\rm H_2O} &=& L_{\rm eq}^{\rm H_2O} \\ L_{\rm g}^{\rm O_2} &=& L_{\rm g}^{\rm H_2O} \\ \\ _{\rm air} \times L_{\rm eq}^{\rm O_2} &=& c_{\rm O_2} \times L_{\rm g}^{\rm H_2O} \end{array}$$

<sup>7</sup> Conversion of the absolutereference measurement to the conditions in the sample is needed for this to apply.

<sup>8</sup> Translucent means that the light travels through the sample, but diffusely.



Figure 5.3. An example of optical fringes removed by the means of beam dithering using tracking coils.

<sup>9</sup> AMSRS is the Applied Molecular Spectroscopy and Remote Sensing Group lead by Prof. Sune Svanberg. since a large portion of the detected light will then be of this kind, which we refer to as short-cut photons, only holding small gas absorption signals or none.

## 5.3 Review

The GASMAS concept was introduced in 2001 by Sjöholm *et al.* [122] and has since then been a research focus for the AMSRS group<sup>9</sup> at the Atomic Physics Division in Lund. Here the technique has been further developed and applications of the technique have been investigated. An overview of the published GASMAS papers and their content is presented in Tab. 5.2.

The first report of GASMAS was on  $O_2$  absorption of embedded gas inside, among others, wood, apple, and polystyrene foam [122]. These samples have been further investigated in succeeding publications. Different types of woods were investigated in [124] and the drying of wood was studied in [132].

The gas-exchange in apples as well as in other fruits and vegetables were studied in [126, 127] with the aim to demonstrate the GASMAS technique for packaging technology applications. Later the GASMAS technique was also applied to packaged food products, such as packaged minced meat, bake-off bread, and milk and juice containers, where it was shown that the technique can be used as a non-intrusive tool for quality control of modified atmosphere packaging (Papers **VII** and **VIII**) - further discussed in Section 6.1.

Polystyrene foam has been the subject of investigations with regards to concentration and porosity. By combining GASMAS data with time-of flight spectroscopy data, the  $O_2$  concentration was measured inside polystyrene foam and the deviation to ambient air was used for porosity assessment [116]. The GASMAS technique as a tool for porosity has thereafter been further investigated on pharmaceutical tablets [129], which has also been an application field of focus for GASMAS [123]. The combination of GASMAS and LIDAR was also demonstrated on polystyrene foam.  $O_2$  was then detected by the DIAL technique to illustrate the possibility to study embedded gas remotely (Paper **VI**).

A GASMAS application that has been extensively investigated is sensing of gas inside the human body, and a review of this is given in Section 6.2.4. Focus has primarily been on the paranasal sinuses ([78, 133] and Papers IX - XII), but the technique has also been applied to the mastoid bone (Paper XIII) and models of neonatal lungs (Paper XIV).

In addition to application-oriented research, technical improvements of the GASMAS technique and instrumentation have also been made. The first GASMAS setup or version of it was used in [116, 122, 124, 126, 128, 132] and was based on an O<sub>2</sub>-sensing Fabry-Perót diode laser. At first the laser was coupled into a multimode fiber and collimated before entering the sample. Nitrogen gas was flushed in the laser passages through ambient air to remove absorption offsets. In 2006 a setup sensing  $H_2O$  at 980 nm with a Fabry-Perót diode laser was assembled and used simultaneously with the previous setup to monitor  $O_2$  and  $H_2O$  in drying wood [132].

To eliminate the absorption offset from ambient air and to get mode-hop free diode lasers, the use of pigtailed DFB lasers<sup>10</sup> was later employed ([78, 123, 133] and Papers IX - XIV, and IV). Since the light then travels through a fiber from the laser to the sample no influence of absorbtion of ambient air is expected. The pigtailed fiber-coupled lasers were accompanied with large interference effects and demanded a balanced detection scheme, presented in Ref. [78], and further improved in Papers VII and XI. VCSEL diode lasers, both pigtailed and non-pigtailed, have also been used in GASMAS setups; [121, 125, 129, 131] and Papers III and V.

In 2007 a new signal-detection scheme, based on the use of synchronized plug-in computer boards and software-based wavelength modulation, dWMS, was introduced [125]. This opened up for compact and flexible GASMAS instrumentation, which was a prerequisite to perform studies outside the laboratory. Two setups, sensing  $O_2$  and  $H_2O$ , respectively, and based on pigtailed-DFB diode lasers, were then merged and clinically adapted (Papers X and XI).

Absorption by gas confined in nano-porous ceramics was published as late as this year for the first time [121], but has already presented additional interesting results (Papers III - V). Studies of gas confined in nano-porous ceramics with GASMAS possess several interesting characteristics. The confinement of the molecules in nm-sized pores disturbs the energy levels of the molecule through wall interactions, causing broadening and minor shifts of the absorption line. Gas analysis of confined molecules thus provides a way to do fundamental studies of these mechanisms, as well as applications. Since the effects are dependent on the size of the confinement, the broadening could, e.g. provide information about the pore size, as shown in Paper V. Furthermore, the extremely high scattering of the nano-porous ceramics, yielding large path lengths, also makes them suitable as a small gas cell, presented in Paper III.

The first reported broadening of confined gas in nm-sized pores was from  $O_2$  in Alumina,  $Al_2O_3$  [121]. Broadening of gas in 70 nm and 18 nm pores was presented. A gas-interaction path length of 78 cm, for a 6 mm thick sample with 70 nm pores and with a porosity of 35%, was obtained.

Later the broadening of  $H_2O$  in alumina was also demonstrated, Paper IV. The diffusion of  $H_2O$  was studied by monitoring the decrease in  $H_2O$  absorption from a sample that had been placed <sup>10</sup> Pigtailing means that the laser is coupled directly from the gain medium to a fiber. in an environment of 100% relative humidity. The diffusion of  $O_2$ and  $H_2O$  was compared by flushing a sample with nitrogen gas and measure the absorption of  $O_2$  and  $H_2O$  simultaneously. In contrast to the  $O_2$  molecules that rapidly diffuse out of the sample, the  $H_2O$  diffusion is much slower and consists of over-layered diffusion curves.

Studies of gas in nano-porous ceramics have been further studied under reduced pressure, Paper  $\mathbf{V}$ , demonstrating how the wall-collision related broadening becomes more significant at lower pressures.

## 5.3.1 Similar work

Up to this point all GASMAS papers published have included members of the AMSRS group, but the interest of pursuing TDLAS in the diffuse optical regime is growing. The use of integrating spheres<sup>11</sup> as gas cells has been around since the 80's [135, 136] and is still an active field [137, 138]. Here the light is sent into the sphere where it scatters around in a diffuse manner and interacts with the gas. Although the absorption path length is unknown and the interaction path length is a distribution, the advantages are a high tolerance for misalignment and the small size. From a 50 mm integrating sphere, an effective path length of over one meter can be achieved [137]. Models of the light-path distribution in integrating spheres have been made [139, 140].

Other gas cells with diffuse light propagation include the ones with diffusers as reflectors [141]. Similarly as the integrating spheres, these cells or open paths have the advantages of high tolerance for misalignment, which, e.g. can be applicable when studying combustion processes when temperature changes induce alignment problems or the harsh environments degrade the optical windows over time [142]. Hodgkinson *et al.* studied the effect of transmissive and reflective optical diffusers inside gas cells and concluded that the diffusers can be used to reduce optical interference fringes [71, 143].

Absorption measurement of diffuse light is also carried out in a number of additional fields, e.g. atmosphere optics, where the path lengths through clouds are enhanced [144, 145], and gas sensing inside aerogel with the use of Fourier spectrometry [146].

The GASMAS technique has gained a high interest from the ISP, International Science Programme, which has enabled spread of the technique. Today GASMAS setups are present in Ghana, Kenya, Sri Lanka, Zimbabwe, and Ecuador.

<sup>11</sup> An integrating sphere is a hollow cavity coated for high diffuse reflectivity with small entrance and exit ports and is typically used to measure a samples optical properties [134]. Table 5.2: Overview of content in publications using the GASMAS technique.

Year	Ref	Covers	
<b>Analy.</b> 2001	sis of gas dispersed in s Sjöholm et al. Opt. Lett. [122]	cattering media Introduce the GASMAS principle Defines the $L_{eq}$ parameter. Illustrates internal pressure assessment: epoxy with 300 mbar gas pores. Measured on wood, apple, sugar, salt, flour, polystyrene foam, and epoxy. Dynamic process of O <sub>2</sub> diffusion in an N <sub>2</sub> -exposed polystyrene foam studie Noted that line broadening due to nano-sized confinement can be expected Instrumentation: Studied lines: O <sub>2</sub> at 759.95 nm (R <sub>17</sub> Q <sub>18</sub> and R <sub>19</sub> Q <sub>19</sub> ) 761.003 nm (R <sub>7</sub> . Fabry-Pérot diode laser coupled into fiber and collimated out to sample Offset elimination with N <sub>2</sub> -flushing Analog lock-in detection Photomultiplier tube (PMT) - active surface 2000 mm <sup>2</sup> Sensitivity: $2.5 \times 10^{-4} \leftrightarrow 1.2$ mm	ied. d. R <sub>7</sub> ) le.
Conce time-r	entration measurement of resolved laser spectroscop	of gas embedded in scattering media by employing absorption and $p_{ij}$	
2002	Somesfalean <i>et al.</i> Appl. Opt. [116]	Combine GASMAS and TOFS for O <sub>2</sub> -concentration extraction Measured 20.4% O <sub>2</sub> in polystyrene foam. Calculated the porosity to 98% by assuming 20.8% O <sub>2</sub> concentration in sample. Reports an $L_{eq} \propto d^2$ -dependency, where d is sample thickness.	the
<i>Laser</i> 2003	spectroscopy of free mod Alnis et al. Appl. Phys. B [124]	lecular oxygen dispersed in wood materials Wood materials analysis GASMAS and TOFS measurements. Fiber-structure and gas-diffusion parameters investigated. Studies of different types of woods.	
<b>Studie</b> 2005	es of gas exchange in fru Persson et al. Proc. FRUTIC [126]	<ul> <li>uits using laser spectroscopic techniques</li> <li>Analysis of gas-exchange in fruits</li> <li>Apples, oranges, mushrooms, and avocados studied.</li> <li>Illustrates the applicability to MAP.</li> <li>O<sub>2</sub> diffusion for peeled and film-wrapped apples.</li> <li>O<sub>2</sub> diffusion for an apple and mushroom in a plastic bag.</li> <li>Reflection and transmission geometries applied.</li> </ul>	
<b>Diode</b> 2006	<i>laser absorption spectra</i> Persson <i>et al.</i> Opt. Laser Eng. [127]	<b>Provide State Sta</b>	
Spectr 2006	oscopic studies of wood- Andersson et al. Opt. Express [132]	<ul> <li>drying processes</li> <li>O<sub>2</sub> and H<sub>2</sub>O studied in drying wood</li> <li>Time series of drying processes.</li> <li>O<sub>2</sub> and H<sub>2</sub>O simultaneously detected at two different sample locations.</li> <li>Investigation of bulk absorption of the two wavelengths used.</li> <li>Instrumentation updates:</li> <li>Two simultaneous measuring setups</li> <li>Studied lines: O<sub>2</sub> at 761.003 nm and H<sub>2</sub>O at 978.509 nm</li> <li>Fabry-Pérot diode lasers (7 mW and 200 mW)</li> <li>Photodiode detector - active surface 100 mm<sup>2</sup></li> </ul>	
<b>On the</b> 2006	e potential of human sin Persson et al. Appl. Phys. B [128]	<b>Proof-of-principle of O</b> <sub>2</sub> -sensing in human sinuses Measurements of a phantom modeling the frontal sinuses. Investigation of varying tissue-phantoms, and air-gap thicknesses. Transducer-detector separation investigated on sinus phantom. Human frontal sinuses studied in a reflection geometry.	20

<b>Appro</b> 2007	pach to optical interferent Persson et al. Appl. Phys. B [133]	ace fringes reduction in diode laser absorption spectroscopy Implementation of dual-beam $O_2$ -GASMAS instrument Reduction of interferences originating from the laser source. Comparison between hardware and software balanced detection schemes. Instrumentation updates:
		Pigtailed DFB diode laser (4 mW) Fiber-carried dual-beam scheme Sensitivity: about $6 \times 10^{-4} \leftrightarrow 2$ mm
Gas n	nonitoring in human sin	nuses using tunable diode laser spectroscopy
2007	Persson <i>et al.</i> I Biomod Opt	$O_2$ and $H_2O$ sensing in human sinuses
	(Paper $IX$ )	Maximally and nontal sinuses investigated. Monte-Carlo simulations with ASAP performed
	(rupor III)	Money Carlo Simulations with HSHI performed. Measurement geometries investigated.
		Data from healthy and unhealthy volunteers presented.
		Monitoring of gas-dynamics demonstrated.
		Normalization of $O_2$ with $H_2O$ introduced.
		Instrumentation updates:
		Studied lines: $O_2$ at 760.445 nm and $H_2O$ at 935.686 nm.
Flexib	ble lock-in detection syste	em based on synchronized computer plug-in boards applied in sensitive
<b>gas sp</b> 2007	Andersson <i>et al.</i>	O <sub>2</sub> -GASMAS instrument based on dWMS and VCSEL
	Rev. Sci. Instr. [125]	Compact flexible instrumentation.
		Gas-dynamic monitoring of bamboo stalk demonstrated.
		WMS-signals $(2f-4f)$ retrieved from human frontal sinus.
		Implementation of synchronized DAO cards
		LabVIEW-based WMS retrieval
		Software lock-in analysis
		Pigtailed and non-pigtailed VCSEL diode lasers (0.3 mW and 0.15 mW) Studied line: O <sub>2</sub> at 760.445 nm
Monte	e Carlo simulations rela	ted to gas-based optical diagnosis of human sinusitis
2007	Persson <i>et al.</i>	Monte-Carlo simulation of human sinus model
	J. Biomed. Opt. [133]	Simulations of measurements on phantom model presented in [128]. Imaging possibilities simulated.
Nonir	wasive characterization	of pharmaceutical solids by diode laser oxygen spectroscopy
2007	Svensson <i>et al.</i>	Characterization of pharmaceutical tablets
	Appl. Spectrosc. [123]	$L_{\rm eq}$ -dependency of compressed tablets.
		Instrument: Dr B-based O <sub>2</sub> -sensing
Simul $tunab$	taneous detection of mo le diode laser spectrosco	plecular oxygen and water vapor in the tissue optical window using py
2008	Persson <i>et al.</i>	Simultaneous detection of $O_2$ and $H_2O$
	Appl. Opt.	Frequency multiplexing employed for dual-gas sensing.
	(Paper $\mathbf{A}$ )	Cross-talk between sensed gases investigated
		Initial clinical tests reported.
		Instrumentation updates (DFB-based fiber based):
		Implementation of a synchronized DAQ card
		LabVIEW-based WMS retrieval
		Pigtailed DFB diode lasers, laser light coupled together into a single fiber Studied lines: $O_2$ at 760.445 nm and $H_2O$ at 935.685 nm
High .	sensitivity gas spectrosco	opy of porous, highly scattering solids
2008	Svensson <i>et al.</i>	System characterization of high-sensitive VCSEL $O_2$ GASMAS
	Opt. Lett. [131]	Fourier based dWMS introduced. Interference-elimination methods investigated: tracking coil vs. sample rota
		tion.
40		Instrument: VCSEL-based, dWMS Sonsitivity: $3 \times 10^{-5} \leftrightarrow 0.1 \text{ mm}$ (60 c)
		(00  s)

Food m	conitoring based on diod	e laser gas spectroscopy
2008	Lewander <i>et al.</i>	$O_2$ -and- $H_2O$ sensing in food packages
	Appl. Phys. B	Proof-of-principle on minced meat, bake-off bread, and milk-carton headspace.
	(Paper $\mathbf{VII}$ )	Gas dynamics monitored.
		Temperature compensation of $H_2O-L_{eq}$ introduced. Instrument: DFB-based, dWMS (Fourier based)
Gas an	alysis within remote por	Pous targets using LIDAR multi-scatter techniques
2008	Appl Phys B	LIDAB and GASMAS combined
	(Paper $\mathbf{VI}$ )	$O_2$ line studied at 760 nm.
		DIAL technique applied.
Gas in	scattering media absorp	c ASMAS muiou
2008	Proc. of SPIE [147]	GASIMAS review
<b>VCSEL</b>	-based oxygen spectrosc	opy for structural analysis of pharmaceutical solids
2008	Appl Phys $B$ [129]	Thorough description of Fourier based dWMS
	11ppi. 1 ilyö. D [120]	Combining GASMAS and TOFS for material analysis.
		Introduces the concept of optical porosity.
		Fast gas-dynamics ( $\tau = 1.6$ s) reported.
		Instrument: VCSEL-based, dWMS
Clinica	l system for non-invasio	the in situ monitoring of gases in the human paranasal sinuses
2009	Lewander <i>et al.</i>	Clinical GASMAS system sensing $O_2$ and $H_2O$ simultaneously
	(Paper XI)	Improved balanced detection scheme
	(1 aper 201)	Fitting of complex time-representation of WMS signals introduced.
		Human sinus TOFS measurements reported.
		Clinical data with good SNR presented.
		Instrument: DFB-based, pigtailed, dWMS
		Sensitivity: $3 \times 10^{-5} \leftrightarrow 1 \text{ mm } (O_2)$
		Detection limit: $2 \text{ mm} (O_2 \text{ and } H_2O)$
Optical	analysis of trapped Gas	3 - Gas in Scattering Media Absorption Spectroscopy
2010	Svanberg Laser Physics [148]	GASMAS review
Laser s	pectroscopy of gas confi	ned in nanoporous materials
2010	Svensson and Shen	$O_2$ confined in nano-porous alumina studied
	Appl. Phys. Lett. [121]	Broadening of $O_2$ absorption line due to tight confinement.
		Unfamiliar lineshape reported.
		Instrument: VCSEL-based, dWMS
Laser d broader	ubsorption spectroscopy on the sector of the	of water vapor confined in nanoporous alumina: wall collision line unamics
2010	Svensson <i>et al.</i>	H <sub>2</sub> O confined in nano-porous alumina studied
	Opt. Express	Broadening of $H_2O$ absorption lines due to tight confinement.
	(Paper $IV$ )	Large absorption studied in direct absorption.
		Diffusion of $O_2$ and $H_2O$ studied.
		Instrument: DFB-based, pigtailed, dWMS
<i>Non-in</i> 2010	vasive diagnostics of the Lewander $et c^{l}$	maxillary and frontal sinuses based on diode laser gas spectroscopy Besults from clinical trial
2010	(Paper XII)	Correlation study between $O_2$ and $H_2O_{Loc}$ is with findings from CT images
	( <b>r</b> )	Maxillary and frontal sinuses studied.
		40 sinus patients examined.

Non-ir	ntrusive gas monitoring	in neonatal lungs using diode laser spectroscopy - Feasibility study
2010	Lewander <i>et al.</i>	Proof-of-principle of gas sensing in lungs
	$(Paper \ \mathbf{XII})$	$O_2$ and $H_2O$ monitored in neonatal lung models made out of boar lungs and tissue phantoms.
		Transmission and reflection geometries studied.
		Position study.
		Instrument: DFB-based, pigtailed, dWMS
Disord	lered strongly scattering	porous materials as miniature multipass gas cells
2010	Svensson <i>et al.</i>	Ceramics as compact multi-pass cells
	(Paper III)	$O_2$ absorption of gas embedded in zirconia, alumina, and titania. Instrument: VCSEL-based
Wall o	collision line broadening	$at\ reduced\ pressures:\ towards\ non-destructive\ characterization\ of$
2010	Xu et al.	Broadening of absorption lines of $\Omega_2$ in nano-porous ceramics for
2010	Tru co wo.	different pressures
	(Paper $\mathbf{V}$ )	Pressures from 75 Torr to ambient studied.
		Shows additive behavior of wall-collision broadening to the pressure broaden-
		ing.
		Instrument: VCSEL-based, pressure chamber

# Chapter 6

# Application of GASMAS

As described in the previous chapter, GASMAS has been applied to a variety of fields. The applications which this thesis are based on are further elaborated in this chapter. Background, applicability, and a review of the GASMAS work carried out within two areas; food packaging and medical applications, are presented. Although the scattering is different and the pores range from µm to cm scale, the gas inside food and the human body cavities can all be studied with GASMAS. Each sample requires specific considerations, such as applicable wavelengths, gases present in the sample, and the optical power needed. Both the presented applications are concluded with an outlook to future work.

# 6.1 Food-packaging applications

The desire of fresh food has set an increased demand on the packaging technology since it is more sensitive to deterioration. Modified atmosphere packaging, MAP, is a well developed packaging technique, based on the control of gas composition inside the package. MAP is today used for a number of food stuffs to increase the shelflife. Following the new packaging techniques, sensing methods are developed to ensure food safety and quality. Many developed sensing techniques are intrusive, requiring gas to be extracted through needles for further analysis, or gas-reacting objects to be placed inside the packages. Monitoring of food packages with GASMAS constitutes an interesting non-intrusive alternative. GASMAS can provide information about the gas in the food stuff or in a surounding headspace, even for packages which do not appear transparent for the naked eye. <sup>1</sup> Already as early as in the 30's, fruits and vegetables were transported in a modified atmosphere.

<sup>2</sup> Examples of commercial sensors are; PBI Dansensor, Wilco etc.



Figure 6.1. Illustration of gas monitoring in an apple in a backscattering-detection geometry (a) and corresponding  $O_2$  absorption signal (b) [126].

### 6.1.1 Modified atmosphere packaging - MAP

Modifying and controlling the surrounding ambient gas in food has been shown to be an effective way to prolong the shelf time of the produce,<sup>1</sup> and is frequently used [149]. Typically, the gas composition is altered by lowering the O<sub>2</sub> concentration and replacing the gas by either N<sub>2</sub> or CO<sub>2</sub>. O<sub>2</sub> is a highly biologically active gas that can hasten chemical breakdown and microbial growth, while N<sub>2</sub> is considered an inert gas and CO<sub>2</sub> can slow the bacterial growth rate [150, 151]. The gas composition is actively changed at the time of packaging, either by flowing gas during the packaging or by first subjecting the product to vacuum followed by an inlet of the desired gas mixture [152]. Examples of food items packaged in a modified atmosphere are cured meat, bread, pasta, fruit, and vegetables. Furthermore pharmaceutical drugs are also sometimes packaged in a modified atmosphere.

#### 6.1.2 Current gas-sensing techniques

Present techniques to monitor gas in packages can be divided into three main tracks; spectroscopic techniques on transparent packages, gas extraction with needles and subsequent gas analysis, and the use of markers within the packages. The first track includes TDLAS techniques applied to glass vials for medical drugs [153], and wine bottles [154]. These methods are non-intrusive in nature, but require known optical path length and optical access to the headspace. The second gas-sensing method is based on extraction of gas and subsequent gas analysis with, e.g. gas chromography, mass spectrometry [155, 156], or IR sensors [157].<sup>2</sup> These well established techniques are flexible, and do not require large sample volumes. However, since the gas is extracted through needles, the technique is intrusive. This causes waste of samples, do not allow repetitive measurements, and is accompanied with gas-extraction issues. The last method, with the placing of sensor discs, reactive to either  $O_2$  or  $CO_2$  [158], has not become a well spread sensing technique [157]. The sensor discs are costly in handling, need transparent packaging material, and are intrusive in the sense that they are inside the sample. However, this method enables repetitive studies.

### 6.1.3 Review

Already in the first publication of GASMAS it was reported on sensing of gas within food products, such as apples, sugar, salt, and flour [122]. Later the gas inside fruits (apples and oranges) and vegetables (mushroom, avocado, and aubergine) was further investigated [126, 128]. It was then shown that the gas could be monitored in a reflection geometry, Fig. 6.1, and that the diffusion of gas intrusion could be measured.

The GASMAS technique was later expanded towards the area of packed food due to the demanding need to non-intrusively access information of the product. Proof-of-principle gas measurements ( $O_2$  and  $H_2O$ ) in packaged minced meat and bake-off bread, as well as headspace gas measurements of a gable-top milk container, demonstrated the applicability of GASMAS to packaged food products; Paper **VII**. The modified-atmosphere headspace of plastic-top juice containers were further analyzed in Paper **VIII**. Variations in  $O_2$  concentration between samples with different expiration dates and storage times were studied as well as larger sample sets.

#### Minced meat

Minced meat, placed in a white polystyrene-foam tray and covered by a transparent thin plastic film, was studied both in a reflection and transmission detection mode; Paper VII. To demonstrate the possibility to monitor temporal slow changes, a time dependence measurement was performed during 3 days. To account for changes in probed gas volume, H<sub>2</sub>O was measured simultaneously, feasible since liquid water was present inside the sample. The temperature dependency of the  $H_2O$  signal, resulting in a concentration change, was accounted for by logging the internal temperature (measured in a parallel sample) and using the Arden-Buck equation (Eq. (5.1)), Fig. 6.2. The temperaturecompensated  $H_2O$  data were then used for normalization of the  $O_2$ data yielding data corresponding to the O<sub>2</sub> concentration, under the assumption that the  $O_2$  and  $H_2O$  sensing laser light probes the sample similarly. The time series showed small changes in probing volume and that the oxygen is consumed by the meat.

#### Bake-off bread

Temporal measurements of a bake-off bun in a modified atmosphere were also demonstrated in Paper VII. As the package was punctured it was noted that the  $O_2$  and  $H_2O$  signals increased. For  $O_2$  this is expected due to the sealed packages holding a close to zero  $O_2$  concentration. For  $H_2O$  this indicated that saturation was not achieved in the sealed package due to lack of liquid water. The result shows that the technique described can be used to check package integrity.

#### Headspace of liquid containers

The assessment of information about the gas inside the headspace of containers for liquids and made out of translucent material, Fig. 6.3, was first demonstrated on a milk carton, Paper VII. Absorption signals of both  $O_2$  and  $H_2O$  with good SNR were obtained. Punctuation measurements verified that the headspace



Figure 6.2. Monitoring of  $H_2O$  inside packaged minced meat. As the sample temperature increases the  $H_2O$  concentration and thus the absorption ( $L_{eq}$ ) increase. By logging the temperature and calculating the corresponding saturation pressure the temperature dependency can be taken into account.



Figure 6.3. Illustration of gas monitoring in headspace of a milk carton and juice container.

atmosphere was similar as ambient air, and the need of normalization of  $O_2$  with  $H_2O$  was clear.

To investigate the suitability of the technique for headspaces with modified atmosphere, further studies were performed on juice containers, laminated carton packages with a polyethylene plastic top and cap, and with a modified atmosphere headspace; Paper **VIII**. In total 60 samples with three different expiration dates (20 samples of each date) were studied. No large variation was noted between the samples with the same expiration date. However, distinct changes in  $O_2$  content were seen between the different expiration-date sets. The  $O_2$  concentration was deduced by perforating samples and monitoring the increase as ambient air flowed into the headspace.

## 6.1.4 Outlook

The current work within the food packaging application is mainly focusing on liquid translucent containers in a joint project together with TetraPak. The project includes further verification of the technique and comparison with another standard technique. To optimize the applicability of GASMAS as a quality tool for liquid containers, additional investigations of the transmission of the bulk material, the need to normalize the  $O_2$  signals with  $H_2O$ , and optimum detection geometry are needed.

Future research work also includes the expansion to other food products, or other packaged goods where the monitoring of the gas composition is of interest.

To make GASMAS a standard gas analysis tool for MAP analysis, the applicability for in-line monitoring should also be further investigated.

# 6.2 Gas sensing in the human body

Gases are fundamental for the human body and are important in certain types of medical diagnostics; see, e.g. Section 3.3, where TDLAS is utilized. Such current diagnostic techniques require that the gas is extracted, for example, through breathing, and then analyzed. The alternative diagnostic technique, GASMAS, provides a way to analyze the gas within the human body *in situ*.

Free gas exists in the human body at a number of locations. These obviously include the respiratory tract organs such as the nose and mouth cavities, the lungs, the paranasal sinuses, and the middle ear. Furthermore, free gas also exists in the stomach, in the intestines, and in some bone structures.

Monitoring of gas inside the human body is limited by the transmission of light in the tissue, restricted by the strong absorption of liquid water (above 1400 nm) and blood (below 600 nm);



**Figure 6.4.** Absorption coefficient of water and hemoglobin. Data taken from [159] and [160].

see Fig. 6.4, as well as by large scattering properties. In the tissue optical window or the therapeutical window, i.e. the transmission region between 600 nm and 1400 nm, where the tissue appears translucent and light to a low extent can pass up to centimeters, a couple of gases exhibit absorption lines; Fig. 6.5.  $O_2$  and  $H_2O$  absorb in this wavelength region and have been studied within the human body, presented in Papers **IX** – **XIII**.

 $O_2$  is an important physiological gas and therefore important to quantify within the human body. However, the diffuse light propagation in tissue prohibits direct evaluation of gas concentration through the Beer-Lambert law, which requires known gas interaction length (further discussed in Section 5.1.1). A solution to this has been shown to be simultaneous monitoring of H<sub>2</sub>O at a wavelength close to the one used for O<sub>2</sub> sensing. The absorption of H<sub>2</sub>O can be used as a measure of mean probed gas distance due to known gas concentration through the saturated humidity and known body temperature which the cavities in the human body exhibit (Paper **IX**). Information about the gas filled volume can thus be obtained through H<sub>2</sub>O monitoring and the ventilation of the cavity can be achieved through diffusion measurement or O<sub>2</sub> and H<sub>2</sub>O sensing.

Sensing of free gas in human body cavities with GASMAS was first demonstrated in 2005 and has since been investigated as a tool to monitor the paranasal sinuses ([128, 133, 161] and Papers IX - XII), and the mastoid process (Paper XIII).



**Figure 6.5.** Absorption lines of gases that absorb within the optical tissue window (top) as well as only the absorption lines of  $O_2$ ,  $H_2O$ , and  $CO_2$  (bottom).

# 6.2.1 Paranasal sinus diagnostics

The paranasal sinuses, Fig. 6.6, are air-filled cavities located in the human skull, which are connected to the nasal cavity via small ventilation channels. The function of the sinuses is debated and suggestions include serving as a way to humidify and heat the air passing into the lungs, being resonators for the speech, or stabilizing the skull.

The sinuses are divided into four subgroups:

- Frontal sinuses Located behind the frontal bone
- Maxillary sinuses Located under the eyes behind the cheek bone
- Ethmoid sinuses Located behind the eyes and the nose
- Sphenoid sinuses Located further back in the skull behind the nose and in front of the hypophysis



Figure 6.6. Anatomy of the paranasal sinuses in the skull. Adapted from [162].

Table 6.1: Factors indicating rhinosinusitis. Adapted from [164].

Major factors Facial pain/pressure (in the presence of other major symptoms) Facial congestion or fullness Nasal obstruction or blockage
Nasal discharge, purulence, or discolored postnasal drainage Hyposmia or anosmia (lack of smelling)
Fever (in the presence of other major symptoms)
Minor factors
Headache
Fever
Halitosis (bad breath)
Fatigue (tiredness)
Dental pain
Cough
Ear pain, pressure, or fullness

#### Rhinosinusitis

The small ventilation channels between the nasal cavity and the sinuses easily get clogged, prohibiting drainage of mucus inside the sinus. Such a state can lead to rhinosinusitis or sinusitis, i.e. an inflammation of the nose and/or the paranasal sinuses. The origin of the rhinosinusitis is mainly viral but can also be bacterial or due to an allergic reaction, as well as swelling from cold. The definition of rhinosinusitis is thus broad and covers many sinus conditions [163].

The rhinosinusitis is classified according to its duration, where an acute sinusitis persists less than 4 weeks and a chronic more than 12 weeks [163, 164]. Furthermore, a recurrent acute rhinosinusitis is defined as an acute rhinosinusitis if it occurs at least four times during one year [165].

The incidence of rhinosinusitis shows large numbers, with estimates that 15% of US population are affected annually [166]. Rhinosinusitis thus constitutes a major socio-economic and health issue with substantial costs including doctor visits, tests, and medical treatments, as well as indirect costs like restricted active days. The cost for treatment of a patient with chronic rhinosinusitis is estimated to be \$2,600 per year [167].

An additional issue related to rhinosinusitis is the prescription of antibiotics. In 2002 rhinosinusitis was the cause for over 20% of the prescriptions in the US [163]. The alarming reports about the increased resistance due to over-prescription of antibiotics are thus highly related to rhinosinusitis and its diagnosis, often without objective facts related to bacterial origin.

Basic diagnostic tools			
Case history and clinical examination			
Endoscopy			
CT scan			
X-ray			
Supplementary diagnostic tools			
Allergy diagnosis			
MRI			
Ultrasound			
Microbiological studies			
Leukocyte count and differentiation			
Antineutrophilic cytoplasmic antibody			
Cytology and nasal mediator			
Saccharin test, electron microscopy studies			
Nasal biopsies			

Table 6.2: Diagnostic techniques for rhinosinusitis. Adapted from [172].

#### Current diagnostic techniques

The majority of the diagnosis of rhinosinusitis is not usually based on objective instrument; instead symptoms and physical examinations, usually made at the general practitioners' offices, are employed [165, 168]. Such diagnoses have shown to lead to a large over-diagnosis of bacterial rhinosinusitis causing an overprescription of antibiotics. A standardized definition has been desirable to facilitate diagnosis of rhinosinusitis and the prevalence of it, and has resulted in that international consensus meetings have defined rhinosinusitis; Tab. 6.1 [167]. Since most of the patients with suspected rhinosinusitis are diagnosed in a primary care setting where no diagnostic tools like  $CT^3$  or endoscopy<sup>4</sup> are routine, such guidelines are helpful. However, studies report on a large over-diagnosis of symptom-defined rhinosinusitis and suggest the addition of objective signs given by, e.g. CT or endoscopy [169]. The European Position Paper on Rhinosinusitis has thus expanded the recommendation of diagnostics to include objective signs found though nasal endoscopy or CT scan. Table 6.2 gives an overview of the used diagnostic tools. Although endoscopy is standard at oto-rhino-larvngological clinics, it is not used in the primary care clinics [170]. Ultrasound imaging is a technique which can aid the diagnosis of rhinosinusitis, but the technique has suffered from weak diagnostic correlation studies [171]. Although it has the favorable characteristics such as being cost effective, noninvasive, and often present at the primary clinics, it is also associated with high operator dependency.

Sinus culture can also be used to verify bacterial acute rhinosinusitis and is standard in pharmaceutical trials. However, due to the discomfort of a trocar or needle it is usually not used in these easier cases, and is only applied to more complex cases [170].

 $^3$  CT, computer tomography, is a medical tool based on X-rays and tomography yielding 3D images.

<sup>4</sup> Endoscopy is a medical tool to look inside hollow organs in the body by inserting a flexible tube with a camera.

#### Clinical applicability of GASMAS

New diagnostic tools for diagnosis of the paranasal sinuses are of high interest due to the common and hard-diagnosed rhinosinusitis, or sinusitis. With the inflammation follows obstruction of the sinus cavity and blockage of the ventilation to the nasal cavity. It has been shown that by using the GASMAS technique, the gas composition can be evaluated and yields data that correlate to the gas-filled volume and the  $O_2$  concentration inside the sinus, meaning the obstruction and ventilation, respectively.

The GASMAS-based diagnosis opens up for the possibility to assess diagnostic valuable information non-intrusively with a simple instrument. The instrumentation can be incorporated into a small device with practical usability. The technique is cost effective and the instrument can be used at the general practitioner's office. The unharmful and non-intrusive nature allows repeatable investigations, making it possible to study the course of the disease as well as recurring problems.



Figure 6.7. Reflection and transmission measurement on slab model. [128]

#### Review

Investigation of GASMAS as a diagnostic tool has so far been pursued mostly to the maxillary and frontal sinuses. The technique was first demonstrated on a sinus phantom made out of plastic Delrin slabs [128], Fig. 6.7. It was shown that the  $O_2$  in the air gap between two slabs could be detected both in a transmission (slabs up to 10 mm) and reflection geometry (through a slab of 10 mm). Monte-Carlo simulations with the software ASAP, based on these geometries was also pursued [133]. Through this work it was demonstrated that when the light scatters back and forth between the scattering slabs. In a transmission geometry with two 10 mm slabs with 10 mm air gap inbetween, about 60% of the detected transmitted light passes only once through the air cavity. The remaining 40% of the photons have additional passages, even up to 13 passages.

The first gas-sensing inside human sinuses was conducted in a backscattering geometry on the frontal sinuses [128]. Although very weak signals were obtained, about 1 mm, they demonstrated communication with the gas inside the sinus. Later, better detection geometries of the frontal sinuses, Fig. 6.8, were found and larger gas absorption signals, about 10 - 20 mm, were obtained.

The possibility to study gas inside the maxillary sinuses was shown on volunteers, first in a transmission geometry [161] and later in a reflection geometry (Paper IX); Fig. 6.8. Reflection mode implies that the light transducer and detector are both positioned on the cheek, separated by a distance, while a transmission mode refers to the light transducer positioned inside the mouth and the detector on the cheekbone. However, it should be noted



Figure 6.8. Detection geometries for maxillary and frontal sinuses.



**Figure 6.9.** Setup including two diode lasers coupled together with one fiber. The instrument interfaces with the patient through a fiber transducer and a detector.



Figure 6.10. Absorption signals of frontal sinus.



Figure 6.11. Data obtained with GASMAS for different sinuses.

that a transmission geometry from the outside could perhaps also be possible.

The differences in measured  $O_2 L_{eq}$  on the right and left side and for different detector positions were shown to be possible to compensate for by normalizing with  $L_{eq}$  for H<sub>2</sub>O (Paper IX). As discussed in Sections 5.1.1 and 5.1.2, H<sub>2</sub>O can serve as a calibration of the probed gas interaction distance if liquid water is present and the temperature is known. First two parallel  $O_2$  and  $H_2O$ sensing setups were used and careful markings of light injection and detector positions were needed. Later (2006) a more clinically adapted system with simultaneous detection of  $O_2$  and  $H_2O$  was built (Papers X and XI). The system is based on two pigtailed DFB diode lasers operating at 760 nm and 935 nm for sensing O<sub>2</sub> and H<sub>2</sub>O, respectively. A LabVIEW controlled synchronized sampling card provides the scanning of the laser wavelengths as well as the sampling of the detected signal. Digital wavelength modulation spectroscopic techniques, dWMS, are applied for sensitive detection and also enables simultaneous dual-gas sensing by the use of two different modulation frequencies, 9 kHz and 10 kHz (presented in Paper  $\mathbf{X}$ ).

The system was used in a clinical trial on 40 patients, where GASMAS data were compared with findings in low-dose CT scans. Examples of the measured absorption signals from a healthy patient's frontal sinus can be seen in Fig. 6.10. The GASMAS data for maxillary and frontal sinuses are shown in Fig. 6.11. The clinical correlation was studied by comparing the  $L_{eq}$  values and the findings from the CT scans. A radiologist evaluated each sinus and graded the obstruction and ventilation according to a standard classification scheme [173]. Obstruction grading: 0 – no abnormality, 1 - partial opacification, and 2 - total opacification. Ventilation grading (Ostiomeatal complex): 0 - not obstructed and 2- obstructed. Good clinical correlation was shown (Paper XII). The transmission detection geometry is the one being investigated and used the most so far, however, due to clinical and practical reasons there is a strive to move over to the reflection geometry. Work has been carried out to study the dependency of light injection and detector position by Monte-Carlo simulations, model experiments as well as studies on human maxillary sinuses. The purpose was to compare the detection of gas inside the maxillary sinus in a reflection and transmission geometry. A tissue phantom with an enclosed gas cavity was constructed. The phantom was constructed of gelatin, with absorbers (ink) and scatterers  $(TiO_2)$ , and a gas-filled ping pong ball.

The obtained experimental results of equivalent path lengths though gas for different detector positions were compared to Monte-Carlo simulated data. The Monte-Carlo simulations were made with a MATLAB script of a semi-infinity geometry with an air-filled sphere (the ping pong ball). The results showed that the


**Figure 6.12.** Transmission and reflection gas measurements of a sinus phantom and also Monte-Carlo simulated data for the reflection and transmission geometry.



**Figure 6.13.** Result from reflection and transmission measurement of a pair of human sinuses. Two reflection positions were analyzed; detector and fiber placed close ( $\sim 1 \text{ cm}$ ) and far ( $\sim 2 \text{ cm}$ ).



Figure 6.14. Left: Human skull with the temporal bone, where the mastoideus is located in the posterior part. Adapted from [174]. Right: Mastoid air cell system. Adapted from [175].

transmission geometry provided reproducible information, and was not sensitive to detector position or geometry variations, contrary to the reflection geometry; Fig. 6.12. The results illustrate the difficulty of extracting oxygen concentration in a reflection measurement geometry since it is sensitive to the position of the detector and laser light transducer as well as the geometry of the sinus and surrounding tissue. These results were also verified on a human sinuses, Fig. 6.13.

## 6.2.2 Mastoid diagnostics

The mastoid is a part of the temporal bone in the skull and is located right behind the ear; Fig. 6.14 left. It consists of hollow air-filled cavities, mastoid cells; Fig. 6.14 right, connected to the middle ear through the mastoid *antrum*. The mastoid process is the outer tip of the posterior temporal bone. The mastoid air cells are also considered a sinus in the skull.

Mastoiditis is an infection in the mastoid process, and is closely connected to middle ear infection (*otitis media*). Mastoiditis even constitutes one of the most common complications of *otitis media*. Earlier mastoiditis was a common consequence from untreated otitis, and was a cause of high mortality of children [176]. As antibiotics were introduced as a treatment of otitis, mastoiditis decreased rapidly. However, today mastoiditis is still a present factor [177]. The majority of the mastoiditis cases occur for children.

Symptoms of mastoiditis include pain, tenderness, fever, and swelling. Diagnosis of mastoiditis is generally based on medical case history and physical examination. Imaging techniques, like MRI and CT can provide additional information. Typical analysis includes monitoring the size of the mastoid air cells system. The volume of the mastoid cells is related to the status of the mastoid.

Seeking medical care early is important as serious consequences can be caused by non-prompt treatment. Severe disease, such as spread to the brain, hearing loss, and facial nerve affection, can occur. Mastoiditis is treated with antibiotics and also by drainage with temporarily inserted tubes [178].

GASMAS provides a way both to monitor the presence of air in the mastoid cells as well as a way to study the gas composition within them, non-intrusively. The GASMAS approach allows a potentially easy diagnostic tool as well as the possibility to do repeated measurements to study, e.g. sick courses.

#### GASMAS work

The first mastoid process GASMAS measurements were conducted in the laboratory on a healthy volunteer and were reported in Ref. [162]. The light was guided with fiber and injected at the tip of the mastoid process and a large area detector  $(18 \times 18 \text{ mm}^2)$  was placed at the flat part of the bone, see Fig. 6.15. The O<sub>2</sub> signal obtained is presented in Fig. 6.16. The demonstration of the proof of principle measurements resulted in the inclusion of monitoring of the mastoid in the already planned clinical trial comparing GAS-MAS and CT data. Since the posterior part of the temporal bone is part of the CT images it was possible to do comparative studies also for the mastoid.

The mastoids of 30 patients were studied in the clinical trial and the results were correlated with CT findings (Paper XIII). From the CT scans both grading of the obstruction (0 - air filled, 1 - partially air filled, and 2 - obstructed) as well as the volume were analyzed. A three dimensional box approximation was used to assess the volume. Out of the 30 patients enrolled only 4 were found to have totally or partially obstructed mastoid air cells. These patients all exhibited low or no gas absorption, which is to be expected. In addition, a few healthy mastoids also resulted in no detected gas signal. This is believed to originate from the light not passing deep enough into the bone to interact with the gas. Of the healthy diagnosed mastoid air cells, a reduced oxygen concentration, compared to the ambient air was noted (a ratio of  $O_2/H_2O$ of 0.7 instead of 1.0 which was observed for the paranasal sinuses studied in these patients). This in accordance to the earlier reported gas composition studied of the mastoid air cells system [179]. Furthermore, correlation between the CT assessed volume and measured  $H_2O$  absorption was obtained.

#### 6.2.3 Neonatal lung diagnostics

The lungs are among the last vital organs in the body to mature in a pregnancy. Prematurely born babies thus often suffer from lung dysfunctions, such as lung injury or respiratory distress syndrome. In Europe and in the US between 6 - 15% [180, 181] of the deliveries are preterm and cause large intensive care costs



Figure 6.15. Detection geometry for gas sensing in the mastoid air cells. The fiber probe and detector are placed behind the ear.



**Figure 6.16.** Signal from the mastoid process in a healthy volunteer [162].

[182]. Care-taking at the neonatal intensive units includes several sophisticated monitoring and regulating systems, controlling and measuring the oxygenation, temperature, respiration, brain activity etc.

The respiratory distress syndrome, the largest cause of premature mortality [183] is caused by insufficient production of surfactant as well as structural immaturity. Surfactant is a compound that distends the alveoli (small air compartments that the lung consists of) keeping them from collapse. The respiratory distress syndrome is treated with respiratory support and surfactant therapy. Continuous positive airways pressure, mechanical ventilation, and the use of additional oxygen are also possible treatments. Although these treatments are life-saving and needed to prevent damage of the lungs, they also constitute an origin of chronical lung diseases. Mechanical ventilation can cause alveolar collapse and pneumothorax (assembling of gas in the *pleura*). Optimization of the lung therapy is needed. Today, e.g.  $CO_2$  levels in the blood and the breathing are monitored, but also X-rays images are used. Using GASMAS to measure gas inside the lungs could provide an additional monitoring tool that is non-invasive and utilizing nonharmful radiation. The amount of gas as well as the  $O_2$  content could be assessed. Measuring the lung volume, by impedance techniques, to optimize the therapy has been reported earlier [184]. The hope is that GASMAS will be able to note regional differences of the lung, monitor the treatment response, and study the gas transport. Improvements of the respiration treatment could thus help to reduce the formation of chronical lung diseases.

## Review

The possibility to assess information on the gas inside the lungs of premature babies has been evaluated in a feasibility study (Paper **XIV**), and was the topic of Anders Bruzelius' master's project [185]. The feasibility study included experiments on models as well as Monte-Carlo simulations. Lung models consisting of an inflated boar lung covered by layers of tissue phantoms (gelatin with added absorbers and scatterers), were studied. The dimension of the lung segment and the thickness of the gelatin tissue phantoms were chosen to correspond to the size of a 1 kg (6 mm tissue slab) and a 3 kg baby (12 mm tissue slab). Large gas absorption signals (about an order of magnitude larger than for the paranasal sinuses) were obtained both in transmission and reflection geometry; Fig. 6.17. It was shown that for the 1 kg babies a transmission geometry would be feasible, whereas the larger babies might require that a reflection detection geometry is applied. The reflection geometry is accompanied with some issues regarding utilizing  $H_2O$  as a reference for  $O_2$  concentration extraction. The assumption that laser light at the wavelength (760 nm and 935



Figure 6.17. Reflection (top) and transmission (bottom) detection geometry for gas sensing in the lung model consisting of an animal lung and a tissue phantom slabs.

nm) in both cases interacts with the same amount of gas can no longer be hold, Fig. 6.18, which makes it not as straight forward to retrieve the  $O_2$  concentration.

## 6.2.4 Outlook

The GASMAS technique shows great promise to become a powerful diagnostic tool in a clinical setting. However, further optimizations are needed regarding the clinical applicability, the clinical interface, and the technique. Verification of the clinical applicability requires further clinical studies where larger sets of clinical data are analyzed. The work on user interface includes both the probe system and the information produced. Technical improvements include optimization of the laser system (optical power, stable lasers, noise reduction, improved data processing etc.) as well as optimization of detection geometry (reflection, transmission etc.). The detection-geometry dependency for  $O_2$  concentration assessment requires further knowledge. Up to this point the most investigated detection geometry is the transmission or semi-transmission case, which has shown good clinical correlation for the paranasal sinuses (Papers IX and XII). However, due to clinical and practical reasons as well as transmission limitations there is a strive to move over to the reflection geometry. In the reflection geometry the different optical properties of the tissue at the two wavelengths might induce important aspects. One possibility to overcome the problem is to utilize other absorption lines of the gases, where the optical properties of tissue are more similar. To use an absorption line of water vapor at 820 nm instead of at 935 nm is one possibility. The absorption of  $H_2O$  is lower here, but in the case of gas sensing in the human body the absorption signal is of the same order as the now sensed  $O_2$ .

Furthermore, within the neonatal lung monitoring the next step is to verify the technique on patients and to adapt the instrument. The model experiments have shown that it should be possible to measure the gas within premature born babies. It should also be noted that the light transmission in the model is most likely lower as compared to the patient case. The optical properties of the neonatal tissue in the abdomen are not well known;<sup>5</sup> thus the model may very well represent a more difficult transmission case than the real situation.



Figure 6.18. Light penetration into a lung in a reflection geometry. The 760 nm and 935 nm laser light interacts with the gas cavities to different extent.

<sup>5</sup> Compared to adults the thoracic wall of neonatals is more transparent, and diagnostic approaches even include the use of transillumination with a flash lamp.

# Comments on the Papers

#### I Quasi zero-background tunable diode laser absorption spectroscopy employing a balanced Michelson interferometer

Z. G. Guan, M. Lewander, and S. Svanberg

A novel absorption technique based on a balanced Michelson interferometer is presented. As light is absorbed by the gas the interferometer becomes unbalanced which results in a zerobackground spectrum. I took part in the planning of the work and contributed significantly to the manuscript.

#### II Fast and sensitive time multiplexed gas sensing of multiple lines using a miniature telecom diode laser between 1529 nm and 1565 nm

*M. Lewander, A. Fried, D. Richter, P. Weibring, and L. Rippe* The paper presents fast multi-species detection using a widely tunable MG-Y diode laser. Sequential scans over individual absorption lines separated by 30 nm are reported. High sensitivity is achieved. I took part in the planning of the instrument. Rippe and I assembled the instrument, and planned and performed all experiments. I programmed the control software, did the data analysis, and wrote the manuscript.

#### III Disordered strongly scattering porous materials as miniature multipass gas cells

T. Svensson, E. Adolfsson, M. Lewander, C. T. Xu, and S. Svanberg

The paper presents highly scattered porous ceramics as miniature gas cells. Long gas absorption path lengths are reported from different ceramics. I was active in the experimental work and took minor participation in the manuscript preparation.

## IV Laser absorption spectroscopy of water vapor confined in nanoporous alumina: wall collision line broadening and gas diffusion dynamics

T. Svensson, M. Lewander, and S. Svanberg

Broadening of absorption lines of  $H_2O$  confined in nano-porous alumina is presented. Simultaneous monitoring of  $O_2$  and  $H_2O$ when subjected to flow of nitrogen gas demonstrate the possibility to measure gas diffusion of the sample. I and Svensson planned and executed the experiments using the instrument presented in Paper **XI**. I analyzed part of the data and prepared corresponding figure for the manuscript.

#### V Wall collision line broadening at reduced pressures: towards non-destructive characterization of nanoporous materials

C. T. Xu, M. Lewander, S. Andersson-Engels, E. Adolfsson, T. Svensson, and S. Svanberg

The paper presents study of wall-collisions broadening within samples of varying pore sizes. The broadening is investigated under different pressures. I contributed in the planning, assembling of the setup, and was part of all the experimental work. I participated in the data analysis and manuscript preparation.

### VI Gas analysis within remote porous targets using LIDAR multi-scatter techniques

Z. G. Guan, M. Lewander, R. Grönlund, H. Lundberg, and S. Svanberg

This paper combines GASMAS with LIDAR technique and monitors  $O_2$  remotely in polystyrene foam and snow. The backscattered diffuse light is filtered out in the focal plane of the telescope, allowing detection of only the light that has penetrated into the sample and interacted with the gas. The paper demonstrate the feasibility for large-scale GASMAS and remote detection. I contributed in the planning of the experiment, worked together with Guan and Lundberg in the laboratory, and was involved in all measurements. I took part in the manuscript preparation with discussions.

#### VII Food monitoring based on diode laser gas spectroscopy

M. Lewander, Z. G. Guan, L. Persson, A. Olsson, and S. Svanberg

The paper demonstrates the possibility to assess information about gas inside food packages non-intrusively. Principle measurements of minced meat, bread and a carton liquid container are reported. The use of  $H_2O$  for quantitative  $O_2$  concentration evaluation is discussed and presented. I was the main contributor in all parts of the work; instrumentation, experimental work, data analysis, and drafting of the paper.

#### VIII Non-intrusive measurements of headspace gas composition in liquid food packages made of translucent materials

M. Lewander, P. Lundin, T. Svensson, S. Svanberg, and A. Olsson

The paper reports from a study of large sample sets of juice containers with a modified atmosphere and illustrates the feasibility to measure the  $O_2$  concentration non-intrusively. Differences between samples of varying storage times are shown. The main focus of the paper is toward the special need within the industry of packaging. I contributed with the planning, experimental work and data analysis. I prepared the figures and wrote parts of the manuscript.

#### IX Gas monitoring in human sinuses using tunable diode laser spectroscopy

L. Persson, M. Andersson, M. Lewander, K. Svanberg, and S. Svanberg

Gas monitoring inside the frontal and maxillary sinuses using GASMAS is presented. Deviations between different detection geometries are eliminated by normalizing the  $O_2$  absorption with  $H_2O$  absorption, measured with two separate setups. It is demonstrated that the ventilation of the sinus cavity can be studied by flushing the nasal cavity with nitrogen gas and monitoring the diffusion. I was part in the assembling of the  $H_2O$ -sensing instrument and participated in the experimental work regarding detection geometries and gas-exchange studies. I contributed to the manuscript in discussions.

### X Simultaneous detection of molecular oxygen and water vapor in the tissue optical window using tunable diode laser spectroscopy

L. Persson, M. Lewander, M. Andersson, K. Svanberg, and S. Svanberg

A compact transportable instrument detecting  $O_2$  and  $H_2O$  in human body cavities is presented. The system is fiber based and couples the light from two diode lasers into a fiber probe and utilizes one detector. The gases are distinguished by different frequency modulations. No crosstalk between the detected gases is shown. The paper includes early clinical data from one maxillary and one frontal sinus. I participated in the assembling of the instrument, wrote the control software, and was part of all the experimental work. I contributed substantially to the revision of the manuscript as well as to discussions and a figure to the manuscript preparation.

#### XI Clinical system for non-invasive in situ monitoring of gases in the human paranasal sinuses

M. Lewander, Z.G. Guan, K. Svanberg, S. Svanberg, and T. Svensson

The paper presents a clinical instrument using GASMAS for detection of gas inside the human sinuses. The instrument is an improvement from an earlier setup, regarding interfering noise, data processing, and data acquisition. Digital wavelength modulation with Fourier filtering is employed. Fitting procedures and WMS retrieval through complex description of the absorption signals are implemented. TOFS data from volunteer sinuses are presented. Preliminary clinical data of  $O_2$  and  $H_2O$  absorption signal with good SNR are reported from the maxillary and frontal sinuses. I was the main responsible for the assembling of the clinical system, the characterization of it, the development of analyzing algorithms, and all the experimental work regarding gas analysis, as well as the drafting of the manuscript.

#### XII Non-invasive diagnostics of the maxillary and frontal sinuses based on diode laser gas spectroscopy

M. Lewander, S. Lindberg, T. Svensson, R. Siemund, K. Svanberg, and S. Svanberg

The paper presents data from a clinical trial with 40 patients, and investigates GASMAS as a diagnostic tool for the paranasal sinuses. The absorption of  $O_2$  and  $H_2O$  were shown to correlate well with gradings of obstruction and ventilation found in computer tomography images. I was the main responsible for the GASMAS instrument, coordinating the clinical trial, performed the examinations with GASMAS, analyzed all the obtained data, did the correlation study, and wrote the manuscript.

#### XIII Method for studying gas composition in the human mastoid using laser spectroscopy

S. Lindberg, M. Lewander, T. Svensson, R. Siemund, K. Svanberg, and S. Svanberg

The paper presents data from a clinical trial with 40 patients, and investigates GASMAS as a diagnostic tool for the mastoid bone. The absorption of  $O_2$  and  $H_2O$  were shown to correlate well with gradings of obstruction found in computer tomography images. I was the main responsible for the GASMAS instrument, coordinating the clinical trial, performed the examinations with GASMAS, and analyzed the GASMAS data. I wrote substantial parts of the manuscript.

### XIV Non-intrusive gas monitoring in neonatal lungs using diode laser spectroscopy - Feasibility study

M. Lewander, A. Bruzelius, V. Fellman, K. Svanberg, and S. Svanberg

The paper reports of gas sensing inside a model of a premature born baby. The model consisted of inflated animal lung tissue and gelatine based tissue phantoms, with realistic dimensions.  $O_2$  and  $H_2O$  monitoring in both transmission and reflection mode were demonstrated. I was the main responsible for the planning of the work, the instrument, the experimental work as well as the data analysis. I wrote parts of the manuscript and prepared figures.

# Acknowledgements

My deepest gratitude to Sune Svanberg for the opportunity to be a PhD student in your group and the mentoring you have given me, both on a professional and personal level. Your belief in me, great knowledge in physics, and hard working spirit has made you a perfect supervisor. I also would like to express my thanks to my co-supervisors; Katarina Svanberg, Stefan Andersson.Engels, and Marcus Aldén. Katarina your medical connections and discussions have been of most importance for my PhD work, and your positive and friendly manners are very much appreciated.

I want to express my thanks to present and former colleagues. Linda Persson, Rasmus Grönlund, and Mats Andersson, your help with introducing me to the projects, the labs, and the research group together with nice social environment are much appreciated and missed. Tomas Svensson, your scientific nature and friendship have meant much to me and I also thank you for introducing me to coffee (it was and will be useful). Zuguang Guan, your happy spirit, good electronics skills, and fun personality are much appreciated. Thanks to Mikkel Brydegaard for interesting discussions and being a nice travel companion. Patrik Lundin, your positive nature together with great physics and techniques skills will take you far - I feel lucky to hand over projects to you. Can T. Xu, deepest thanks for all your assistance and support in the finishing of this thesis, it has meant very much to me. Our hard work in the lab, in front of the computer, long math derivations, and your nice company will be missed. Erik Alerstam, thanks for always being up for a coffee, a lunch, a discussion, some TOFS measurements, or some Monte-Carlo simulations. I also want to thank all other members of the group, including visiting researchers and master students; Gabriel Somesfalean, Hiran Jayaweera, Benjamin Anderson, Anna-Lena Sahlberg, Anders Bruzelius, and the rest of you.

I also want to express my thanks to the Atomic Physics Divisions, with Claes-Göran Wahlström as Head of Division. The nice administration staff make everything run smoothly.

All collaboration partners are acknowledged; Sven Lindberg, Roger Siemund, and Vineta Fellman of the Medical Faculty; Annika Olsoon at Packaging Logistic Division; Fredrik Hansen at TetraPak; Zhongshan Li and Joakim Bood at the Combustion Physics Division. I also want to send my appreciations to the group at NCAR led by Alan Fried, which I had the opportunity to visit for 6 months and gain invaluable experience. Alan, your hospitality, leadership, and knowledge are very much appreciated. Lars Rippe, our long discussions, early and long work hours, hospitality, and positive nature are very much appreciated. Petter Weibring, Scott Spuler, and Dirk Richter are also acknowledged. It was a pleasure to work with you.

Last but definitely not least I want to thank my family and friends for strong support and encouragement. I am grateful for my grandparents, my parents, and all my siblings. I feel very fortunate to have such a large family. Special thanks go to my Mom Ingrid for believing in me, and my Grandmother Gunnel for your great interest in my research. Magnus, your love and support throughout the years have meant very much to me. Åsa, Jennie, and many other friends are also deeply acknowledged for being highlights in my life.

This work was economically supported by direct grants from the Swedish Research Council, a Linnaeus grant to the Lund Laser Centre, through the Vinnova PIEp-IDRE and NGIL programmes, and the Knut and Alice Wallenberg Foundation.

# REFERENCES

- C. N. Banwell. Fundamentals of Molecular Spectroscopy. McGraw-Hill (1972).
- [2]. G. Herzberg. Molecular Spectra and Molecular Structure. Read Books (2007).
- [3]. J. J. Sakurai. Modern Quantum Mechanics. Addison-Wesley (1994).
- [4]. C. Zender. Radiative Transfer in the Earth System (2008). URL http: //dust.ess.uci.edu/facts.
- [5]. L. S. Rothman, I. E. Gordon, A. Barbe, D. C. Benner et al. The HI-TRAN 2008 molecular spectroscopic database. Journal of Quantitative Spectroscopy & Radiative Transfer 110, 533–572 (2009).
- [6]. L. S. Rothman, D. Jacquemart, A. Barbe, D. C. Benner M. et al. The HITRAN 2004 molecular spectroscopic database. Journal of Quantitative Spectroscopy & Radiative Transfer 96, 139–204 (2005).
- [7]. L. S. Rothman, A. Barbe, D. C. Benner, L. R. Brown et al. The HITRAN molecular spectroscopic database: edition of 2000 including updates through 2001. Journal of Quantitative Spectroscopy & Radiative Transfer 82, 5–44 (2003).
- [8]. L.S. Rothman, C.P. Rinsland, A. Goldman, S.T. Massie, D.P. Edwards, et al. . The HITRAN molecular spectroscopic database and HAWKS (HITRAN Atmospheric Workstation): 1996 edition. Journal of Quantitative Spectroscopy & Radiative Transfer 60, 665–710 (1998).
- [9]. T. H. Maiman. Stimulated optical radiation in ruby. Nature 187, 493–494 (1960).
- [10]. E. D. Hinkley. High-resolution infrared spectroscopy with a tunable diode laser. Applied Physics Letters 16, 351–354 (1970).
- [11]. E. D. Hinkley. Laser spectroscopic instrumentation and techniques long-path monitoring by resonance-absorption. Optical and Quantum Electronics 8, 155–167 (1976).
- [12]. G. Galbacs. A review of applications and experimental improvements related to diode laser atomic spectroscopy. Applied Spectroscopy Reviews 41, 259–303 (2006).
- [13]. M. W. Sigrist, R. Bartlome, D. Marinov, J. M. Rey, D. E. Vogler and H. Wächter. *Trace gas monitoring with infrared laser-based detection* schemes. Applied Physics B **90**, 289–300 (2008).
- [14]. M. Lackner. Tunable diode laser absorption spectroscopy (TDLAS) in the process industries - A review. Reviews In Chemical Engineering 23, 65–147 (2007).
- [15]. J. Workman, M. Koch and D. J. Veltcamp. Process analytical chemistry. Analytical Chemistry 75, 2859–2876 (2003).
- [16]. I. Linnerud, P. Kaspersen and T. Jæger. Gas monitoring in the process

industry using diode laser spectroscopy. Applied Physics B 67, 297–305 (1998).

- [17]. P. A. Martin. Near-infrared diode laser spectroscopy in chemical process and environmental air monitoring. Chemical Society Reviews 31, 201– 210 (2002).
- [18]. M. G. Allen. Diode laser absorption sensors for gas-dynamic and combustion flows. Measurement Science & Technology 9, 545–562 (1998).
- [19]. A. Fried and D. Richter. Infrared Absorption Spectroscopy. In D. E. Heard, editor, Analytical Techniques for Atmospheric Measurement Wiley-Blackwell (2007).
- [20]. H. I. Schiff, G. I. Mackay and J. Bechara. The use of tunable diode laser absorption spectroscopy for atmospheric measurements. Research on Chemical Intermediates 20, 525–556 (1994).
- [21]. A. W. Mantz. A review of the applications of tunable diode-laser spectroscopy at high-sensitivity. Microchemical Journal 50, 351–364 (1994).
- [22]. K. Song and E. C. Jung. Recent developments in modulation spectroscopy for trace gas detection using tunable diode lasers. Applied Spectroscopy Reviews 38, 395–432 (2003).
- [23]. J. Wang. New strategies of diode laser absorption sensors. Technical Report TSD-141 Department of Mechanical Engineering, Stanford University (2001).
- [24]. P. Werle. A review of recent advances in semiconductor laser based gas monitors. Spectrochimica Acta Part A 54, 197–236 (1998).
- [25]. P. W. Werle, P. Mazzinghi, F. D'Amato, M. De Rosa, K. Maurer and F. Slemr. Signal processing and calibration procedures for in situ diodelaser absorption spectroscopy. Spectrochimica Acta Part A 60, 1685– 1705 (2004).
- [26]. P. Werle, F. Slemr, K. Maurer, R. Kormann, R. Mücke and B. Jänker. Near- and mid-infrared laser-optical sensors for gas analysis. Optics and Lasers in Engineering 37, 101–114 (2002).
- [27]. M. G. Allen, K. L. Carleton, S. J. Davis, W. J. Kessler, C. E. Otis, D. A. Palombo and D. M. Sonnenfroh. Ultrasensitive dual-beam absorption and gain spectroscopy - applications for near-infrared and visible diodelaser sensors. Applied Optics 34, 3240–3249 (1995).
- [28]. P. Weibring, D. Richter, J. G. Walega and A. Fried. First demonstration of a high performance difference frequency spectrometer on airborne platforms. Optics Express 15, 13476–13495 (2007).
- [29]. D. Richter and P. Weibring. Ultra-high precision mid-IR spectrometer I: Design and analysis of an optical fiber pumped difference-frequency generation source. Applied Physics B 82, 479–486 (2006).
- [30]. P. Weibring, D. Richter, A. Fried, J. G. Walega and C. Dyroff. Ultrahigh-precision mid-IR spectrometer II: system description and spectroscopic performance. Applied Physics B 85, 207–218 (2006).
- [31]. R. T. Ku, E. D. Hinkley and J. O. Sample. Long-path monitoring of atmospheric carbon-monoxide with a tunable diode laser system. Applied Optics 14, 854–861 (1975).
- [32]. Y. Gerard, R. J. Holdsworth and P. A. Martin. Multispecies in situ monitoring of a static internal combustion engine by near-infrared diode laser sensors. Applied Optics 46, 3937–3945 (2007).
- [33]. G. B. Rieker, H. Li, X. Liu, J. T. C. Liu, J. B. Jeffries, R. K. Hanson, M. G. Allen, S. D. Wehe, P. A. Mulhall, H. S. Kindle, A. Kakuho, K. R. Sholes, T. Matsuura and S. Takatani. *Rapid measurements of* temperature and H<sub>2</sub>O concentration in IC engines with a spark plugmounted diode laser sensor. Proceedings of the Combustion Institute **31**, 3041–3049 (2007).

- [34]. T. N. Anderson, R. P. Lucht, S. Priyadarsan, K. Annamalai and J. A. Caton. In situ measurements of nitric oxide in coal-combustion exhaust using a sensor based on a widely tunable external-cavity GaN diode laser. Applied Optics 46, 3946–3957 (2007).
- [35]. R. K. Hanson, P. A. Kuntz and C. H. Kruger. *High-resolution spec*troscopy of combustion gases using a tunable IR diode-laser. Applied Optics 16, 2045–2048 (1977).
- [36]. A. Lytkine, A. Lim, W. Jger and J. Tulip. Gas temperature measurements using widely tunable long-wavelength VCSEL. Applied Physics B 90, 323–327 (2008).
- [37]. W. Q. Cao and Y. X. Duan. Current status of methods and techniques for breath analysis. Critical Reviews in Analytical Chemistry 37, 3–13 (2007).
- [38]. K. D Skeldon, C. Patterson, C. A. Wyse, G. M. Gibson, M. J. Padgett, C. Longbottom and L. C. McMillan. The potential offered by real-time, high-sensitivity monitoring of ethane in breath and some pilot studies using optical spectroscopy. Journal of Optics A 7, S376–S384 (2005).
- [39]. C. Roller, K. Namjou, J. D. Jeffers, M. Camp, A. Mock, P. J. Mc-Cann and J. Grego. Nitric Oxide Breath Testing by Tunable-Diode Laser Absorption Spectroscopy: Application in Monitoring Respiratory Inflammation. Applied Optics 41, 6018–6029 (2002).
- [40]. L. G. Sandström, S. H. Lundqvist, A. B. Petterson and M. S. Shumate. Tunable diode laser spectroscopy at 1.6 and 2 μm for detection of Helicobacter pylori infection using C-13-urea breath test. IEEE Journal of Selected Topics in Quantum Electronics 5, 1040–1048 (1999).
- [41]. S. Koletzko, M. Haisch, I. Seeboth, B. Braden, K. Hengels, B. Koletzko and P. Hering. Isotope-selective nondispersive infrared spectrometry for detection of helicobacter-pylori infection with C-13-urea breath test. Lancet 345, 961–962 (1995).
- [42]. C. E. Wieman and L. Hollberg. Using diode-lasers for atomic physics. Review of Scientific Instruments 62, 1–20 (1991).
- [43]. J. C. Camparo. The diode-laser in atomic physics. Contemporary Physics 26, 443–477 (1985).
- [44]. S. Wang. Principles of distributed feedback and distributed Braggreflector lasers. IEEE Journal of Quantum Electronics QE10, 413–427 (1974).
- [45]. H. Kogelnik and C. V. Shank. Coupled-wave theory of distributed feedback lasers. Journal of Applied Physics 43, 2327–2335 (1972).
- [46]. W. Zeller, L. Naehle, P. Fuchs, F. Gerschuetz, L. Hildebrandt and J. Koeth. DFB lasers between 760 nm and 16 μm for sensing applications. Sensors 10, 2492–2510 (2010).
- [47]. K. Iga. Surface-emitting laser Its birth and generation of new optoelectronics field. IEEE Journal of Selected Topics In Quantum Electronics 6, 1201–1215 (2000).
- [48]. J. Wang, S. T. Sanders, J. B. Jeffries and R. K. Hanson. Oxygen measurements at high pressures with vertical cavity surface-emitting lasers. Applied Physics B 72, 865–872 (2001).
- [49]. P. Vogel and V. Ebert. Near shot noise detection of oxygen in the A-band with vertical-cavity surface-emitting lasers. Applied Physics B 72, 127–135 (2001).
- [50]. B. Scherer, J. Wöllenstein, M. Weidemüller, W. Salzmann, J. Ostermann, F. Rinaldi and R. Michalzik. Measurement of the pressure broadening coefficients of the oxygen A-band using a low cost, polarization stabilized, widely tunable vertical-cavity surface-emitting laser. Microsystem Technologies 14, 607–614 (2008).

- [51]. J. M. Ostermann, F. Rinaldi, P. Debernardi and R. Michalzik. VCSELs with enhanced single-mode power and stabilized polarization for oxygen sensing. IEEE Photonics Technology Letters 17, 2256–2258 (2005).
- [52]. D. C. Hovde and C. A. Parsons. Wavelength modulation detection of water vapor with a vertical cavity surface-emitting laser. Applied Optics 36, 1135–1138 (1997).
- [53]. J. Chen, A. Hangauer, R. Strzoda and M. C. Amann. Experimental characterization of the frequency modulation behavior of vertical cavity surface emitting lasers. Applied Physics Letters 91, 141105 (2007).
- [54]. V. Weldon, J. O'Gorman, J. J. PerezCamacho, D. McDonald, J. Hegarty, J. C. Connolly, N. A. Morris, R. U. Martinelli and J. H. Abeles. Laser diode based oxygen sensing: A comparison of VCSEL and DFB laser diodes emitting in the 762 nm region. Infrared Physics & Technology 38, 325–329 (1997).
- [55]. F. Koyama. Recent advances of VCSEL photonics. Journal of Lightwave Technology 24, 4502–4513 (2006).
- [56]. A. Hangauer, J. Chen, R. Strzoda, M. Ortsiefer and M. C. Amann. Wavelength modulation spectroscopy with a widely tunable InP-based 2.3 μm vertical-cavity surface-emitting laser. Optics Letters 33, 1566– 1568 (2008).
- [57]. V. Weldon, D. McInerney, R. Phelan, M. Lynch and J. Donegan. Characteristics of several NIR tuneable diode lasers for spectroscopic based gas sensing: A comparison. Spectrochimica Acta Part A 63, 1013–1020 (2006).
- [58]. V. Jayaraman, Z. M. Chuang and L. A. Coldren. Theory, design, and performance of extended tuning range semiconductor-lasers with sampled gratings. IEEE Journal of Quantum Electronics 29, 1824–1834 (1993).
- [59]. T. L. Koch and U. Koren. Semiconductor-lasers for coherent optical fiber communications. Journal of Lightwave Technology 8, 274–293 (1990).
- [60]. B. G. Lee, M. A. Belkin, R. Audet, J. MacArthur, L. Diehl et al. Widely tunable single-mode quantum cascade laser source for midinfrared spectroscopy. Applied Physics Letters 91, 231101 (2007).
- [61]. M. Lackner, M. Schwarzott, F. Winter, B. Kogel, S. Jatta, H. Halbritter and P. Meissner. CO and CO<sub>2</sub> spectroscopy using a 60 nm broadband tunable MEMS-VCSEL at similar to 1.55 μm. Optics Letters 31, 3170-3172 (2006).
- [62]. W. Zeller, M. Legge, J. Seufert, R. Werner, M. Fischer and J. Koeth. Widely tunable laterally coupled distributed feedback laser diodes for multispecies gas analysis based on InAs/InGaAs quantum-dash material. Applied Optics 48, B51–B56 (2009).
- [63]. P. C. D. Hobbs. Building Electro-Optical Systems Making it All Work. John Wiley & Sons (2000).
- [64]. D. Herriott, R. Kompfner and H. Kogelnik. Off-axis paths in spherical mirror interferometers. Applied Optics 3, 523–526 (1964).
- [65]. J.A. Silver. Simple dense-pattern optical multipass cells. Applied Optics 44, 6545–6556 (2005).
- [66]. J. U. White. Long optical paths of large aperture. Journal of the Optical Society of America 32, 285–285 (1942).
- [67]. J. A. Silver and A. C. Stanton. Optical interference fringe reduction in laser-absorption experiments. Applied Optics 27, 1914–1916 (1988).
- [68]. D. Masiyano, J. Hodgkinson, S. Schilt and R. P. Tatam. Self-mixing interference effects in tunable diode laser absorption spectroscopy. Applied Physics B 96, 863–874 (2009).

- [69]. D. S. Bomse, Stanton A. C. and J. A. Silver. Frequency modulation and wavelength modulation spectroscopies: comparison experimental methods using a lead-salt diode laser. Applied Optics 31, 718–731 (1992).
- [70]. C. D. Mansfield and H. N. Rutt. Evaluation of multiple beam interference effects in infrared gas spectroscopy. Measurement Science & Technology 10, 206–210 (1999).
- [71]. J. Hodgkinson, D. Masiyano and R. Tatam. Gas cells for tunable diode laser absorption spectroscopy employing optical diffusers. Part 1: single and dual pass cells. Applied Physics B 100, 291–302 (2010).
- [72]. J. Reid, M. Elsherbiny, B.K. Garside and E.A. Ballik. Sensitivity limits of a tunable diode-laser spectrometer, with application to the detection of NO<sub>2</sub> at the 100-ppt level. Applied Optics 19, 3349–3354 (1980).
- [73]. N. Y. Chou, G. W. Sachse, L. G. Wang and T. F. Gallagher. Optical fringe reduction technique for FM spectroscopy laser spectroscopy. Applied Optics 28, 4973–4975 (1989).
- [74]. H. C. Sun and E. A. Whittaker. Novel etalon fringe rejection technique for laser-absorption spectroscopy. Applied Optics 31, 4998–5002 (1992).
- [75]. J. Chen, A. Hangauer, R. Strzoda and M. C. Amann. Tunable diode laser spectroscopy with optimum wavelength scanning. Applied Physics B 100, 331–339 (2010).
- [76]. C. B. Carlisle, D. E. Cooper and H. Preier. Quantum noise-limited FM spectroscopy spectroscopy with a lead-salt diode-laser. Applied Optics 28, 2567–2576 (1989).
- [77]. C. B. Carlisle and D. E. Cooper. Tunable-diode-laser frequencymodulation spectroscopy using balanced homodyne detection. Optics Letters 14, 1306–1308 (1989).
- [78]. L. Persson, F. Andersson, M. Andersson and S. Svanberg. Approach to optical interference fringes reduction in diode laser absorption spectroscopy. Applied Physics B 87, 523–530 (2007).
- [79]. C. R. Webster. Brewster-plate spoiler a novel method for reducing the amplitude of interference-fringes that limit tunable-laser absorption sensitivities. Journal of the Optical Society of America B 2, 1464–1470 (1985).
- [80]. V. V. Liger. Optical fringes reduction in ultrasensitive diode laser absorption spectroscopy. Spectrochimica Acta Part A 55, 2021–2026 (1999).
- [81]. A. Fried, J. R. Drummond, B. Henry and J. Fox. Reduction of interference-fringes in small multipass absorption cells by pressure modulation. Applied Optics 29, 900–902 (1990).
- [82]. S. So, E. Jeng and G. Wysocki. VCSEL based Faraday rotation spectroscopy with a modulated and static magnetic field for trace molecular oxygen detection. Applied Physics B DOI: 10.1007/s00340-010-4002-1 (2010).
- [83]. C. Dyroff, P. Weibring, A. Fried, D. Richter, J. G. Walega, A. Zahn, W. Freude and P. Werle. *Stark-enhanced diode-laser spectroscopy of* formaldehyde using a modified Herriott-type multipass cell. Applied Physics B 88, 117–123 (2007).
- [84]. P. Werle and S. Lechner. Stark-modulation-enhanced FM-spectroscopy. Spectrochimica Acta Part A 55, 1941–1955 (1999).
- [85]. A. N. Dharamsi, P. C. Shea and A. M. Bullock. Reduction of effects of Fabry-Perot fringing in wavelength modulation experiments. Applied Physics Letters 72, 3118–3120 (1998).
- [86]. J. Gustafsson, N. Chekalin and O. Axner. Improved detectability of wavelength modulation diode laser absorption spectrometry applied to window-equipped graphite furnaces by 4th and 6th harmonic detection.

Spectrochimica Acta Part B 58, 111-122 (2003).

- [87]. P. Kluczynski and O. Axner. Theoretical description based on Fourier analysis of wavelength-modulation spectrometry in terms of analytical and background signals. Applied Optics 38, 5803–5815 (1999).
- [88]. O. E. Myers and E. J. Putzer. Measurement broadening in magnetic resonance. Journal of Applied Physics 30, 1987–1991 (1959).
- [89]. M. L. Olson, D. L. Grieble and P. R. Griffiths. Second derivative tunable diode laser spectrometry for line profile determination I. Theory. Applied Spectroscopy 34, 50–56 (1980).
- [90]. G. V. H. Wilson. Modulation broadening of NMR and ESR line shapes. Journal of Applied Physics 34, 3276–3285 (1963).
- [91]. J. Reid and D. Labrie. 2nd-harmonic detection with tunable diodelasers - comparison of experiment and theory. Applied Physics B 26, 203–210 (1981).
- [92]. R. Arndt. Analytical line shapes for Lorentzian signals broadened by modulation. Journal of Applied Physics 36, 2522–2524 (1965).
- [93]. L. C. Philippe and R. K. Hanson. Laser-diode wavelength-modulation spectroscopy for simultaneous measurement of temperature, pressure, and velocity in shock-heated oxygen flows. Applied Optics 32, 6090– 6103 (1993).
- [94]. S. Schilt, L. Thevenaz and P. Robert. Wavelength modulation spectroscopy: combined frequency and intensity laser modulation. Applied Optics 42, 6728–6738 (2003).
- [95]. J. A. Silver. Frequency-modulation spectroscopy for trace species detection: theory and comparison among experimental methods. Applied Optics 31, 707–717 (1992).
- [96]. J. M. Supplee, E. A. Whittaker and W. Lenth. Theoretical description of frequency-modulation and wavelength modulation spectroscopy. Applid Optics 33, 6294–6302 (1994).
- [97]. X. Zhu and D. T. Cassidy. Modulation spectroscopy with a semiconductor diode laser by injection-current modulation. Journal of the Optical Society of America B 14, 1945–1950 (1997).
- [98]. T. Fernholz, H. Teichert and V. Ebert. Digital, phase-sensitive detection for in situ diode-laser spectroscopy under rapidly changing transmission conditions. Applied Physics B 75, 229–236 (2002).
- [99]. K. Duffin, A. J. McGettrick, W. Johnstone, G. Stewart and D. G. Moodie. Tunable diode-laser spectroscopy with wavelength modulation: A calibration-free approach to the recovery of absolute gas absorption line shapes. Journal of Lightwave Technology 25, 3114–3125 (2007).
- [100]. A. J. McGettrick, K. Duffin, W. Johnstone, G. Stewart and D. G. Moodie. Tunable diode laser spectroscopy with wavelength modulation: A phasor decomposition method for calibration-free measurements of gas concentration and pressure. Journal Of Lightwave Technology 26, 432–440 (2008).
- [101]. J. C. Schotland. Continuous-wave diffusion imaging. Journal Of The Optical Society of America A 14, 275–279 (1997).
- [102]. D. H. Griffel. Applied Functional Analysis. Dover Publications, Inc. (2002).
- [103]. G. Marchesini, B. R. Webber, G. Abbiendi, I. G. Knowles, M. H. Seymour and L. Stanco. Herwig 5.1 - A Monte-Carlo event generator for simulating hadron emission reactions with interfering gluons. Computer Physics Communications 67, 465–508 (1992).
- [104]. A. Z. Panagiotopouloss. Direct determination of phase coexistence properties of fluids by Monte-Carlo simulation in a new ensemble.

Molecular Physics 61, 813-826 (1987).

- [105]. B. C. Wilson and G. Adam. A Monte-Carlo model for the absorption and flux distributions of light in tissue. Medical Physics 10, 824–830 (1983).
- [106]. E. Alerstam, W. C. Y. Lo, T. D. Han, J. Rose, S. Andersson-Engels and L. Lilge. Next-generation acceleration and code optimization for light transport in turbid media using GPUs. Biomedical Optics Express 1, 658–675 (2010).
- [107]. Erik Alerstam, Tomas Svensson and Stefan Andersson-Engels. Parallel computing with graphics processing units for high speed Monte Carlo simulation of photon migration. Journal of Biomedical Optics Letters 13, 060504 (2008).
- [108]. L. H. Wang, S. L. Jacques and L. Q. Zheng. MCML Monte Carlo modeling of light transport in multilayered tissues. Computer Methods and Programs in Biomedicin 47, 131–146 (1995).
- [109]. G. Strang and G J Fix. An Analysis of the Finite Element Method. Prentice-Hall (1973).
- [110]. E. Alerstam, S. Andersson-Engels and T. Svensson. White Monte Carlo for time-resolved photon migration. Journal of Biomedical Optics 13, 041304 (2008).
- [111]. J. Swartling, J. S. Dam and S. Andersson-Engels. Comparison of spatially and temporally resolved diffuse-reflectance measurement systems for determination of biomedical optical properties. Applied Optics 42, 4612–4620 (2003).
- [112]. A. Kienle, L. Lilge, M. S. Patterson, R. Hibst, R. Steiner and B. C. Wilson. Spatially resolved absolute diffuse reflectance measurements for noninvasive determination of the optical scattering and absorption coefficients of biological tissue. Applied Optics 35, 2304–2314 (1996).
- [113]. A. Torricelli, A. Pifferi, P. Taroni, E. Giambattistelli and R. Cubeddu. In vivo optical characterization of human tissues from 610 to 1010 nm by time-resolved reflectance spectroscopy. Physics in Medicine and Biology 46, 2227–2237 (2001).
- [114]. S. J. Matcher, M. Cope and D. T. Delpy. In vivo measurements of the wavelength dependence of tissue-scattering coefficients between 760 and 900 nm measured with time-resolved spectroscopy. Applied Optics 36, 386–396 (1997).
- [115]. F. Bevilacqua, D. Piguet, P. Marquet, J. D. Gross, B. J. Tromberg and C. Depeursinge. In vivo local determination of tissue optical properties: applications to human brain. Applied Optics 38, 4939–4950 (1999).
- [116]. G. Somesfalean, M. Sjöholm, J. Alnis, C. af Klinteberg, S. Andersson-Engels and S. Svanberg. Concentration measurement of gas embedded in scattering media by employing absorption and time-resolved laser spectroscopy. Applied Optics 41, 3538–3544 (2002).
- [117]. T. Svensson. Pharmaceutical and Biomedical Applications of Spectroscopy in the Photon Migration Regime. PhD thesis, Lund University, Lund Reports on Atomic Physics, LRAP 392 (2008).
- [118]. Gustav Mie. Beiträge zur optik trüber medien, speziell kolloidaler metallösungen. Annals of Physics 330, 377–445 (1908).
- [119]. J. M. Schmitt and G. Kumar. Optical scattering properties of soft tissue: a discrete particle model. Applied Optics 37, 2788–2797 (1998).
- [120]. V. Tuchin. Tissue Optics. SPIE Press (2007).
- [121]. T. Svensson and Z. J. Shen. Laser spectroscopy of gas confined in nanoporous materials. Applied Physics Letters 96 (2010).
- [122]. M. Sjöholm, G. Somesfalean, J. Alnis, S. Andersson-Engels and S. Svan-

berg. Analysis of gas dispersed in scattering media. Optics Letters **26**, 16–18 (2001).

- [123]. T. Svensson, L. Persson, M. Andersson, S. Svanberg, S. Andersson-Engels, J. Johansson and S. Folestad. Noninvasive characterization of pharmaceutical solids by diode laser oxygen spectroscopy. Applied Spectroscopy 61, 784–786 (2007).
- [124]. J. Alnis, B. Anderson, M. Sjöholm, G. Somesfalean and S. Svanberg. Laser spectroscopy of free molecular oxygen dispersed in wood materials. Applied Physics B 77, 691–695 (2003).
- [125]. M. Andersson, L. Persson, T. Svensson and S. Svanberg. Flexible lock-in detection system based on synchronized computer plug-in boards applied in sensitive gas spectroscopy. Review of Scientific Instruments 78, 113107 (2007).
- [126]. L. Persson, B. Anderson, M. Andersson, M. Sjöholm and S. Svanberg. Studies of gas exchange in fruits using laser spectroscopic techniques. In Proceedings of FRUTIC 05: Information and technology for sustainable fruit and vegetable production (2005).
- [127]. L. Persson, H. Gao, M. Sjöholm and S. Svanberg. Diode laser absorption spectroscopy for studies of gas exchange in fruits. Optics and Lasers in Engineering 44, 687–698 (2006).
- [128]. L. Persson, K. Svanberg and S. Svanberg. On the potential of human sinus cavity diagnostics using diode laser gas spectroscopy. Applied Physics B 82, 313–317 (2006).
- [129]. T. Svensson, M. Andersson, L. Rippe, S. Svanberg, S. Andersson-Engels, J. Johansson and S. Folestad. VCSEL-based oxygen spectroscopy for structural analysis of pharmaceutical solids. Applied Physics B 90, 345–354 (2008).
- [130]. A. L. Buck. New equations for computing vapor-pressure and enhancement factor. Journal of Applied Meteorology 20, 1527–1532 (1981).
- [131]. T. Svensson, M. Andersson, L. Rippe, J. Johansson, S. Folestad and Andersson-Engels S. *High sensitivity gas spectroscopy of porous, highly scattering solids.* Optics Letters **33**, 80–82 (2008).
- [132]. M. Andersson, L. Persson, M. Sjöholm and S. Svanberg. Spectroscopic studies of wood-drying processes. Optics Express 14, 3641–3653 (2006).
- [133]. L. Persson, E. Kristensson, L. Simonsson and S. Svanberg. Monte Carlo simulations related to gas-based optical diagnosis of human sinusitis. Journal of Biomedical Optics 12, 054002 (2007).
- [134]. P. Elterman. Integrating cavity spectroscopy. Applied Optics 9, 2140– 2142 (1970).
- [135]. R. M. Abdullin and A. V. Lebedev. Use of an integrating sphere as a multipass optical-cell. Soviet Journal of Optical Technology 55, 139–141 (1988).
- [136]. S. Tranchart, I.H. Bachir and J.L. Destombes. Sensitive trace gas detection with near-infrared laser diodes and an integrating sphere. Applied Optics 35, 7070–7074 (1996).
- [137]. J. Hodgkinson, D. Masiyano and R. P. Tatam. Using integrating spheres as absorption cells: path-length distribution and application of Beer's law. Applied Optics 48, 5748–5758 (2009).
- [138]. E. Hawe, P. Chambers, C. Fitzpatrick and E. Lewis. CO<sub>2</sub> monitoring and detection using an integrating sphere as a multipass absorption cell. Measurement Science & Technology 18, 3187–3194 (2007).
- [139]. E. S. Fry, G. W. Kattawar, B. D. Strycker and P. W. Zhai. Equivalent path lengths in an integrating cavity: comment. Applied Optics 49, 575–577 (2010).

- [140]. J. T. O. Kirk. Modeling the performance of an integrating-cavity absorption meter: theory and calculations for a spherical cavity. Applied Optics 34, 4397–4408 (1995).
- [141]. T. Iseki, H. Tai and K. Kimura. A portable remote methane sensor using a tunable diode laser. Measurement Science & Technology 11, 594–602 (2000).
- [142]. J. Chen, A. Hangauer, R. Strzoda and M. C. Amann. Laser spectroscopic oxygen sensor using diffuse reflector based optical cell and advanced signal processing. Applied Physics B 100, 417–425 (2010).
- [143]. D. Masiyano, J. Hodgkinson and R. P. Tatam. Use of diffuse reflections in tunable diode laser absorption spectroscopy: implications of laser speckle for gas absorption measurements. Applied Physics B 90, 279– 288 (2008).
- [144]. J. Pukite, S. Kuhl, T. Deutschmann, U. Platt and T. Wagner. Accounting for the effect of horizontal gradients in limb measurements of scattered sunlight. Atmospheric Chemistry and Physics 8, 3045–3060 (2008).
- [145]. T. Wagner, F. Erle, L. Marquard, C. Otten, K. Pfeilsticker, T. Senne, J. Stutz and U. Platt. *Cloudy sky optical paths as derived from differential optical absorption spectroscopy observations*. Journal of Geophysical Research-atmospheres **103**, 25307–25321 (1998).
- [146]. Yu. Ponomarev, T. Petrova, A. Solodov, A. Solodov and A. Danilyuk. Experimental study by the IR spectroscopy method of the interaction between ethylene and nanopores of various densities. Atmospheric and Oceanic Optics 23, 266–269 (2010). 10.1134/S1024856010040044.
- [147]. S. Svanberg. Gas in scattering media absorption spectroscopy-GASMAS. In Proceedings of SPIE vol. 7142 (2008).
- [148]. S. Svanberg. Optical analysis of trapped Gas Gas in Scattering Media Absorption Spectroscopy. Laser Physics 20, 68–77 (2010).
- [149]. M. R. Baroni L. Torri, B. Baroni. Modified Atmosphere. Artek snc (2009).
- [150]. J. Farber, L. Harris, M. Parish, L. Beuchat, T. Suslow, J. Gorney, E. Garrett and F. Busta. *Microbiological sfety of controlled and modified atmosphere packaging of fresh and fresh-cut produce*. Comprehensive Reviews in Food Science and Food Safety 2, 142–160 (2003).
- [151]. C. A. Phillips. Review: Modified atmosphere packaging and its effects on the microbiological quality and safety of produce. International Journal of Food Science & Technology **31**, 463–479 (1996).
- [152]. I. J. Church and A. L. Parsons. Modified atmosphere packaging technology - A review. Journal of the Science of Food and Agriculture 67, 143–152 (1995).
- [153]. A. C. Templeton, Y. R. Han, R. Mahajan, R. T. Chern and A. R. Reed. Rapid headspace oxygen analysis for pharmaceutical packaging applications. Journal of Pharmacy Technology 26, 44–61 (2002).
- [154]. M. Cocola, I. Fedel and G. Tondello. A new device for the measurement of gaseous oxygen in closed containers. In Proceedings of the 3rd international Multi-conference on Engineering and Technological Innovation (2010).
- [155]. J. M. Cook, R. L. Karelitz and D. E. Dalsis. Measurement of oxygen, nitrogen, and carbon-dioxide in beverage headspace. Journal of Chromatographic Science 23, 57–63 (1985).
- [156]. B. Johnson. Headspace analysis and shelf life. Cereal Foods World 42, 752-754 (1997).
- [157]. Dmitri B. Papkovsky. Sensors for Food Safety and Security. In F. Baldini, A. N. Chester, J. Homola and S. Martellucci, editors, Optical

Chemical Sensors vol. 224 of NATO Science Series II: Mathematics, Physics and Chemistry pp 501–514. Springer Netherlands (2006). URL http://dx.doi.org/10.1007/1-4020-4611-1\_24.

- [158]. M. Smolander, E. Hurme and R. Ahvenainen. Leak indicators for modified-atmosphere packages. Trends In Food Science & Technology 8, 101–106 (1997).
- [159]. G. M. Hale and M. R. Querry. Optical-constants of water in 200-nm to 200-µm wavelength region. Applied Optics 12, 555–563 (1973).
- [160]. S. Prahl. Tabulated Molar Extinction Coefficient for Hemoglobin in Water (2010). URL http://omlc.ogi.edu/spectra/hemoglobin/ summary.html.
- [161]. L. Persson, M. Andersson, T. Svensson, M. Cassel-Engquist, K. Svanberg and S. Svanberg. Non-intrusive optical study of gas and its exchange in human maxillary sinuses. In Dietrich Schweitzer and Maryann Fitzmaurice, editors, Proceedings of SPIE: Diagnostic Optical Spectroscopy in Biomedicine IV. SPIE vol. 6628 (2007).
- [162]. L. Persson. Laser Spectroscopy in Scattering Media for Biological and Medical Applications. PhD thesis, Lund University, Lund Reports on Atomic Physics, LRAP 385 (2007).
- [163]. W. Abuzaid and E. R. Thaler. Etiology and Impact of Rhinosinusitis, In Rhinosinusitis. Springer (2008).
- [164]. D. C. Lanza and D. W. Kennedy. Adult rhinosinusitis defined. Otolaryngology-Head & Neck Surgery 117, S1–S7 (1997).
- [165]. J. A. Eloy and S. Govindaraj. Microbiology and Immunology of Rhinosinusitis, In Rhinosinusitis. Springer (2008).
- [166]. V. K. Anand. Epidemiology and economic impact of rhinosinusitis. Annals of Otology Rhinology and Laryngology 113, 3–5 (2004).
- [167]. D. W. Kennedy and E. R. Thaler, editor. *Rhinosinusitis*. Springer (2008).
- [168]. M. Lindbaek and P. Hjortdahl. The clinical diagnosis of acute purulent sinusitis in general practice - a review. British Journal of General Practice 52, 491–495 (2002).
- [169]. R. Tahamiler, S. Canakcioglu, S. Ogreden and E. Acioglu. *The accuracy of symptom-based definition of chronic rhinosinusitis*. Allergy **62**, 1029–1032 (2007).
- [170]. K. A. Kölln and B. A. Senior. Diagnosis and Management of Acute Rhinosinusitis, In Rhinosinusitis. Springer (2008).
- [171]. T. Puhakka, T. Heikkinen, M. J. Makela, A. Alanen, T. Kallio, L. Korsoff, J. Suonpaa and O. Ruuskanen. Validity of ultrasonography in diagnosis of acute maxillary sinusitis. Archives of Otolaryngology-Head & Neck Surgery 126, 1482–1486 (2000).
- [172]. C. Bachert, K. Hormann, R. Mosges, G. Rasp, H. Riechelmann, R. Muller, H. Luckhaupt, B. A. Stuck and C. Rudack. An update on the diagnosis and treatment of sinusitis and nasal polyposis. Allergy 58, 176–191 (2003).
- [173]. V. J. Lund and I. S. Mackay. Staging in rhinosinusitus. Rhinology (Utrecht) **31**, 183–184 (1993).
- [174]. Wikipedia. Mastoid part of the temporal bone (2010). URL http: //en.wikipedia.org/wiki/Mastoid\_part\_of\_the\_temporal\_bone.
- [175]. L. Corbeel. What is new in otitis media? European Journal of Pediatrics 166, 511–519 (2007).
- [176]. J. Spratley, H. Silveira, I. Alvarez and M. Pais-Clemente. Acute mastoiditis in children: review of the current status. International Journal of Pediatric Otorhinolaryngology 56, 33–40 (2000).

- [177]. C. D. Bluestone and J. O. Klein. Otitis Media in Infants and Children. BC Decker Inc. (2007).
- [178]. D. Zanetti and N. Nassif. Indications for surgery in acute mastoiditis and their complications in children. International Journal of Pediatric Otorhinolaryngology 70, 1175–1182 (2006).
- [179]. L. Hergils and B. Magnuson. Human middle ear gas composition studied by mass spectrometry. Acta oto-laryngologica 110, 92–99 (1990).
- [180]. M. M. Slattery and J. J. Morrison. Preterm delivery. The Lancet 360, 1489 – 1497 (2002).
- [181]. R. L. Goldenberg, J. F. Culhane, J. D. Iams and R. Romero. *Epidemi-ology and causes of preterm birth*. The Lancet **371**, 75 84 (2008).
- [182]. W. M. Gilbert, T. S. Nesbitt and B. Danielsen. The cost of prematurity: quantification by gestational age and birth weight. Obstetrics & Gynecology 102, 488 - 492 (2003).
- [183]. L. B. Ware and M. A. Matthay. Medical progress The acute respiratory distress syndrome. New England Journal of Medicine 342, 1334–1349 (2000).
- [184]. M. van Veenendaal, M. Miedema, F. de Jongh, J. van der Lee, I. Frerichs and A. van Kaam. Effect of closed endotracheal suction in high-frequency ventilated premature infants measured with electrical impedance tomography. Intensive Care Medicine 35, 2130–2134 (2009).
- [185]. A. Bruzelius. Sensing of Free Gas in Human Tissue with Diode Laser Spectrscopy - Application to Lung Monitoring in Premature Neonates. MSc Thesis, Lund University, Lund Reports on Atomic Physics, LRAP 420 (2010).