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1 Introduction

This booklet is intended as an introduction to the field of tunable diode laser spectroscopy (TDLS) and its applications for different analytical tasks. A special emphasis is placed on process analytics and the requirements of different measurement environments. The text assumes a recognition of the special problems in applying measurement instruments in an industrial environment.

1.1 Background, history

In the middle of the 19th century, spectral analysis was developed by Gustav Kirchhoff and Robert Bunsen. Optical spectroscopy originated through the study of visible light dispersed according to its wavelength by a prism. Since then, spectroscopic methods have played an important role in the study of chemical and physical processes in the atmosphere.

The ozone layer was discovered using optical spectral analysis
UV absorption of ozone was discovered
Methane and carbon monoxide in the atmosphere was studied
Spectral analysis was developed by Gustav Kirchhoff and Robert Bunsen
The semiconductor laser was developed

Figure 1 History of optical spectral analysis

The UV absorption of ozone was first discovered around 1880 and in 1926 the ozone layer was discovered using optical spectral analysis. Methane and carbon monoxide in the atmosphere was first studied by optical spectroscopy in 1949. Many important gases have absorption in the infrared (IR) and near infrared (NIR) spectral regions. The absorption lines of gases at atmospheric pressure are narrow so by using highly monochromatic light, such as that emitted from a laser, it is possible to probe these lines individually and perform very selective measurements.
Soon after the first semiconductor diode laser was developed in 1962 by US groups at the General Electric Research Center and at the IBM T.J. Watson Research Center, diode laser spectroscopy began to be used for the detection, identification, and measurement of molecular and atomic species in the gas phase. The applications of diode lasers to spectroscopy have rapidly grown as the quality and variety of diode lasers available has increased. Initially, there was a drive from the research community to explore these lasers in atmospheric and earth sciences.

The first semiconductor lasers for spectroscopy were made of lead salts and had to be cooled to liquid helium temperatures. The first use of these lasers for atmospheric sensing was made in 1976 by Hinkley [Ref. 1]. In the following years there was a rapid progress in laser quality and in 1983 TDLS was used for sensing of trace gases in the stratosphere [Ref. 2]. From the late 1980’s the telecom industry made huge investments in the development of semiconductor lasers covering the wavelength range 1300 nm – 1650 nm for use in fiber optic systems. The drive to use the existing fiber optic network to carry an increased amount of data stimulated the development of the optical wavelength-division multiplexing (WDM) technique, where the data traffic is carried over several spectral channels.

The advent of the room temperature vertical cavity surface emitting laser (VCSEL) in 1988 offered a viable source for sensing at the shorter wavelengths, most notably oxygen in the 760 nm region. Due to their high quality standards, room temperature operation and stable operating characteristics these lasers were very well suited for the application of TDL in process analytical instruments that have requirements on long periods of stable and unattended operation. As shown in figure 2, the gradual maturity of the technology enabled the progress of TDLS technology from the science laboratories to the development of spectroscopic instrumentation for field use that can operate unattended for very long periods of time. A number of startup companies were founded in the mid-nineties for exploring various industrial applications.

The near infrared wavelength range (NIR) is suitable for measuring a number of gases such as H2O, CO, CO2, NO, HCl, all important for combustion control. However, the line strengths are generally two
orders of magnitude below the strength of the transitions in the fundamental absorption bands. However, the low noise and high quality of telecom grade lasers makes it possible to design TDLS instruments capable of detecting fractional absorption on the order of $10^{-5} - 10^{-6}$ which to a large extent compensates for the low line intensities in the NIR. There is large potential for improving performance of existing measurement applications and creating new applications for TDL instrumentation by going to longer wavelengths. Moreover, several important gases such as sulfur dioxide have no suitable absorption bands at all in the NIR but can be measured in the mid-infrared (MIR). Today, there are many, more or less exotic, laser types covering the entire MIR wavelength range (3 – 10 µm). However, for commercial instruments that require 24/7 operation with minimum maintenance for extended periods of time, the main contender is the semiconductor laser and the extension of this technology to new wavelength ranges as shown in Figure 2.

![Wavelength regions for room temperature TDLs](image)

Figure 2  Wavelength regions for room temperature TDLs

During the last decade, the progress in diode laser fabrication, exploring new semiconductor material systems such as gallium antimonide (GaSb) has extended the wavelength range of commercial TDL instrumentation to 2.9 µm where several important gases such as CO, CO$_2$, CH$_4$ and NH$_3$ are accessible in regions reasonably free of water interference. For wavelengths longer than 2.9 µm there is still a lack of viable room temperature single mode lasers suitable for TDLS instrumentation. For wavelengths in the range ~4.3 µm to ~12.5 µm CW room temperature quantum cascade (QC) DFB lasers are commercially available. The market penetration for diode laser instruments for
process monitoring applications utilizing QC lasers is still, however, in its infancy. Considerable research efforts are also underway in several laboratories to develop semiconductor lasers that operate in the 3-4 µm emission wavelength range, as this will enable detection of hydrocarbons using diode laser spectroscopy.

Diode lasers, for which the emission wavelength is determined by the inherent bandgap energy of the optically active material, are extending their wavelength range for room temperature single-mode operation beyond 3 µm, enabling high sensitivity detection of several important hydrocarbons. The GaSb-based inter-band cascade laser (ICL) has a large potential to cover the spectral region from 3.5 µm up to the wavelengths where commercial QC lasers are readily available. This will fill the present day gap in the wavelength coverage and enable the use of TDLS in the entire infrared wavelength region.

1.2 Application examples

Here we present some of the most common applications for TDLs in process analytics. The first applications for TDLs were found in the power industry in emission monitoring and combustion control. Different opportunities were then found in the iron and steel industry. Most recently, TDL analyzers have been introduced for different applications in the chemical industry. The application areas can be divided into combustion, environment, process and safety, and storage and transportation.

TDL applications in municipal waste incinerators

A municipal waste incinerator (MWI) offers a multitude of opportunities for TDL analyzers. The potential to increase the efficiency and reduce the maintenance of the plant has made the TDL the de facto standard in this industry. Figure 3 shows a schematic view of an MWI and the measuring points where the TDL has proven to be the preferred technology.
In an MWI, mixed waste is incinerated and the energy generated is used for district heating or generation of electrical power. The varying humidity of the fuel burned makes it important to have real-time monitoring of the water vapor in the furnace as shown in the figure above. A very important factor when optimizing a combustion process is the amount of excess air in the combustion zone, which is why it is important to monitor the residual oxygen concentration in the flue gas. The combustion is efficient if the fuel is burnt out to a very high extent. If too much air is fed into the combustion zone, unnecessary cooling occurs and the power generated will be lower. Excess air is also connected with increased NO$_x$ emissions. If, on the other hand, the plant is operated under conditions of an oxygen shortage, an increase of CO emissions will occur. For these reasons, optimizing and continuously monitoring the amount of excess air is important for keeping the combustion process optimal.

In situ measurements of the oxygen concentration directly in the hot combustion zone using a TDL analyzer have proven to be very useful for optimizing the combustion process. This is also today one of the
largest application for TDL analyzers in the power industry and the technology is rapidly replacing the zirconia oxide (ZrO₂) probes used earlier. Figure 4 show a comparative measurement between a TDL measurement and the oxygen value given by the ZrO₂ used by the plant [Ref. 3].

![Figure 4](image)

Vergleich der O₂-Betriebsmessung mit der NIR-Messung

Figure 4  Comparative measurement between a TDL instrument and a zirconia oxide probe

For removal of nitrogen oxides in the flue gas, de-nitrification reduction processes are employed. Ammonia or urea is used as a reducing agent to convert the nitrogen oxides to nitrogen and water. The ammonia is fed via spray nozzles to the gas flow and the amount of NH₃ must be continuously adjusted to the current NO content in the combustion. The amount of NH₃ must be large enough to allow for an efficient NOₓ reduction. However, it is important to avoid a large unused amount of NH₃ or ammonia slip downstream in the process. Excess NH₃ slip leads to salt formation which is presented as a solid accumulated on surfaces. The salt might plug parts of the catalyst, increasing the pressure drop and causing catalyst deactivation. It might also plug the air pre-heater, decreasing its efficiency. The ammonia salt will also cause corrosion when absorbing moisture from the gas. NH₃ slip monitoring is today one of the most popular applications for TDL analyzers. Ammonia is a “sticky” gas which requires heated sample lines. The in-situ monitoring capability of the TDL analyzer has resulted in more reliable and faster measurements of NH₃ slip.
Increased environmental concerns and regulatory demands have forced MWI plants to remove HCl from flue gases. To minimize HCl emissions, the flue gases are cleaned in a so-called bag house filter by using hydrated lime. The lime is injected into the gas stream and then forms a layer on the filter bags downstream, where it is continuously absorbing the HCl from the emission gas. Since the lime is consumed in this process, it has to be removed as soon as its adsorption capabilities are finished. TDL analyzers are installed to measure the concentration of HCl just before and after the bag house filter. The HCl concentration in the raw gas before the filter then controls the injection of the new or re-circulated lime, and the analyzer after the filter is used to verify the levels emitted from the plant. By in situ monitoring of the HCl concentration, the removal process is made more efficient and the consumption of lime is reduced.

**TDL applications in coal-fired power plants**

Energy consumption in the G20 increased by more than 5% in 2010. Oil and coal combined represents over 60% of the world energy supply. Coal is still, and certainly will be in the foreseeable future, one of the most important energy sources in the world, contributing about 27% of the energy supply. The average efficiency of a coal-fired power plant in converting the stored energy in coal to electricity is about 30%. Therefore, there exists a large potential for improvement using combustion optimization. In order to minimize the environmental impact there is also similar forms of flue gas treatment as can be found in an MWI plant. Figure 5 shows schematically a coal-fired power plant with some of the important measuring points for process analytics. In Table 1, the most interesting measuring points for a TDL analyzer are indicated.
**Figure 5**  Schematic view of a coal-fired power plant

**Table 1**  Measurement locations in a coal fired power plant

<table>
<thead>
<tr>
<th>MP</th>
<th>Plant location</th>
<th>Component</th>
<th>Measurement range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Coal silo</td>
<td>CO</td>
<td>0-5%</td>
</tr>
<tr>
<td>2</td>
<td>After coal mill</td>
<td>O₂</td>
<td>0-10%</td>
</tr>
<tr>
<td>3</td>
<td>Combustion chamber</td>
<td>O₂</td>
<td>0-10%</td>
</tr>
<tr>
<td>4</td>
<td>Air pre-heater</td>
<td>O₂</td>
<td>0-10%</td>
</tr>
<tr>
<td>5</td>
<td>deNOₓ stage</td>
<td>CO, O₂</td>
<td>0-500 ppm, 0-10%</td>
</tr>
</tbody>
</table>
The arguments for oxygen monitoring for combustion optimization are very similar to those for an MWI plant. Combustion is the conversion of primary chemical energy contained in the coal into heat through the process of oxidation at high temperatures. The oxygen required for the combustion is supplied as part of the combustion air that is fed to the process. In a perfect combustion the amount of oxygen supplied is just sufficient to burn all combustibles completely. In real combustion, however, an excess volume of oxygen (air) must be supplied due to insufficient mixing of fuel and oxygen. Too high an oxygen content will cause increased NO\textsubscript{x} content and energy losses through dilution with cool air. Too low an oxygen content will cause increased formation of CO. Therefore, the excess air value is an important parameter for an optimal combustion process and economic plant operation. User benefits include higher efficiency since less excess air has to be heated, leading to costs savings on electric power. Using a TDL analyzer, the oxygen concentration and the gas temperature can be derived in real time. Oxygen concentration and gas temperature are measured simultaneously in the same gas volume from the same set of absorption lines by analyzing the relative strengths of the lines (see chapter “3.3.5 Spectroscopic measurement of gas temperature” on page 56).

Monitoring of the CO levels in the coal silo and after the electrostatic filter is a safety application where the objective is to prevent self-ignition in the silo. The TDL is installed to measure the concentration of CO right inside the coal silo, enabling a very fast measurement response. Especially while the silo is filled with coal, high dust loads occur in the gas path which is why it is important to avoid absorption paths that are too long. Electrostatic filters, used for trapping of dust particles by electrostatic attraction, are very common in coal-fired power plants. Because of the high field strength, spontaneous discharges can occur in the electrostatic filters. It is important to prevent flue gases with an excess CO concentration to enter the filter, since the gas is flammable and can be ignited by electric sparks. Therefore, fast and continuous monitoring of the CO content of the flue gas upstream...
of the filter (Figure 5) is a key issue for safe filter operation. As shown in Figure 5, the coal combustion plant includes a denitrification stage very similar to the one used in a waste incinerator. However, for the larger coal combustion plants the deNO\textsubscript{x} stage uses selective catalytic reduction and the TDL application is to optimize this process measuring ammonia and humidity in the same manner as in the MWI plant. The NH\textsubscript{3} levels here are in the range 0 – 10 ppm.

**TDL applications in the metal industry**

The applications in the metal industry are characterized by very difficult installation conditions with high temperatures, high dust load and the fact that the hot gas often gives spectral interference problems.

Production of today’s many different types of steel is carried out in a series of partly alternative steps. Steel converters are used in the iron and steel industry to convert pig iron into high quality steel by removing mainly carbon and other impurities and adding special alloys. Special furnaces (converters) are used to run this process which requires the supply of energy and air or oxygen. Producing steel and metal is an energy consuming process in every step. Therefore, the potential of energy savings in combination with increased demands on quality control, reduced production time and reduction of greenhouse gas have created incentives for new methods to monitor and control the production processes. The off-gas of the process delivers key data for process optimization. In order to achieve precise measurement results and short response time it is essential that these measurements are made in situ. Below are some application examples:

**Safety application; measurement of oxygen in coke oven gas**

The most common steel making technology uses coke in a blast furnace (BF), both as a reducing agent and as a source of thermal energy. Coal is converted to coke in large coke oven batteries. The coking process consists of heating coal in the absence of air to drive off the volatile compounds. The resulting coke is a hard, but porous carbon material that is used for reducing the iron in the blast furnace. The BF process involves reduction of ore to liquid metal in the blast furnace and refining in convertor to form steel. During the operation
of coke ovens there are gases produced containing high levels of CO. This exhaust gas has a high calorific value and therefore is usually used as a combustible in a close-by power plant for energy recovery. High levels of CO, however, lead to the risk of explosion in the presence of oxygen. Therefore, the plant operator needs to measure the content of oxygen in this gas in order to be sure that it is close to zero (measurement range normally 0-2%) otherwise an explosion can occur. The gas is guided from the coke oven to the power plant in a gas pipe, which normally has an average diameter of two meters. The gas in the pipe is wet and dusty. A TDL placed in the duct will measure the O₂ level within the pipe accurately, in real time and with no drift.

Figure 6  Oxygen sensing with a TDL in a coke oven gas duct

**Process optimization by real-time monitoring of converter off-gas**
The basic oxygen furnace (BOF) is very common for making steel by blowing air or oxygen into molten iron. A vessel (converter) is first charged with molten pig iron from the blast furnace. Then a water-cooled lance is lowered into the vessel through which pure oxygen is blown into the melt at high pressure. The oxygen combines with the carbon contained in the molten iron to form gaseous CO and CO₂, which are separated from the molten metal and released from the melt as part of the off-gas. The whole process is completed in 15 to 20 minutes. Measurements in the off-gas of a converter requires that they
can be performed in very hostile environments. Heavy and varying dust loads as well as temperature variations in the range of 100-1800 °C and severe turbulence have to be considered when designing a measurement system for these applications. Their concentration levels and concentration variations over the process runtime is sometime called the melting curve and it directly reflects the de-carbonization progress and provides important information about progress and endpoint of de-carbonization. Conventional extractive analyzers have been typically used in steel mills for converter gas analysis. The TDL-based in situ analyzer has shown great potential for saving cost and energy due to the real-time control of important process parameters.

Increasing efficiency and safety in aluminum smelters
The aluminum smelting process is today well established and the same in most plants. Aluminum oxide (alumina) is dissolved in an electrolytic bath of molten cryolite (sodium aluminum fluoride) within a large carbon- or graphite-lined pot. A large electric current is passed through the electrolyte, typically 150,000 amperes. Molten aluminum is then deposited at the bottom of the pot and is subsequently siphoned off. A basic focus in the aluminum producing industry is the high energy consumption. Therefore, fluorine containing auxiliary ma-
material (cryolite) is added to the electrolytic reduction of aluminum oxide. This leads to a reduction of the melting point, but as an unwanted drawback HF-containing emissions are released. HF emissions are very problematic in terms of toxicity and are therefore subject to numerous regulations. Continuous control of the emitted HF gas is necessary to ensure safety of workers and the environment. To minimize the emissions of HF, the flue gases are cleaned in a so-called dry filter. These filters contain aluminum oxide particles which adsorb the HF on their surface. Since the adsorption capabilities are limited, the filter material has to be exchanged periodically. Optimizing the time for the exchange of filter material is crucial for process optimization, cost control and for environmental control. One challenge for the sensor design is the large magnetic fields produced by the currents.

Figure 8  TDLS in aluminum manufacturing

**TDL applications in chemical / oil & gas**

Product quality, plant safety and resource efficiency depend directly on the availability of reliable process data. For this reason, process analytics is an integral part of a modern chemical plant. Process analytical systems are needed to deliver exact data on the composition, concentration or purity of the product streams. The range of analytic equipment used includes gas chromatographs, infrared gas analyzers, and analyzers for paramagnetic measurement of oxygen. Accurate measuring results are needed in any environment, whether under
corrosive operating conditions or in hazardous areas. The implementation of TDL technology into the chemical / oil & gas industries is still in its infancy. However, in selected applications where the selectivity and short response time of the TDL is important, the technology is rapidly gaining acceptance. A few applications where TDL analyzers already have made a large impact are presented below.

Oxygen monitoring is especially important in the chemical industry. Whenever oxygen is part of a chemical reaction its concentration needs to be controlled to prevent explosive atmospheres forming. For the same reason, safety monitoring is also important in chemical storage facilities. Competing technologies such as paramagnetic sensors or ZrO$_2$ sensors have difficulties since the environment can contain a varying background of gases, often combustible, that can lead to large measurement errors. Also, the chemicals involved are often quite challenging for a sampling system.

**Oxygen in the manufacturing of propionic acid**

Propionic acid inhibits the growth of mold and some bacteria at the levels between 0.1 and 1% by weight. As a result, most propionic acid produced is consumed as a preservative for both animal feed and food for human consumption. Propionic acid is the most effective and most tested hay preservative available today. This application accounts for about half of the world production of propionic acid. Propionic acid is also useful as an intermediate in the production of other chemicals, especially polymers.

Propionic acid is manufactured by the reaction of propionaldehyde (manufactured from ethylene) and oxygen in an oxidizer. At the output of the reactor there is a mixture of hydrocarbons including propionic acid and oxygen. There is a need to measure the oxygen concentration quickly and reliably at the output of the oxidation reactor. The oxygen concentration has to be as high as possible for an efficient reaction but kept below the explosive limit of 11%.
Extractive oxygen sensors such as paramagnetic analyzers generally measure a value that is too low. The problem is that propionic acid “eats” oxygen in the sample line. This means that when the sample finally reaches the analyzer, the oxygen concentration will have decreased. Another problem is that propionic acid easily condensates and that just a drop of condensate in the sample results is a fatal error to a paramagnetic system. The accuracy and the short response time of TDL technology makes it possible to run the oxidizer with a higher oxygen concentration and still have a greater security level in the process.

**Measurement of oxygen level in a thermal oxidizer**

Thermal oxidizers (or thermal incinerators) are combustion systems that control the emissions of volatile organic compounds (VOCs). The oxidation breaks the molecular bonds of any HC to ultimately convert them into CO₂ and H₂O when the correct circumstances are created. Thermal oxidation is capable of a very high VOC destruction efficiency, but the fuel consumption and cost to heat the VOC laden process can be severe.

To ensure sufficient thermal oxidation with the lowest possible fuel consumption, it is crucial to measure and optimize the O₂ concentration. Today, paramagnetic analyzers are used; however, this technology is considered much too slow. Also, the potential presence of various unknown HCs causes interference which is difficult, if not impossible, to compensate for. In order to optimize the combustion, a TDL can be used to measure the O₂ concentration in situ, quickly and reliably on the output of the thermal oxidizer, despite the harsh conditions.
**Oxygen slip in vinyl chloride monomer plants**

Vinyl chloride monomer (VCM) is a colorless, flammable gas used as feedstock in the production of polyvinyl chloride (PVC). In the production, ethylene, chlorine and oxygen are converted into VCM and water. The three process steps involved in the manufacturing are direct chlorination, oxychlorination and EDC cracking. In direct chlorination, EDC (1,2-dichlorethane, “DC-EDC”) is formed by a highly exothermal direct chlorination reaction of ethylene and chlorine. In oxychlorination, EDC (1,2-dichlorethane, “Oxy-EDC”) and water are formed by the catalytic reaction of ethylene with hydrogen chloride and oxygen. The EDC is then cracked at high temperatures in a fuel-heated furnace. VCM and HCl are formed together with various by-products. Some EDC remains unconverted in this process and is recycled. The three process sections above are combined into one complete VCM synthesis process, in which only VCM and water are formed.

![Diagram of VCM manufacturing process]

**Figure 10  Schematic illustration of the VCM manufacturing process**

Ethylene, oxygen and hydrogen chloride are fed into a fluidized bed reactor for the oxychlorination process. In this reaction not all components are completely consumed and “oxygen-slip” will be seen at the output of the oxychlorination reactor. It is important to optimize the oxygen level for effective formation of EDC but also keep this slip below the explosion limit. In direct chlorination it is important to avoid the formation of oxygen in the chlorine line from any moisture impurities in the HCl. This a safety application where the oxygen level should be as close to zero as possible. In these applications TDLs have increased the efficiency and improved the safety of the process through their higher accuracy and faster response.
**Oxygen in flare gas**

Flare systems are used for safe disposal of waste combustibles from oil wells, refineries, and other chemical or petrochemical plants. There are two types of flares, ones that operate continuously and others that are used only in case of emergencies. Various leaks of air into the system can cause an increase in the O$_2$ concentration and possibly lead to an explosion. The O$_2$ concentration is measured in the gas stream going to the flare. Reliability is the most crucial feature required for accurate measurement, even with a varying background of HCs. A short response time will also enhance safety in the plant.

![Flare Measurement Point](image)

**Figure 11 Measurement point in flare gas measurement**

Paramagnetic O$_2$ analyzers have historically been used for this application. One problem with this technology is that the large amount of hydrocarbons interferes with the O$_2$ measurement. This interference is difficult, if not impossible to compensate for due to the large variety of hydrocarbons that can be diverted to flare depending on what is occurring in the process.

The recent progress in performance and wavelength coverage of room temperature semiconductor lasers has made it possible to detect hydrocarbons in their main absorption band. This is why the number of applications and the performance of hydrocarbon sensing in the chemical and in the oil/gas industry will increase. This will lead to a successive replacement of traditional technologies in time critical applications such as process and quality control.
Laser Spectroscopy Theory

Using a prism, white light from the sun or a light bulb can be split into all the visible colors as well as electromagnetic radiation that is invisible to the eye.

![Electromagnetic spectrum](image)

A molecule such as oxygen (O\textsubscript{2}) or water vapor (H\textsubscript{2}O), absorbs light only at certain particular colors or wavelengths in the infrared or ultraviolet. These absorbing wavelengths are characteristic of the molecule and are called its spectrum. When the energy of an incoming photon matches one of the internal energy of a molecule, the photon is captured and the molecule makes a transition to a higher level of internal energy. At infrared wavelengths, the spectrum results from excitation of vibrational and rotational energy levels in the molecule, while at visible and ultraviolet wavelengths the spectrum occurs when electrons orbiting the molecule change state.

![Example of vibrational modes in water](image)

Due to the unique properties (i.e. mass distribution and atomic-bond strength) of the different molecules, the absorption spectra in the infrared spectral region have a very distinct shape that is characteristic to the specific molecule. The infrared spectral region is therefore commonly called the fingerprint spectral region. This distinctness can be used to identify the molecules of an unknown gas or to quantify the concentration of molecules in a gas mixture.

In principle, any light source could be used for spectroscopy. However, in order to acquire any meaningful information about the gas, the light source has to match absorption features in the gas. While a light bulb followed by a wavelength selective filter, prism or grating in principle can be used to measure gas concentrations, it usually does...
not work very well. Splitting apart the different wavelengths with high enough resolution is difficult and little power is actually diverted into each wavelength bin. A laser on the other hand puts out a single pure color, or wavelength, so all its power is concentrated at this single wavelength. Laser spectroscopy is an extremely effective tool for the detection and quantification of molecular trace gases. The demonstrated detection sensitivity ranges from ppmv, ppbv to even sub-ppbv levels depending on the specific gas species and the detection method employed. The laser narrow line width makes it possible to tune over a single line in the gas spectrum. Therefore, it is necessary to know something about molecular lines and their shape and how they are influenced by pressure and temperature.

Tunable diode laser spectroscopy (TDLS) is a highly selective, sensitive and versatile technique for measuring trace species. The diode laser source is ideal for optical spectroscopy because of its narrow line width, tunability, stability, compactness, and ability to operate at room temperature. In addition to concentration, it is also possible to determine the temperature, pressure, velocity, and mass flux of the gas under observation since the technique analyzes the detailed properties of the absorption lines. TDLS has rapidly become the most commonly used laser-based technique for quantitative measurements of species in gas phase. Today, the technique is widely used for environmental monitoring, remote sensing, and process gas analytics.

The basic TDLS measurement setup is fairly simple, as shown in Figure 14. In principle, all you need is a laser diode at the right wavelength which is tunable, a gas cell and a detector.

![Figure 14 Basic setup for laser spectroscopy](image_url)
The entire power of the light source is directed into an extremely narrow region. The exact wavelength of the laser can be tuned slightly over the absorption line by changing the laser temperature and/or current. The laser light passes through the gas sample and the laser power transmitted through the sample is detected as a function of the laser wavelength. When the laser emission wavelength coincides with a resonant absorption in the molecule we see a sharp absorption signal.

2.1 Spectroscopy – molecular absorption

The spectrum of a molecule consists of a large number of lines, often grouped in bands, that are spread over many wavelengths, at each of which some percentage of the light can be absorbed.

For a diatomic molecule, the energy states can be represented by plots of potential energy as a function of inter-nuclear distance.

![Energy levels in a diatomic molecule](image)

Electronic transitions occur so rapidly that the inter-nuclear distance cannot change much in the process.

Vibrational transitions in the infrared occur between different vibrational levels of the same electronic state. Rotational transitions occur between rotational levels of the same vibrational state if the radiation is in the microwave range. In the infrared, normally the transitions often involve combination vibration-rotation transitions. In order for a
molecule to absorb a photon it is necessary for it to have a dipole moment due to non-uniform distribution of positive and negative charges on the various atoms. That is, some kind of charge distribution so it can act as an antenna. This is why nitrogen does not absorb at all in the infrared while a molecule like hydrogen fluoride has very strong absorption in the infrared. The A-band of oxygen plotted in Figure 16 arises from a transition of vibration levels of the \( b^1\Sigma_g^+ - X^3\Sigma_g^+ \) electronic transition of molecular oxygen through its magnetic dipole moment. It is the paramagnetic property of the molecule and the fact that the transition also involves an electronic state that is the reason for its absorption in the near infrared.

Figure 16  The A-band of oxygen around 760 nm

In general, it is the vibrational transition that determines the wavelength region of the spectrum and it is the rotational transitions that generate the fine structure of the spectra. If the pressure is very high or the molecule very large the rotational lines tends not to be well resolved. The population of the different states depends on the gas temperature, which is why the intensity of certain absorption line is temperature dependent.

2.1.1 Line width broadening

The center wavelength of the transition in the molecule is given by the internal energy levels of the molecule, as shown above. However, when analyzed by optical spectroscopy, the energy levels appear to be broadened into absorption lines of a certain width. This occurs since in spectroscopy you are always looking at a large group of individual
molecules and the value measured transition wavelength of each individual molecule has a spread around an average value given by the internal molecular state. The line width broadening mechanisms that are relevant for the measurement of gaseous atmospheric constituents are Doppler broadening and collisional broadening. The former mechanism is induced by the motion of the absorbing molecules, while the latter mechanism originates from collisions of molecules at elevated gas pressure. It is only at a very low gas pressure and temperature that the natural line width given by the finite lifetime of the states due to the uncertainty principle (typical 15 kHz) is relevant, which is why we omit this here.

The shape of the absorption lines is described by the spectral line shape function $\chi(v - v_0)$, which peaks at the line center defined by $h v_0 = E_2 - E_1$, the energy difference between the states. In spectroscopy you often plot the spectra versus the frequency of light in wave numbers cm$^{-1}$ which is related to the wavelength as $\nu = \frac{1}{\lambda} = f/c$ where $c$ is the speed of light ($c = 2.997925 \text{ m/s}$).

**Velocity (Doppler) broadening**

The dominant line broadening in low pressure gases at room temperature is caused by the Doppler shift of the transition frequency due to the thermal motion of the molecules. In the atmosphere the molecules are moving randomly with the velocities given by the Maxwell thermal velocity distribution. The number of molecules in a velocity interval $dv_r$ is given by

$$\frac{dN(v_r)}{N_{Total}} = \left( \frac{M}{2\pi kT} \right)^{\frac{1}{2}} e^{-\left(\frac{Mv_r^2}{2kT}\right)} dv_r$$

where $v_r$ is the line of sight velocity component, and $M$ the molecular mass. Using the expression for the Doppler shift and integrating over all velocity components we obtain the total Doppler broadened line shape which is a Gaussian

$$\chi(v - v_0) = \frac{S}{\sqrt{\pi \Delta v_D}} e^{-\frac{(v-v_0)^2}{\Delta v_D^2}}$$
Where

$$\Delta v_D = v_0 \sqrt{\frac{2kT}{M}} \ln 2$$

As can be seen, this line shape is dominating for shorter wavelengths (higher frequencies $v_0$), higher temperatures and smaller molecules with a low molecular mass. The total line shape is comprised by contribution from very many individual molecules with a spread in wavelength due to the Doppler shift as illustrated below.

![Illustration of the inhomogeneous broadening due to the Doppler effect](image)

**Pressure (collisional) broadening**

The atoms in a gas frequently collide with each other and with the walls of the containing vessel, interrupting the light emission and shortening the effective lifetime of the excited state.

Based on the kinetic theory of gases the mean time between collisions $\tau_{col}$ is given by

$$\tau_{col} = \frac{\text{mean free path}}{\text{mean speed}} = \frac{\bar{l}}{v} \approx \frac{1}{\sigma_s P} \sqrt{\frac{\pi M k T}{8}}$$

Where $\sigma_s$ is the collision cross section and $P$ the pressure.
Figure 18  *Collision broadening*

The phase of the oscillating dipole will randomly be interrupted by collisions. The frequency spectrum of the radiated energy is derived by Fourier transformation of the interrupted waveform, a Lorentz shaped line

\[
\chi(v - v_0) = \frac{1}{\pi} \frac{\Delta v}{(v - v_0)^2 + \Delta v^2}
\]

Where the line width \(\Delta v_L\) is

\[
\Delta v_L = \Delta v_{L,0} \frac{P}{P_0} \sqrt{\frac{T_0}{T}}
\]

We see that this broadening is dominating for higher pressures and at longer wavelengths.

Figure 19  *Pressure broadening of an absorption line*

**The Voigt line shape**

The line shape of the oxygen molecule is actually a result of a mix of these two line shapes. This profile is called the Voigt line shape and is calculated as the convolution between a Gaussian and a Lorentz line
shape. However, for the pressure and temperature encountered in process analytical applications it is standard to assume the Lorentz line shape in performing the curve fit. Without going into the mathematical expression for the Voigt line shape, Figure 20 illustrates the different line shapes discussed.

![Figure 20](image)

Comparison between the Doppler, Voigt and Lorentz line shapes

2.2 Laser absorption spectroscopy – Beer-Lamberts law

The amount of power absorbed by the gas depends upon the number of molecules present times the cross section times the optical path length. Therefore, the gas concentration can be expressed as:

$$Concentration = \frac{\text{How much light is absorbed by the gas molecules}}{[\text{Absorption coefficient for the gas}] \times [\text{Path Length}]}$$

From this expression we see that we need to separate the absorption of light by molecules from the absorption of light from other factors such as dust and dirt in the measurement path. To determine the gas concentration, we measure the amount of power absorbed at a characteristic wavelength, and divide it by the cross section and by the path length. The absorption is given by Beer-Lamberts law, which states that the fraction of photons absorbed over a path $\delta$ L is constant. This constant is called the absorption coefficient.
Figure 21  *Beer–Lamberts law*

\[
\frac{\delta I}{I} = -\alpha(v)c\delta L
\]

The absorption coefficient \( \alpha(v) \) varies rapidly with the optical frequency \( v \) for gaseous species as the frequency of the light passes a resonance (an absorption line) in the molecule. Integrating over the path \( L \) gives

\[
\int_{I_0}^{I_R} \frac{\delta I}{I} = -\int_0^L \alpha(v)c\delta L
\]

With the solution

\[
\ln I_R - \ln I_0 = -\alpha(v)cL \Rightarrow I_R = I_0 e^{-\alpha(v)cL}
\]

For small values of the absorption \( \alpha(v)L \) this is approximated with

\[
I_R = I_0 T e^{-\alpha(v)L} \Rightarrow I_R = I_0 T \left[1 - c\alpha(v)L\right] = BG - I_0 T c\alpha(v)L
\]

What we have here is a background signal BG and a small absorption signal. This is actually the direct absorption signal and the DC component BG can typically make up more than 99.9% of the total signal.

The absorption of the laser light comes from two different kinds of sources. Dust, dirt and other components that are so spectrally broad that they act as a constant absorption over the wavelength scan of the laser. This broad absorption is indicated by \( \sigma \). All the gas components, \( i \), in the path that have a molecular transition in the scanned wavelength region contribute to the absorption, so the total absorption coefficient is

\[
\text{Number of molecules} = \alpha \delta L \\
\text{Gas Conc} = c
\]
\[ \alpha(v) = \sigma + \sum \alpha_i(v) \]

For the received signal we have the total absorption comprising broadband attenuation and the total molecular absorption:

\[ I_R = I_0 e^{-\left(\sigma + \sum c_i \alpha_i\right) L} = I_0 e^{-\sigma L} e^{-\sum c_i \alpha_i L} = I_0 e^{-\sum c_i \alpha_i L} \]

We have defined a transmission value \( T \) which will vary significantly with the path length \( L \) and the amount of dust and dirt \( \sigma \). Figure 22 illustrates the fast drop in transmission when using long measurement path lengths. Increasing the path length from 1 to 10 meters decreases the transmission \( T \) two orders of magnitude.

![Transmission as a function of path length](image)

Figure 22  *Transmission as a function of path length*

For the gas component \( i \), the absorption coefficient is \( \alpha_i(v) = S_i c(v - v_0) N_i(p,T) \), where \( S_i \) is the molecular line intensity and \( N_i \) is the number of absorbing molecules per \( \text{cm}^3 \) of atmosphere and \( c(v - v_0) \) is the normalized absorption line shape with its center frequency \( v_0 \) shown for CO at 6390.82 \( \text{cm}^{-1} = 1564.7 \) nm. There are two main reasons for the temperature dependence of the absorption coefficient \( \alpha_i(v) \) namely, the temperature dependence of the line intensity \( S_i \) of the molecule and the temperature variation of the
number of molecules in the path. The ideal gas law gives the number of absorbing molecules from the gas i, at the partial pressure $p_i$ as $N_i = N_L (T_0/T)(p_i/p)$ where $T$ and $p$ are the actual gas temperature and pressure respectively, $T_0$ is the reference temperature at STP (273.16 K, 1 atm). $N_L$ is the number of molecules in one mole at STP.

![Figure 23](image)

**The normalized absorption line shape $c(\nu - \nu_0)$ of CO at $\nu_0 = 6390.82 \text{ cm}^{-1}$**

### 2.3 Spectroscopic databases

The most widely used spectroscopic database is HITRAN [http://www.cfa.harvard.edu/hitran/](http://www.cfa.harvard.edu/hitran/). This large database was developed and then made public domain. HITRAN stands for HIgh-resolution TRANsmission molecular absorption database, and the initial work on this started at the US Air Force in 1961. The first edition of this came out on a magnetic tape (The McClatchey tape) in 1973 and was freely distributed. Today, you can download the database from the Hitran web site. The present edition is Hitran 2008. There even exists a free software package, HAWKS (HITRAN Atmospheric Workstation) software, which can manipulate, filter, and plots the line-by-line data as well as the absorption cross-sections, in Windows, UNIX, and MAC operating systems. Here you plot spectra at different gas temperatures since Hitrans contains information about the line strength $S$ for each transition.

There is also a Special Issue of the Journal of Quantitative Spectroscopy and Radiative Transfer (JQSRT) volume 110, numbers 9-10,
June/July 2009 that includes 17 articles describing background information related to HITRAN. The standard reference is given in [Ref. 4]. In order to correctly estimate the performance at higher temperatures typical for combustion applications, it is necessary to use the HITEMP, the high-temperature molecular spectroscopic database which can be downloaded from the Hitran web site [Ref. 55]. There is a very useful web tool, Spectralcalc, for plotting Hitran data and other spectral information http://www.spectralcalc.com/info/about.php.

Another database that also includes many organic compounds is the vapor phase spectral library from Pacific Northwest National Laboratory (PNNL). The data can be accessed through a web site at NIST in USA http://webbook.nist.gov/chemistry/.

One of the more useful set of FTIR data for ammonia in the telecom wavelength range can be found in the dissertation of Lene Lundsberg-Nielsen [Ref. 7].
3 Tunable Diode Laser (TDL) Spectroscopy

3.1 Unique advantages for TDL in process gas analytics

In situ trace-gas detection for environmental monitoring and process analytics has been performed by several techniques other than laser spectroscopy. These techniques include mass spectrometry (MS), gas chromatography (GC) and chemo-luminescence detection.

While MS can provide very high sensitivity, selectivity is often limited due to mass overlap between certain molecules. For example, the water isotopes $^{17}$H$_2$O and HDO both have the mass $M = 19$. This mass overlap thus requires pre-preparation of the molecular species to be detected. It should be noted, though, that mass spectrometry is advantageous over laser spectroscopy for the detection of very large molecules.

Gas chromatography (GC) is a technique where the molecular species to be measured has to be transported through a column, the walls of which are coated with a liquid or polymeric substance. The interaction of the gaseous molecular species with the walls of the column causes the different species of the sample gas mixture to leave the column at different times. This effect is due to the different adsorption coefficients of the different molecules. The molecular species can thus be identified qualitatively by the time they require to pass through the column. Quantitative detection is then performed by, e.g. a flame-photometric detector or by a mass spectrometer. Due to the principle of GC, only sequential measurements of different species can be performed. In addition, the required time for a measurement can be relatively high. Depending on the length of the column, measurement times often reach 5 - 10 minutes or more. Particular for near in situ process measurements, this measurement time is often too long to detect rapid fluctuations in chemical processes.

Chemo-luminescence relies on the chemical reaction of the molecular species of interest with the surface of a polymeric dye. The reaction energy excites the dye molecules, and a fraction of this excitation energy is emitted as photons (luminescence) when the excited molecules return to their energetic ground state. Chemo-luminescence has been used for in situ measurements of ozone and nitrogen oxides.
Chemo-luminescence offers the advantage of relatively fast measurements (around 10 Hz). The technique is highly selective, but it has only been developed for the detection of a few gaseous species. The chemical reactions that take place during the measurement are irreversible, and regular replacement of the dye is required. Chemo-luminescence is not an absolute measurement technique, and regular calibration is necessary.

Tunable Diode Laser analyzers are one of the most robust process analyzers available making fast, accurate measurements of gases directly in situ in harsh process environments where typical conditions are high temperature or pressure and varying transmission conditions. The TDL is very well suited for corrosive and “sticky” gases since the technology does not require gas sample conditioning. There is generally no, or very small, cross interference from other gases and the response time is very short. TDL analyzers have been continuously developed maintaining their technological edge in response to increasingly demanding standards in process and emission control.

Oxygen is an important, widely used gas in industrial processes. Therefore, there is great demand for in-line monitoring of oxygen concentration for the enhancement of combustion efficiency and reduction of environmental pollution. TDL technology here offers a highly sensitive, highly selective and fast time response trace gas detection technique for these applications. With the use of the semiconductor laser diode laser and by precisely tuning the laser output wavelength to a set of single isolated absorption lines of the gas, the TDL technique offers gas concentration measurement with very high sensitivity and selectivity. The TDL analyzer requires very little maintenance and generally has very long calibration intervals. The improved measurement quality and low cost-of-ownership obtained by going to an in situ technology has led to a trend where TDL is replacing other technologies, including GCs, in an increasing number of applications.

### 3.2 Laser sources for TDL in process gas analytics

Diode lasers are manufactured for different applications such as fiber optic communication, optical storage, and sensing. Important properties of the lasers include wavelength, power, coherence, cost, and operating temperature. For gas sensing applications the most impor-
tant property is the spectral coherence; the laser has to operate at one single emission wavelength. However, new types of single mode lasers are under development. Efforts to improve mid-infrared diode lasers are of special interest to the molecular gas sensing community because of the high sensitivity that can be achieved in this region. The efforts focus on achieving room temperature operation and single frequency output through novel device structures.

A laser is basically an oscillator working at optical frequencies. In order to get an oscillator to work, both gain and feedback are needed. In a diode laser the amplification (gain) is provided by applying a current in the forward direction of the laser diode. This current creates a traffic jam of holes and electrons at the p-n junction. In this congestion, holes and electrons recombine and release energy as light if the band gap of the material has the right structure. The cleaved facets of a conventional diode laser create the oscillator feedback. When the light bounces back and forth between the mirrors, the number of photons increases in a coherent way by stimulated emission, as once predicted by Einstein.

The first laser diodes were incredibly inefficient and short lived p-n homo-junction devices. Today, a large number of structures exist where the current is confined in a narrow region in order to increase the efficiency of the device.

![Basic edge-emitter laser structures](image)

Figure 24 Basic edge-emitter laser structures

A laser can only operate at those wavelengths for which an integral multiple of half-wavelengths fit into the cavity. There are an infinite number of integral multiples of the cavity length. However, only a finite number will fit into the gain profile of the laser gain material. Thus, the maximum possible longitudinal mode output of the laser is the intersection of the set of possible longitudinal modes with the gain curve, see Figure 25.
A diode laser gas analyzer needs a light source of narrow emission line width. There are two main options when designing the diode laser cavity for single wavelength (single mode) output; make the laser cavity short enough to allow only one mode under the gain curve (VCSEL) or introduce a wavelength selective element external or internal to the cavity. Figure 26 shows a schematic structure of a typical DFB laser using InP-based materials. In the DFB laser, oscillation is allowed for only one of the longitudinal modes by the built-in grating structure.
tive layer after the initial growth. Then a grating is defined by etching or e-beam lithography. After the definition of the grating a regrowth is performed. In some material systems this etching and regrowth is very difficult, which is why Nanoplus GmbH pioneered the application of a lateral metal grating outside the active layer, as seen in Figure 27. This fabrication method has been very successful in producing DFB lasers in other material systems for longer wavelengths.

![Figure 27 Schematic drawing of a laterally-coupled distributed-feedback DFB laser with a metal grating structure and an active region](image)

More complicated structures have been developed to allow for the selection of modes over a greater wavelength range. By separately controlling the current to the two segments a widely tunable laser with a large tuning range is obtained by the vernier action of the two segments. A laser for the simultaneous detection of several hydrocarbons such as methane and ethane in the 3.3 µm has recently been demonstrated.

![Figure 28 Monolithically tuneable DFB laser](image)
The vertical cavity surface emitting laser (VCSEL) uses a vertical resonator, perpendicular to the p-n junction. Since the active layer is parallel to the emission area, it is possible to obtain a round, low-divergence beam by defining a circular output coupler. In the case of a vertical resonator, the length $L$ of the gain medium is defined by the distance between the DBR mirrors on the top and at the bottom of the structure which is sufficiently short to allow for only one single longitudinal mode. In order to achieve laser operation, the limited gain by short active layer must be compensated by more efficient feedback. This is provided by the use of highly efficient Distributed Bragg Reflectors as resonator mirrors.

Figure 29  *Continuous and step tuning of the two segment laser*
Figure 30  *Vertical cavity surface emitting laser (VCSEL)*

The resonator mirrors are typically made up of twenty to forty alternating layers of Al$_x$Ga$_{(1-x)}$As and AlAs, each layer 1/4 thick, which give a reflectivity in the order of 99.9% – 99.99%. The high resonator efficiency and small gain medium volume combine to give threshold currents of only a few mA.

The output power of single mode VCSEls currently available is typically less than 1 mW. However, several more sophisticated VCSEL laser structures are presently emerging, which produce single mode output power approaching 5 mW.

The laser light from a VCSEL will tune within the gain profile as the laser temperature is varied, which allows the device to be temperature-tuned over a range of several nanometers, without mode hopping. The typical tuning with device temperature is similar to a DFB laser at the same wavelength. The small junction area of the VCSEL will increase the current density and the resistance through the device. This creates strong localized heating, which is why the VCSEL typically will tune two orders of magnitude more than an edge emitter. Table 2 shows a comparison of some selected laser parameters between a DFB from Sarnoff and a VCSEL from Avalon, both operating at 761 nm.
Table 2  Comparison of some selected data between a DFB and a VCSEL operating at 761 nm

<table>
<thead>
<tr>
<th></th>
<th>VCSEL</th>
<th>DFB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Center Wavelength</td>
<td>761 nm</td>
<td>761 nm</td>
</tr>
<tr>
<td>Line Width</td>
<td>3 MHz</td>
<td>30 MHz</td>
</tr>
<tr>
<td>Temperature Tuning</td>
<td>33 GHz/K</td>
<td>33 GHz/K</td>
</tr>
<tr>
<td>Current Tuning</td>
<td>100 GHz/mA</td>
<td>1 GHz/mA</td>
</tr>
<tr>
<td>Threshold Current</td>
<td>3 mA</td>
<td>20 mA</td>
</tr>
<tr>
<td>Cavity Length</td>
<td>( L \approx \lambda = 761 \text{ nm} )</td>
<td>( L \approx 500 \mu \text{m} )</td>
</tr>
</tbody>
</table>

The only manufacturer able to produce classical DFB lasers in Al\(_x\)Ga\(_{1-x}\)As at 761 nm was Sarnoff Corp. They have, however, stopped delivering these lasers due to low yield. Today, Nanoplus Gmbh delivers 761 nm DFB lasers manufactured with a procedure that avoids the regrowth process. Due to the high cost of the Nanoplus 761 nm lasers, VCSEL lasers are today the main type used for oxygen measurements. At wavelengths above 1200 nm it is difficult to manufacture a mirror structure with sufficient reflectivity to realize a VCSEL laser. Only Vertilas Gmbh has managed so far and they are manufacturing VCSELS for spectroscopic applications in the wavelength range of 1.3 \(\mu\)m to 2 \(\mu\)m.

For wavelengths longer than 4.5 \(\mu\)m, the quantum cascade (QC) laser offers room temperature single mode operation. Their application in process monitoring has been limited to some special applications such as plasma monitoring in etching processes and breath analysis for medical applications. The cost of the laser, the more complicated bias and modulation scheme needed has so far prevented wide spread use of their application. An excellent review can be found in reference 8.

3.3 Signal processing techniques for TDL spectroscopy

As discussed in chapter 2.2, in the most basic diode laser spectrometer the emission wavelength of the tunable diode laser is tuned over the characteristic absorption lines of a species in the gas in the path of the laser beam. This causes a reduction of the measured signal intensity, which can be detected by a photodiode, and then used to
determine the gas concentration and other properties such as gas temperature. The main disadvantage of absorption spectrometry (AS) as well as laser absorption spectrometry (LAS) in general is that it relies on a measurement of a small change of a signal on top of a large background. Any noise introduced by the light source or the optical system will deteriorate the detectability of the technique. The sensitivity of direct absorption techniques is therefore often limited to an absorbance of $10^{-3} - 10^{-4}$, far away from the theoretical limit that would be in the $10^{-7}$ range. Since this is insufficient for many types of applications, direct absorption spectroscopy (DAS) is normally not used in its simplest mode of operation.

There are basically two ways to improve on the situation; one is to reduce the noise in the signal, the other is to increase the absorption. The former can be achieved by the use of more advanced signal processing, whereas the latter can be obtained by placing the gas inside a cavity (chapter “3.4 Cavity enhancement techniques” on page 58) in which the light passes through the sample several times, thus increasing the interaction length. It is also possible to enhance the signal by performing detection at wavelengths where the transitions have larger line strengths. This is achieved using fundamental vibrational bands or electronic transitions instead of overtones.

### 3.3.1 Direct absorption spectroscopy (DAS)

The most direct approach is to apply a rapid, repetitive current sweep onto the laser bias which generates an amplitude modulation and a wavelength sweep and then use signal averaging to combine data from many sweeps in order to improve the signal-to-noise ratio. The laser wavelength will sweep back and forth across the absorption line twice per cycle, which is why the absorption sampling rate is twice the modulation rate if spectra are collected both on the up and down ramp. The detector signal will contain both amplitude (optical power) modulation and wavelength modulation with the contribution from the power modulation dominating the absorption signal. Typically, the amplitude modulation can be on the order of $1 - 10\%$ of the total laser power while the signal from the molecular absorption can give a fractional absorbance $10^{-4} - 10^{-5}$ at the sensitivity limit. Moreover, the amplitude modulation coming from the laser will vary strongly over
the laser wavelength scan since the laser I-P curve normally is not linear enough on this scale. In order to obtain adequate resolution in the A/D-conversion over the line this DC-component should be removed. Figure 31 shows schematically a setup for direct absorption spectroscopy where a current ramp is superimposed on the laser bias current. Also shown in the figure an analog subtraction circuit can be implemented that removes the fundamental component of the AM background signal (BG) before the A/D converter. In this circuit the output signal from the detector is subtracted from the modulation signal going to the laser. By optimizing the amplitude and phase of the signal coming from the signal generator, the fundamental AM component of the signal can more or less be completely removed. However, the low frequency 1/f noise and fluctuations accompanying the fundamental AM component still remains after the subtraction. This noise has to be further eliminated by e.g. application of rapid scanning, filtering or balanced detection schemes in order to reach a relative intensity level of 10^{-5}, i.e. the level typical for the WMS technique, see further description below.

Figure 31  *Schematic setup for direct absorption spectroscopy*

The detected absorption signal $\alpha L$ contains the transmission $T$ and the laser output intensity $I_0$ but in DAS this information is contained in the detected signal as shown in the equation below.

$$I_R = I_0 T e^{-\alpha L} \approx I_0 T [1 - c\alpha L] = BG - I_0 \alpha cL$$

The direct absorption technique retains the true shape of the absorption line and provides a means to perform calibrated measurements by including enough of the region around the absorption feature. The direct absorption technique also decreases the requirement on the laser wavelength modulation capability since it does not use an addi-
itional modulation on top of the wavelength scan. The rapid scan creates a signal at a higher detection frequency which also moves the spectral information to higher frequencies and makes it possible to filter out noise at lower frequencies. After the subtraction of the ramp, adjusted in amplitude and phase, we are left with raw spectra that can be digitized and digitally signal processed to yield the DAS spectra. Since we know how much we have subtracted we still have the normalization of the total transmission through the process, IT/IR, intact. In order to calculate the concentration while taking care of varying process conditions that can induce line broadening, the raw spectrum is curve fitted to an analytical model (see chapter “3.3.3 Normalization and calibration” on page 49).

**Noise and sensitivity issues in DAS**

Using a modulation of 100 kHz and an analog subtraction circuit, a noise level of approximately $1.5 \times 10^{-5}$ has been claimed for a DAS system [Ref. 9]. However, since this DAS signal processing scheme fails to address the problem with the laser excess noise, the detected signal will still contain high noise levels at lower frequencies. The claimed performance would rely on the laser having a low noise level and very small etalon problems.

In order to improve on this situation, a separate reference signal could be derived from the laser itself. In principle, dual-beam approaches that divide the signal beam into one which passes through the absorbing medium, and into a reference beam, which does not pass through the absorbing medium, should allow cancellation of common-mode excess laser amplitude noise. In practice, however, conventional dual-beam measurements are severely limited by the balancing requirements in the two detection channels. For example, if the target detectivity is approximately $10^{-6}$ and the laser amplitude noise in the detection bandwidth is 1% of the mean intensity, then the laser intensity incident upon the two detectors must be balanced to less than 1 part in $10^4$. Even if this balance could be achieved in a laboratory setup, it would be impractical to maintain in a field instrument. This double beam laser noise cancellation scheme was greatly improved by Hobbs et. al. by designing an auto balancing ratiometric detector (BRD), which claims shot-noise limited noise equivalent re-
Residual absorption of $10^{-7}$ [Ref. 100, Ref. 111].

In practical use, however, the BRD system has shown serious problems in true process conditions. Operation during rapid changes in laser light transmission is difficult. In many processes particles are present and particulate loading changes. The BRD circuit requires a well defined detector/reference-detector ratio of laser power. This is achieved by splitting the laser light using a beamsplitter before the light transmits across the process. During the transmission through the process, dust load changes the amount of laser power that is received by the measurement detector. This changes the measure/reference detector power ratio in an unpredictable way that has direct and significant effects on the noise cancellation efficiency. The BRD circuit has also shown sensitivity to ambient temperature induced measurement drift during environmental cycling of the circuit. For these reasons the circuit has been deemed unsuitable for process analytical instrumentation.

**Figure 32** *Block diagram of a generic all-electronic laser noise suppression scheme*

Today’s instruments using DAS rely on high speed data acquisition and FPGA signal processing. By modulating the laser and sampling the detector signal at an extremely high frequency and subsequently filtering the detector signal in an FPGA, the laser noise can be reduced to allow sensitivities approaching those of WMS systems. The signal processing strategies used must remove the laser 1/f-noise and base line fluctuations while maintaining as much of the absorption line shape as possible.
3.3.2 Wavelength modulation spectroscopy (WMS)

The ease with which diode lasers are modulated in amplitude and frequency makes it very attractive to use more advanced modulation techniques to achieve a higher sensitivity. Wavelength-modulation spectroscopy is a well established technique to increase the signal-to-noise ratio in tunable diode laser spectroscopy. In this technique the absorption signal is transformed into a periodic signal by modulating the emission wavelength of the tunable laser source with an additional sinusoidal signal added to the current ramp scanning the spectrum. [11].

Figure 33 Schematic setup for wavelength modulation spectroscopy

The current through the laser is

\[ i_{lc}(t) = i_{bias} + i_{scan}(t) + i_{\alpha} \cos(2\pi f + \phi) \]

The laser output intensity is then

\[ I_L(t) = I_{L,0} + I_{L,1}(t) \cos(2\pi f + \phi) \]

Where \( I_{L,0}(t) \) contains the slowly varying intensity due to the bias and the scan, and \( I_{L,1} \) is the intensity modulation index. The emission frequency will vary according to

\[ v(t) = v_0 + v_{ramp} + v_{\alpha} \cos(2\pi ft) \]

The laser is mounted on a thermo electric cooler (TEC) where the temperature is adjusted so that the wavelength scan is performed around \( v_0 \), close to the absorption line center. If we enter the expression for the emission frequency into Beer-Lamberts law we get for small absorptions.

\[ I_D \approx \eta I_D T \left[ 1 - c\alpha(v)L \right] = \eta I_D T \left[ 1 - c\alpha(v_0 + v_{ramp} + v_{\alpha} \cos(2\pi ft))L \right] \]

The variation of the light intensity from the laser across the ramp is
included into $I_D(\eta)$. $\eta$ is an instrumental gain. This is now a periodic function that can be expanded in a cosine Fourier series.

$$\alpha(v_0 + v_{\text{ramp}} + v_\alpha \cos \omega t) = \sum_{n=0}^{\infty} \chi_n(v_0, v_{\text{ramp}}) \cos(2\pi nt)$$

Modulation of $v$ thus produces a signal $S(v_0, v_{\text{ramp}}, t)$ that has components which are periodic with the modulation frequency $\omega = 2\pi ft$ and its higher harmonics ($2\omega, 3\omega, ...$). Figure 34 shows how the first four harmonics looks as the laser is scanned over the absorption line. It is most common to use the second harmonic since it does not have a DC-component and it gives a maximum at the line center.

![Figure 34](image)

Figure 34  View of the detector signal for the first four harmonics of the Fourier expansion as the laser is scanned over the absorption line

The pressure and temperature dependence of the second harmonic spectrum can be larger than that of the direct absorption signal depending on the modulation amplitude used. In practice, the absorption line is often slightly over-modulated in order to decrease the temperature and pressure dependence and filter out unwanted etalons.

Demodulation of the signal $S(v_{\text{ramp}}, v_\alpha, t)$ is done with a lock-in amplifier. The lock in amplifier effectively selects a Fourier component by multiplying the signal with a reference with an adjusted phase and integrating over the signal, see Figure 35.
Detected signal at nf from the lock-in is

\[ S_{nf}(\theta) = \frac{1}{\tau} \int_{0}^{\tau} S(t) \cos(2\pi ft - \theta) dt \]

Demodulating at the modulation frequency 1f yields a signal proportional to the first harmonic of the signal, demodulation at twice the modulation frequency 2f yields a signal proportional to the second harmonic which is the one most commonly used. An analytical expression for the second harmonic of the Lorentzian lineshape function has been derived by Kluczynski et al. [12].

\[ S_{2f}(v_{ramp}, v_a) \approx \eta T \left[ \chi_2 I_{L,0}(\nu) + \frac{\chi_1 + \chi_3}{2} I_{L,1}(\nu) \cos(\phi_1) \right] \alpha_0 c L \]

This expression is very compact and suitable for numerical computing and is used for concentration calculation in real process instruments. The first term in the bracket is the second harmonic of the Lorentzian line function multiplied by the intensity from the laser. The second term represents the mixing of the signal from the absorption line and the signal coming directly from the intensity modulated laser. For a laser with a small intensity modulation index like VCSEL, the signal will be more or less identical to the theoretical one from a pure second harmonic. For lasers with a high intensity modulation index a distortion of the line due to the second term in the bracket will occur.
Figure 36  Effect of laser power modulation on the detected WMS signal

It was first determined by Reid and Labrie [Ref. 12], that for a sinusoidal modulation of the laser emission frequency, the maximum second derivative signal at the line center is achieved by adjusting the modulation amplitude to $\nu_a = 2.2 \gamma$, where $\gamma$ is the half width half maximum (HWHM) of the lineshape function.

3.3.3 Normalization and calibration

In order to make accurate absolute measurements of the gas concentration, there is a need to normalize the measured spectra with the laser intensity. Depending if you are using DAS or WMS you need to normalize differently. A common task of a TDLS-based gas analyzer is to achieve high sensitivity and accuracy under varying conditions. To improve the sensitivity of the analyzer we should use optimized signal processing, normally least squares curve fitting. At a given sensor bandwidth, least squares curve fitting is the best method to filter the measurement noise, because it gives the smallest variance on the fitted concentration values. Moreover, the fitting to a model of the absorption line returns the correct concentration value even if the line is broadened by other gas molecules in the process or by an elevated pressure. The opposite can also happen, line narrowing due to elevated gas temperatures or by the presence of gases such as hydrogen or helium.
**Direct absorption**

The basic direct absorption signal is as shown before; here we introduce an instrumental gain.

\[ S_{DAS} = \eta I_0 T e^{-a(v-v_0) cL} \eta I_0 T \tilde{\alpha} - \alpha (v-v_0) cL^2 = \eta I_0 T \tilde{\alpha} - \alpha_0 \chi (v-v_0) cL^2 \]

From chapter “2.2 Laser absorption spectroscopy – Beer-Lamberts law” on page 29, we know that the absorption coefficient is \( \alpha_i(v) = \alpha_0 \chi (v-v_0) \), where \( \alpha_0 = S_i N_i \) is the molecular absorption coefficient for gas \( i \), \( S_i \) is the line intensity of the transition and \( N_i \) is the number of absorbing molecules per cm\(^3\) of atmosphere and \( \chi (v-v_0) \) is the normalized absorption line shape with its center frequency \( v_0 \).

If we record a part of the baseline where the absorption \( \alpha \) is zero we are left with the value of \( \eta I_0 T \) which is all we need to get an absolute value of the concentration. The recorded absorption signal \( \eta I_0 T c \alpha L \) has then to be fitted to a mathematical model of the absorption line in order to correctly retrieve the gas concentration. The absorption line is most often modeled as Lorentzian.

\[ \chi (v-v_0) = \frac{1}{\pi} \frac{\Delta v}{(v-v_0)^2 + \Delta v^2} \]

Where the half width half maximum line width \( \langle \Delta v \rangle \) is

\[ \Delta v = \Delta v_0 \left( \frac{p}{p_0} \right) \left( \frac{T}{T_0} \right) \]

\( \Delta v_0 \) is the line width at STP, \( p \) and \( T \) is the gas pressure and temperature respectively.

Figure 37 shows the transmission for 10% of CO over a 1 meter path for the pressures 1 and 2.5 atmospheres. The temperature is ambient. In the figure we have also indicated some measurement points over the one atmosphere curve for illustration purposes. In reality the analyzer normally record 100 – 256 points over an absorption line. In practice, an offset and a tilt is often added to improve the fit. Let the buffer index be \( x \) and the function to spectral fitting spectrum is

\[ \text{Spectrum}(x) = \alpha_0 \chi (x-x_0) cL \]

Using the expression for the fitted spectrum, the curve fitting algorithm...
will change the value of the width $\Delta \nu$ and the line strength $\alpha_0$ until the measured data points $Y_i$ fit to the mathematical curve in the “best way”. The criterion is that the sum of the least squares, Chi-square, over the curve is minimized.

$$X^2 = \sum_i \frac{(Y_i - S(x_i))^2}{S(x_i)}$$

The signal processing flow is schematically illustrated below.

**Figure 37**  Transmission for 10% of CO over 1 meter path for the pressures 1 and 2.5 atmospheres

**Figure 38**  Signal processing flow for direct absorption spectroscopy

**Wavelength modulation spectroscopy**

In WMS the received signal at the second harmonic is
\[ S_{2f}(\nu_{ramp}, \nu_a) \approx \eta T \left[ \chi_2 I_{L,0}(\nu) - \frac{\chi_1 + \chi_3}{2} I_{L,1}(\nu) \cos(\varphi_1) \right] \alpha_0 c L \]

Where the mean intensity is \( I_0 \), the intensity modulation index of the laser is expressed in mW/mA, and \( \chi_1(\nu_d, \nu_a) \), \( \chi_2(\nu_d, \nu_a) \), and \( \chi_3(\nu_d, \nu_a) \) are the three first harmonics of the modulated Lorentzian line shape (see chapter “3.3.2 Wavelength modulation spectroscopy (WMS)” on page 46). To make life easier we define the detuning from the line center as \( \nu_d = \nu - \nu_0 \). Every Fourier component is derived from the expression of the Lorentzian line and contains all information about the line intensity and line width of the absorption line. Moreover, in addition to the pressure dependence due to the broadening of the basic absorption line all components are also dependent on the applied wavelength modulation amplitude which we need to retrieve or calibrate. For detailed expression of the analytical functions of the harmonics of the Lorentzian line, see [Ref. 11] and [Ref. 13]. Since the WMS 2f-signal is zero outside the absorption line we have no information about the value of the received intensity and the transmission or the gain applied by the electronics. We need to find \( \eta I_0 T \) and this has to be derived separately. The most common method is to have a separate DC channel for detection of the intensity. This channel has to handle the total received intensity but the requirements on resolution of this measurement are moderate. During the measurement of the normalization factor \( \eta I_0 T \) the wavelength modulation is normally turned off.
Figure 39  Second harmonic signal for 10% of CO over 1 meter path for the pressures 1 and 2.5 atmospheres

We have also here, just as an illustration shown that the measured data points also in WMS can be fitted to an analytical expression for the second harmonic of the absorption line shape. The fitting is performed in the same manner by minimizing Chi square. The fitting function is however in this case

\[
\text{Spectrum}(x) = \alpha_0 \left[ \chi_2(x, \nu_a)I_0 - \frac{\chi_1(x, \nu_a) + \chi_3(x, \nu_a)}{2} I_1 \right]cL
\]

The signal processing flow for WMS is schematically illustrated below.

Figure 40  Signal processing flow for WMS

Since the WMS signal is dependent on the wavelength modulation
amplitude, $v_a$, we are determining this parameter by introducing a well calibrated reference gas in the measurement channel. As we know all parameters such as concentration, and line width we can derive $v_a$ from the fit to the reference line and store it as a fixed parameter in the curve fit. The FM index of the laser, $v_a / i_a$, normally changes very slowly. As shown in Figure 41, a separate reference channel can be built in to the instrument. The big advantage here is that we get a self-calibrating system that can compensate for any changes in the laser. Moreover, for some lasers the FM index varies over the scan. An on-line measurement using a reference cell can compensate for this.

It is clear that this signal processing scheme produces the same information as the direct absorption scheme. Since we are continuously retrieving the line amplitude and the line width it is possible to retrieve the original lineshape in real time. This is not at all necessary but emphasizes that the WMS signal processing scheme, if performed properly, gives exactly the same information about the “true process conditions” as that obtained by an analyzer based on direct absorption. The reason to use WMS in spite of its greater complexity, is that it gives an extra edge in sensitivity when detecting small molecules.

3.3.4 Comparison between direct absorption spectroscopy and wavelength modulation spectroscopy

Wavelength modulation spectroscopy has traditionally been the preferred method for detecting small molecules at very low absorption. It is difficult to obtain high performance gas detection using direct absorption spectroscopy in its most basic form. The reason is the large background signal that has to be removed. As an example, 100 ppm CO at 300K gives absorption of 0.0001% from the 100% level. This is a small signal with a large offset. Just subtracting the background will leave a lot of fluctuations on the base line. DAS retains the original lineshape of the spectra and the signal of absorption gives the total intensity, which is why there is no need for additional signal processing to obtain the normalization. For broadened spectra, due to elevated gas pressure or broadening typical for larger molecules DAS is advantageous since no additional broadening of the spectra occur due to the modulation scheme.
Figure 41  *Absorption of 100 ppm CO. Notice the scale is from 0.9999 to 1.0000*

The sensitivity limit of WMS is typically two orders of magnitude better than that obtained with direct absorption spectroscopy. The reason for this is that the modulation scheme moves the signal away from the large signal fluctuations at lower frequencies. The signal is detected in an optimum pass band around the modulation frequency avoiding the laser noise and the noise in the measurement channel due to varying dust load, flames and turbulence.

Figure 42  *Schematic illustration of WMS and the low frequency noise component encountered in process analytics*

Moreover the second harmonic signal is centered around a zero base line and can be amplified quite easily. Figure 43 shows the second harmonic signal from 100 ppm CO.
Figure 43  The second harmonic signal from 100 ppm CO

The drawbacks with wavelength modulation spectroscopy are; WMS needs more complicated signal processing, WMS needs to be normalized to the received light intensity using a separate detection scheme and WMS adds an additional broadening to the detected spectra. Moreover, recent progress in digital signal processing has seen the DAS based system performance approaching the performance of the WMS system by the use of advanced filtering techniques to remove the low frequency background.

It is clear that all the information in the absorption line can be retrieved using curve fitting independent of if you are using WMS or DAS. You just have to use the right model. This conclusion is confirmed by the successful deployment worldwide of both WMS and DAS instruments in process analytics over recent decades.

3.3.5 Spectroscopic measurement of gas temperature

The common method in laser spectroscopy of measuring temperature is to compare the ratio between two absorption lines which have different temperature coefficients. The difference is due to the fact that different transitions are populated differently depending on the type of transitions that are involved. Some transitions are more easy to excite and other more complicated vibration-rotation modes require higher temperatures to be excited. The strength S of an absorption line changes with temperature according to
where $T_0$ (K) is reference temperature and $Q$ is the absorber’s partition function. The factors $\nu_{0,i}$ (cm\(^{-1}\)) and $E_{i}^{\nu}$ (cm\(^{-1}\)) are the center frequency and lower-state energy of the $i$th transition and $T$ is the actual temperature in the path.

The R-branch of the oxygen A-band offers several possibilities to measure temperatures around 600-1600 °C with high sensitivity since several absorption lines have a lower-state energy around 1000 cm\(^{-1}\). The penalty for using these lines is that the line strength is slightly weaker than in the P-branch. The problem with this temperature measurement method is that two absorption lines must be found which are close enough to be measured with a single laser, but which still have different temperature behaviour to give high temperature resolution. This limits the number of possible choices of absorption lines quite a lot. The conclusion is therefore that the concentration and the temperature should be measured close to the band-head of the R-branch where absorption lines meeting these requirements can be found. If we are measuring the two lines in the same scan, using DAS or WMS, and take the ratio of the integrated absorption for each line we obtain a function only of the gas temperature. All other factors such as gas concentration and pressure are the same. The ratio $R$ is then just the ratio of the different line strengths

$$R = \frac{S_1(T_0)}{S_2(T_0)} \exp \left[ -\left( \frac{hc}{k} \right) \left( E_1^{\nu} - E_2^{\nu} \right) \left( \frac{1}{T} - \frac{1}{T_0} \right) \right]$$

We see that we need a large difference in the lower state energies to obtain a good temperature resolution. These values are available in the Hitran database. Using two absorption lines in the R-branch of the oxygen band around 760 nm Sandström et al. managed to measure oxygen and temperature in situ in a reheating furnace during production [Ref. 15]. The reheating furnace is used for heat treatment of steel in the manufacturing process. The chosen absorption lines
in this work enabled an estimation of the gas temperature to a 25 °C accuracy in a controlled environment at 1000 °C and an oxygen concentration of 20%×m.

![Figure 44](image.png)  
**Figure 44** *R-branch absorption lines of oxygen vs temperature*

![Figure 45](image.png)  
**Figure 45** *Temperature measured with TDL and thermocoupler*

### 3.4 Cavity enhancement techniques

The sensitivity of a laser spectrometer is proportional to the signal-to-noise ratio (SNR) of the recorded data. The signal is determined by the gas concentration and by the absorption path length. While the gas concentration cannot readily be increased to reach a higher signal level, the absorption path length can be increased using multipass absorption cells. Multipass absorption cells have been developed as a means for signal enhancement, as the absorption signal is directly proportional to the interaction length of the laser radiation.
and the trace gas. External cavities can either be of multi-pass type, i.e. Herriott or White cells, of non-resonant type (off-axis alignment), or of resonant type, most often working as a Fabry–Pérot (FP) etalon. Multi-pass cells, which typically can provide an enhanced interaction length of up to ~2 orders of magnitude, are nowadays common together with TDLAS.

3.4.1 Multi-path cell

Herriott invented a design that comprises only two concave spherical mirrors with equal radius of curvature. The mirrors are separated by a distance close to the mirror radius of curvature. The front mirror contains a coupling hole through which the laser beam is coupled into the cell, as depicted in Figure 46. If the laser beam is directed onto a circle on the rear mirror, the spots on the mirrors form a circular spot pattern. After a number of passes through the cell, the laser beam exits the cell through the same coupling hole but in an inverted angle. This reentrant condition depends on the mirror radius of curvature and the mirrors separation and acts to stabilize the optical path. Absorption path lengths of up to 50 meters are feasible for a cell with a base length of 0.5 m and mirrors with 10 cm diameter. The design was later improved using astigmatic mirrors which have enabled path lengths up to 250 meters for a cell with a base length of 1 meter.

![Schematic view of a Herriott cell](image)

Figure 46  Schematic view of a Herriott cell

3.4.2 Integrated cavity output spectroscopy (ICOS)

Resonant cavities can provide much larger path length enhancements, the enhancement is in the order of the finesse of the cavity,
F, which, for a balanced cavity with high reflecting mirrors with reflectivities of ~99.99–99.999%, can be \( \sim 10^4 \) to \( 10^5 \). A problem with resonant cavities is although a high finesse cavity has very narrow cavity modes, often in the low kHz range while many diode lasers have free-running line widths in the MHz range, which is why it is difficult to utilize the full potential of the technology. One of the most commonly used techniques is integrated cavity output spectroscopy (ICOS) or the non-resonant variety off-axis ICOS (OA-ICOS). The basic operating concept of the off-axis ICOS is based on injecting the laser light into the optical cavity in an off-axis configuration with respect to the on-axis cavity alignment formed by the two highly reflective dielectric mirrors. Unlike traditional absorption measurements, the optical path length in the off-axis ICOS method is effectively infinite as the entering laser light bounces back and forth retracing the same path on each cycle. The effective path length of the cavity is given by the mirror reflectivity. Therefore, using highly reflective astigmatic mirrors with \( R > 99.99\% \) the laser beam can travel 10,000 passes, lengthening a 20 cm long cavity to an optical path length of 2,200 meters.

Figure 47  *Off-axis integrated cavity output spectroscopy (OA-ICOS)*

The off-axis alignment configuration off-axis ICOS is intrinsically robust. The cavity effective path length does not depend on the exact laser beam alignment, only on the losses in the cavity. Therefore, the design is tolerant against mechanical vibrations. The absorption intensity signal is acquired in the same way as with conventional TDL. The injected laser light wavelength is scanned over the entire spectral feature of the absorption peak. Quantitative measurement of the probed species concentration can be derived from the transmitted intensity signal. One problem with ICOS is that the transmitted light in-
tensity becomes very low due to the high reflectivity of the mirrors. For this reason it can only be used with very good detector electronics.

LGR markets more than 10 different ICOS analyzers with very high sensitivities. The EAA-22 ammonia analyzer has a specified sensitivity of 0.6 ppb. The CDA-22 CO$_2$ analyzer specifies a measurement precision of 150 ppb over a 5 second response time and 50 ppb using 100 seconds integration.

3.4.3 Cavity ring-down spectroscopy (CRDS)

Cavity ring-down spectroscopy is based on a measurement of the difference of the rate at which light intensity leaks out of a stable optical cavity with and without the absorbing gas present. Cavity ring-down spectroscopy (CRDS) has its origins in technology developed by the aerospace industry for characterizing high reflectivity mirrors. Its application to molecular absorption measurements was first described by O’Keefe and Deacon at Los Gatos research in 1988. The basis of all cavity ring-down techniques is a measurement of the decay of light within a high finesse optical cavity. In most applications, the cavity is formed from a pair of high-quality plano-concave mirrors, see Figure 48, often having reflectivities greater than 0.9999.

![Diagram of cavity ring-down spectroscopy](image-url)

Figure 48  Cavity ring-down spectroscopy (CRDS)

In the most basic version of the technique, a pulse of laser light is directed onto the back face of one of the mirrors, and the small amount of light coupled through the mirror into the cavity is repeatedly reflected backwards and forwards between the two mirrors. The intensity of the trapped pulse will decrease by a fixed percentage during each round trip within the cell due to both absorption and scattering by the medium within the cell and reflectivity losses. The result is that the amount of light within the cavity decays exponentially with time.
The exponential decay is recorded by positioning a sensitive photo detector behind the second mirror to detect the tiny amount of light leaking out of the cavity through the mirror on each pass. The time constant $\tau$ of the decay is given by:

$$\tau = \frac{L}{c_{\text{light}} \left[ (1 - R) + \alpha(\nu)cL \right]}$$

Where $d$ is the cavity length, $c_{\text{light}}$ the speed of light, $1 - R$ the cavity loss in the absence of a sample, where $R$ is the mirror reflectivity, and $\alpha(\nu)$ is the absorption coefficient of an absorbing species with the concentration $c$ present over the path length $L$ in the cavity. Two ring-down times are compared on and off the absorption line, $\tau_{\text{off}}$ and $\tau_{\text{on}}$ respectively.

$$c = \frac{1}{\alpha c_{\text{light}}} \left( \frac{1}{\tau_{\text{on}}} - \frac{1}{\tau_{\text{off}}} \right)$$

Because the measured decay constant is independent of the absolute intensity of light injected into the cavity, CRDS has the distinct advantage over single-pass techniques that it is largely insensitive to noise caused by shot-to-shot fluctuations in the intensity of the pulsed laser source. The great utility of the CRDS method lies as much in the extremely high sensitivity as in the simplicity of the technique. Absolute concentrations are easily inferred from the absorption data that CRDS provides. CRDS concentration detection limits for many species have been demonstrated to be in the part-per-billion to part-per-trillion range. Although this technique can provide a significant improvement in the sensitivity of infrared absorption analysis, pulsed laser sources generally do not possess the high frequency resolution necessary for many IR applications, which is why the technique has been limited to some special applications such as trace gas analysis in the semiconductor industry and greenhouse gas emissions detection.

### 3.5 Sample modulation techniques

When the wavelength of the diode laser is tuned over an absorption line, a periodic, slowly drifting, fringe structure is superimposed on the desired signal from the absorption of the target gas. This etalon effect
is in reality the limiting factor independent of modulation schemes. The problem of fringe reduction remains the main challenge in order to improve the ultimate sensitivity of a TDL spectrometer. A reduction of the fringes below a fractional absorption of $10^{-5} - 10^{-6}$ generally requires some selective modulation of the sample spectral feature and investigation of the rest of the optical setup. The most basic approach is to switch between ambient and background signals by emptying the absorption cell in order to subtract the background fluctuations. This “sample modulation” is very slow, especially for sticky, polar substances like ammonia and the exchange time is much longer than the drift time of the etalons. A more promising approach is the use of an additional fast modulation of a spectral feature to separate disturbing background effects from the molecular feature of interest. The most commonly used schemes for rapidly modulating an absorption line are the Zeeman and Stark effects.

3.5.1 Faraday modulation spectroscopy

Faraday modulation spectroscopy (FAMOS) is a spectroscopic technique for detection of paramagnetic molecules in general. The technique is often used for trace gas detection of oxygen and nitric oxide (NO). The technique utilizes the fact that, in the presence of a magnetic field, a transition in a paramagnetic molecule can rotate the polarization plane of linearly polarized light tuned to that transition. By placing the sample between nearly crossed polarizers, the rotation is monitored as an alteration of the detected optical power. Modulation of the magnetic field and performing phase sensitive detection of the signal at the modulation frequency does not only provide noise reduction as the wavelength modulation spectrometry (WMS) technique does, it also largely suppresses background signals originating from optical interference effects and possible spectral interferences from non-paramagnetic gases. The magnetic field is applied by running an alternating current in a solenoid surrounding the absorption cell.
The technique has recently been successfully applied for oxygen detection utilizing VCSEL lasers and for NO detection using QC lasers [Ref. 17, Ref. 18]. Sensitivity limits for oxygen was around 30 ppm×m [Ref. 17] and for NO 4.5 ppb×m with a response time of 1 second [Ref. 18].

3.5.2 Stark modulation spectroscopy

The Stark effect can be used to modulate the absorption coefficient of a rotational-vibrational absorption line by applying a modulated external electric field to the gas. The electric field causes a splitting of the ground state and the excited state of the absorption transition. As a result, the lineshape of the absorption transition becomes deformed. This deformation results in an amplitude modulation for any given point of the absorption line. The amplitude-modulated absorption signal can be detected by means of a lock-in amplifier which is referenced to the Stark modulation frequency. Stark modulation spectroscopy is selective since it only modulates the absorption line and it reduces the influences of optical interferences and other molecular absorbers that do not show a Stark effect. The technique employs a very high electrical field strength, which is why it has a very limited application in field instrumentation. Figure 50 shows a TDL setup for Stark spectroscopy. A laser beam is passed through an absorption cell that has two electrodes inside. A high voltage supply generates an alternating electrical field perpendicular to the laser beam. The alternating field generates an intensity variation. A lock-in amplifier performs phase sensitive detection of the signal at the electrical field modulation frequency. Figure 51 shows a direct absorption TDL spectrum of formaldehyde for the cases field on and field off, from [Ref. 16].
Figure 50  *Setup for Stark modulation spectroscopy*

Figure 51  *A direct absorption spectra of formaldehyde for the cases when the field is on and the field is off*

In practical application, the enhancement of Stark modulation is often limited to one order of magnitude due to problems with maintaining the high field in the cell.
4 References


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