Application of Tunable Diode Laser Spectroscopy for atmospheric trace gas detection:
Improvements to detect Formaldehyde and Formic acid at the same laser temperature

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Contents

Abstract

In the last few decades the tunable diode laser absorption spectroscopy technique has been well established in the field of atmospheric trace gas detection. The detection of trace gases in the atmosphere yields to a better understanding of the physics and chemistry of the atmosphere. It allows a deep insight in air mass motions and is a powerful tool for air quality controls. The TDLAS method is mainly used in the mid-infrared region of the electromagnetic radiation spectrum and records rotational-vibrational absorption lines of molecules. By using the mid-infrared spectral region most of the atmospheric trace gas species can be measured.

Most of the TDLAS instruments uses lead-salt lasers in the range of 3 to 30 μm. To get an outstanding specification with detection limits in the sub-ppbv range, multipass reflection cells are used. By reducing the pressure in the absorption cell, overlaps with other species can be minimized. This high selectivity and sensitivity of TDLAS systems allows measurements of species with low concentrations in the atmosphere, such as HNO_3, HONO, CO and formaldehyde.

Here we report about a TDLAS instrument setup, a TAMS (Tropospheric air monitoring system) which is reconfigured for HCHO and formic acid measurements. The aim is a modification of the instrument to detect formaldehyde and formic acid without changing the laser temperature. This would provide a much improved efficiency and duty cycle between measurements. To run the system after an idle time of approximately six months, preliminary tests are necessary. These tests and other tests are described in the experimental part of the thesis. Problems with the laser diode required a switch to an other diode. This laser diode has a different wave number range and a detection of HCHO and HCOOH was no longer possible. To use the general instrument setup, a detection of 12CO/13CO isotopes came into the focus of the work.

The theory of TDLAS and the importance of the selected species in the atmosphere, are part of the first two chapters. A detailed characterization of the instrument is given in chapter 3 and in chapter 4 all tests and modifications on the instrument are described.

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Chapter 1

Theory of Tunable Diode laser absorption spectroscopy

Tunable lead-salt lasers were first used for high-resolution spectroscopy in the mid-infrared region of the electromagnetic spectrum in the 1960s. About a decade later, an atmospheric application with long-path cells and measurements of some species at a detection limit of 20ppt [Eurotrac 1997] was developed. Tunable diode laser absorption spectroscopy became a powerful tool to measure trace gases in the atmosphere. Varied designs and improvements of the basic components for TDLAS instruments opened the way to measurements at different types of instrument platforms such as ground-based stations, aircraft and ships. A compact design of a TDLAS instrument, which builds the basis of this project, is especially developed for ground-based and airborne measurements. Particularly the use of aircraft affords the determination of trace gases and their concentrations throughout the troposphere. With the use of small aircraft research on weather situations of special interest, like thunderstorm clouds, are possible.

Tunable diode laser spectroscopy is most used in the mid-infrared and is based on the detection of single isolated rotational-vibrational absorption lines of molecules. Most atmospheric species show absorption lines in the mid-infrared and with typical concentration of about 1 ppb, the very small absorption cannot be detected by regular spectroscopy methods with absorption cells of up to 10cm length. To be able to detect these small absorptions, two developments are important. First, TDLAS uses a multi-pass absorption cell, which yields to a path length up to 100m. Different types of multi-pass absorption cells have been developed in the last decades and three of them are commonly used in atmospheric applications. These are the Herriott cell (Herriott et al 1964), the astigmatic Herriott cell (Herriott and Schulte 1965) and the White cell (White 1942). The current instrument setup uses a double corner cube White cell, developed by Wienhold *et al.* The second way to come down to measurements in the ppb region, is to use modulation spectroscopy. The diode laser is then modulated over the absorption line width. The frequency can be varied between 100Hz and 2 GHz.

More details about quantitative IR-absorption spectroscopy, lead-salt lasers and modulation spectroscopy are given in the following sections.

1.1   Absorption Spectroscopy

Absorption Spectroscopy is based on the Lambert-Beer law. It describes the intensity decrease of electromagnetic radiation when a volume with absorber molecules is passed via the path length l. The Lambert-Beer law is shown in the following formula.

$$I(\nu) = I_0(\nu) \cdot e^{-\alpha(\nu) \cdot L} \tag{1.1}$$

The intensity of the radiation by transmittance of the volume without absorber molecules is given as I_0. The path length is L and $\alpha(\nu)$ is the absorption coefficient. The absorption coefficient shows a dependency from the absorption cross section $\sigma(\nu)$ which is characteristic for each absorbing species.

$$\sigma(\nu) = \alpha(\nu) \ N \tag{1.2}$$

This equation gives a relation between the absorption coefficient and the concentration of the absorbing species in the volume. N is the concentration.

The exponent of the Lambert-Beer law can also be named as the optical density and is frequency dependent.

1.2   Quantitative IR-Absorption spectroscopy

Infrared spectroscopy is based on the interaction of electromagnetic radiation with the dipole moment μ of a molecule. In the case of right conditions for an interaction between the oscillating electric field of the radiation and the dipole moment, a change in energy of the molecule from a lower to a higher state is accomplished. The energy of infrared radiation is able to influence the vibrational and rotational states of a molecule, where the electronic states are unaffected. Vibrational transitions can be described by a harmonic oscillator and the rotational value by a rigide rotator. The two different types of transitions affect each other and a band-spectrum can be detected in an IR spectroscopic experiment. Within a vibrational band, a number of closely spaced absorption lines can be observed. These are a result of the simultaneous change of the rotational state while a change in the vibrational quantum number occurs. A vibrational- rotational spectrum of HCl is shown in figure 1.1. The branch of lines on the high-energy side correspond to changes with $\Delta J = +1$ and this branch is called R-Branch. A change of $\Delta J = -1$ yields to a P-branch in the lower-energy part of the spectrum. The change of transition state with $\Delta J = 0$ is not allowed in case of the selection rule. So a Q-branch near the band-origin does not appear.
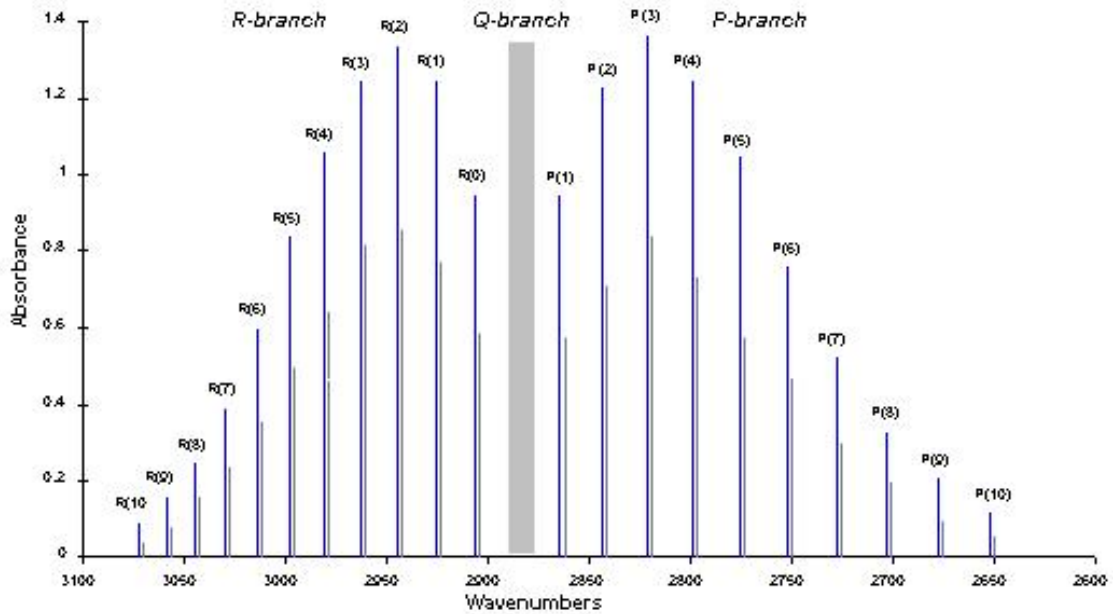
Figure 1.1: IR spectrum of HCl Source: web.nmsu.edu

For quantitative IR-spectroscopy it is important to recognize that the absorption lines of a spectrum are not infinitely sharp and without any width, but spread over a range of wavelength and accordingly frequencies. The maximum in intensity is at the line centre. Three types of line shapes are important and have to be known for spectroscopic purposes. The Doppler broadening is based on a statistical theory and a MAXWELL velocity distribution is assumed. Therefore the line shape looks like a Gaussian curve and the line width (standard deviation) depends on temperature. At high pressures the collisions of molecules affect a broadening of the line shape. The result is known as the Lorentz profile. For pressure ranges, used in most of the spectroscopic measurement techniques (a few torr up to 110 torr), both effects on line shapes result in a overall description which is the Voigt function. The process to get the Voigt function from Doppler and Lorentz functions is a convolution.
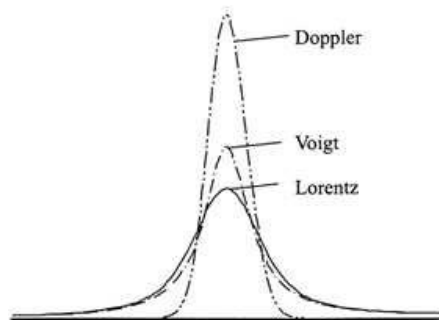

Figure 1.2: Types of line shapes: Doppler, Lorentz and Voigt profile

Calculations of profiles for different measurement conditions show a lower impact of pressure broadening for sampling and cell pressures between 10 to 50 torr. This fact of well resolved IR Voigt line shapes for individual and little groups of absorption

lines, makes the IR spectroscopy so useful. Interferences from the same molecule or other molecules in the sample are minimized and a modulation technique can be applied.

1.3   Tunable diode lead salt lasers

Lasers, used for TDLAS can be divided into two classes [Fehér 1995]. Gallium-arsenide based lasers in the region of 0.6 to 6 μm and the lead-salt lasers, ranging between 3 to 30 μm. The latter shows a high spectral brightness and narrow emission band width [Wienhold 1998].

Tunable diode lead-salt lasers are similar to GaAs-lasers used in communications. The typically 300 x 250 μm wide laser diodes, are made by crystals of lead-salt semiconductors. Salts like $Pb_{1-x}Sn_xSe$ with different stoichiometric compositions build a p-n-junction. When a current of a few milli-Ampere is led through the pn-junction, a lasing action takes place. The wavelength is determined by the energy gap and is temperature dependent. One divides lasers into two types: Type I emits wavelengths between 3000 and 4000 cm^{-1} and is operated at temperatures below 77K. Lasers of type II are operated above 77K and can be cooled by liquid nitrogen. Their wavelengths are typically between 3050 and 900 cm^{-1}. With change of temperature, a tuning of about $100 cm^{-1}$ can be achieved and the rate is about $5 cm^{-1}$/K. Tuning via the current is more accurate and equals about 0.05 cm^{-1}/mA. The typical output for lead salt lasers is 0.1-0.5mW and enough for detections through a multi-pass reflection cell with a path length of 100m. The Output beam of a laser diode has a divergent behaviour and, therefore a specific optic, right after the laser, is required to focus the laser beam.

1.4   Modulation Spectroscopy

The very small signals from trace gases in the atmosphere can not be detected by conventional spectroscopy methods, as they use direct absorption. The small changes would not be seen in a big signal. Therefore, the application of modulation spectroscopy is useful. The benefit of this method is a direct proportionality between detected signal and the concentration of the species. It also allows the measurement at a frequency, where the laser noise is small. The modulation technique can be divided into two types. For Wavelength modulation spectroscopy (WMS) the modulation frequency is lower than the absorption line width and usually 50kHz. The second type is the frequency modulation spectroscopy (FMS), where the modulation frequency is usually greater than the absorption line width and of the order of 500 MHz to 2GHz.

The TDLAS system in this work uses wavelength modulation and therefore we concentrate on this method in the following section.

A modulation of typically 50kHz is added to the laser current. This produces a sinusoidal change of the laser emission frequency. A narrow-band and phase sensitive amplification of the signal at the detector is accomplished by a lock-in amplifier. The Fourier transformation of the periodic of the detector signal, yields an amplification of the n-th Fourier compound of the n-th basis frequency. For TDLAS application, the 2nd Fourier compound is used and is comparable with the 2nd derivation of the signal. Therefore, a best result for a detected signal is achieved by demodulation with twice the modulation frequency. With the second harmonic the maximum is at line centre and the baseline is around zero Volts. These characteristics of the signal are useful. With higher harmonics the signal decreases significant.

Chapter 2

Atmospheric trace gases

Formaldehyde, formic acid and $^{12}CO/\ ^{13}CO$ Isotopes

In this work the species of interest are formaldehyde and formic acid. Their importance in the atmosphere and, therefore, their quantitative measurement are discussed in the following chapters. This chapter will give an overview about the characteristics and behaviors of these substances in the atmosphere. In this case, since the laser to measure HCHO and HCOOH stopped functioning, a switch to another laser was necessary. Consequently the measurement of these species was no longer possible. The characteristics of the second laser allow the measurement at CO absorption lines. Thus, CO and especially its isotopes in the atmosphere are the subject of this work. The characteristics are described in the last section of this chapter.

2.1 Formaldehyde in the Atmosphere

Formaldehyde plays an important role in tropospheric chemistry and in understanding chemical mechanisms of the atmosphere and their oxidative capacity. With measurements of formaldehyde, chemical transport models can be validated.

Formaldehyde is released to the atmosphere by different sources. Natural sources are forest fires, plant volatiles and microbial products as well as reactions of compounds in seawater. A part of formaldehyde in the atmosphere comes from refineries where fuel combustion and catalytic cracking takes place. Formaldehyde can also be formed by photochemical oxidation of reactive organic gases in the presence of ozone and NO_x which can be found in polluted areas [Finlayson-Pitts].
A typical amount of formaldehyde in ambient air is 2-39 ppb (Seinfeld) and the atmospheric lifetime of HCHO can vary between hours and days and depends on the presence and reaction of different compounds. So the photolysis of HCHO yields to a lifetime of 3.8-8.6h and in respect to reactions with OH and HO_2 a residence time of 6.2h up to 1.5 days can be reached. In highly polluted areas the reaction with OH and HO_2 is in competition with photolysis. With respect to NO_3 the lifetime of formaldehyde in the atmosphere is 8 to 80 days [Finlayson-Pitts]. As the

lifetimes show, the major reaction of formaldehyde in the atmosphere is the reaction by photolysis. For this reaction two paths are known.

$$HCHO \; + \; h\nu \; \longrightarrow \; H \; + \; HCO \tag{2.1}$$

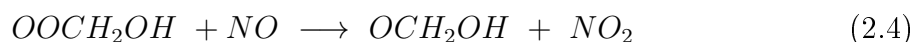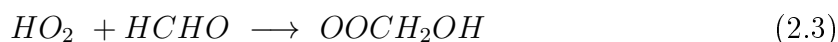$$HCHO \; + \; h\nu \; \longrightarrow \; H_2 \; + \; CO \tag{2.2}$$

The first shown path is the most important one and a major source for free radicals in the atmosphere. Free radicals are important species in the atmosphere. They are part of the self-cleaning mechanism of the atmosphere in case of their participation in loss-reactions of harmful substances. Free radicals also control most of chemical processes in the troposphere, such as ozone production. To understand all these free radical processes it is important to know about formaldehyde in quantitative ways.

2.2 Formic acid in the Atmosphere

Formic acid counts to the acids in the atmosphere and is one of the most abundant carboxylic acids there. Typical values in the troposphere are around 5 to 10ppb. The sources are not well understood, but a seasonal variation dependent on temperature seems to be present. This seasonal and temperature dependency point to a microbial source. Besides natural or human made sources of formic acid, a production by atmospheric processes is known. These processes are photochemically led and occur in the gas-phase by reaction of ozone-alkenes or in cloud water via hydrolysis of aldehydes and a aqueous-phase reaction. The behaviour of formic acid in cloud water depends strongly on the pH-value of the aqueous phase.
An other way to form formic acid is a path via formaldehyde. There the fast reaction of formaldehyde with HO_2 leads to a peroxy radical. In the presence of NO and oxygen formic acid is formed in two steps as shown below [Finlayson-Pitts 1986].

$$HO_2 \; + HCHO \; \longrightarrow \; OOCH_2OH \tag{2.3}$$

$$OOCH_2OH \; + NO \; \longrightarrow \; OCH_2OH \; + \; NO_2 \tag{2.4}$$

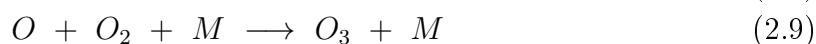$$OCH_2OH \; + O_2 \; \longrightarrow \; HCOOH \; + \; HO_2 \tag{2.5}$$

This scheme shows, that an understanding of formaldehyde and formic acid chemistry, especially their quantitative appearance, can help to obtain information about NO and therefore NO_x chemistry. In addition NO as well as the entire NO_x group plays an important role in understanding the natural troposphere.
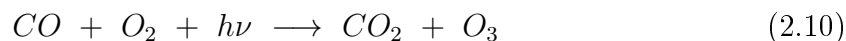
2.3   CO Isotopes in the Atmosphere

Carbon monoxide is a diatomic gas which is released to the earth's atmosphere mostly by volcanic activities and by anthropogenic emissions. Two thirds of the carbon monoxide in the atmosphere has an anthropogenic origin. The atmospheric lifetime of the molecule is about two to four months and the concentration is highly variable. Trends of an increasing amount of the global CO were observed in the 1980s. Recently a decrease of carbon monoxide can be observed. The rates of change are different for the northern and the southern hemisphere.

Carbon monoxide does not count directly to the greenhouse gases, but has an indirect effect on climate change. CO reacts in the atmospheric oxidation cycle with the OH radical. This reaction affects a remove of one of the most oxidising species of the atmosphere, the OH radical. Because the hydroxyl radical is the key compound for the methane depletion reaction, the decrease of the Greenhouse gas CH_4 is less for low OH concentrations. Furthermore, each loss reaction of OH, affects one molecule of ozone. The atmospheric oxidation process is given as follows.

$$CO \; + \; OH \; \longrightarrow \; CO_2 \; + \; HO_2 \tag{2.6}$$

$$HO_2 \; + \; NO \longrightarrow \; NO_2 \; + \; OH \tag{2.7}$$

$$NO_2 \; + \; h\nu \; \longrightarrow \; NO \; + \; O \tag{2.8}$$

$$O \; + \; O_2 \; + \; M \; \longrightarrow \; O_3 \; + \; M \tag{2.9}$$

The net reaction is:

$$CO \; + \; O_2 \; + \; h\nu \; \longrightarrow \; CO_2 \; + \; O_3 \tag{2.10}$$

To understand the related effects and for a quantitative determination of these processes, the concentrations of CO as one of the key compounds need to be known. Therefore measurements for CO sources and sink reactions are necessary. A combinatory use of IR spectroscopy with the effect of isotopic fractionation, gives access to required information. The isotopic fractionation is a shift of the percentage of isotopes of an element based on physical or chemical processes. The fractionation is also a thermodynamic process and thus temperature dependent. The key value for this effect is the factor of fractionation α, who gives the relation between the isotope rates of two samples. The method allows comparing the isotope rates of different samples. This can for example be non reacted CO and CO in an air sample which is radiated and which already reacts with OH or other species.

Chapter 3

Instrumental

This chapter contains a complete description of the actual TDLAS instrument setup. It starts with the optical and mechanical setup, followed by the gas flow system and finally the electronics and data acquisition.

The instrument in total is developed for its application on ground-based measurements or in aircrafts. Therefore it is built up compact and all components fit into two flight racks. One rack holds the optics including liquid nitrogen dewars, pump for the White cell and computer with data acquisition board. The second rack holds the permeation sources and all control boards.

3.1   Optical and mechanical Setup

The type of lead-salt diode laser used in this setup requires a cooling to cryogenic temperatures. A specially developed liquid nitrogen (LN2) cryostat [Riedel, Knothe; Deutsches Patent 1993] is therefore used. This cryostat makes it possible to cool multiple Laser diodes in separated and indepenent cold-heads to temperatures between 80K and 150K. The cooling principle is based on a hydrostatic equilibrium between nitrogen vapour and liquid nitrogen. The liquid nitrogen runs through small pipes towards the cold stations where the laser diodes are placed. There, the liquid nitrogen evaporates and is then directed back to the LN2 tank via an orifice. The diameter of the orifice limits the nitrogen mass flow and allows a crude alignment of the cooling. The exact temperature at the cool fingers is measured by PT1000 and the exact regulation of the temperature is accomplished by active heating. The temperature and current, set to the diode, are controlled and driven by a LDC 800 control unit (Profile GmbH, Germany). For an efficient use of the liquid nitrogen reservoir, an insulating vacuum between LN2 tank and evaporator is necessary.

Two laser diodes with different wave number ranges are placed in separated cold heads. In total three cold head positions are available with this instrument. The divergent laser beam emitted by a diode is collimated by an aperture transformation from 1:2 to 1:7. This is realised by a 26° off-axis ellipsoid (OAE) mirror. The OAE mirror is housed in a box together with two flat mirrors. This combination forms a mirror objective which is justable in three dimensions with orthogonal axes

[Riedel 1993]. Between the mirror objective and the following beam pass, a pin-hole and a visible laser, like a Helium-Neon laser, can be set as a point light and an alignment for the optical pass is possible. The same position can be used for a wavelength determination with a special monochromator described by [Riedel 1993]. The monochromator can also be used for mode characterisation of the laser diode. The laser beam is then directed by different optical elements (mirrors) to the White cell. The laser and White cell are placed on different levels of the instrument rack. Therefore the beam is directed through a hole in the optical plate and coupled into a double corner cube White cell. The White cell has a basic length of 0.5 m and a volume of approximately 2.7 L. This special type of a White cell is developed by Wienhold et al in the 1990s. Additional to the three-mirror system of a standard White Cell, the improved version contains two corner cube mirrors. This modifications lead to a better mechanical stability as well as to a significant reduction of Etalon structures.A smaller cell diameter can be used. The total path length can be varied around 64 m and includes 128 passes.

The outgoing beam from the multipass reflection cell is directed to the upper level of the optical plate by mirrors. A CaF_2 beam splitter splits the beam into a signal and reference path. 95% of the beam is lead to the signal detector and 5% to a reference detector. The beam splitter is again followed by mirrors and the path towards the reference cell includes a reference cell of 8 cm length. The HgCdTe detectors (Kolmar Technologies Inc.) are liquid nitrogen cooled.

3.2 Gas flow system

For simultaneous measurements of formaldehyde and formic acid, a gas flow containing both species from permeation devices is required. For this purpose zero air is directed through the permeation sources and diluted by zero air from a second gas bottle. The original setup did not cover a gas flow system for these purposes. The modification process is described in the experimental part of this thesis. The following section contains information about the components of the gas flow system and the calibration of the TDLAS instrument.

Permeation sources offer access to well define flow rates of a species of interest. A permeation source is basically built by a heater whith a Teflon (PTFE) tube containing the substance as a solid or liquid. A picture of the permeation source of HCHO is given below.
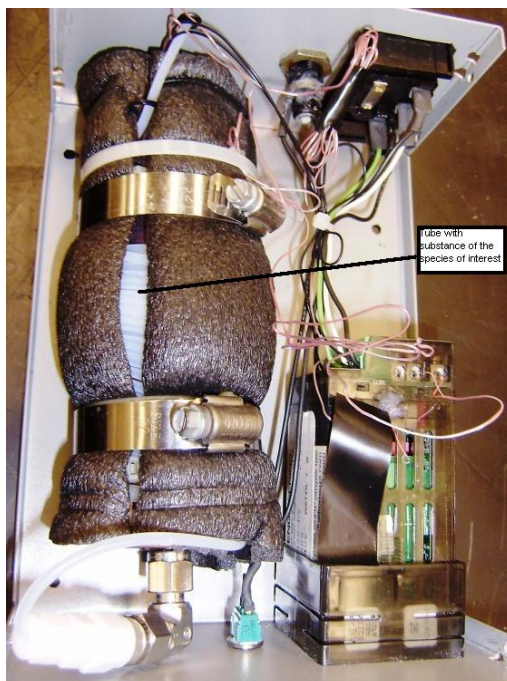
Figure 3.1: Assembly of a Permeation source used for the current TDLAS setup. The tube with the substance is wounded around the heater.

The tube with the substance in it, emit permanently and the amount emitted depends on temperature and pressure. Permeation source temperatures used in the experiment are $45.0°C$. To bring the emitted substance to the measurement cell, a 1/8" Teflon tube with a constant zero air flow is used. Teflon tubes are used to minimize surface effects. The gas flow from the permeation sources usually needs to be diluted which can be done by a PTFE line from a second zero air gas bottle. The gas is then directed to the White Cell. For a better detection limit and to minimize the overlap of absorptions from other species in the air sample, the pressure of the White Cell is reduced to 50 mbar. The pressure of the White Cell is measured and controlled by a Baratron (MKS 122A-00100DD). For quantitative measurements of air samples, background signals and calibrations are required The calibration is usually a standard addition. The flow from the permeation source is added to ambient air, which is sampled by an inlet system. The White cell then needs to be flushed between the ambient, background measurement and the two calibrations for HCHO and HCOOH. A flushing time of 15 seconds allows an exchange of the gases to 99% [Schiller 2008].

3.3   Electronics and Data acqusition

Different electronical compounds are necessary to run the TDLAS instrument. A schematic of the system is shown in the following figure.
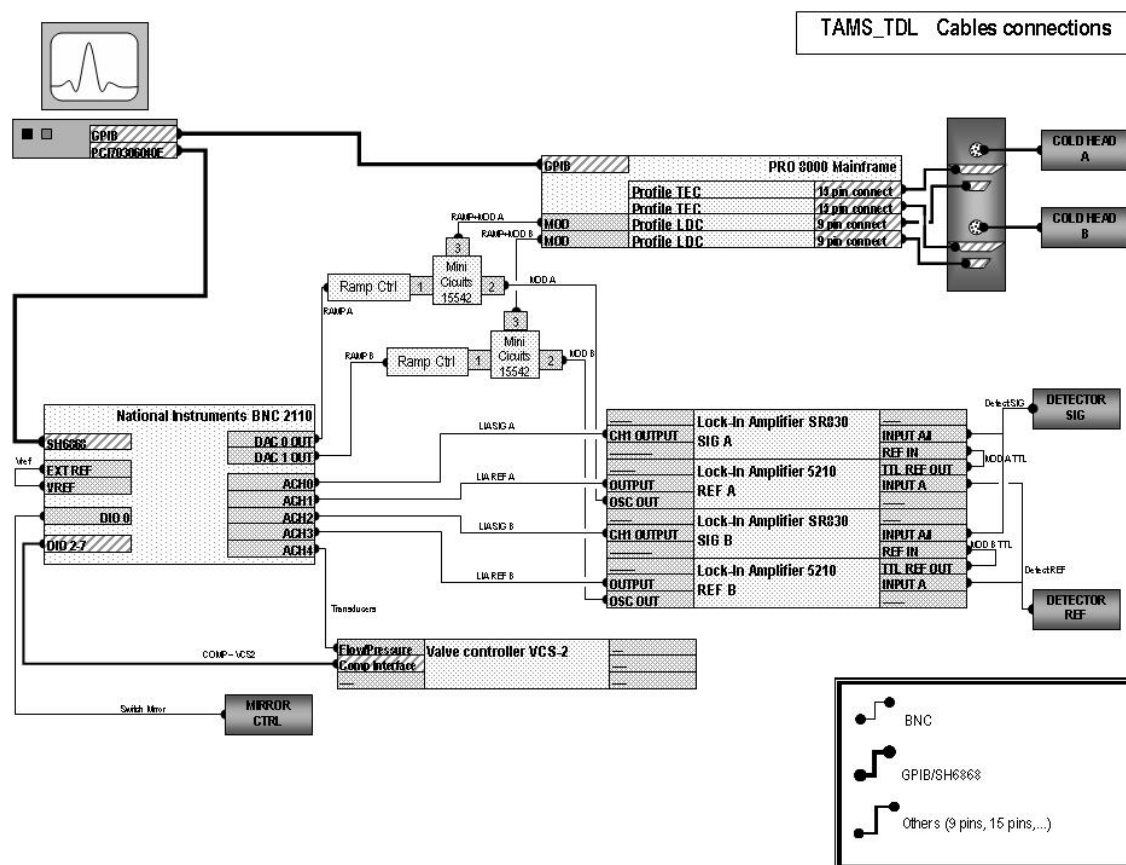

Figure 3.2: Schematic of the TAMS electronics.

First of all, a control of the laser diode is important. The laser controller is a LDC 8000 (Profile GmbH, Germany) and regulates the laser temperature and current to a constant value. This ensures a constant laser wavelength. An electrical board with modulation and ramp controller allows to set ramp times and modulation frequencies to the laser current. With the saw tooth current ramp a scan across the absorption line is possible.

The detected signal is pre-amplified and then triggered to the lock-in amplifier. The lock-in amplifier convolves the signal with the reference signal and demodulates the signal. An analog-to-digital converter gives a digital signal out which can be processed by further hard- and software.

All information about the electronics and signals go to a National Instrument Board BNC 2110 and from there to a GPIB interface which is the connection to a windows based Computer. The active control of the parameters and the demonstration of the signal are done by a Labview user surface. This surface is written by former group members and can be modified if needed.

Chapter 4

Experimental and Results

4.1 Preliminary Tests

To test the state of the instrument, tests of different components are necessary. The first section of this chapter describes the preliminary tests and measurements, which are done at the beginning of the project. Basic tests at electrical connections and crude optic alignments are not going into detail description.

4.1.1 Evacuation of the dewar

A soft vacuum in the LN2 cryostat, because of severlas months of disuse, shortens the time period in which LN2 is held by the dewar. First tests show a standing time of LN2 in the dewar from less then 20 hours. To improve the standing and consequently the operation time for one fill, an evacuation of the dewar was required. The evacuation was done with a turbo pump. A first evacuation is run over four days and a second run, one week later, was run for two days. The final pressure in the dewar is 10^{-2} mbar. The standing time is improved to approximately 28 hours and the operation time up to eight hours. An improvement of these times ensures a permanent constant cryogenic temperature of the cold heads. Consequently, a constant cryogenic temperature over night, when fills are not possible. This avoids an accumulation of air and water vapour in the lines between LN2 reservoir and cold heads. Especially water vapour can block the lines and a lacking cooling of the laser diodes would be the result. A blocking of one line was observed with the very first filling of the tank. About one hour was required to cool down to 79.77K. After the dewar evacuation and regular fills, a blocking is not observed again.

4.1.2 Calibration of the Formaldehyde Permeationsource

Permeation rates need to be determined frequently. This is also done at the beginning of the project. The permeation rate of formaldehyde can be determined by a UV-spectrometric measurement. From the reaction of formaldehyde with the disodium salt of chromotropic acid in concentrated sulfuric acid, a stable mono-cationic dibenzoxanthylium product results. This reaction product strongly absorbs UV-light at 580 nm.

Experimentation

A solution of chromotropic acid in concentrated sulphuric acid is prepared. The mixing ratio of chromotorpic acid to sulfuric acid is about M 1:9. The loss of reaction ability is approximately 0.036% per day.

The Permeation source is pre-heated for three days without a gas flow. The gas flow of 20 sccm is started two hours before starting the reactions. Three measurements, each with 5 mL of the standard solution are done. Parts of the chromotropic acid solution are weighted in wash bottles and pre-heated to $70°C$ up to $85 °C$ for 15 minutes. At these temperatures the reaction yield is much better then at room temperature. The PTFE tube from the permeation source is placed into the liquid and the gas flow bubbled through for approximately one hour. For spectrometric measurements the reaction solution is cooled down to room temperature and the solution is pipetted into a cuvette of 14 mm path length. The transmission is set to 100% by an empty cuvette. With the values of transmission, the calculated concentrations and the spectrometer specifications, the permeation rates can be determined. Two measurements at different permeation source temperatures are done. The results are presented in the following table.

Sample	Permeation rate
1	$5.507*10^{-8}$ g/min
2	$7.595*10^{-8}$ g/min
3	$8.072*10^{-8}$ g/min

Table 4.1: Measured permeation rates of the formaldehyde permeation source at 26.5 $°C$.

Sample	Permeation rate
1A	$1.624*10^{-7}$ g/min
2A	$1.605*10^{-7}$ g/min
3A	$1.504*10^{-7}$ g/min

Table 4.2: Measured permeation rates of the formaldehyde permeation source at $45.0°C$.

For the measurements at $25.6°C$, the first value need to take out, because the gas tube is not placed in the solution, as it is done for measurements 2 and 3. This seems to have an effect on the reaction rate, and can be ascribed to a loss of gas in the solution when the tube is not placed under the liquid surface. The average permeation rates are as follow:

Permeationrate at 25.6$°C$: $7.834*10^{-8}$ g/min = 78.34ng/ min
Permeationrate at 45.0$°C$: $1.578*10^{-7}$ g/min = 157.8ng/ min

It is obvious, that the permeation rate is higher for higher temperatures at the same pressure and zero air flow. A increase of temperature from $25.6°C$ to $45.0°C$ leads to an increase of permeation rate by the factor of approximately 2.

4.1.3 Calibration of the formic acid permeation source

A characterisation of the formic acid permeation source was not possible because of an unusable Ion-chromatography instrument. A determination by titration against a strong base, like sodium hydroxide, was not attempted since for the small amounts of formic acid emitted by the permeation source, the wet-chemistry method of titration would lead to a great inaccuracy.

4.2 Gas flow System modification

For atmospheric measurements of trace gases air samples are directed by an air inlet system to the measurement cell, the White Cell. The gas flow system must provide a selection possibility for the type of gas introduced into the absorption cell. The types of gases, needed for quantitative measurements, are ambient air from the inlet system, background air and calibration gas.

ambient air = the air which need to be measured
background = zero air
calibration = ambient + air from permeation source

The aim is to measure formaldehyde and formic acid simultaneously. For this purpose, the given gas flow setup need to be modified. In previous projects, the system was used to measure one species, background and calibration gas. To measure HCHO and HCOOH, with background and calibration, a new connection of the mass flow controller, valves and tubes is necessary.

The calibration is based on standard addition where a known amount of the species produced by the permeation source is added to ambient air. The amount of substance emitted by the permeation sources and, forwarded by a flow of 20sccm of zero air, needs to be diluted. A schematic picture of the developed gas flow system is shown in the following picture.
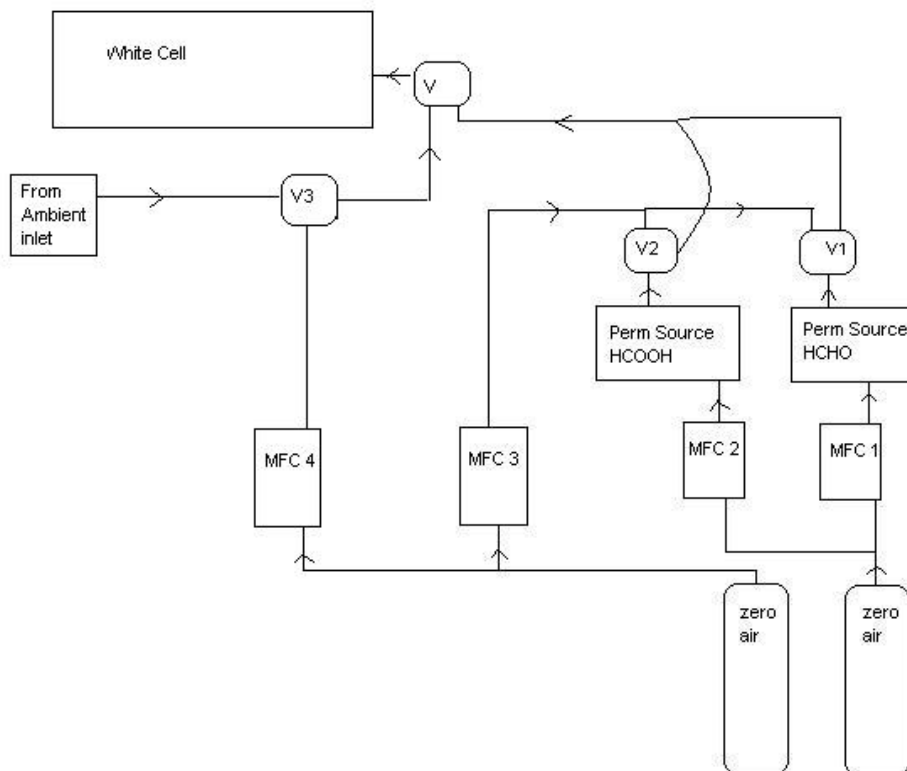
Figure 4.1: Gas flow system for ambient air, background and calibration gas.

As shown in the right part of the schematic, valve V3 allows a selection between ambient air and background flow. The background is zero air, with a regulated flow by the mass flow controller MFC 4. The calibration gas is zero air led through the permeation source. The flow through the permeation sources is controlled by, MFC 1 for HCHO and, MFC 2 for formic acid. The set flow of zero air through the HCHO and HCOOH permeation sources is 20 sccm. A further dilution is made possible by setting valves V1 and V2 into the air flow. Via these valves, zero air from a second gas bottle can be mixed to the permeation source gas flows. A flow control of air, coming from the second zero air bottle, is given by MFC 3. The output of Valves V1 and V2 is connected by a y-piece and forwarded to the valve next to the White Cell. In case of separated calibrations, the lines from HCHO and HCOOH can be connected by the y-piece. If a calibration for HCHO is running, valve V2 from HCOOH will be closed and the line is used only by the HCHO gas flow controlled by valve V1, and reversed.

4.3 Data acquisition

The operation and data acquisition for the TDLAS instrument is accomplished by a Windows based computer. For this research project, a new computer needed to be set up. The system of the computer is Windows XP and the TDLAS instrument procedure is based on Labview 5.1 and Data acquisition card (DAQ Card 6062E)

Version 6.8. These are older versions of National Instrument Software, and may be not compatible with the Windows operating system. All required installations are done, but a stable working system could not be set up. Different sub-vi (virtual instruments, which can be written and included to the total program) are missed. The GPIB interface, to receive and send data from/to the instrument, is not accepted from the computer. New installations as well as up- and downgrades are tried. A downgrade to Windows 98 did not help, since a machine based on Windows 98 is also missing sub-vi's. These problems with software and hardware could not be solved. Consequently, the instrument was run manually. The display of signals is done on an oscilloscope.

4.4 Tests to measure formaldehyde and formic acid

The first intention of the project is to measure formaldyde and formic acid with one laser diode at the same laser temperature. The absorption lines for the species of interest are taken from the HITRAN Database. For formaldehyde the C-O stretching at 1759 cm^{-1} is selected for measurements. The absorption line for formic acid is overlapping the formaldehyde line at $1759cm^{-1}$.

To detect the selected absorption line for formaldehyde, the already installed laser diode (432-hv-1-15) can be used. The diode was cooled to 92K and the current was set to 775mA, which is below the maximal current set by the laser control board. When the laser diode was tried to switch on, an error message appears on the control board. A cable damage was assumed, since the laser diode can be switched on for short time frames, but finally shows no reaction. A cable damage or a loose contact was eliminated by circuit tests. It was assumed, that the diode is damaged and can no longer be used.

A change of the laser diode was considered. An applicable diode could not be found and a change of the diode for the cold head place would impact a warming-up of the LN2 dewar and a repeated evacuation. Since the general setup of the TDLAS instrument could still be used and, a second laser, placed in one of the other cold heads can be used, a switch to this laser diode is nearby. Due to a different wave number range of this laser, formaldehyde and formic acid can no longer be measured. To detect this species, a new laser diode needs to be found and mounted into the cold head station.

4.5 Tests to measure Carbon monoxide isotopes

The laser diode (397-HV-1-184) in the second cold head was previously used to measure CO. The characteristic wave number is $2105cm^{-1}$. Absorption lines for CO can be found in the HITRAN database. The absorption line for CO usable for detections with the TDLAS system is $2174cm^{-1}$. For this wave number, strong absorptions by other species are minimal. The focus of the project is to detect $^{12}CO/^{13}CO$ isotopes. The relation of intensities for the isotopes is approximately

99:1.

The switch to this laser diode, placed in another cold head around the cryostat, needed a check of the laser beam alignment. This was done by using a HeNe-Laser on a pinhole. The alignment up to the White Cell input is basically good. The characteristic beam pattern of the double corner cubic White Cell, with dots in four rows, can be seen. An extreme loss of intensity is observed for the laser beam coming out of the White Cell. This can due to on dust particles in the White Cell, which leads to scattering of the laser beam. Consequently, the laser beam hitting the detectors was too low in intensity to give a significant signal.

Nonetheless, the function of the detectors is verified. A clear signal on the oscilloscope can be seen, when the laser is directed to the detector without the complete optical path with mirrors and White Cell in between.

Like the optical path needs to be aligned, also the focus of the laser beam on the mirror objective is checked and improved. For this purpose the mirror objective can be moved in three orthogonal axes. With this alignment and the low beam intensity of the White cell output beam, tests for temperatures and currents are done. The only information about the laser diode is the maximum temperature and the characteristic wave number. Many combinations of temperatures and currents are tried to find the laser line. Until the end of the project the laser line could not be found. This will be part of future work on the TDLAS setup for CO measurements.

Chapter 5

Conclusions

In this project, a Tunable diode laser instrument to measure the trace gases HCHO, HCOOH and CO isotopes is used. The aim of this work was to develop the current instrument setup to detect formaldehyde and formic acid by using one laser temperature. For this purpose, the instrument setup is characterised and preliminary tests are done. This includes a characterisation of the permeation sources, which shows a strong temperature dependency of the emitted amount of species by a permeation source. This emphasizes the importance of regular tests and characterisations of the permeation devices. Also the evacuation of the liquid nitrogen dewar by a turbo pump is important. A good vacuum and regular fills of the cryostat with liquid nitrogen, ensures a constant cryogenic temperature for the laser diodes. This will be very important, once the laser and absorption line of the species is found. Changes in temperature will also change the line centre and comparable measurements will be more difficult.

The difficulties in the laser beam alignment could be seen in this project. Especially disturbances of the beam by dust in the White Cell play an important role. A significant loss of intensity can be observed. Furthermore, disturbances by etalons and other optical aberrations yield to a loss of intensity. A detection of a signal with the detectors can be impossible. A careful alignment and a good knowledge about aberrations and their appearance are therefore important.

The effects of optical disturbances impact the tests with the laser diode to measure CO isotopes. The laser line for the CO laser can not be found during the project period. Tests on the White Cell with a minimized mode should be part of future work with the TDLAS instrument. As well as these tests and improvements, the software problem need to be solved by future students.

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