Detection of CO in combustion flues via line-of-sight absorption by use of a quantum cascade distributed feedback laser
(Theoretical considerations)

Master’s Thesis

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Abstract

This master’s thesis is part of a project initiated by Sydkraft, Vattenfall and Lund Institute of Technology, aiming at developing a robust and simple method for monitoring the concentration of CO in combustion products by laser spectroscopy.

The method proposed comprises infrared absorption spectroscopy, using a pulsed and thermoelectrically cooled quantum cascade laser, operating in a frequency interval around $4.6 \mu m$, where interfering peaks from other species in the combustion process are as sparse as possible. The idea is to investigate the transmission line profile of a rotational transition between the first and second vibrational energy levels of the molecule. One of the parameters determining the observed line profile is the concentration of CO. Thus, the concentration can be deduced by performing a non-linear least-squares curve fit of a theoretical profile, generated via molecular constants in the HITRAN database.

The aim is to take a first step in investigating whether useful data can be acquired under combustion conditions, using the type of laser mentioned.
Preface

This is the story of a diploma work that eventually proved to be subject to an unfortunate non-delivery of the QCL device essential for the intended measurements. There was one device, which was accidentally overheated and therefore destroyed. (However operating at an unsuitable wavelength for measurements at flame temperatures, this device could have been used for simpler, room temperature measurements in a cell.)

Be all that as it may, no measurements were made, so I’ve had a lot of time to write a bulky theory section, some of which may very well be left out by the majority of readers. One option would have been to skip or rewrite some of the theory sections, but I’ve decided to include them as they are, to open up for readers less educated in physics. I can imagine that this approach, providing relatively large amounts of text, require some guidance for the reader, which is why I have decided to add this short preface.

The general tip is to start by reading the summary in section 4. Doing so, the reader may freely exclude everything that exceeds the frames of his or her purposes.
1 Introduction

The task in this diploma work is almost self-motivating; in addition to CO being a regulated criteria pollutant, it’s a well-known fact that a high concentration of CO indicates incomplete combustion. Thus, the idea of monitoring the CO concentration, while manipulating various parameters of the combustion process, is not far fetched.

An example flame of special interest would be the one in a biomass furnace, possibly several meters across. Sydkraft and Vattenfall use furnaces that apply a two-stage combustion with the first stage being very fuel rich, after which air is injected, making the second stage lean. This way, temperatures are kept low, which limits the production of nitric oxides. Between the first and second stage, however, deposition onto the furnace walls of an organic acid, whose production is related to the production of CO, causes corrosional thinning of the wall. The goal for Sydkraft and Vattenfall is to minimise this corrosion via feedback control of the furnace, based upon the monitoring of the CO concentration. In this scenario, it makes sense to measure over a short pathlength, close to the wall, were the temperature is around 1000K\(^1\). These are features making it fairly easy to build a probe, which eliminates the great problems with optical thickness that would have been brought about by an optical pathlength of several meters, and also limits the amount of obstructing CO\(_2\) lines that would be the result at a higher temperature.

The principles of measurement presented in this thesis are not new. For example, the possibility of using tunable IR diode lasers for measurement of CO concentration was shown in 1977 [1]. Using the same type of equipment, flame temperature measurement via CO absorption lines was performed shortly thereafter [2]. As a more recent example, a more high-powered, thermoelectrically cooled, pulsed IR QC\(^2\) laser was used for measurement of atmospheric CO [3]. The invention of the first QC laser in Bell laboratories 1994 [4,5], is considered a breakthrough in IR spectroscopy, and further development led to the thermoelectrically cooled, pulsed and tunable QC-DFB\(^3\) lasers of today. Features that make them especially interesting are the ease of use (no cryogenics), and the relatively high power-to-size ratio. Such a device has not yet, to the best of our knowledge, been used for monitoring CO in a biomass furnace. As mentioned before, this is the ultimate goal of the project, and to get started, some basic spectroscopic measurement in a laboratory flame and evaluation of the performance of the QC laser have to be done, a task that was originally the diploma workers allotment.

Since the QC laser was not delivered, interest will be focused mainly on theoretical considerations regarding the method of measurement. Possible problems encountered when trying to evaluate the concentration of CO in a biomass furnace are discussed, and an experimental setup for testing the method in a methane flame is proposed.

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1 From personal communication with Prof. Mark Linne.
2 Quantum cascade.
3 Quantum cascade distributed feedback.
2 Theory

2.1 Bare Essentials of Combustion

Since this work deals with a diagnostic method rather than the combustion process itself, the treatment of combustion is kept very sparse. This short overview will treat only the concept of equivalence ratio and how this is used to describe lean, balanced and rich combustion.

A short schematic of a combustion process comprising an organic fuel and air can be written as

\[ F \text{ fuel} + A \text{ O}_2 + 3.76N_2 \rightarrow \text{combustion products} + X \text{ N}_2 \text{.} \]

where \( F, A \) and \( X \) may be expressed in for example mol/s.

The equivalence ratio, \( \Phi \), for an arbitrary combustion process, is defined as

\[ \Phi = \frac{\text{(moles fuel)/(moles oxygen)}_{\text{real mixture}}}{\text{(moles fuel)/(moles oxygen)}_{\text{stoichiometric mixture}}} \],

where stoichiometric combustion applies to a hypothetical case, were the combustion is complete, so that the only end products are H\(_2\)O and CO\(_2\) (i.e. we have \( X = 3.76 * N_2 \), since no nitric oxides are formed).

Hence, for the combustion process above, we may write

\[ \Phi = \frac{F/A}{(F/A)_{st}} \],

where \((F/A)_{st}\) is the fuel-to-oxygen ratio for the stoichiometric case.

This implies that when \( \Phi = 1 \), the combustion can generally be expected to be complete. We call this balanced combustion. When \( \Phi > 1 \), the combustion is said to be rich, and when \( \Phi < 1 \), it’s said to be lean.

To some extent, CO is actually formed in lean and balanced combustion, as well as in rich. In order to minimise emissions of CO and other pollutants, one often aims at running the combustion process as lean as possible. However, in the biomass furnaces run by Sydkraft and Vattenfall, a two-stage combustion process is used: Initially very rich combustion is applied, resulting in low temperatures, which keeps production of nitric oxides low. At the second stage, more air is inserted, which completes the combustion without reaching the high temperatures at which large amounts of nitric oxides are formed. Thus, in this work, interest is focused upon both lean and rich combustion.
2.2 Molecular Physics

The method of CO detection described in this thesis is pure absorption spectroscopy within the fundamental and hotband rotational/vibrational transitions of the CO molecule. The temperatures in furnaces of interest to us have been found to lie between 1000K and 1600K\(^4\), and IR radiation will be used as the means of excitation of the molecule. As a result, no electronic excitation will occur, so we will address the electronic ground level. Therefore, the description of electronic energy levels will be kept rather sparse, and more attention will be paid to the physics behind rotational and vibrational energy levels. A spectrum of a typical heteronuclear diatomic molecule (very suitably chosen to be CO) will be explained as an orientation to the issues of spectroscopic measurement via line-of-sight absorption.

2.2.1 The diatomic molecule

The simplest way of describing a diatomic molecule is the classical dumbbell, as depicted in Figure 1.

![Figure 1: The diatomic molecule](image)

In Figure 1, the locations of the electrons around the nuclei are left out. In different energy levels, of course the electron orbits take on different appearances, and via electrostatic interaction affect the distance \( R \) between the nuclei. Furthermore, the molecule may rotate about any of the axes \( x \) or \( y \), which also affects \( R \), due to the elasticity of the bond between the elements. (To a first approximation, rotation about the \( z \)-axis is assumed to have negligible effects on the energy levels of the molecule.)

In the following, an attempt will be made to refresh the reader’s (and the authors) memory of the basic principles in evaluating the energy levels of a diatomic molecule. The full mathematical treatment will be left out.

\(^4\) From unpublished material of Christer Löfström.
The Schrödinger equation

To compute the possible energetic states for the molecule, one would have to solve the Schrödinger equation, which in its simplest form is written:

\[ H\psi = E\psi \]

As is known to every plausible reader of this thesis, the Hamilton operator, \( H \), consists of the sum of kinetic energy of all the particles within the molecule, and the potential energy of every possible interaction between them. In the case of the diatomic molecule, we have

\[(T_N + T_e + V_{NN} + V_{ee} + V_{eN})\psi = E\psi ,\]

where the kinetic energy of the nuclei and the electrons are designated by \( T_N \) and \( T_e \). \( V_{NN} \) and \( V_{ee} \) represents the potential energy of the nucleus-nucleus and electron-electron electrostatic repulsion, and \( V_{eN} \) represents the electron-nucleus attraction.

Now, with the centre of mass as the origin, using position vectors for the nuclei and the electrons (\( R_1, R_2 \) and \( \vec{r} \)), and assuming some familiarity with conventions in physics, the ingredients of the Hamiltonian can be written as below.

Kinetic energy:

\[
T_N = -\frac{\hbar^2}{2m_1} \nabla^2 R_1 - \frac{\hbar^2}{2m_2} \nabla^2 R_2
\]

\[
T_e = -\frac{\hbar^2}{2m_e} \sum_i \nabla^2 \vec{r}_i
\]

Potential energy:

\[
V_{NN} = \frac{Z_1Z_2\epsilon^2}{4\pi\epsilon_0 |R_1 - R_2|}
\]

\[
V_{ee} = \sum_{i \neq j} \frac{\epsilon^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}
\]

\[
V_{eN} = -\sum_i \frac{Z_1\epsilon^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_1|} - \sum_i \frac{Z_2\epsilon^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_2|}
\]

Solving the Schrödinger equation as given above, is not possible in closed form. Simplifications are commonly made, and the commonest one is the Born-Oppenheimer approximation. This makes use of the fact that the electrons are much lighter and move a lot faster than the nuclei. Thus, the Schrödinger equation can be solved for different, fixed values of \( \vec{R}_1 \) and \( \vec{R}_2 \), and then one can study the variation of the eigenvalues as a function of \( \vec{R} = \vec{R}_1 - \vec{R}_2 \), i.e. the distance between the nuclei. With \( \vec{R}_1 \) and \( \vec{R}_2 \) fixed, \( T_N \) equals zero and \( V_{NN} \) is just a number, so the full molecular Hamiltonian is reduced to an electronic one, \( H_{el} = T_e + V_{ee} + V_{eN} \).
The approximation is equivalent to a separation of the molecular wave function into an electronic and a nuclear part:

$$\psi = \psi_e(\vec{r}, \vec{R}) \chi_n(\vec{R}_1, \vec{R}_2),$$

where the electronic wave function, $\psi_e$, can be evaluated, again using the Schrödinger equation, which is then written in terms of the remaining Hamiltonian as

$$(T_e + V_{\text{ex}} + V_{\text{el}})\psi_e = E_e \psi_e.$$ 

Empirically, it’s well established that electronic energies are a lot greater than the vibrational ones, which in turn are a lot greater than the rotational ones, i.e.

$$E_e \gg E_v \gg E_r.$$ 

This justifies further mathematical manipulation to separate the nuclear wave function into a vibrational part, only dependent upon internuclear distance, and a rotational part, dependent on the angular orientation of the molecule;

$$\chi_n(\vec{R}_1, \vec{R}_2) = \psi_v(R)\psi_r(\theta, \phi),$$

giving, for the Schrödinger equation

$$(H_e + H_v + H_r)\psi_e(\vec{r}, \vec{R})\psi_v(R)\psi_r(\theta, \phi) = (E_e + E_v + E_r)\psi_e(\vec{r}, \vec{R})\psi_v(R)\psi_r(\theta, \phi).$$ 

The full analysis of this expression requires separation of variables and some other mathematical tricks. The interested reader is directed to [6], where the treatment is reviewed in further detail. However, an overview of the electronic, vibrational and rotational states will be given in the following.
Electronic energy levels

Plotting the energy of the two lowest electronic states against internuclear distance, produces a plot according to Figure 2. In each electronic state there are of course several vibrational states, and within each of these, several rotational states. The separation between the electronic levels is in the order of an eV.

By convention, the vibrational quantum numbers are designated \( v'' \) and \( v' \), where the primes are for distinguishing between lower and upper level, respectively. The same goes for the rotational quantum numbers, \( J'' \) and \( J' \). Since the scope of this thesis does not include electronic transitions, but resides entirely within the ground electronic level, nothing will be said about the expression for electronic energies. For a detailed description, refer to [6].

Vibrational energy levels

Let’s leave the upper electronic levels behind and peer into the electronic ground state. The general way of approaching an expression for the vibrational levels is by describing the potential well with a so called Morse potential, which have been depicted in Figure 3, together with a harmonic potential approximation. For the sake of mathematical lucidity, the treatment will be made using the harmonic approximation.

Figure 2: The potential wells of the two lowest electronic levels.
Figure 3: The Morse potential and the harmonic potential approximation.

For small deviations $x = R - R_0$ from the equilibrium intermolecular distance, we apply the Morse potential, given by

$$V = D_e (1 - e^{-βx})^2,$$

(1)

where $D_e$ is the dissociation energy as depicted in Figure 3, and $β$ is an empirically chosen constant for the molecule in question. (1) may be Taylor expanded, which gives

$$V = D_e β^2 x^2 \left(1 - \frac{βx}{2} + ... \right)^2$$

(2)

The leading term of this Taylor expansion,

$$V = D_e β^2 x^2,$$

(3)

represents the harmonic potential depicted in Figure 3. Comparison with the expression for the potential in classical harmonic motion under a restoring force gives an expression for the spring constant. We have

$$F = -kx \quad \leftrightarrow \quad V = -\int kx \, dx = \frac{kx^2}{2},$$

where use of (3) gives us the spring constant as

$$k = 2D_e β^2.$$
Making use of the classical result for the vibrational frequency,

\[ \nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}}, \]

we get

\[ \nu_0 = \frac{\beta}{2\pi} \sqrt{\frac{2D}{\mu}}, \tag{5} \]

where \( m \) conventionally has been replaced by the reduced mass, \( \mu = \frac{m_1m_2}{m_1 + m_2} \).

Quantum mechanically, however, we have to put our confidence in the Schrödinger equation:

\[ \left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + D_\psi \beta^2 x^2 \right) \psi_\nu = E_\nu \psi_\nu, \]

which, correctly treated [6], can be shown to have energetic eigenvalues given by

\[ E_\nu = \hbar \nu_0 \left( \nu + \frac{1}{2} \right). \tag{6} \]

For most practical purposes, the vibrational energy is commonly expressed in wavenumbers and designated by \( G_\nu \):

\[ G_\nu = \frac{10^{-2}}{hc} E_\nu = \frac{\hbar \nu_0}{hc} \times 10^{-2} \left( \nu + \frac{1}{2} \right), \]

giving

\[ G_\nu = \omega_\nu \left( \nu + \frac{1}{2} \right) \text{ cm}^{-1}, \tag{7} \]

where the vibrational constant, \( \omega_\nu = \frac{\nu_0}{c} \times 10^{-2} \), is expressed in units of \( \text{cm}^{-1} \).

For spectroscopic purposes, the treatment above is not accurate enough; due to the anharmonicity of the Morse potential well, terms of up to the third order in the Taylor expansion may have to be included in the treatment of the Schrödinger equation. This introduces anharmonicity correction terms in the full expression for the vibrational energies:
\[ G_v = \omega_e \left( v + \frac{1}{2} \right) cm^{-1} - \omega_e \chi_e \left( v + \frac{1}{2} \right)^2 + \omega_e \gamma_e \left( v + \frac{1}{2} \right)^3 cm^{-1}, \]  

(8)

To evaluate this expression for a specific molecule, \( \omega_e \) and the anharmonicity constants, \( \omega_e \chi_e \) and \( \omega_e \gamma_e \), can be retrieved from spectroscopic data tables.

As an example, for the ground electronic state of CO, designated \( X^1\Sigma^+ \), we have [7]

\[
\begin{align*}
\omega_e &= 2169.81358 \text{ cm}^{-1} \\
\omega_e \chi_e &= 13.28831 \text{ cm}^{-1} \\
\omega_e \gamma_e &= 0 \text{ cm}^{-1}.
\end{align*}
\]

Population of vibrational energy levels

The population occupying a vibrational energy level \( v \) is given by the Boltzmann distribution as [8]

\[
N_v = \frac{N}{Q_v} e^{-G_{\text{v}}/kT},
\]

(9)

where \( N \) is the total number of molecules within the electronic level in question, and the vibrational partition function \( Q_v \) is given by

\[
Q_v = 1 + e^{-G_{\text{v}}/kT} + e^{-2G_{\text{v}}/kT} + \cdots = \sum_{v=1}^{\infty} e^{-vG_{\text{v}}/kT}.
\]

(10)

In order to appreciate the population of vibrational states as given above, a plot of the vibrational distribution of CO is presented in Figure 4.

Figure 4: The population of the first few vibrational levels at different temperatures.
Rotational energy levels.
As an approach to evaluating the rotational energy levels, the molecule is to a first approximation regarded as a rigid rotator, where the nuclei rotate around the centre of mass. An attempt to illustrate the scheme is made in Figure 5.

Figure 5: The rigid rotator

Use may now be made of the classical expressions for the moment of inertia,

\[ I = m_1R_1^2 + m_2R_2^2 = \text{(via the definition of center of mass)} = \mu R_0^2, \]

and angular momentum, \( \bar{L} = I\omega \).

With designations according to Figure 5, the rotational energy can be calculated in a classical fashion as

\[ E_r = \frac{1}{2} \left( m_1v_1^2 + m_2v_2^2 \right) = \frac{1}{2} \left( m_1R_1^2 + m_2R_2^2 \right)\omega^2 = \frac{I\omega^2}{2} = \frac{(I\omega)^2}{2I} = \frac{I^2}{2\mu R_0^2}, \]

(11)
Inserting the quantum mechanical result for the angular momentum, $[\mathbf{L}]^2 = J(J+1)\hbar^2$, into (11), we have

$$E_r = \frac{\hbar^2}{2\mu R_0^2} J(J+1).$$

(12)

For spectroscopic purposes the energy is often expressed in wave numbers, whereby the rotational energy is expressed as

$$F_j = \frac{10^{-2}}{\hbar c} E_r = \frac{\hbar \times 10^{-2}}{4\pi c \mu R_0^2} J(J+1).$$

This is more commonly written as

$$F_j = B \cdot J(J+1) \quad cm^{-1},$$

(13)

which defines the rotational constant,

$$B = \frac{\hbar \times 10^{-2}}{4\pi c \mu R_0^2} \quad cm^{-1}.$$  

(14)

Since the internuclear bond is really elastic rather than rigid, however, the internuclear distance $R_0$ increases somewhat due to the rotation. Using (4), this can be accommodated by equating the centripetal force to the restoring force, which gives

$$F = 2D\beta^2 (R - R_0).$$

(15)

In addition, the vibration of the molecule increases the average value of $R^2$, which can be accounted for by replacing the fixed factor $1/R_0^2$ in the rotational constant with the expectation value of $1/R^2$:

$$B = \frac{\hbar \times 10^{-2} \psi^* (R) \frac{1}{R^2} \psi (R) dR}{4\pi c \mu}.$$

(16)

These manipulations lead to corrections for rotation and vibration according to

$$F_j = B \cdot J(J+1) - D_j J^2 (J+1)^2 \quad cm^{-1}$$

(17)
In (17), $B_v$ is the corrected rotational constant, given by an expansion

$$B_v = B_e - \alpha_e (v + \frac{1}{2}) + \gamma_e (v + \frac{1}{2})^2,$$

(18)

where $B_v$ is the same as $B$ given by (14), $\alpha_e$ accounts for the rotational increase of $R$, and $\gamma_e$ accounts for the interaction between rotation and vibration.

The vibrationally corrected centrifugal distortion constant, $D_v$, can be deduced via spectroscopic data tables providing $D_e$ and $\beta_e$, which is the correction term for interaction between rotation and vibration, such that

$$D_v = D_e + \beta_e (v + \frac{1}{2}).$$

(19)

All the aforementioned constants with subscript $e$, as well as the internuclear distance $R_0$, can be retrieved from spectroscopic data tables.

For the CO molecule in the ground electronic state, the interaction between rotation and vibration is weak, so $\gamma_e$ and $\beta_e$ can be neglected, and we find [7]

$$B_c = 1.93128087 \text{ cm}^{-1},$$

$$\alpha_c = 0.01750441 \text{ cm}^{-1},$$

$$D_c = 6.12147 \cdot 10^{-6} \text{ cm}^{-1}.$$ 

**Population of rotational energy levels**

For the population of rotational levels, one has to take into account that each state of an atomic system with a total angular momentum $J$, has a $(2J + 1)$-fold degeneracy. Therefore, the distribution is given by [8]

$$N_J = \frac{N}{Q_r} (2J + 1)e^{-F_J/kT},$$

(20)

where $N$ is the number of molecules within the vibrational state in question, and the rotational partition function $Q_r$ is given by

$$Q_r = 1 + 3e^{-F_1/kT} + 5e^{-F_2/kT} + \cdots = \sum_{J=0}^{\infty} (2J + 1)e^{-F_J/kT}.$$ 

(21)

An appreciation of the distribution of rotational levels as given above, can be seen in the plot of Figure 6.
Transition rules

Before dealing with transition rules, it should be mentioned that the treatment of vibrational and rotational states could be taken further. For spectroscopic measurements of the relatively simple CO molecule, however, the analysis above provides good agreement with measurements.

A quantum mechanical discussion about selection rules is not included here, but it turns out that the selection rules for vibrational transitions are quite loose. The harmonic oscillator assumption, combined with the Frank Condon principle [9], predicts $\Delta v = \pm 1$. Since we know harmonicity to be merely an approximation, we’re not surprised to see that also $|\Delta v| > 1$ is possible, allthough the transition probability for $\Delta v = \pm 1$ is typically the largest.

For a combined rotational/vibrational transition in an electronic $\Sigma$-state with $\Lambda = 0$, $\Lambda$ being the total electronic angular momentum along the internuclear axis, the rotational selection rule is $\Delta J = \pm 1$. The CO-state of interest here is exactly such a state, so for the infrared absorption spectroscopy presented in this diploma work, the selection rules can be summarised:

$\Delta v = 1$, $\Delta J = \pm 1$

Absorption lines originating from transitions with $\Delta J = -1$ are said to create a P-branch in the spectrum, while the transitions with $\Delta J = +1$ create an R-branch.

In analogy, $\Delta J = 0$ transitions create a Q-branch. These transitions take place only if the molecule exhibits angular momentum along the internuclear axis. (The CO molecule being straight, this is impossible in the ground electronic state, where $\Lambda = 0$.)

The notation of absorption lines often follow $X_{J''}$ or $X(J''')$, where $X$ is P, Q, or R, and $J''$ is the rotational quantum number at which the transition starts.
2.2.2 The CO spectrum

The infrared molecular line intensities, $S^5$, are given for 38 different species in the HITRAN database [10], allowing the spectrum to be rather swiftly modelled, using for example the program HITRAN-PC. Modelled at 1200K, the fundamental CO spectrum, i.e. the one at the lowest energy, then appears as in Figure 7.

![Figure 7: Screendump of the CO spectrum, as modelled with HITRAN-PC.](image)

In Figure 7, we can clearly distinguish two similar patterns, both centered around a central gap. To explain the appearance of this spectrum, we may once again peer into the ground electronic state, to consider some possible vibrational transitions.

For the vibrational states of the CO molecule, (8) may be reduced to

$$G_v = \omega_v \left( v + \frac{1}{2} \right) \text{cm}^{-1} - \omega_x v^2 \text{ cm}^{-1},$$

(22)

which specifies that the spacing between vibrational states decreases with increasing vibrational quantum number $v$, as depicted in Figure 8.

![Figure 8: The designation of vibrational excitations](image)

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1 The meaning of ‘$S$’ this will be explained in section 2.3.1
In Figure 8, also an orientation of the designation of the first couple of transitions is given. The fundamental transition \( \nu' = 0 \) to \( \nu' = 1 \) and one hotband transition \( \nu' = 1 \) to \( \nu' = 2 \), both marked in bold, are the ones of primary interest to this work, and specifically the ones we should focus on to explain the spectrum in Figure 7.

The required photon energies for these transitions are given by

\[
\Delta G_{1e,0} = G_{\nu' = 1} - G_{\nu' = 0} \approx 2143 \text{ cm}^{-1},
\]

and

\[
\Delta G_{2e,1} \approx 2116 \text{ cm}^{-1}.
\]

Interestingly, these are the positions of the gaps in Figure 7. Thus, one can rightfully suspect that the stronger pattern, centered at 2143 cm\(^{-1}\), emanates from the 1 \( \leftarrow \) 0 vibrational transition, and the weaker one, centered at 2116 cm\(^{-1}\), from the 2 \( \leftarrow \) 1 transition.

Taking into account the vibrational distribution of Figure 4 and the rotational distribution of Figure 6, one would not be surprised by the plot of both vibrational and rotational population versus energy in Figure 9. The plot has been calculated using a temperature of 1200K.

Figure 9: The distribution of the three first vibrational states, and the rotational states within them.
To get an appreciation for the locations of the absorption lines along the wavenumber-axis, let’s neglect correction terms and form an approximative expression for the photon energy required for a transition to take place:

\[
\Delta E = E - E' \approx G_v + B' (J + 1) - G_{v'} - B'' J' (J' + 1)
\]  

(23)

For the P-branch transitions, we have \(\Delta J = -1\) \(\Rightarrow J = J' - 1\), insertion of which gives

\[
\Delta E = (G_v - G_{v'}) + (B - B'')J^{12} - (B + B')J'', \quad J'' = 1, 2, 3, \ldots
\]  

(24)

The difference in vibrational energy, \((G_v - G_{v'})\), can be assumed to be constant, and since we’ve seen that \([\text{refer to (16)}]\)

\[
B \propto \frac{1}{R^2},
\]

where \(R^2\) increases due to both vibration and rotation, we also know that \(B\) is less in the upper state, i.e. \(B < B''\).

Therefore, terms two and three of expression (24) are negative for all \(J'' \geq 1\), and we can conclude that \(\Delta E\) will decrease exceedingly with higher \(J''\), creating a P-branch to the left of the central gap, as seen in Figure 7. The shape of the branch is of course determined by the rotational distribution in the lower vibrational state; compare with Figure 9.

For the R-branch, insertion of \(J = J'' + 1\) into (23) leads to

\[
\Delta E = (G_v - G_{v'}) + 2B + (3B - B'')J'' + (B - B')J^{12}, \quad J'' = 0, 1, 2, \ldots
\]  

(25)

Assume that the two leftmost terms are constant. The \(J''\)-dependent terms would exhibit a straight line with \(k = 2B''\) if \(B = B'\), but essentially a concave parabola as long as \(B < B''\). Creating a plot with \(J''\) on the x-axis, and on the y-axis a slight modification of the \(J\)-dependent terms (created via division by \(B'\));

\[
(3 \frac{B}{B''} - 1)J'' + (\frac{B}{B'} - 1)J^{12},
\]

may help to further clarify the behaviour of (25). An attempt to do so is presented in Figure 10.
Using imagination and Figure 10, we will see the absorption lines of the R-branch climb up the energy scale, starting at a distance of $2B'$ from the band origin at $\Delta E = (G_v - G_{v'})$, then getting closer and closer with higher $J''$. Sooner or later they will come to a point were they start to travel back, creating a so-called band head. In the case of CO, the difference in $B$ is sufficiently small for us not to experience this reverse at 1200K. The rotational levels at which the top of the parabola is reached are poorly populated at this temperature, and the R-branch becomes as simple and nice as in Figure 7. Just as for the P-branch, the shape is determined by the population of rotational levels in the lower vibrational state.
2.3 Absorption Spectroscopy

Since quantum cascade lasers of today are tunable only in a relatively narrow interval, and also quite expensive, it’s essential to find a suitable line for measurement before ordering the laser. Therefore, the spectrum has to be modelled using plausible conditions and concentrations of other species in the sample mixture. This can be done using data from the HITRAN database [10], and for example the program HITRAN-PC. The conventions described below are the ones used by this program.

2.3.1 Transmission and Absorption

The intensity after transmission of monochromatic light through a path $L$ in a sample of gas is given by the Beer-Lambert law as

$$I(v, L) = I_0 \cdot e^{-\alpha(v)P_aL},$$

(26)

where $I_0$ is the initial intensity and the optical depth, $\alpha(v)P_aL$, can be separated into $\alpha(v)$, the linear absorption coefficient dependent on $v$, the frequency in $cm^{-1}$, $P_a$, the partial pressure of the gas in $atm$, and finally $L$, the optical pathlength in $cm$.

The transmission is defined as

$$T(v, L) = \frac{I(v, L)}{I_0},$$

(27)

and the absorption as

$$A(v, L) = 1 - T(v, L).$$

(28)

The linear absorption coefficient can be related to the molecular line intensity, $S$, by

$$\alpha(v) = S \cdot g(v - v_0) \cdot N,$$

(29)

where $g(v - v_0)$ is the normalised lineshape function, $v_0$ is the frequency at the line centre and $N$ is the number of absorbing molecules per $cm^3$ per $atm$. $N$ is calculated following the ideal gas law, as

$$N = N_L \cdot \frac{296}{T},$$

(30)

where Lochsmidt’s number, $N_L = 2.479 \cdot 10^{19} cm^{-3} atm^{-1}$, is the number of absorbing molecules at 296 K.
To sum up, (26), (27) and (29) implies that the transmission of monochromatic light can be written as

$$T_{\text{mono}}(\nu, L) = e^{-S g(\nu - \nu_0) N_P a L}.$$  \hfill (31)

### 2.3.2 Broadening processes

The line shape function $g(\nu - \nu_0)$ can be either a Lorentzian profile for calculation of pressure broadening, or a Gaussian for Doppler broadening. HITRAN-PC can also convolve the two, creating a Voigt profile for calculation of the combined effect.

The pressure broadened profile is thus given by a Lorentzian function

$$g_p(\nu - \nu_0) = \frac{\gamma_p}{\pi [(\nu - \nu_0)^2 + \gamma_p^2]},$$  \hfill (32)

where the pressure broadened HWHM, $\gamma_p$, is calculated using the air-broadened halfwidth parameter, $g$, found in the HITRAN database, and the total background pressure, $P_r$, provided by the user, as

$$\gamma_p = g P_r.$$  

The Doppler broadened profile is given by a Gaussian function

$$g_D(\nu - \nu_0) = \frac{\sqrt{\ln 2}}{\gamma_D} \cdot e^{-\frac{\ln 2 (\nu - \nu_0)^2}{\gamma_D^2}},$$  \hfill (33)

where $\gamma_D$ is the Doppler halfwidth given by

$$\gamma_D = \frac{\nu_0}{c} \sqrt{\frac{2RT\ln 2}{M}}.$$  

Here, $R$ is the gas constant, $T$ is the temperature in Kelvin and $M$ is the molecular weight.

If one is only interested in the location and the maximum of the absorption line, plots without the broadened profiles can be created. In this case, only the maximum of every spectral line is calculated and drawn, and we have

$$g_{L\max} = \frac{1}{\pi \gamma_p} = 0.318 \ , \ \text{and} \ \ g_{D\max} = \frac{\sqrt{\ln 2}}{\gamma_D} = 0.469.$$  

28
2.3.3 Transmission of polychromatic light

Taking into account the broadening effects, and using (31), we can conclude that the HITRAN-PC program assumes the light source to be monochromatic, whereby the transmission is given by

\[ T_{\text{mono}}(\nu, L) = e^{-S g_{\nu}(\nu-v_{0}) \cdot N \cdot P_{\lambda} \cdot L}, \]  

(34)

where the line profile, \( g_{\nu}(\nu-v_{0}) \), is a convolution of the line profiles for doppler and pressure broadening. This results in a so-called Voigt profile, hence the index V. The effect of scanning the absorption line with a laser with an extremely narrow spectral distribution is depicted in Figure 11.

**Figure 11:** When the line is overswept by an extremely narrow-banded laser, the line profile for the data points follow approximately the model deduced from the Beer-Lambert law.

The QC laser device intended for the measurements in this diploma work is actually not monochromatic, but has a spectral distribution similar to a Lorentzian function. Hence, the expression for transmission has to be adjusted, for predictions of the spectrum to come out fairly accurate.

Let \( v_{L} \) be the centre frequency of the laser and assume that the spectral distribution of the laser is dependent upon a function \( g_{L}(\nu-v_{L}) \), satisfying

\[ \int_{-\infty}^{\infty} g_{L}(v-v_{L}) \, dv = 1, \]

(35)

furthermore specifying the spectral density of the laser as

\[ p(\nu-v_{L}) = \frac{I}{c} g_{L}(\nu-v_{L}), \]

(36)

where \( I \) is the irradiance of the laser and \( c \) is the speed of light.
The line function $g_L(v - v_0)$ is a linear measure for the probability of absorbing a photon with frequency $v$, and in analogy, one may regard the transmission curve, given by (34), as a measure of the probability that an incoming photon will be transmitted by the sample volume. This implies that at any centre frequency $v_L$ of the spectral distribution of the incoming photons, the resulting transmission is an overlap integral of the laser line profile $g_L(v - v_L)$ and the line transmission curve given by (34). Hence, the mathematical expression for transmission of polychromatic light is given by

$$T_{\text{poly}}(v_L, L) = \int_{-\infty}^{\infty} g_L(v - v_L) e^{-S g_F(v' - v_0) N P_a L} \, dv'.$$

(37)

The schematic depiction of Figure 12 is intended to further clarify the effect of scanning the line with a laser with for example a Lorentzian spectral distribution.

![Schematic Figure 12](image)

**Figure 12:** When the spectral distribution of the laser is wider, the resulting line profile for the data points is given by an overlap integral of the laser line function and the profile of the absorption line.

By comparing (37) with the expression for a cross-correlation;

$$f(x) * g(x) = \int_{-\infty}^{\infty} f(h) g(h + x) dh,$$

(38)

and specifying

$$h = v - v_L$$
$$h + x = v - v_0$$

which gives $x = v_L - v_0$, we arrive at the conclusion that the transmission of polychromatic light can be described by a cross-correlation:
\[
T_{poly}(x, L) = \int_{-\infty}^{\infty} g_L(h) e^{-Sg_L(h+x)NP_L} dh,
\]

or, if so preferred,

\[
T_{poly}(x, L) = g_L(x) * T_{mono}(x, L).
\]

Please note that in (39) and (40), \( x \) is simply the difference between the centre frequencies for the laser and the line, i.e. the detuning.

When the spectral distribution of the laser is very narrow, \( g_L(v - v_L) \) is commonly approximated by a Dirac delta function, which results in the expression (34). Measurements using a laser that has a wider spectral distribution, may allow \( g_L(v - v_L) \) to be approximated by a Lorentzian function with a FWHM, \( \Delta v_{1/2} \), equal to the manufacturers specification, or determined experimentally. We then have

\[
g_L(v - v_L) = \frac{\Delta v_{1/2}}{2\pi(\Delta v_{1/2}^2 + (v - v_L)^2)}.
\]

The deduction of \( \Delta v_{1/2} \) can be done in a fashion similar to the one in [11].

Finally, it should also be mentioned that since the laser is pulsed, the irradiance exhibits a temporal distribution, which has to be taken into account if the pulse duration is in the same order of magnitude as the time of rotational/vibrational interaction and rotational energy transfer via collisions. In this case, however, the time scales of the latter are both in the picosecond region, and the laser pulse duration is a few tens of nanoseconds, so steady state can be assumed to prevail during the entire duration of the pulse. Thus, the temporal distribution of the laser irradiance can be ignored.
2.4 Gaussian beams

The amplitude distribution of a laser often exhibits a Gaussian profile along any axis perpendicular to the beam. Being highly divergent and invisible, an infrared QC laser beam poses obvious problems to collimation and alignment. Therefore, calculations using the theory for Gaussian beam propagation has to be made, in order to get a rough idea on how to place the optics, before the fine-tuning of the system can take place. Hence, applicable parts of this theory are summarised in the following. For a full treatment, the reader is directed to [12].

2.4.1 Free-space propagation

The irradiance of a Gaussian amplitude distribution as a function of distance $r$ from the centre, is given by

\[
I(r) = \frac{2P}{\pi w^2} e^{-2r^2/w^2},
\]

where $P$ is the total beam power and $w$ is the radius where the intensity has fallen to $1/e^2$ (or 0.135) of its centerline value. Approximately 86% of the total power is contained within $w$, which is referred to as the beam radius. In Figure 13 a schematic of a propagating Gaussian beam is depicted, defining the waist radius $w_0$, the far-field divergence half angle $\theta$, and the beam radius $w(z)$ as a function of distance from the waist.

![Equiphase surfaces](image)

Figure 13: The beam profile along the line of propagation for a Gaussian beam.

A plane wave with a waist radius $w_0$ will remain collimated only for a finite distance, and eventually diverge as a spherical beam with a spreading half angle,

\[
\theta = \frac{\lambda}{\pi w_0}.
\]
The radius of the beam, \( w(z) \), can be calculated as

\[
w^2(z) = w_0^2 \left[ 1 + \frac{z^2}{z_R^2} \right],
\]

(44)

where \( z_R = \frac{\pi w_0^2}{\lambda} \) is the Rayleigh range, defined as the distance on either side of the waist where the beam area has doubled.

### 2.4.2 Propagation by a lens

A Gaussian beam with waist radius \( w_0 \), propagated by a lens with focal length \( f \), at a distance \( d \) from the waist, is depicted in Figure 14. We focus our interest at the resulting waist radius \( w_0' \), at distance \( d' \) from the lens.

![Figure 14: The profile for a Gaussian beam propagated by a lens](image)

Given \( w_0 \), \( d \), and \( f \), the relations are

\[
\frac{1}{w_0^2} = \frac{1}{w_0'^2} \left( 1 - \frac{d}{f} \right)^2 + \left( \frac{z_{R1}}{f} \right)^2 \quad \text{and} \quad d' = f + \frac{(d - f)f^2}{(d - f)^2 + z_{R1}^2},
\]

(45)

where \( z_{R1} = \frac{\pi w_0^2}{\lambda} \) is the Rayleigh range of the incoming beam.

These expressions still hold if the lens is replaced with for example an off-axis mirror. Also, the direction of propagation is unimportant, i.e. ‘counting backwards’ is perfectly adequate.
2.5 The Quantum Cascade Laser (QCL)

2.5.1 Background
New doors have opened in nano technology, since the introduction of molecular beam epitaxy (MBE), which allows deposition of semiconductor materials, molecular layer by molecular layer, onto a suitable surface. By stacking alternating materials in epitaxial layers of carefully chosen composition and thicknesses (in the order of magnitude of some nanometers), and applying a suitable bias voltage normal to the layers, one can engineer the wave functions for the electronic motion across the layers, creating conditions necessary for laser action. A schematic of a typical QCL design, with a lasing structure manufactured via MBE, is presented in Figure 15[13,14]. The InGaAs layers have a lower refractive index than the lasing region, and thus co-operate with this in creating a waveguide. Due to the high refractive index relative to air of the semiconductor materials used, the front- and back facet of the waveguide serves as mirrors, providing a laser cavity. Some QCL’s come with coated end-facets, for even higher reflectivity. The purpose of the top grating is to limit the spectral width of the laser via the distributed feedback mechanism, which will be treated in section 2.5.3.

Figure 15: A schematic of a typical QCL, with a portion of the lasing nano structure, as seen with a transmission electron microscope. Photons, created via laser action in the structure, travel parallel to the epitaxial layers and normal to the ridges of the top grating, and leave the device through the front facet. (The figure is a mix of out-of-context figures, cut from [13] and [14].)
The principle of wave function engineering is called quantum confinement, and is based upon the fact that when an electron is confined within a sufficiently narrow space by a large potential on either side, i.e. a quantum well, the Schrödinger equation allows only certain, discrete energy levels. (If the space is not so narrow, each state gets wider with respect to energy, creating an energy band.) Furthermore, if two wave functions in adjacent wells have approximately the same energy, and the barrier between the wells is sufficiently thin, they can resonate. This means that they degenerate, creating a new wave function, which is a linear combination of the two, and extends through both wells.

The result of stacking all these different layers of semiconductor materials, is thus a series of quantum wells with different widths, arranged in a certain slope with respect to potential. This slope depends on the applied bias voltage, the widths of the quantum wells (and the barriers), and the composition of the semiconductor materials used. The resulting electronic wave functions across a portion of the structure may be designed to be either truly discrete, or sufficiently overlapping and close enough to each other, to be referred to as energy minibands. In literature, these minibands are often drawn as shaded polygons, though sometimes as ‘forests’ of wave functions, and sometimes not at all. Figure 16[13] presents schematic energy diagrams for some common types of quantum cascade lasers, with conduction band profiles and moduli squared of relevant wave functions. The direction of electronic propagation is ‘downhill’ in all cases. Note that the x-axes in Figure 16 are perpendicular to the epitaxial layers as they are seen in Figure 15.

By efficiently feeding electrons to an upper level and extracting them from a lower, population inversion and thus laser action can take place, provided that the lifetime for the upper state is larger than for the lower state. The significance of the quantum cascade laser is that the layers are arranged periodically, so that the lower laser state of one period is connected to the upper laser state of the next period via either one lower level and a miniband, or just a miniband [compare Figure 16 a) and d)]. An electron entering into a lower laser state through an optical transition, is thus quickly extracted and injected to the upper laser state of the next period via a combination of phonon emission and tunnelling.

Typically, the period is repeated 20-70 times, so that every electron travelling across the whole lattice gives rise to several tens of photons, hence the name quantum cascade laser (QCL). Since the invention of the QCL in Bell laboratories in 1994 [9,10], a lot of designs have been tested and evaluated, some examples of which can be found in Figure 16. For readers interested in further detail, an overview of QCL designs dated 2001 and earlier, is presented in [13]. Here we will concentrate on the so-called bound-to-continuum design [15,16], which is the design of the laser intended to be used in this thesis.
Figure 16: Energy diagrams and conduction-band profiles for QCL's with a:

a) 2QW (two-quantum-well) active region. Note that the miniband of the injection region is not drawn. Straight arrows indicate the direction of electronic propagation, and wavy arrows indicate optical transitions.

b) 3QW active region, for some time the most common type among high-performance QCL's.

c) SL (superlattice) active region, where the lasing transition takes place between two minibands, rather than between two discrete levels. Note that the lower laser level is connected to the upper level of the next stage via a miniband, crossing the injector region. (Very faintly shaded in this picture.) The quantum wells of the SL structure are kept at approximately equal potential by screening the applied electric field via carefully modulated doping of the injector region with extrinsic electrons, hence the ladder-like appearance.

d) so-called ‘chirped’ SL active region, which requires no doping, since the bias voltage is compensated for inside the active region by gradually decreasing the width of the wells in the direction of electronic propagation\(^6\).

\(^6\) This will be explained further in the following section.
2.5.2 QCL based on a bound-to-continuum transition

Since bound-to-continuum lasers are a development of the SL-QC and the chirped SL-QC, we’ll start with a brief description of these.

The superlattice QC laser (SL-QCL)

In a SL-QCL, the epitaxial layers are designed to create two minibands in the superlattice, rather than a set of discrete levels, as can be seen in Figure 16 c). This is achieved by stacking a series of equal potential wells, wherein the resulting wave functions end up at the same energy, and thus can resonate across the whole superlattice. The lasing transition then generally takes place between the lowest level of the upper miniband, and the uppermost level of the lower miniband.

The energy levels of the wave functions inside a quantum well are dependent upon the width of the well. Thus, in order to create resonating wave functions across an SL structure consisting of quantum wells of equal widths, the potentials of these quantum wells have to be kept at the same level. Since the potential structure is biased when an external field is applied, this requires that the field is screened from the SL region.

The quantum wells of the superlattice structure in Figure 16 c) are kept at approximately equal potential by screening the applied electric field with extrinsic electrons, brought about by carefully modulated doping of the injector region. However, lasers designed via this approach have the disadvantage of high waveguide losses and spectral broadness, among other things due to scattering of photons towards the impurities necessary for doping. A lot of effort has been taken to keep doping levels low, and this has lead to the development of the so-called chirped SL-QCL, which is totally free of dopants.

The Chirped SL-QC laser

The principle of chirping is illustrated in Figure 17. In order for resonating energy levels to exist under biased conditions, the well width is chirped, which means that where the potential is high, the wells are wider in order to allow electronic levels closer to the bottom of the well. Going down the potential slope, the wells become narrower, allowing levels higher and higher relative to the bottom of the well. This allows the biased structure to exhibit levels all at the same absolute energy, and thus minibands with an appearance close to the one in a doped SL-QC can be constructed. [See Figure 16 c) and d).]
Figure 17: The principle of a chirped superlattice. Narrowing/widening of the quantum wells forces the wave function to a higher/lower energy relative to the bottom of the well. This way, wave functions of several adjacent wells can be brought into resonance when a suitable bias voltage is applied.

The Bound-to-Continuum QC laser

The bound-to-continuum design is an even further development of the chirped SL-QC. The difference is an additional, narrow quantum well, just at the beginning of the superlattice, as seen in Figure 18 [15]. This well, followed by a very thin barrier, creates a wave function extending far into the superlattice, with a maximum close to the injection barrier. Since this wave function, providing the upper laser state, is well separated from the upper miniband of the superlattice, it doesn’t have to be confined by separating the structure into an active region and an injection/relaxation region.

Figure 18: Energy diagram of a bound-to-continuum lasing structure. The arrow indicates the lasing transition.
There are several features making the bound-to-continuum structure a strong candidate in the quest for high-performance QCL’s:

1) The upper laser state is strongly coupled to the lower states in the miniband of the previous period (to the right in Figure 18), providing resonant tunnelling of electrons into the upper laser state.

2) The high separation in energy between the upper miniband of the superlattice and the upper laser state, provides that the injection efficiency into the laser state is not severely reduced by injection into the upper miniband.

3) The multitude of energy states present in the lower miniband decreases the probability that electrons will be injected into the lower laser state.

4) The lifetime of the lower laser state can be expected to be very short, since the efficient intrasubband scattering in the miniband below makes electron extraction from the lower laser state very fast.

In other words, the probability of electron injection into the upper laser state is vastly bigger than the probability of injection into the lower state, from which also the electron extraction is very fast. These characteristics provide excellent conditions for a high degree of population inversion, and thus, high gain. A more detailed argument about population inversion and gain can be found in [15].

2.5.3 Distributed Feedback (DFB)

We will now address the “Grating and lateral contact layer” of Figure 15. This has been deliberately left out of the argument so far, because it’s a feature separated from the laser action mechanism described in the previous sections. In the design of the laser used in this work, the grating is of the same type as the one in Figure 15, which is an air-semiconductor Bragg grating of the first order, providing so-called index-coupled DFB. Figure 19 illustrates the situation.

Figure 19: A schematic sideview of the waveguide, with the lasing region marked in gray. Due to the large difference between the refractive indices of the semiconductor and air, the electric field of the oscillating mode (not drawn) will see a periodic shift in the effective refractive index. The transverse distribution of the beam intensity is indicated as \( u(x) \).
Due to the high refractive index of the semiconductor used, the result of creating a grating on the top of the waveguide, is that the electric field of the oscillating mode will see an effective refractive index \( n_{\text{eff}}(z) = \langle n(x, z) \rangle_z \), that depends periodically on the longitudinal \( z \)-coordinate. The notation \( \langle \ldots \rangle_z \) denotes a weighted spatial average taken over the \( x \)-coordinate, i.e. normal to the lasing structure; the weight is determined by the distribution of the beam intensity \( |\mu(x)|^2 \). In accordance with Bragg’s ideas of scattering from a periodic array of elements, the beams in the waveguide are effectively coupled to each other when the freespace wavelength of the radiation is such that

\[
\lambda = \lambda_B = \frac{2\langle n_{\text{eff}} \rangle \Lambda}{l},
\]

(46)

where \( \langle n_{\text{eff}} \rangle \) is the average value of \( n_{\text{eff}} \) along the \( z \)-coordinate, \( \Lambda \) is the grating period, and \( l \) is the order of the grating. This means that we would expect a reflection maximum (⇔ transmission minimum) at the Bragg wavelength for light falling into the grating from either side of the waveguide.

A precise description of the DFB mechanism when applied in a laser would require an analytical treatment exceeding the frames of this work. The interested reader is directed to [17], while we focus on some interesting results, presented in [12]. Let’s consider the intensity transmittance \( T = |E_f(0, 0) / E_f(0, L)|^2 \), where \( E_f(x, z) \) is the electric field of the forward beam, and \( L \) is the length of the grating. When the reflectivities of the waveguide end facets are both assumed to be zero (\( r_1 = r_2 = 0 \)), a transmittance minimum occurs, just as one would expect, exactly at the Bragg wavelength, while several maxima, i.e. several modes, are present, symmetrically located at both sides. The situation for a laser with a first order grating is depicted in Figure 20.

![Figure 20: Schematic of the behaviour of a laser with a first order Bragg grating, where the end facet reflectivities are both zero.](image-url)
The situation in Figure 20 is clearly not desireable; the goal is to enhance only one mode, and several solutions are possible. One is to provide a shift in the grating equal to $\lambda_B / 4$ at $z = L / 2$, which actually creates a very narrow transmission maximum right at the Bragg wavelength [12]. Another is to suppress either of the two strongest modes through deposition of end facet coatings, thus achieving different reflectivities.

In the laser used in this work, the high refractive index of the waveguide relative to air results in end facet reflectivities $r_1 = r_2 \approx 30\%$, and suppression of the undesirable modes is achieved via careful selection of the length $L$ of the resulting laser cavity. (Only modes with $m(\lambda / 2) = L$, where $m$ is an integer, can exist as a standing wave in the cavity provided by the end facets.) Also, perhaps surprising, unforeseeable imperfections in the Bragg grating contribute to the suppression of modes. Thus, manufacturing of a DFB laser is not an exact science, and often many specimens have to be made in order to achieve one device meeting up to the desired performance.

### 2.5.4 Tuning the laser

The performance of the laser at its optimum at about $-30^\circ$ C, so the microscopic structure is mounted onto a thermo element, and inserted into a water cooled housing. The emission frequency of the laser can be adjusted by feeding the device with an additional, rapidly ramped, sub-threshold current, which periodically heats the waveguide faster than heat can be carried away via the thermo element. Due to the thermal expansion of the Bragg grating, this makes the cavity resonate at a longer wavelength. Auxiliary circuits allow accurate measurement of the bias current via an oscilloscope, and its relation to the wavelength can be determined via reference spectra.

The easiest way to achieve the tuning in an experimental situation, is to use a function generator to apply a sawtooth or triangle tension, in our case via the so-called ‘Bias-T’ device [18]. The positive slope of the ramped current is then set to a duration that covers many laser pulses, tuning the radiation a little bit towards longer wavelengths pulse by pulse.


2.6 Data Evaluation

Once transmission spectra are collected, they will have to be evaluated in a suitable way to determine the concentration of CO. Using HITRAN data, theoretical spectra of the line chosen for measurement can be created, and among the parameters that determine the amplitude and shape of the line, is the concentration of CO in the sample mixture. The plan is to determine the set of parameters that give the best fit of the theoretical spectra to the experimental spectra, and this will be done using a least squares fitting method.

2.6.1 The Weighted Least-Squares Method

What we’ve been considering so far is transmission versus frequency, so the theoretical description will be limited to this, with an additional example of how to treat a variable that can’t be directly measured. In section 3.2.2, we will further refine the treatment so that it applies to the experimental data, which are merely voltages and currents.

Assume that the experimental datapoints are denoted \((v_i, T_i)\). The transmission is subject to additive measurement noise, i.e. \(T_i = T + \varepsilon_i\), where \(T\) can be predicted by a function

\[
T = F(v, p_1, \ldots, p_n).
\]

\(p_1, \ldots, p_n\) is the set of parameters determining the behaviour of the function, e.g. pressure, pathlength, temperature, and concentration of CO. Figure 21 illustrates the situation.

Figure 21: Measured transmission spectrum (crosses) of an arbitrary line, compared with a theoretical spectrum (solid curve).
The best fit to the experimental data points is given by the parameter values which

\[ Q^2 = \sum_{i=1}^{N} (T_i - F(v_i))^2 \frac{1}{\sigma_{T_i}^2}, \]  

(47)

where the factor \( 1/\sigma_{T_i}^2 \) is for weighting the contribution from each datapoint
according to it’s uncertainty [19]. Note that \( \sigma_{T_i} \) is not known a priori, but has to be
inferred from the measured data. The detailed procedure can be done via any software
capable of performing a least-squares non-linear fit, and the programming will not be
dealt with here. The interested reader is directed to references [19] and [20], and
literature on some suitable programming language.

In many cases, the uncertainties can be considered to be the same within suitably
chosen intervals along the frequency axis. We then denote the data points

\[ (v_j, T_j), \]

where \( i = 1, \ldots, N \) refers to the intervals and \( j = 1, \ldots, n \) refers to the datapoints within
each interval. The uncertainty within each interval is then estimated as

\[ \sigma_{T_{ij}}^2 = \frac{1}{n-1} \sum_{j=1}^{n} (T_{ij} - \bar{T}_i)^2, \]

where \( \bar{T}_i \) is the mean value of the transmission in each interval, i.e.

\[ \bar{T}_i = \frac{1}{n} \sum_{j=1}^{n} T_{ij}. \]

We may now use these values in equation (47), which is adjusted to

\[ Q^2 = \sum_{i=1}^{N} (\bar{T}_i - F(\bar{v}_i))^2 \frac{1}{\sigma_{T_i}^2}, \]  

(48)

where we have also introduced the mean value of the frequency, \( \bar{v}_i \), in each interval in
analogy with the argument above.

In our case, a direct measurement of \( \nu \) is not possible. What can be measured, is the
sub-threshold current that is used to control the emission frequency of the laser. By
acquiring reference spectra of a known species, for example N₂O (refer to Appendix
A), possibly combined with spectra taken through an etalon, the relation between the
frequency of the emitted photons and the bias current can be determined. For
example, we may find a linear relationship between the frequency \( \nu \) and the mean
current \( C_i \) within each interval, according to
We have chosen $C$ to denote the bias current, to avoid confusion with the intensity, $I$, in following sections. One can estimate $\hat{a}$ and $\hat{b}$ using a linear least-squares method in a similar fashion as above. This clearly introduces uncertainties also in $v$, which have to be taken into account. Our problem will then be somewhat expanded, and the software used will be set to find the parameter values that minimise

$$Q^2 = \sum_{i=1}^{N} (\bar{T}_i - F(\bar{v}_i))^2 \frac{1}{\hat{\sigma}_{T_i}^2} + \sum_{i=1}^{N} (\bar{v}_i - v(\bar{C}_i))^2 \frac{1}{\hat{\sigma}_{v_i}^2},$$

where $\hat{\sigma}_{v_i}$ can be treated in the same fashion as $\hat{\sigma}_{T_i}$, i.e. taken to be the same in certain intervals, in which

$$\hat{\sigma}_{v_i}^2 = \frac{1}{n-1} \sum_{j=1}^{n} (v_{ij} - \bar{v}_i)^2,$$

where

$$\bar{v}_i = \frac{1}{n} \sum_{j=1}^{n} v_{ij}.$$

Quite often, however, $v(\bar{C}_i)$ can be determined accurately enough to allow us to use (48) directly. Hence, which method is to be preferred has to be evaluated in each specific case, and depends on the repeatability of the frequency sweep, i.e. the physical properties of the laser, as well as of auxiliary equipment.
3 Method

3.1 Choosing Approach

As described in section 2.3.1, the HITRAN-PC program generates spectra, based on HITRAN data and parameters such as temperature, pathlength, partial pressures of the components in the sample of interest, and so on. Another program, called STANJAN, can be used to calculate the steady-state partial pressures of the different product species in a combustion process, based on the relative amounts of reactants (C, O, H, and N), as well as temperature and total pressure. It’s thus possible to combine these programs to evaluate which line in the CO spectrum that is most suitable for measurement under flame conditions.

3.1.1 Basic Considerations and A General Spectral Survey

When choosing a line for measurement, the greatest concern in this work has been avoiding interference from other combustion products. The final goal is to perform in-situ measurements in a biomass furnace, so the simulations of the spectra should clearly be performed using high-temperature data. Since the HITRAN database was initially intended for atmospheric applications, it contains mostly room-temperature data, and, for only a few species, data suitable for 1000K, 1500K and solar temperatures. The only two species of interest to us, for which high-temp data at 1000K is obtainable, is H₂O and CO₂. Perhaps a lucky coincidence, this proved to suit us well, since early simulations, using all species for which HITRAN contains data, indicated that the ones expected to cause trouble is primarily H₂O and CO₂, and, to a very limited extent, NO. Even though it would be desirable to use high-temp data for CO and NO, these molecules were assumed to be simple enough for the predictions to come out fairly accurate. Thus, for the analysis of the spectral behaviour of the combustion products, a data file was created, containing high-temp data for H₂O and CO₂, and room-temperature data for CO and NO.

Since burning biomass would be quite cumbersome for a first laboratory experiment, we’re hoping to start evaluating the technique for measurements in ordinary, laminar flame combustion of CH₄. For stoichiometric combustion of CH₄ and air, we have

\[
CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2,
\]

allthough a STANJAN run with relative reactant amounts according to

\[
\begin{align*}
\text{C} & : \quad 4 \\
\text{H} & : \quad 4 \\
\text{O} & : \quad 15.04 \\
\text{N} & : \quad 1
\end{align*}
\]

yields partial pressures of the relevant product species according to

- H₂O \( 1.9011 \cdot 10^{-1} \text{ atm} \)
- CO₂ \( 9.5050 \cdot 10^{-2} \text{ atm} \)
- NO \( 2.0864 \cdot 10^{-6} \text{ atm} \).

\[ \text{CH}_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2, \]

allthough a STANJAN run with relative reactant amounts according to

\[
\begin{align*}
\text{C} & : \quad 4 \\
\text{H} & : \quad 4 \\
\text{O} & : \quad 15.04 \\
\text{N} & : \quad 1
\end{align*}
\]

yields partial pressures of the relevant product species according to

- H₂O \( 1.9011 \cdot 10^{-1} \text{ atm} \)
- CO₂ \( 9.5050 \cdot 10^{-2} \text{ atm} \)
- NO \( 2.0864 \cdot 10^{-6} \text{ atm} \).
In order to get an overall view of the spectral situation, the whole range of the CO spectrum was simulated via HITRAN-PC. This was done applying a CO concentration of 1% and assuming a Φ = 1 situation, thus using the data above on behalf of the other products. The result can be seen in Figure 22. Since furnace temperatures have been found to lie between 1000K and 1600K, the temperature was set to 1300K. In our measurements, we intend to use a McKenna burner with a flame diameter around 5 cm, why the pathlength was chosen accordingly.

Figure 22: The first, tentative, simulated spectrum, assuming that Φ = 1 and [CO] = 1%. The environment of the HITRAN-PC program can also be seen, with the menu at the top, providing 80’s style interactivity.

Although a good number of possible lines could be found in between H₂O lines in the P-branch of the CO spectrum (to the left in Figure 22), these were early discarded after consultations with Larry S. Rothman, the originator of HITRAN. The primary reason for this is that the software is not very good at foreseeing the behaviour of the CO₂ lines at high temperatures, unless one stays around 2300 cm⁻¹. From Figure 22, it’s pretty clear that this directs us to the R-branch, and that we should focus on a region not too far away from the central gap of the CO spectrum, to avoid the massive onslaught of CO₂ lines. This has been done in Figure 23, where also the pair of CO lines eventually found to be most promising is marked with an arrow.
Figure 23: Zooming into a portion of the R-branch. The arrow indicates the pair of lines eventually found to be the most promising one.

Further investigation yields that the pair of lines marked out in Figure 23 actually are the best candidates, as is made probable by Figure 24. Here also broadening mechanisms has been included in the simulation, creating Voigt profiles for the spectral lines.

Figure 24: The pair of clean R-branch CO lines at 2173 cm\(^{-1}\).

These are the cleanest couple of lines before the massive lobe of CO\(_2\) lines predicted by the software. Lying around 2173 cm\(^{-1}\) (or 4.602 \(\mu\)m) these lines are also closer to 2300 cm\(^{-1}\) than the lines in the P-branch, which makes it less probable that reality will surprise us with additional CO\(_2\) lines, obstructing the view. The designation of these lines are \(R(7)\) for the strongest line, originating from a \(v'' = 0\) to \(v' = 1\) transition (fundamental), and \(R(15)\) for the weaker one, originating from a \(v'' = 1\) to \(v' = 2\) transition (hotband).

Being the result of one fundamental and one hotband transition, and also close enough for both to be scanned within the tuning range of the QCL, these two lines are especially interesting. This is because theoretically, the features mentioned allows temperature measurements based on calculations of the redistribution among vibrational levels according to temperature. (Naturally, this would also require that the rotational redistribution within each vibrational level were taken into account.)
3.1.2 Simulations of Spectra From Furnaces

Lean-burn Furnaces

The question is what things might look like in an actual furnace. A biomass furnace has a diameter of several meters, and thus the potential pathlength is large. It seems like a nice thought to use the whole diameter of the furnace to maximise the sensitivity of the method. However, it turns out that at a pathlength of, for example 3m, the transmission will be approximately zero all over the wavelength region we are investigating here, which is due primarily to CO\(_2\) lines adding up to an extreme optical thickness in the entire frequency region of interest. In order to perform line-of-sight measurements in the heart of a big, lean-burn furnace, this implies that the pathlength has to be reduced, for example by building a water cooled, fibre optic probe, with windows protected by flows of inert gas. Although difficult, this option may still be possible, which is why we’ve chosen to treat the case.

Assuming a lean burn, \(\Phi = 0.8\), a pathlength of 30 cm and a temperature of 1000K (implying that we position the probe quite high in the furnace, i.e. far from the flame front), yields a spectrum according to Figure 25. The concentration of CO has been set to 0.1%. The red line in Figure 25 is a composite spectrum, i.e. a sum of the contributions of all species included in the run, roughly predicting what we actually will see in our measurements. This situation looks quite good; if we know about the contribution of CO\(_2\) and H\(_2\)O, the spectrum can be corrected for this, and reasonable data can be achieved.

![Figure 25: A simulation of the situation in a furnace with \(\Phi = 0.8\), a pathlength of 30cm and a temperature of 1000K.](image)

An attempt to move closer to the flame front, i.e. raising the simulation temperature, will give us an idea of the limitations of the method. See Figure 26.
At 1100K, the lines of interest begin to get obstructed, primarily by CO₂ lines.

A glance at the ‘noisy’ spectrum of Figure 26 implies that it’s a good idea to try to measure at a point in the furnace where the temperature stays around 1000K.

The previous concerns indicate that determination of CO concentration in an average furnace flue, at least down to a concentration of 0.1%, is possible via the method proposed, as long as temperature and pathlength are kept at suitable values. This would require a probe to be built, supposedly creating a pathlength of 30cm, and inserted into the furnace at a position were the temperature is not too much above 1000K.

**Two-stage biomass furnaces**

We’ll now address the application of special interest to Vattenfall and Sydkraft, which is performing measurements in a two-stage biomass furnace. The ultimate interest is directed to the concentration of an organic acid corroding the walls in between the combustion stages, so the measurements are preferably done close to the wall, over an arbitrarily short pathlength. Imagining a location where temperatures are around 1000K, somewhere between the first, rich combustion stage and the leaner second stage, a simulation according to Figure 27 was done.

![Figure 26](image)

**Figure 26:** At 1100K, the lines of interest begin to get obstructed, primarily by CO₂ lines.

![Figure 27](image)

**Figure 27:** A simulation with Φ = 1.2, corresponding to a CO concentration of 2%. A pathlength of 1 cm was applied to obtain these data.
As can be expected from the rather high value of $\Phi$, the concentration of CO is quite high, which makes it beneficial to use a short pathlength to avoid optical thickness of the stronger line. We have started with considering situations in which the absorption is less than 30%, to keep open the possibility of applying an approximative, simplified linear model in the least squares fit. The fact that the pathlength has to be brought down to 1 cm to obtain the nice spectral behaviour of Figure 27, is slightly discouraging on behalf of the proposed simplifications. It would be preferable to be able to measure over a longer pathlength in order to minimise the relative amount of the sample volume that is disturbed by the probe. Perhaps, one should at this moment consider giving up on the idea of a linear approximation, and turn to the somewhat more cumbersome method of non-linear least squares curve fitting, described in sections 2.6.1 and 3.2.2.

According to a simulation with $\Phi = 1.4$, bringing us to a CO concentration of 3.9%, the spectrum would appear as depicted in Figure 28. This situation poses no problems to a non-linear curve fit, whereas one should start being hesitant towards any simplifications to linear models. Also, the problem with the short pathlength prevails.

![Figure 28: A simulation with $\Phi = 1.4$, corresponding to a CO concentration of 3.9%.

In order to facilitate for somebody to resume this project in the future, the limitations of the method are illustrated in Figure 29 and Figure 30. Imagining a least squares non-linear fit method to be used in the data evaluation, these situations should provide information suitable for determination of the CO concentration. Which pathlength is to be preferred, depends on the situation in the furnace of interest. If the CO concentration can be expected to stick to 6% or lower, it would be preferable to use the longer pathlength of 5 cm, as in Figure 29, whereas a higher upper detection limit require a shorter pathlength, as in Figure 30. 
Having made the considerations above, we can conclude that the method should be successful for CO concentrations of up to 6%, which however requires a non-linear least squares curve fit and a pathlength no longer than 5 cm. If one is satisfied with concentrations of up to for example 2%, one should still choose a non-linear model, since this allows measuring over a longer pathlength, thus reducing probe interferences with the sample volume.

3.1.3 Simulations of spectra from a flame

It’s now appropriate to evaluate the method, performing simple measurements in a flame. Thus different flame situations has to be simulated in order to find a plausibly successful experimental approach. What has to be estimated before measurement, is at which temperatures (i.e. at what height in the flame) and for which values of $\Phi$ we can expect to acquire reliable results in a test run of the method. The estimated temperature in a Methane/Air flame is around 1500K\(^7\). Thus, for a start, spectra were generated at this temperature, for different values of $\Phi$ and with a pathlength equal to the flame diameter, which is 6 cm. Two of these can be seen in

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\(^7\) From personal communication with Christian Brackman
Figure 31, where the composite spectra are rather discouraging, due to the relatively high amount of CO\textsubscript{2} background. In a), the amount of CO is about 0.7%, and in b), it is around 2%. An option is to move higher up the flame, where the temperature is lower and the obstruction by CO\textsubscript{2} lines can be expected to be less pronounced.

Figure 31: Two simulated spectra for flame conditions at 1500K with a) $\Phi = 10^{3}$, yielding $[\text{CO}] = 0.7\%$, and b) $\Phi = 10^{3}$, yielding $[\text{CO}] = 2\%$. The pathlength is 6cm.

Simply assuming that a height in the post flame with a temperature of around 1200K\textsuperscript{8} can be reached, spectra were generated at this temperature, with all other settings identical to the ones used for Figure 31. The most promising of these spectra can be found in Figure 32.

\textsuperscript{8} From personal communication with Christian Brackman
Figure 32: A simulation of a spectrum from a flame with $\Phi = 1.03$, at a point in the flame where the temperature is 1200K.

Thus, we can conclude that if we can achieve a 6cm diameter flame with $\Phi = 1.03$, corresponding to a CO concentration of approximately 5%, and find a spot in this flame where the temperature is 1200K, these are good starting values for a test run to evaluate the method.
### Experimental Procedure

#### 3.2.1 Setup

The beam of a QCL often exhibits a divergence half angle of 30 degrees in the vertical direction, and 20 degrees in the horizontal. Thus, it has to be collimated, preferably using mirrors rather than lenses, so that no chromatic aberration will occur. Since the beam is infrared and therefore invisible, collimation and alignment is not an easy task.

The absence of chromatic aberration, together with the use of pellicle beamsplitters, facilitates the insertion of an ordinary red laser beam, in order to have a strict reference of alignment during the whole experiment. It’s also preferable to use two detectors to be able to monitor the pulse-to-pulse variation. We propose the experimental setup depicted in Figure 33. Regarding the alignment procedure, some hints can be found in Appendix B, and for swift identification of the different pieces of equipment, there are some photos in Appendix C.

![Figure 33: Schematic of the proposed experimental setup.](image)

The data to be collected is the detector voltage before the flame, \( U_0 \), the detector voltage after the flame, \( U_T \), and the bias current, \( C \), the denotation of which is chosen to avoid confusion with the intensity, \( I \), in the following description of the data evaluation.
3.2.2 Data Acquisition and Treatment

One basic consideration in the experimental procedure is how quickly we need to scan the line. In the stable flame of a McKenna burner, this doesn’t really matter, but we feel that some consideration should be taken for the application of ultimate interest. We have currently no information about the characteristic timescale of turbulence in the bio-mass furnaces of Sydkraft and Vattenfall. Thus, we have chosen to make an educated guess of the timescale. Considering the size of the furnaces in question, which have diameters of around 5m, we have estimated that not much will change in an optical pathlength of 5 to 30 cm within 0.01s. Hence, we might as well aim for scanning the line within this time also during the laboratory flame measurements.

The optimum pulse duration and period time of QC lasers differ between different specimens, but can generally be expected to be around 50 ns and 2.5 µs, respectively.

Please note that these values correspond to a duty cycle (duration /period) of 2%, which is a bit above the general maximum recommendation of 1%. It’s thus a good idea always to consult the manufacturer, to be certain not to overheat the diode. To be on the safe side, it’s very wise to use a somewhat shorter pulse or longer period than the ones stated in the data sheet for the specific laser.

As mentioned in sections 2.5.4 and 2.6.1, the tuning of the laser is achieved via heating the waveguide with a ramped sub-threshold current. This is preferably achieved using a function generator to apply a sawtooth voltage, which controls the current through the QCL via the ‘Bias-T’ device [18]. The timescale being 0.01s, it would be suitable to set the period of the sawtooth current to 100Hz. A pulse repetition period of 2.5 µs corresponds to a pulse frequency of 400 KHz, which gives us 4000 pulses in one scan, i.e. we acquire 4000 datapoints in one scan. The detailed technical procedure of data collection is left for the next researchers. Instead, the following will be dedicated primarily to the data evaluation, the treatment of which will be kept as short as possible, and again, interested readers are directed to [19] and [20].

A suitable, digital oscilloscope, the data acquisition of which is preferably trigged by some appropriate value of the bias current, can be used to collect the 4000 data points. These can be expected to lie within a tube in a three-dimensional data space, as depicted in Figure 34. The dashed lines are intended to indicate the approximate plane of the tube. The widening of the tube in the $U_T$ dimension, at low values of $U_T$, is due to the detector noise being strong relative to the signal in this region, which increases the uncertainty of $U_T$. 

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9 From personal communication with Joachim Walewski and Mark Linne
Since the spectral width of the laser can be expected to be wider than the spectral step between each collected value of the bias current $C$, the tube can be divided into for example 100 segments along the $C$-axis, within each of which the frequency can be considered to have the same value. We can then denote the datapoints

$$(C_y, U_{0y}, U_{Tj}), \quad i = 1, \ldots, 100, \quad j = 1, \ldots, 40,$$

where the index $i$ refers to the segments, and the index $j$ refers to the datapoints within each segment.

Having 40 data points within each segment, we are provided good statistical conditions for the creation of 100 new points $(\overline{C}_i, \overline{U}_{0i}, \overline{U}_{Ti})$, which are the mean values of the data points within each segment, with respect to all three dimensions. These can be created via a computer program called WFIT [20]. This program calculates mean values and standard deviations for the data, following the mathematical procedure below, where we have replaced absolute numbers with the designations $N$ and $n$, for the sake of generality.

Let the number of segments be $N$, and let the number of data points within each segment be $n$. We can now find the mean values for the bias current, $\overline{C}_i$, with corresponding estimated uncertainties, $\sigma_{C_i}$, according to

$$\overline{C}_i = \frac{1}{n} \sum_{j=1}^{n} C_y, \quad \sigma_{C_i} = \frac{1}{n-1} \sum_{j=1}^{n} (C_y - \hat{C}_j)^2 \quad i = 1, \ldots, N$$
The same can be applied for $\overline{U}_{0i}$ and $\overline{U}_{Ti}$:

$$
\overline{U}_{0i} = \frac{1}{n} \sum_{j=1}^{n} U_{0ij}, \quad \hat{\sigma}_{0i} = \frac{1}{n-1} \sum_{j=1}^{n} (U_{0ij} - \overline{U}_{0i})^2 \quad i = 1, \ldots, N
$$

$$
\overline{U}_{Ti} = \frac{1}{n} \sum_{j=1}^{n} U_{Ti j}, \quad \hat{\sigma}_{Ti} = \frac{1}{n-1} \sum_{j=1}^{n} (U_{Ti j} - \overline{U}_{Ti})^2 \quad i = 1, \ldots, N.
$$

Now, how do we perform the least squares fit? Comparing with the previous expression for the transmission, given by (37), we have

$$
I_{Ti} = I_0 \int_{-\infty}^{\infty} g_L(v'-v) e^{-Sg_r(v'-v_0)NP_aL} dv' + B,
$$

(49)

where we have added a background intensity contribution, $B$, to compensate for the fact that the detector will be subject so some IR radiation emitted by the flame. Since (49) is a very complicated expression, let’s simplify to

$$
I_{Ti} = I_0 f(v, p_1, \ldots, p_k) + B,
$$

(50)

where $p_1, \ldots, p_k$ are the parameters we choose to consider.

Assuming that each interval contains only one frequency, which is dependent upon the bias current, we have

$$
v = g(\overline{C}_i),
$$

where the function $g$ can be determined from a reference spectrum of N$_2$O. (Refer to Appendix A.)

Combining this with the fact that the intensities are proportional to the detector voltages;

$I_{Ti} \propto \overline{U}_{Ti}$ and $I_{0i} \propto \overline{U}_{0i}$,

(50) may be written

$$
\overline{U}_{Ti} = \alpha \overline{U}_{0i} f(g(\overline{C}_i), p_1, \ldots, p_k) + \beta,
$$

(51)

where $\alpha$ is the so called calibration constant, and $\beta$ is the background, expressed in volts.

$\beta$ is easily estimated as the value of $U_r$ with a burning flame and no laser pulses.
After this, \( \alpha \) can be estimated from a couple of laser pulses in a situation where we have no absorbing flame, i.e. the integral in expression (49) equals 1 and we have \( \beta \approx 0 \), giving

\[ \overline{U_T} = \hat{\alpha} \overline{U_0}, \]

where \( \overline{U_T} \) and \( \overline{U_0} \) are the average values of the detector voltages measured during these pulses. Now, with \( \hat{\alpha} \) and \( \hat{\beta} \) determined, lets introduce another function \( F \) such that (51) can be even further simplified to

\[ U_T = F(C_i, p_i, \ldots, p_k, \hat{\alpha}, \hat{\beta}). \]  

(52)

It’s now easy to see how the weighted least squares method, as described in section 2.6.1, can be utilised in this situation. The task is to program a computer to estimate the parameter values \( \hat{p}_1, \ldots, \hat{p}_k, \hat{U}_0, \hat{C}_i \) that minimise the function

\[ Q^2 = \sum_{i=1}^{N} \left( U_{T_i} - F(C_i, \hat{p}_1, \ldots, \hat{p}_k, \hat{\alpha}, \hat{\beta}) \right)^2 \frac{1}{\sigma_{U_{T_i}}} + \sum_{i=1}^{N} \left( U_{0i} - \hat{U}_0 \right)^2 \frac{1}{\sigma_{U_{0i}}} + \sum_{i=1}^{N} \left( C_i - \hat{C}_i \right)^2 \frac{1}{\sigma_{C_i}}. \]

Note that the values of \( \hat{\alpha}, \hat{\beta}, \hat{\sigma}_{U_{T}}, \hat{\sigma}_{U_{0}}, \hat{\sigma}_{C} \) are estimated before this operation, whereas \( \hat{p}_1, \ldots, \hat{p}_k, \hat{U}_0, \hat{C}_i \) are the results of the operation. If so desired, one can also estimate \( \hat{\alpha} \) and \( \hat{\beta} \) via the least squares fit, but it makes sense to use all the data that can be experimentally acquired.

If everything is done right, one of the parameters \( \hat{p}_1, \ldots, \hat{p}_k \) will be the concentration of CO, and we’re done. It should be mentioned, however, that we have not as yet considered one additional problem

Variations of the measured detector voltages have two causes:

- detector noise
- pulse-to-pulse variations of the laser output.

The additive noise from the two detectors is assumed to be uncorrelated, but this is not the case for pulse-to-pulse variations. Fluctuation in pulse energy causes the detector voltages before and after the flame to vary in the same fashion, i.e. these quantities are indeed statistically correlated.

Although common least-squares fitting schemes do not consider this type of correlation, they may be applied never the less, but on the expense of precision of the estimated function parameters. For cases where the correlated data to be fitted depend linearly on each other, e.g. the detector voltages above, there exists an appropriate, ready-to-use variant of least-squares fitting, which is discussed in detail in [20]. For similar experiments it has been found that the precision can be improved by as much as a factor of three, when this method is applied.
Because of limited space we do not discuss this subject any further, but direct the interested reader to the reference mentioned. A program interface written in MATLAB® for weighted least-squares fitting of correlated quantities has been developed at our division and may be downloaded from http://www.forbrf.lth.se. In addition to carrying out the fitting above, this interface provides uncertainties for the estimated function parameters [refer to equation (52)].
4 Summary and Outlook

Although the QCL intended for the measurements in this project was never delivered, which left us with the option to treat the issue merely on a theoretical level, we hope that a future resuscitator of this project will find interest in some of the considerations taken.

Most of the theoretical treatment of combustion, molecular physics and Gaussian beams in section 2.1, 2.2, and 2.4 may perhaps be excluded by the majority of readers. Although the physics behind the function of the QCL, described in section 2.5, is of no importance for the measurements, we hope that this section may serve as a decent introduction to the concept of QCL, and that it will provide some basic understanding for the mechanisms used.

What we hope to be of more interest to the reader is the treatment of the transmission of polychromatic light in section 2.3.3, and the use of this to evaluate the CO concentration via HITRAN constants and the weighted least-squares non-linear fitting method, described in sections 2.6 and 3.2.

Especially, we hope that the analysis of simulated spectra in section 3.1 will provide some readiness for the limitations that equivalence ratios, pathlength and temperature introduces to the applicability of the method proposed. We look at some different combustion situations, and conclude that the method might work in an ordinary lean-burn furnace, that it should work well in the two-stage biomass furnaces of Sydkraft and Vattenfall, and that it would be a good start to evaluate the method for a methane flame. Suitable conditions when doing so are discussed, and in section 3.2 we move on to the experimental setup and a more detailed treatment of data.

It should be pointed out, that all considerations in this thesis have been made under the assumption that the burning of biomass spectroscopically equals combustion of methane. Whether this is the case may very well be an object for discussion; just as an example, the flame should contain all sorts of sulphur compounds that might possibly give rise to obscuring lines in the spectrum.

The division is still waiting for Alpes Lasers to deliver the QCL, and for the time being, the project is put on hold. A programme for data evaluation via the least-squares fitting method, described in section 2.6.1 and 3.2.2, is currently being written by Dr. Joachim Walewski. When the QC laser arrives, we hope that his work and this thesis may provide a foundation for a resurrection of the project.

To facilitate the overtake, we’d like to present a list of equipment that are applicable to this project and present at the Division of Combustion Physics.
Present Equipment

Lasers
*Alpes Lasers* Quantum Cascade Laser Starter Kit (without laser diode) 1 set
*Edmund Optics* Laser Diode Module, 635nm + mirror-type holder 1 set

Detectors
*Oriel* HgCdZnTe 2 –12 µm (opt. 10,6 µm) at room temp + preamp. 1 set
*VIGO-System Ltd* DRB-1 + Peltier cooler + preamp 1 set

Optics
*Melles Griot* Parabolic off-axis mirror 02POA013, f = 19.1 mm 1 pcs
*Melles Griot* Parabolic off-axis mirror 02POA013, f = 38.1 mm 1 pcs
Mirrors, flat ~20mm*20 mm (one is pretty badly oxidized) 5 pcs
Window UVCaF2 dia = 25.4 mm, th = 6 mm 8 pcs
Window Zaphire dia = 30 mm, th = 1.9 mm 5 pcs
Window CaF2 dia = 25.4 mm, th = 3 mm (both used, one badly) 2 pcs
*Edmund Optics* Pellicle beam splitter 1 pcs

Miscellaneous
- *Tektronix* 3054 Four-Channel Digital Oscilloscope
- Cell, 40cm, with CaF2 windows. Can be used for measurements on CO at low temperatures.
- Cell, 30cm. May be completed with CaF2 windows and used to collect reference spectra of N2O.

The alert reader may have noted that the list contains only one Pellicle Beamsplitter, whereas the setup in section 3.2.1 proposes two. In addition, the division doesn’t own the ‘Bias-T’ device mentioned in section 3.2.2. We’ve chosen to propose this setup anyway, since it would facilitate the experiment to a great extent. Also other pieces of equipment are desireable; for example it would be preferable to use two matched detectors to eliminate the need to correct for differences in the relationship between intensity and output voltage. In addition, the VIGO detector was found to greatly out-perform the Oriel detector, regarding sensitivity. Hence, we’d like to present a list of desireable additional equipment:

Desireable Additional Equipment

Pellicle beam splitter 1 pcs
*VIGO-System Ltd* DRB 1 + Peltier cooler + preamp 1 set
*Alpes Lasers* ‘Bias-T’ device 1 pcs
Function generator for control of the bias current via ‘Bias-T’ 1 pcs

An even further improvement of the experimental setup would be a computer with a data acquisition card and proper software, to control the whole process of trigging and data acquisition.
5 Acknowledgements

Of course, I’d like to thank my supervisor, Prof. Mark Linne, who has had to stand my every now and then popping into his office (which has been next door to mine), asking all sorts of ignorant questions. One of his greatest achievements might have been when I had accidentally destroyed the QCL, ran up to his office to tell him about it, pale and shaky and wondering how he would react, just to hear: ‘Go grab yourself a beer! … These things happen.’ That saved my day, and probably the rest of the week.

Prof. Linne’s co-supervisor, moreover my friend, Dr. Joachim Walewski, has spent a lot of time explaining physics and mathematics to me, which has been necessary after my having spent one year of studying pedagogy, forgetting approximately everything about ‘hardcore’ physics. He’s also been jerking me around to all sorts of social behaviour; drinking beer, watching films and theatre plays, teaching me about history, philosophy, the swedish language and so much more. Thanks a lot!

I’d like to thank Prof. Marcus Aldén for letting me use the equipment at the division, my successesfull destruction of one QCL device included. I’m also indebted to Prof. Per-Erik Bengtsson, who was my first contact at the division, and helped me to get this diploma work in the first place.

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Before I start getting deeper into trouble, mentioning more persons and forgetting about others, let me just say: Thanks a lot, all you nice and special people at the Division of Combustion Physics!

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Appendix A – N₂O reference spectrum

Below is depicted a HITRAN-PC simulation of an N₂O spectrum from a 30cm cell with 0.1% N₂O in N₂. The total pressure is 0.01 atmospheres. The advantage of this option is that a 30cm cell already exists at the division of combustion physics, albeit lacking CaF₂ windows.

However, the option of building a 1cm cell, allowing 1% of N₂O in N₂, which should be easier to mix, seems at bit more appealing:
Appendix B – Where to put the mirrors

Alignment of an invisible beam is not an easy task. In order to be able to deduce where to place the parabolic off-axis mirrors, the theory of Gaussian beam propagation, described in section 2.4, was used to write a simple MATLAB® program, which provide the opportunity to juggle with the parameters d4, wd, and wF, as defined by Figure 35. The results are all the other parameters, ending up with the beam waist at the laser. Thus, the distances d3, d2, and d1 can be roughly determined, eliminating some of the tentative nature of the physical alignment procedure.

Figure 35: A schematic of the essential components in the experimental setup, intended to help in understanding the matlab program 'beamsetup.m'.

We hope that the program code\textsuperscript{11}, containing a lot of comments, will be self-explanatory. The beam from a QCL often exhibits a divergence half angle of 30 degrees in the vertical direction, and 20 degrees in the horizontal. With this knowledge, some juggling with d4, wd, and wF, has given the result displayed in the Matlab screen below. (All distances are given in meters.)

Enter desired distance from burner focus to closest mirror and detector, d4. > .7
Enter desired beam radius at the collection mirror, wF. > .021
Enter desired beam radius at the detector, wd. > .002

\[
\begin{align*}
    & w03 = 0.000616 \\
    & w02 = 0.000016 \\
    & d3 = 0.019582 \\
    & d2 = 0.205621 \\
    & d1 = 0.046765 \\
\end{align*}
\]

We hereby find the required beam waist of the laser, \( w01 = 3.7307e-006 \), which corresponds to a beam divergence halfangle of 25.7 degrees.

This is close enough for a decent start. The fine-tuning of the system has to be made by scanning the beam with the detector. At our division, Mark Linne is the master of this art.

\textsuperscript{11} The code can be found on a disc kept by Mark Linne.
Appendix C – Photos of the equipment

The experimental setup, as depicted in Figure 33, but without the extra pellicle and detector. The McKenna burner shown here lacks the gas flow controller units, the flame stabiliser and the hoses for water cooling.

Some close-ups of the QCL, collimation mirrors, pellicle and the little diode reference laser, with its mirror-type holder, modified by the author and Rutger Lorentzon.

The auxiliary equipment for the QCL and the detector. The black box on the picture to the right is the detector preamp, whereas the white is the control unit for the thermo-electric cooling. The auxiliary equipment for the QCL is described in the manual [18].