Investigations of infrared chemiluminescence emission from laboratory flames

Master of Science thesis by Andreas Pettersson

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Abstract

So far most optical combustion diagnostic techniques based on spectroscopic investigations have been made in the UV/visible region of the spectrum. There are, however several difficulties associated with measurements in this spectral region, for example non accessible species and exhibition of structure less spectra from large hydrocarbons. In the IR-region many of these issues are avoided. In this diploma work the IR-chemiluminescence from laboratory flames have been investigated. An IR-camera was used for detection of the spectra produced by the major emitters in the IR-range. Due to the rareness of the IR-camera, very few similar measurements in this region have been performed before.

The purpose of this thesis was to try to detect and identify major species with transitions in the IR-range mainly CO, CO$_2$, and H$_2$O. Measurements were performed in laboratory flames with three different fuel/air mixtures. The result indicates that it is possible to identify the major emitters in these spectral regions but the emission from minor emitters and intermediate species are too weak to detect and identify.
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1 Introduction

1.1 Background

Most optical combustion diagnostic techniques based on spectroscopic analyses so far have been made in the UV/visible region. Several difficulties arise from measurements in this spectral region. Some species do not have accessible transitions for example CO$_2$, CO, H$_2$O or H$_2$. There is also a problem if predissociative states are reachable which preclude fluorescence emission detection. This spectral region also contains broad and structureless spectra originally from hydrocarbon molecules. However in the IR-range of the spectrum several of the species mentioned above have strong vibrational-rotational transitions: CO$_2$, CO, and H$_2$O. The transitions in the IR-range can be detected using spatially resolved techniques as compared to conventional line-of-sight absorption techniques. As the detectable species in this spectral region have separate spectral features there is a possibility of species identification. There are challenges with measurements in this region as well, for instance a considerable line overlap and spectral interference makes species identification more difficult. Although the technique is associated with several issues which have to be addressed it opens possibilities for temporarily, spatially and spectrally resolved measurements.

1.2 Purpose

The purpose of this thesis is to try to detect and identify species with major transitions in the IR-range mainly CO, CO$_2$, and H$_2$O.

1.3 Disposition

In chapter two theories concerning this thesis are discussed. The theory of molecular spectroscopy is rigorously treated, flame chemistry and blackbody theory are addressed and some information is given concerning the HITRAN database. Chapter three focuses on the experimental details of the work. All components are briefly discussed as well as more detailed description of the spectrometers, the gratings, the IR-camera and the blackbody built for the experiment. This chapter also treat the emission measurements and the wavelength calibration. In chapter four the resulting spectra are presented and analysed. In the last chapter conclusions are drawn and future work is discussed.
2 Theory

The theory part of this thesis is focused on molecular spectroscopy although both flame chemistry and blackbody theory is discussed. This chapter also contains information about the HITRAN database.

2.1 Molecular physics

Since diatomic and triatomic molecules are present in high concentrations in combustion especially when focusing in the IR-spectra it is essential to have a basic understanding of the molecular physics governing these types of molecules.

A molecule emits or absorbs energy through three different processes: rotational, vibrational and electronic transitions. The time scales for these interactions are \( \sim 10^{-12} \text{ s} \), \( \sim 10^{-14} \text{ s} \) and \( \sim 10^{-15} \text{ s} \) respectively. According to the Born-Oppenheimer approximation it is possible to treat these three modes separately. The approximation states that the variation effects of the electronic wave function due to vibrations and rotations are very small. Normally this is true but in some exceptional cases the approximation breaks down, for example if the potential curves of two different electronic states are closely situated or overlap. The approximation leads to separate Schrödinger equations for the three energy modes. In this thesis we are mostly concerned with the transitions emitting energy in the IR-region. For this reason the spectra of vibrating and rotating transitions are derived and discussed while the electronic interaction has been left out.

When it comes to triatomic molecules we are mainly interested in the theories involving H\(_2\)O and CO\(_2\) since these are the main products of combustion and both highly active in the IR-region. The complexity in the calculations increases with the number of atoms but it is still possible to use the diatomic model as a base and extend it to include more atoms.

2.1.1 Schrödinger Equation

The first step of forming a new system of wave mechanics now known as quantum mechanics was developed at the turn of last century. Maxwell’s prevailing equations clearly stated that light is a motion of waves but several new theories indicated that a new perspective was needed:

- Max Planck presented a solution to the problem with the Rayleigh-Jeans\(^1\) formula at higher frequencies, the ultraviolet-catastrophe. It included a quantization of light into small energy-radiating oscillators (photons), each of them having the energy \( E_n = h\nu \). Einstein later proved this theory to be true through his work with the photoelectric effect for which he was awarded the Nobel Prize in physics in 1921.
- Niels Bohr was able to calculate the energy levels in the hydrogen atom by assuming quantified electronic angular momentum. For this he was honoured with the Nobel physics Prize in 1922.

---

\(^1\) Rayleigh-Jeans classical calculation for the energy density in a black body: \( \rho(\nu) = \frac{8\pi}{c^3}\chi^2kT \). This treatment leads to the “ultraviolet catastrophe: \( U = \int_0^\infty \rho(\nu)d\nu = \int_0^\infty \frac{8\pi}{c^3}\chi^2kTd\nu \to \infty \)
• Louis de Broglie postulated in his wave theory of matter that all particles can be described as waves with a wavelength given by: \( E = h \nu \) and was awarded the Nobel Prize in physics in 1929.

Erwin Schrödinger however was the first who successfully summarise these theories into one single equation, the Schrödinger equation \([1]\). It should be mentioned that Schrödinger too was awarded the Nobel Prize in physics together with Dirac in 1935:

\[
-\frac{\hbar^2}{2m} \nabla^2 \Psi + W \Psi = i\hbar \frac{\partial \Psi}{\partial t}
\]  

(2.1)

For a particle with mass, \( m \), moving in space and affected by the potential \( W(x,y,z,t) \) it is possible to calculate the matter of waves \( \Psi(x,y,z,t) \) through this time-dependant equation. Using the Hamiltonian operator the time-independent Schrödinger equation (S.E.) is expressed in its’ simplest form:

\[
H \Psi = E \Psi
\]  

(2.2)

Quantization of energy in a molecule follows directly from solutions to this equation. Through interpretations of the wave function, \( \Psi \), and boundaries of the equation, the limitations of quantum numbers to the solutions are set.

2.1.2 Molecular Structure

2.1.2.1 Rotating molecule

Rotating transitions in a molecule concerns the spectroscopy mainly in the microwave region from 1 \( \mu \)m to 1 cm. It is included in this thesis because it also affects the IR-region. In this spectral region the rotation appears as a perturbation on the vibration of the molecule and with high enough resolution it is possible to detect the rotation lines in the vibrating molecule. In Figure 2-1 a diatomic rigid molecule is shown (the bonding distance, \( r_0 = r_1 + r_2 \), between two atoms are assumed to be fixed).

![Figure 2-1. A diatomic rigid rotator with centre of gravity at C.](image-url)
The atomic masses are noted as $m_1$ and $m_2$ respectively, and the total reduced mass of the system is $\mu = \frac{m_1 m_2}{m_1 + m_2}$. The rotation of the molecule around the centre of gravity, $C$, can be resolved into three perpendicular rotational components. Thus the molecule has three principal moments of inertia, one about each axis, $I_x$, $I_y$, and $I_z$. In this case it can be seen from Figure 2-1 that $I_y = I_z$ and that $I_x$ is very small compared to the other two. This leads to one principal moment of inertia:

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$$

(2.3)

Classically the angular momentum, $L$, and the energy, $E$, are defined as:

$$L = \frac{I \omega}{\hbar}$$
$$E = \frac{L^2}{2I} \Rightarrow E = \frac{I^2 h^2}{2l}$$

(2.4)

Quantum mechanically the angular momentum is associated with the operator, $\mathbf{L}$, and can be put into the Hamiltonian operator $\mathbf{H}$. Now the S.E. for the system can be solved and the quantized energy of the rotator is given by:

$$\mathbf{H}_{\text{rot}} = \frac{\hbar L^2}{2I} \Rightarrow \text{solving the S.E.: } \mathbf{H} \psi = E \psi \Rightarrow |L| = \hbar \sqrt{J(J + 1)}$$

and $E_J = \frac{\hbar^2}{2I} J(J + 1) = B J(J + 1)$ \[\text{cm}^{-1}\]

(2.5)

Here the rotational quantum number $J = 0, 1, 2\ldots$ Often the rotational constant, $B$, is used for simplicity. For diatomic molecules $B$ varies around 10 cm$^{-1}$. Now it is possible to derive a rotational diagram of the rigid rotator. The left part of Figure 2-2 shows a diagram of discrete energy levels of a rigid rotator. The distance between the levels grows quadratically with increasing $J$.

![Figure 2-2. A diagram showing the energy levels and transitions of the rigid and the non rigid rotator respectively.](image-url)
The eigenfunctions to the S.E. of the rigid rotator are so called surface harmonics:

\[ \Psi_r = N_r P_J^{M_r}(\cos \vartheta) e^{i M r} \]  \hspace{1cm} (2.6)

For the quantum number, \( M \), yields: \( M = J, (J-1), (J-2), \ldots, -J \). \( M \) represents the component of the angular momentum in direction of a given axis. \( P_J \) is a function of the angle, \( \vartheta \), and \( N_r \) is a normalisation constant [2].

For a diatomic rigid molecule to emit or absorb energy it must be associated with a change in the dipole moment. This applies to all heteronuclear molecules since these possess a permanent dipole moment. During the rotation the dipole component changes periodically with a frequency equal to the rotational frequency. For diatomic molecules with equal atoms no permanent dipole moment exists and therefore no energy is emitted. Homonuclear diatomic molecules such as, \( \text{N}_2, \text{O}_2, \text{and H}_2 \) are therefore IR-inactive and do not emit radiation via rotational transitions.

The wave number of the emitted or absorbed light quantum for the rotational transitions in the rigid rotator is:

\[ \sigma_{\text{rot}} = \frac{E'}{hc} - \frac{E''}{hc} \left[ \text{cm}^{-1} \right] \]  \hspace{1cm} (2.7)

Where \( E' \) and \( E'' \) are the rotational energies in the upper and lower states respectively. For the actual absorption or emission frequencies there are selection rules for the quantum number, \( J \), which must be accounted for. Without going into details it should be mentioned that the selection rules for \( J \) is derived from further evaluation of the dipole moment. An evaluation of \( J \) also states that the dipole moment must take a non zero value in order to emit or absorb energy in accordance with previous discussion.

The selection rule for rotational transitions is: \( \Delta J = J' - J'' = \pm 1 \), where the quantum number “jumps” one step at the time (see Figure 2-2). With this selection rule for \( J \) it is now possible to derive a theoretical spectrum for a simple rigid rotator. From the equation above we have:

\[ \sigma_{\text{rot}} = \frac{E'}{hc} - \frac{E''}{hc} = BJ' (J'+1) - BJ'' (J''+1) = \ldots = 2B(J + 1) \]  \hspace{1cm} (2.8)

The spectrum then consists of equidistant lines with the line separation of \( 2B \) beginning with \( J = 0 \). The rotational frequency is quantized which is different from the classical case where it can take any value.

The assumption that the rotating molecule is completely rigid is however an approximation. Due to centrifugal effects, the internuclear distance will expand with increased rotation. This leads to variation in the moment of inertia, \( I \), and the rotational constant, \( B \). Considering a non rigid rotator (the bar in Figure 2-1 is replaced with a mass less spring) the rotational wave number is given by [2]:

\[ \varepsilon_J = \frac{E}{hc} = B \left[ 1 - uJ (J+1) \right] J (J+1) = BJ (J+1) - DJ^2 (J+1)^2 \]  \hspace{1cm} (2.9)
Here $D$ is termed the centrifugal distortion constant. It can be shown by assuming a small restoring force to compensate for the small displacement from the equilibrium position in the diatomic molecule [2]:

$$D = \frac{4B^3}{\omega^5} \left[ \text{cm}^{-1} \right]$$  

(2.10)

It is known that the vibrating frequency, $\omega$, always is much greater then $B$ so $D/B << 1$. The effect of this distortion term can be seen in the right part of Figure 2-2. The effect is more obvious for higher rotational levels and it should be noted that Figure 2-2 is an exaggeration. It is possible to include cubic and even higher order distortion terms:

$$\varepsilon_J = \frac{E}{hc} = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + ... \left[ \text{cm}^{-1} \right]$$  

(2.11)

These terms however are of little experimental interest since they are scarcely resolvable. The selection rule is still valid in the case of the non rigid rotator, which gives the spectrum for the rotation lines according to the following equation:

$$\sigma_{rot} = 2B(J + 1) - 4D(J + 1)^3$$  

(2.12)

The line spacing is no longer equidistant as before but is slightly decreasing with increasing $J$. The effect is small however, since $D << B$.

The fundamentals of the rotational diatomic model can be used in the triatomic case with some modifications. We can define at least two groups of molecules according to their moments of inertia, $I_A$, $I_B$ and $I_C$:

- **Linear molecules:** All atoms are arranged at a straight line and thus has the following moments of inertia: $I_A = I_B$ and $I_C = 0$. All diatomic molecules thus belong to this category (Figure 2-2). The CO₂ molecule for example is arranged as O – C – O and is therefore also included in this group.

- **Asymmetric tops:** $I$ differ in all directions: $I_A \neq I_B \neq I_C$. Most molecules belong in this category for example H₂O.

There are more categories of molecules for example spherical tops and symmetric tops but they will not be covered in this thesis.

Equation 2.12 applies to the linear group of molecules. For the linear molecule to be microwave active, i.e. emit and absorb energy through pure rotational transitions, it still has to possess a permanent dipole moment. If a molecule have a centre of symmetry it possess no change in the dipole moment due to rotation and is therefore microwave inactive for example CO₂(O-C-O). Depending on the moment of inertia a larger molecule have a smaller rotational constant, $B$. This results in much smaller spacing between the spectral lines for large molecules.
In the case with the asymmetric tops there is no general equation that can be derived as in the other situations. The energy levels and the transition frequencies vary depending on the structure of the molecule and the atoms involved.

### 2.1.2.2 Vibrating molecule

The vibrational transitions mainly occur in the infrared region and are of great interest in this work. We begin by assuming a diatomic molecule where the vibrations are introduced as a harmonic oscillator. For the harmonic oscillator the potential energy, $V$, is known and the vibrational frequency, $\nu_{\text{osc}}$, is:

$$V = \frac{1}{2} kx^2 \quad \text{and} \quad \nu_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$  \hspace{1cm} (2.13)

Where $x$ is the displacement from the equilibrium position and $k$ is the force constant. Inserting the potential energy into the S.E. the allowable vibrational energy levels are calculated as:

$$\frac{d^2\Psi}{dx^2} + \frac{\mu}{\hbar^2} (E - \frac{1}{2} kx^2) \Psi = 0$$  \hspace{1cm} (2.14)

and $E_v = \hbar \sqrt{\frac{k}{\mu}} (v + \frac{1}{2}) = h \nu_{\text{osc}} (v + \frac{1}{2})$ or $E_v = \sigma_{\text{osc}} (v + \frac{1}{2}) \hspace{1cm} [cm^{-1}]$

The vibrational quantum number $v = 0, 1, 2...$ The vibrational frequency, $\nu_{\text{osc}}$, is the same as for the classical case meaning that even in the classical harmonic oscillator the frequency can only take one value. This is different from rotational frequency.

The energy levels are equally spaced with a “zero point of energy” at level $v = 0$.

![Figure 2-3. The allowed vibrational energy levels and the probability density distribution.](image-url)
The eigenfunctions of the S.E. are found to be Hermite orthogonal polynomials [2]:

$$\Psi_v = N_v e^{-1/2(\alpha x^2)} H_v(\sqrt{\alpha x})$$  \hspace{1cm} (2.15)

$N_v$ is a normalisation constant. The probability density distributions, $\Psi_v \Psi_v = |\Psi_v|^2$, are also plotted in Figure 2-3 for different values of $v$. The probability density reveals that it is more likely to find the molecule at the end positions than at the equilibrium point for excited vibrational states. There is also a small probability to find the molecule outside the turning points.

By evaluating the dipole moment of the molecule as in the case of rotation the selection rules for $v$ is derived. The vibrating molecule as well as the rotating molecule must have a change in the dipole moment to be able to emit and absorb light. The selection rule is similar to that of rotation: $\Delta v = v' - v'' = \pm 1$. For the transition wave number yields:

$$\sigma = \frac{E'}{hc} - \frac{E''}{hc} = \sigma_{osc} (v' + \frac{1}{2}) - \sigma_{osc} (v'' + \frac{1}{2}) = ... = \sigma_{osc} \left[ \frac{\text{cm}^{-1}}{\text{cm}^{-1}} \right]$$  \hspace{1cm} (2.16)

Equation 2.16 also shows that the energy levels are equally spaced. Even though the harmonic oscillator model is a fairly good approximation for lower excited levels it fails in accuracy when it comes to the higher levels. In order to correct for the inaccuracy at the higher levels it is therefore necessary to evaluate the anharmonic oscillator. If higher order deviation terms are introduced the energy levels for the anharmonic oscillator can be derived from the S.E. [2]:

$$\varepsilon_v = \sigma_x (v + \frac{1}{2}) - \sigma_x x_v (v + \frac{1}{2})^3 + \sigma_y y_v (v + \frac{1}{2})^3 + ...$$ \hspace{1cm} (2.17)

$v$ is as before the vibrational quantum number and since $\sigma_x$, $\sigma_y$, and $\sigma$ can be considered to be perturbation terms $\sigma_y << \sigma_x << \sigma$. The function is also called the Morse function. The anharmonic oscillator is schematically plotted in Figure 2-4 along with the harmonic oscillator (dashed line).

![Figure 2-4. The vibrational levels of the anharmonic oscillator.](image)
The distance between the energy lines are no longer equally spaced but is slightly decreasing with increasing \( v \). The selection rules for the anharmonic oscillator differ from the harmonic case: \( \Delta v = \pm 1, \pm 2, \pm 3, \ldots \) This is also illustrated in Figure 2-4. However the intensity of these “over tone” transitions is rapidly decreasing with increasing \( v \). The dissociation energy, \( D_e \), is plotted in the same figure which shows where the discrete energy levels goes into a continuous spectrum. The transition wave number is in the order of \( 10^3 \) cm\(^{-1}\).

### 2.1.2.3 Vibrating rotator

The diatomic molecule rotates and vibrates at the same time. The molecule can vibrate 100-1000 times during one rotation. As the molecule vibrates its’ rotational moment of inertia changes which effects the rotational constant, \( B \), and the centrifugal distortion constant, \( D \). This effect is approximated by defining a mean value for \( B \) and \( D \) in a certain vibrational state in the following way:

\[
\begin{align*}
B_v &= B_e - \alpha_e (v + \frac{1}{2}) \\
D_v &= D_e + \beta_e (v + \frac{1}{2})
\end{align*}
\]  

(\ref{rotation-constant-definition})

Here \( B_e \) and \( D_e \) are the constant values defined for the non vibrating rotation above. \( \alpha_e \) and \( \beta_e \) are small corrections compared to \( B_e \) and \( D_e \). The rotational wave number in a given vibrational state is obtained by:

\[
\varepsilon_{J,v} = \frac{E_{v,J}}{\hbar c} = B_v J(J+1) - D_v J^2 (J+1)^2 + \ldots \quad [\text{cm}^{-1}]
\]  

(\ref{rotational-wave-number})

\( D_v \) is so small it is often neglected. For both vibration and rotation we have:

\[
\varepsilon_{J,v} = \omega_e (v + \frac{1}{2} - \omega_e x_e (v + \frac{1}{2})^2 + \ldots + B_v J(J+1) - D_v J^2 (J+1)^2 + \ldots \quad [\text{cm}^{-1}]
\]  

(\ref{vibrational-energy})

Now it is possible to combine the two energy modes into one single energy diagram.

---

Figure 2-5. The rotation energy levels (short lines) drawn for each vibration state (long lines). Transitions between vibrational modes \((v_0\) and \(v\)) are included.
Consider a transition from \(v'\) (higher state) to \(v''\) (lower state). It is now possible to present the transition as a sum of the vibrational and rotational contributions:

\[
\sigma = \sigma_{\text{vib}} + \sigma_{\text{rot}} = \left( \frac{E_{\text{vib}}(v') - E_{\text{vib}}(v'')}{hc} \right) + \left( \frac{E_{\text{rot,v}}(J') - E_{\text{rot,v}}(J'')}{hc} \right) = \sigma_0 + B' v' J' (J'+1) - B'' v'' J'' (J''+1)
\]

This formula can also be verified by the vector sum in Figure 2-5. Implementing the selection rule for \(J\) (\(\Delta J = \pm 1\)) and replacing \(J''\) with \(J\):

\[
\sigma_R = \sigma_0 + 2B' v' + (3B' - B'') J + (B' - B'') J^2; \quad J = 0, 1, 2, \ldots\text{ and } \Delta J = +1
\]

\[
\sigma_P = \sigma_0 - (B' - B'') J + (B' - B'') J^2; \quad J = 1, 2, \ldots\text{ and } \Delta J = -1
\]

These two sets of lines are called R and P branches respectively. The two branches can be combined in equation 2.23:

\[
\sigma = \sigma_0 + (B' + B'') m + (B' - B'') m^2 \Rightarrow B' v' \Rightarrow \sigma = \sigma_0 + 2Bm
\]

\[
m = -1, -2, -3 \quad \text{for P - branch}
\]

\[
m = 1, 2, 3 \quad \text{for R - branch}
\]

Sometimes it is not necessary to include the vibrational effect on the rotation constant and it is set to \(B\) in both vibrational states. From equation 2.23 it is easy to see that the R-branch starts in \(\sigma_0\) and is shifted towards higher frequencies while the P-branch starts in \(v_0\) and is shifted towards lower frequencies. \(m = 0\) corresponds to the forbidden line at \(\sigma_0\) also known as the band origin. For sufficiently high values of \(m\) the R-branch converges and goes towards shorter frequencies. This is the Fortrat parabola and is illustrated in Figure 2-6.

![Figure 2-6. The Fortrat parabola along with the spectral lines associated with different values of \(m\).](image)
There are a few more correction terms that affect the calculations slightly, but they will not be accounted for in this thesis.

For the polyatomic vibrations it is important to consider the shape of the molecule. The internal configuration of the atoms in the molecule becomes fundamental for understanding the different spectra associated with the molecule and gets more complicated as the number of atoms involved increase. A molecule with \( N \) atoms has \( 3N \) degrees of freedom, one for each coordinate. The vibrational motion of a molecule is governed by its' fundamental frequencies. If the number of degrees used to describe the rotation around the centre of mass and translation are removed since neither of these corresponds to any vibrational motion it is possible to distinguish \( 3N-6 \) fundamental vibrations. In the case of a linear molecule this number is changed to \( 3N-5 \) fundamental vibrations. The different vibrational modes represent stretching and bending of the molecule. Leaving the classical treatment and solving the S.E for these vibrations an evaluation of the selection rule for the quantum number \( \nu \) is needed similar to the diatomic vibrational case. The molecule has to change its’ dipole moment in order to be IR-active which is exactly the same as in the evaluation of the diatomic case. The evaluation of \( \nu \) also results in three different types of overtones i.e. superpositions of the fundamental vibrations. The multiple bands are defined for frequencies around \( 2\nu, 3\nu, \ldots \) etc. where \( \nu \) is the fundamental vibration. The summary bands and difference bands are overtone combinations of vibrations that involve \( \nu+\nu_k \) and \( \nu-\nu_k \) respectively. If such superpositions of fundamental vibrations have similar frequencies a resonance phenomenon is introduced and the intensity is enhanced in this spectral region. However in the normal case the intensity of the fundamental mode is much stronger than that of superpositions.

Depending on whether the molecule is linear or non linear the selection rules differ slightly. Consider for example the linear molecule \( \text{CO}_2 \). The vibrations of this molecule can be divided into parallel or perpendicular vibrations:

**Parallel vibrations:**

Selection rules: \( \Delta J = \pm 1 \) \hspace{1cm} \( \Delta \nu = \pm 1, \pm 2, \pm 3, \ldots \)

These rules are identical with those of the anharmonic diatomic oscillator. The spectrum then consists of the P and R branch with lines equally spaced at each side of the forbidden band origin. A large molecule corresponds to a small rotational constant, \( B \), with closely spaced spectral lines. If the molecule is large enough it becomes impossible to resolve the rotation lines. Figure 2-7(a) shows a spectrum with poor resolution. Figure 2-7(b) displays the opposite situation where the resolution is high and the P and R-branches is clearly visible.
Perpendicular vibrations:

Selection rules: $\Delta J = 0, \pm 1$, $\Delta v = \pm 1, \pm 2, \pm 3$...

Note here that the band origin is no longer forbidden. $\Delta J = 0$ or the Q branch is visible in the spectrum and consists of superimposed lines near the band centre. As for the parallel vibration the size of the molecule must be sufficiently small to be able to resolve the rotational lines.

In the non linear case the situation gets more complicated and the details are not covered here.

2.1.2.4 Transition strength

The thermal distribution of the rotational levels is modelled by the Boltzmann factor, $e^{-E/RT}$. The population $N_J$ at level $J$ is then given by:
Here $T$ is the temperature, $k$ the Boltzmann constant, $B$ the rotational constant and $N_0$ is the population in the lowest level. This function starts at $N_J/N_0 = 1$ ($J=0$) and then decreases exponentially as $J$ increases.

The other factor governing the distribution is the possibility of degeneracy in the energy states. Any atomic system with total angular momentum $J$ consists of $2J+1$ levels. Thus the system is said to have a $(2J+1)$-fold degeneracy. This gives the relative population in $J$:

$$N_J \propto (2J+1) e^{-Bh(J+1)/kT}$$  \hfill (2.25)

Equation 2.25 starts at 1.0 and then increases with $J$ until a maximum value is reached. It can be seen that the maximum value of the function corresponds to the nearest integer value of:

$$J = \left\lfloor \frac{kT}{\sqrt{2\hbar cB}} \right\rfloor$$  \hfill (2.26)

The value of $B$ determines how fast the distribution diminishes. It should be noted that the sum of all populated states ($N_{TOT} = N_1 + N_2 + \ldots + N_J + N_{J+1} + \ldots$) always must be the same. This effects the population for different temperatures. For a low temperature the level of maximum population ($J_{MAX}$) is low but the population ($N_{J=MAX}$) on that level is quite high. In return not so many levels $J$ are populated at all. If the temperature is increased ($J_{MAX}$) is increased but ($N_{J=MAX}$) is decreased. Naturally more levels are also populated.

The vibrational population distribution is also modelled by the Boltzmann factor with the vibrational transition energy. The distribution is:

$$N_e/N_0 = e^{-\hbar c\omega_0/\hbar kT} \left(1 - e^{-\hbar c\omega_0/\hbar kT}\right)$$  \hfill (2.27)

As the temperature increases the population of excited vibrational states slowly increases and the population of the ground state decreases at the same rate. The population of the vibrational excited states are however increasing at a much slower rate than for the rotational case.

2.2 Flame-chemistry

Without going into details of the complexity of flame chemistry some things should be mentioned about the basics in numerical modelling of flame phenomena. The emission from a flame can arise as a result of a thermal population of higher quantum levels (described in preceding text), by chemiluminescent chemical reactions yielding products in excited states [11] or by soot emission. The chemiluminescence effect is partly the reason which makes the study of emission more complex than absorption.

Complete combustion of a hydrocarbon with oxygen (air) can be written as:

$$[A] \text{ (oxidant)} + [B] \text{ (fuel)} \rightarrow [C] \text{ (CO}_2) + [D] \text{ (H}_2\text{O)} + \ldots$$  \hfill (2.28)

This reaction is called the balanced stoichiometric equation. Equation 2.28 only gives information of the start reactants and the end products and reveals nothing about the
reactions in between. These in-between reactions are nevertheless important because they determine the rate of the reaction. Breaking this reaction into elementary reactions and following them step by step makes it possible to fully understand the whole procedure of the combustion. But these elementary reactions are quite numerous, only in a stable premixed flame there could be hundreds of elementary reactions involved. The chemical species involved in the elementary reactions are both stable and unstable and the chain reactions proceed by collisions between these intermediate species. The chain-reaction starts with breaking of stable molecules into unstable ones. The final end-reactions produce stable molecules from unstable ones. Often these end-products are created in excited states and cause a chemiluminescent radiation when they go back to their ground state [12].

2.3 The HITRAN database

The HITRAN software (trans.exe) provides molecular transmission spectrum of individual gases over the spectral range from near UV/visible (0.44 µm) to the far-IR-field. The database contains absorption line strength parameters for 705,000 individual vibrational-rotational absorption lines of 32 different molecules including H₂O, CO₂, and CO. By providing the HITRAN software with the parameters governing the experimental environment it is possible to simulate a spectrum over some spectral range of interest. This can be used for comparison with the experiment.

There are several input parameters needed for the software to calculate the spectrum. The temperature of course affects the transition strength. The path length is used to determine the depth over which the transmission spectrum is calculated. The partial pressure i.e. the mole fraction is given as input for each selected specie. The total pressure is also given (since this experiment is simulated on a laboratory flame this parameter is set to atmospheric pressure). The spectral range is selected as well (for this experiment the interval should be somewhere within 1 to 5.5 µm) It is possible to choose the type of line broadening that should be used (the temperature dependant Doppler-broadening seems to the best approximation of this experiment).

To be able to give the correct input overall temperature and the correct mole fraction of each molecule existing in the measurement zone another program was used. This program simulates a stable premixed flame. As input parameters the reacting fuel and the equivalent ratio is given and the output values calculated by the program are the mole fraction of the species left in the burned region and the overall flame temperature. Table 1 shows the result from calculations of the temperature and mole fraction for a stable premixed CH₄/air flame.
Flame type | stoichiometric composition when $\phi = 1$ (% fuel) | IR-detectable major species | partial pressure = mole fraction $x(j) * P_{tot}(1atm)$ | adiabatic temperature [K]
--- | --- | --- | --- | ---
methane - air | CH$_4$ | H$_2$O, CO$_2$, CO, OH, NO | H$_2$O=0.180, CO$_2$=0.08, CO=0.019, OH=0.007, NO=0.004 | 2432

Table 1. The mole fraction and the adiabatic flame temperature for a premixed stable CH$_4$/air flame.

The equivalence ratio is chosen to be one for the calculation as seen in Table 1. The major species and their mole fractions are expressed as parts of the total pressure (one atmosphere). In Figure 2-9 an absorption spectrum including H$_2$O, CO$_2$, and CO from the HITRAN database between 1 and 5.5 $\mu$m is plotted.

This spectrum can be used as a first rough indicator of where to expect strong emission lines although the absorption spectrum should not be exactly compared with the emission experiment.
2.4 Blackbody theory

By definition a blackbody is a perfect absorber i.e. all radiation falling on a blackbody surface, independent on wavelength or angle of incidence, is absorbed. In this sense the blackbody is a perfect emitter at the same time.

If a closed cavity is assumed in which constant temperature can be kept it will absorb and emit electromagnetic radiation continuously and equilibrium will arise when the absorption and emission are equal. The energy density in the cavity is given by:

$$\rho = \left\langle \varepsilon \frac{1}{2} E^2 \right\rangle + \left\langle \mu \frac{1}{2} H^2 \right\rangle$$

(2.29)

Here $\varepsilon$ and $\mu$ are the dielectric constant and the magnetic permeability respectively. As can be seen equation 2.29 is a function of the electric field, $E(t)$, and the magnetic field, $H(t)$, and the brackets indicates a time average. The spectral energy distribution $\rho(\nu)$ is:

$$\rho = \int_0^\infty \rho(\nu) d\nu$$

(2.30)

If a small hole is created in the cavity and the spectral intensity is measured it can be shown that for a blackbody yield [10]:

$$I_\nu = \frac{c}{4n} \rho_\nu$$

(2.31)

Where $n$ is the refractive index of the medium inside the cavity. $I_\nu$ and $\rho_\nu$ are universal functions only dependant on the frequency, $\nu$, and the temperature, $T$, of the cavity.

Solving Maxwell’s equations for a general cavity with proper boundary conditions gives:

$$\nabla^2 E - \frac{1}{c^2 n} \frac{\partial^2 E}{\partial t^2} = 0$$

(2.32)

It is now possible to calculate the number of resonant modes, $N(\nu)$, that exists within the cavity between frequency 0 and $\nu$:

$$N(\nu) = \frac{8\pi \nu^3}{3e^3}$$

(2.33)

$V$ is the volume of the cavity. From equation 2.33 the number of modes per unit volume and unit frequency, $p(\nu)$ is:

$$p(\nu) = \frac{1}{V} \frac{dN}{d\nu} = \frac{8\pi \nu^2}{e^3 c^3}$$

(2.34)

Thus the spectral energy distribution is $\rho(\nu) = p(\nu) \langle E \rangle$ which is equal to the number of resonant modes multiplied with the average energy of each mode. According to Planck the energy and its’ average value of one mode could be written as:

$$E = n h \nu \text{ with } \langle E \rangle = \frac{h \nu}{e^{h \nu/kT} - 1}$$

(2.35)
Where \( n \) is a positive integer. Equation 2.36 finally gives the spectral energy distribution:

\[
\rho(\nu) = \frac{8\pi\nu^2}{c^3} \frac{h \nu}{e^{h\nu/kT} - 1} \tag{2.36}
\]

Figure 2-9 shows the typical blackbody curve for two different temperatures.

Figure 2-10. Plot of the thermal distribution \( \rho(\nu) \) as a function of frequency \( \nu \) at \( T = 2000K \) and \( 3000K \) respectively [10].
3 Experimental considerations

Here the experimental details are discussed. The spectrometers, gratings, IR-camera, blackbody and calibration of the IR-camera are treated thoroughly. The last part of this chapter concerns the emission measurements and the wavelength calibration.

The set-up used for the experiment is shown in Figure 3-1. A brief description of the components involved is followed by more detailed information of the spectrometer and the IR-camera.

![Figure 3-1. Experimental set-up. Number 1, 2, and 3 are attached to the wall. Number 4, 5, 6, 7 and 8 are placed on a table. Below this figure is an explanation for each component involved in the experiment.](image)

1. Air flow. The pressure from the tube was held at approximately 1 bar for all experiments.
2. CH₄, H₂ and CO-gas in separate tubes were used as fuel in the flame. In each flame the air and fuel were premixed before entering the burner. The gas pressure for the fuel was held at about 1 bar.
3. Cold water was used to cool the burner.
4. A gas-flow control was used to manipulate the ratio of fuel and air. This made it possible to perform the experiments with both rich and lean flame types. Two gas-flow meters regulated the pressure between the gas tubes and the gas-flow control for air and fuel respectively. The gas flow meter, which controls the gas flow, is calibrated for ethene (C₂H₄) and a correction factor must be accounted for when using some other gas than ethene. This correction factor is dependent of the molecular weight of the gas.
5. The McKenna burner produced a “semi”-stable flame.
6. A CaF$_2$-lens focused the flame on the entrance slit of the spectrometer. This type of lens has a good transmission in the mid-IR spectral range and was therefore suitable for the experiment.

7. The spectrometer imaged the flame on the detector. Two different spectrometers were used. They are both of Czerny-Turner type but with different focal lengths and different gratings. The SP150 Acton was used for low resolution spectra and the Triax320 for the high resolution spectra.

8. The spectrum was detected on a 256x256 InSb Focal Plane Array (FPA) inside the IR-camera.

3.1 Spectrometers and gratings

A spectrometer system produces a spectrally dispersed image of the source. The spectral techniques are similar for the two spectrometers used in the experiment. Figure 3-2 shows the Czerny-Turner principle for grating spectrometers.

![The Czerny-Turner grating spectrometer.](image)

The illumination source is focused on a small entrance slit. A spherical mirror collimates the image on the grating. The spectrally dispersed images of the slit, one for each of the constituent wavelengths is then focused on the focal plane and detected. The grating is placed in a turret in the spectrometer. By rotating the turret it is possible to scan across the spectral range defined by the grating.

The key criterions when evaluating a spectrometer are the ability to discriminate spectral images of the source, spectral resolution, and the ability of the optical system to gather light, throughput.

The entrance slit defines the throughput. The larger the entrance slit, the more light can be directed to the detector and thus improving the throughput. The entrance slit is stated as f/number and is a ratio of the diameter over the focal length of the smallest optical element in the system. However there is a trade off between the throughput and the resolution due to increased acceptance of more rays further off the optical axis. Such increased aberration

![The Czerny-Turner grating spectrometer.](image)
effects limits the spectral resolution. The spectral resolution of the spectrometer is depending on the properties of the grating and the quality of the optics.

When defining the properties of the grating it is appropriate to begin with the grating equation:

$$m\lambda = a \left( \sin \theta_i + \sin \theta_m \right)$$  \hspace{1cm} (3.1)

Here $a$ is the grating constant, $\theta_i$ and $\theta_m$ is the angle of the incident and diffracted beam respectively (also seen in Figure 3-2), and $m$ is the order of the diffracted pattern. At $\theta_i = -\theta_m$ and thus $m = 0$ light of all wavelengths appears in a zeroth-order peak (no diffraction).

With higher orders of $m$ the grating produces spectral lines on either side of the principal maximum. The intensity decreases with the distance from the zeroth order due to the constraining diffraction envelope. For some gratings the diffraction envelope maximum is shifted to a higher order to avoid overlapping of constituent wavelengths. Such gratings are called blazed gratings. The blazing angle is defined as:

$$\theta_b = \frac{\theta_i - \theta_m}{2} \text{ with the grating equation: } m\lambda = a \left( \sin \theta_i + \sin \left( 2\theta_b - \theta_i \right) \right)$$  \hspace{1cm} (3.2)

A commonly used special case is called the Littrow mount. In this case the incident rays are close to the groove face normal, which gives $\theta_b = \theta_i$ and $\theta_m = -\theta_i$ and equation 3.1 becomes:

$$\text{Littrow: } m\lambda = 2a \sin(\theta_i)$$  \hspace{1cm} (3.3)

Each value of $m$ gives a spectrally resolved range which is detectable; however the intensity decreases with increasing $m$. It should be noted that for different orders the spectral ranges might partially overlap. The non overlapping spectral range for a specific order is called the free spectral range, $F$:

$$F = \frac{\lambda_i}{m}$$  \hspace{1cm} (3.4)

Here $\lambda_i$ is the shortest detectable wavelength of the incident beam. The angular dispersion of the grating is defined from the grating equation as:

$$D = \frac{\partial \theta_m}{\partial \lambda} = \frac{m}{a \cos(\theta_m)}$$  \hspace{1cm} (3.5)

This is the angular separation per unit wavelength. When the focal plane array is used for detection at the focal plane it is more convenient to use the linear dispersion:

$$D_{\text{linear}} = \frac{\partial v}{\partial \lambda} = f \frac{\partial \theta_m}{\partial \lambda} = fD$$  \hspace{1cm} (3.6)
Here \( f \) is the focal length of the spectrometer. Often the plate factor (the reciprocal of the linear dispersion) is used as measurement. The plate factor gives the wavelength range per unit length on the FPA in [nm/mm]. The ability of the grating to produce well defined closely spaced spectral lines at a certain order is defined by the resolving power:

\[
R = \frac{\lambda}{(\Delta \lambda)_{\text{min}}} = ... = mN
\]  
(3.7)

\( N \) is the number of illuminated grooves on the grating and \((\Delta \lambda)_{\text{min}}\) is the smallest wavelength range resolvable.

The specifications for the different spectrometers used in the experiment are summarised in Table 2 which gives a rough theoretical estimation of the differences of the two spectrometers. By comparing the focal length of the spectrometers the linear dispersion of the TRIAX320 should be enhanced by approximately a factor two.

<table>
<thead>
<tr>
<th>Spectrometer</th>
<th>SP150 ACTON</th>
<th>TRIAX320</th>
</tr>
</thead>
<tbody>
<tr>
<td>Focal length, ( f )</td>
<td>150 mm</td>
<td>320 mm</td>
</tr>
<tr>
<td>( f/\text{number} )</td>
<td>4</td>
<td>4.1</td>
</tr>
<tr>
<td>Entrance slit</td>
<td>Manually controlled</td>
<td>Automatically controlled</td>
</tr>
<tr>
<td>Ruled gratings ordered</td>
<td>150 g/mm, blazed at 4 ( \mu )m</td>
<td>300 g/mm, blazed at 4 ( \mu )m, 100 g/mm, blazed at 3 ( \mu )m</td>
</tr>
</tbody>
</table>

Table 2. Specification for the spectrometers.

The theoretically calculated key figures for the gratings are listed in Table 3. The first order was used in all cases \((m = 1)\). The resolution was calculated for the blazing wavelength, \( \lambda_b \), with the Littrow approximation. Table 3 is used for comparison with the actual set-up to indicate the accuracy of the experiment. The plate factor indicates a theoretical improvement of the TRIAX320 with a factor of five compared to the SP150. The cost of higher dispersion is decreasing intensity. The most detailed spectra are obtained with the TRIAX320 using a small entrance slit. This will however be at the cost of low throughput. The minimum intensity detectable is determined by the properties of the IR-camera.
Table 3. Theoretical key figures for the gratings used in the experiment.

<table>
<thead>
<tr>
<th>Spectrometer and grating</th>
<th>SP150 Acton 150 g/mm blazed at 4 µm</th>
<th>TRIAX320 300 g/mm blazed at 4 µm</th>
<th>TRIAX320 100 g/mm blazed at 3 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate factor (1/fD)</td>
<td>42.4 nm/mm or 26.5 cm⁻¹/mm</td>
<td>8.33 nm/mm or 5.21 cm⁻¹/mm</td>
<td>30.9 nm/mm or 34.3 cm⁻¹/mm</td>
</tr>
<tr>
<td>Bandpass Chip width ≈ 1 cm</td>
<td>424 nm</td>
<td>83.3 nm</td>
<td>309 nm</td>
</tr>
<tr>
<td></td>
<td>265 cm⁻¹</td>
<td>52.1 cm⁻¹</td>
<td>343 cm⁻¹</td>
</tr>
<tr>
<td>Bandpass/pixel Pixel width = 30 µm</td>
<td>1.27 nm/pixel</td>
<td>0.25 nm/pixel</td>
<td>0.93 nm/pixel</td>
</tr>
<tr>
<td></td>
<td>0.80 cm⁻¹/pixel</td>
<td>0.16 cm⁻¹/pixel</td>
<td>1.03 cm⁻¹/pixel</td>
</tr>
<tr>
<td>Grating width Grating width</td>
<td>32 mm</td>
<td>67 mm</td>
<td>67 mm</td>
</tr>
<tr>
<td>(Δλ)ₘᵡₜ</td>
<td>0.83 nm</td>
<td>0.19 nm or</td>
<td>0.42 nm or</td>
</tr>
<tr>
<td></td>
<td>0.52 cm⁻¹</td>
<td>0.12 cm⁻¹</td>
<td>0.47 cm⁻¹</td>
</tr>
</tbody>
</table>

3.2 IR-camera

The photo detective material used in the camera is of InSb type (Indium antimonide). The pixel number is 256×256 pixels. The chip is an intrinsic semiconductor, which uses a direct band gap as spectral response. The camera is cooled with liquid nitrogen to a temperature of about 77 K and this produces an energy gap of about 0.23 eV corresponding to a maximum detectable response wavelength of 5.5 µm [8]. To keep the camera at a constant operating temperature vacuum has to be retained inside the camera. The camera is very sensitive and it is necessary that the operating temperature is constant during the measurements in order to get reliable results. Figure 3-3(a) shows the band gap as a function of the temperature. The full spectral “window” of the camera is from 1 to 5 µm. This is mostly due to a dependence of the detector quantum efficiency with the operating temperature.

![Figure 3-3(a) and (b). The energy gap as a function of the temperature (a), and the quantum efficiency as a function of the wavelength in µm [8]. The temperature in Kelvin is given at each of the curves in (b).](image)
As seen in Figure 3-3(b) the quantum efficiency is independent of the temperature down to about 60 K (the figure given at the side of the curve in Figure 3-3(b) is the temperature in Kelvin). When the temperature is further decreased the quantum efficiency decreases for longer wavelengths. Thus the sensitivity of the camera at a given wavelength is dependent on the quantum efficiency, the operating temperature and the resistance. During the measurements the detector temperature was controlled continuously.

In the case with the SP150 the camera was mounted onto the spectrometer in the focal plane. In this way the camera directly detects the focused spectrum without using a camera lens. The TRIAX320 and the camera however were separated and a camera lens was used to focus the focal plane of the spectrometer. Since the number of optical components was increased for the set-up with TRIAX320 this had a negative effect on the experiment with the TRIAX320 but it is hard to evaluate the significance of this effect.

In order to suppress the background and enhance the signal the computer summarized a lot of pictures to one integrated image. Many of these integrated images then were recorded in one following sequence. The operating frequency used in the experiment was about 75 Hz and the integration time 10 \( \mu s \). The number of integrated pictures (frames) was 1000.

It should be mentioned that the IR-camera used in the experiment is quite unique. Not many measurements of the emission in the IR-range like this have been made because of lack of an IR-camera with such sensitivity.

3.3 Blackbody

A blackbody was built for an accurate intensity calibration of the IR-camera. A blackbody by definition is a cavity with a very small hole made in the cavity wall which makes the blackbody used in the experiment more of a “greybody”. A greybody is close to a blackbody for sufficiently high temperatures but fails in accuracy for lower temperatures. Since the block built was heated it can be approximated to a blackbody and we will use the term blackbody. A small blackbody that is easy to use is preferable and therefore the size of the body was an important specification. The time it takes to heat the blackbody is also quite shortened if the size of the body is small. The sketch of the body is shown in Figure 3-4(a) and (b).

![Figure 3-4(a) and (b). The heating block (left block in (a)) and the cooling block (right block in (a)) with a hole in the middle so they could be put together into one single blackbody radiator (b).](image_url)
The body consists of two aluminium blocks as shown in Figure 3-4(a). The left block in the figure has been prepared with a heating wear that is inserted inside the block. The pattern of the heating wear inside the block is supposed to improve the uniformly heating of the body. Another important aspect is the thickness of the heating block. Since the heating block is closest to the camera it has to be thick enough so that the heat becomes homogenously distributed in the block. For a good calibration the camera must detect a uniform radiating area. The surface close to the camera also has to be smooth to avoid shadow effects. The heating wire is connected to a variable power supply. The heating wire can reach a temperature around 300-400 °C but since the blackbody is made of solid aliquin the heating process is quite slow a maximum blackbody temperature has been reached around 90 °C. The limitation of the maximum reachable temperature is also due to heat transfer through convection in air. The right part of Figure 3-4(a) shows the cooling block. It is simply a piped tunnel where a cold water flow is connected. The two blocks are attached to each other with a screw in the middle as seen in Figure 3-4(b). The dimension of the whole body is 200×300×10 mm. The colour of the blocks is black so the radiation from the surroundings is absorbed by the blackbody. In this way the only radiation the camera is able to detect during the calibration is from the blackbody radiation.

3.4 Intensity calibration of the IR-camera

The pixels on the FPA are very sensitive and a proper intensity calibration of the camera is required. Even when manufacturing the chips there are a small number of pixels on every chip which are none responding or “dead”. The result of a “dead” pixel is small black dots appearing in the images. An intensity calibration would compensate for these dead pixels and reduce the number of black dots. It would also make the pixels equally sensitive detectors so the measurements are not dependant on where on the chip the detection occurs. A well calibrated camera has a sensitivity of about 20 mK which is extremely good for this kind of detector. Often it is possible to detect a bad calibration with the human eye by observing the spectrum on the computer display. An intensity calibration lasts as long as the given temperature restrictions are held. Every time the camera has to be refilled with liquid nitrogen a new calibration has to be performed. A badly calibrated image contains randomly organized patterns and systematically reappearing defects, which makes it impossible to perform any analysis.

The calibration method used in the experiment was a two-point calibration. The lens cap was put on the camera and the room temperature was used as the first calibration point. The second calibration point was the body temperature by pushing the palm of the hand on the camera. The blackbody was more reliable as a uniform radiation source than a lens cap and a hand. With this method the blackbody could be placed in front of the camera and used for both calibration points by heating and cooling it. The lower calibration point was set to around 17 °C and the higher to around 55 °C. The lower point should not be below room temperature. The reason for setting the second point to 55 °C was mainly time related.

For the measurements with the SP150 spectrometer a simple calibration method with the hand and the lens cap was performed. The blackbody calibration was performed for the high resolution spectrometer, TRIAX320.
3.5 Emission measurements

The measured premixed flames and their balanced stoichiometric equations are:

- Methane – air: \( \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \)
- Hydrogen – air: \( 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \)
- Carbon monoxide – air: \( 2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 \)

These are the major product species occurring in the flame. As can be seen from the reactions the CH\(_4\)/air flame contains both H\(_2\)O and CO\(_2\) whereas the H\(_2\)/air- and CO/air-flames only contains H\(_2\)O and CO\(_2\) respectively. In this way it was possible to identify the H\(_2\)O- and CO\(_2\)-lines in the CH\(_4\)/air spectrum by comparing them to the other two spectra. There are three controllable factors which determined the intensity in the spectra:

- The equivalence ratio, \( \Phi \)
- Where in the flame the measurements were performed or the height above the burner, \( h \)
- Width of the entrance slit

Changes of these factors were observed as variations of the intensity in the emission spectra. Measurements performed very close to the surface of the burner contained emission from some of the unburned gas and some of the intermediate species. As mentioned in the theory chapter the slit width partly decided the sharpness of the spectrum. A broad entrance slit made it possible to detect weak parts of the spectrum but details in the spectrum were smeared out and the resolving power decreased. The entrance slit could only be accurately determined with the TRIAX320 since this spectrometer had an automatic entrance slit. Shown in Appendix are the variable factors which the measurements were performed. Apart from these three variable factors there were other factors affecting the spectrum for example the calibration of the camera and distances between the experimental objects but it is harder to estimate the effect of these factors.

The spectral range from 1 to 5.5 \( \mu \text{m} \) was scanned stepwise. The control device connected to the spectrometers gave a rough estimation of the steps in terms of absolute wavelength and using MATLAB the images were put together covering the whole range.

One spectral “step” was equal to the bandpass of the spectrometer. The measured bandpass was approximately 500 nm and 150 nm for the SP150 and the TRIAX320 spectrometer respectively. These were compared to the theoretical bandpasses in Table 3 (424 nm and 83 nm for the SP150 and the TRIAX320 respectively). For the SP150 spectrometer the calculated and the measured bandpass are quite similar but for the TRIAX320 the deviation is larger.

Figure 3-5(a) and (b) shows examples of a spectral image and a spectrum using the SP150 spectrometer with a spectral range of 500 nm. Figure 3-6(a) and (b) displays a spectral image detected using the TRIAX320 with a range of 150 nm. The lines in Figure 3-5(a) and Figure 3-6(a) are spectrally resolved images of the entrance slit. The colour variation in the figures
represents intensity variations. The x-axis of the diagram in Figure 3-5 and Figure 3-6 is the width of the focal plane array in pixels.

Figure 3-5(a) and (b). (a) is a spectral image of CH₄/air ($\phi = 1.68$) flame at approximately 3 $\mu$m (estimated with the control device) using the SP150. (b) is the spectrum showing the intensity variation over the spectral image.

Figure 3-6(a) and (b). (a) is a spectral image of CH₄/air ($\phi = 1.85$) flame at approximately 2.9 $\mu$m (estimated with the control device) using the TRIAX320. (b) is the spectrum showing the intensity variation over the spectral image.

3.6 Wavelength calibration

Since the control device only gave a rough estimation of the absolute wavelength scale a calibration of the devices was needed to obtain the correct absolute wavelength. Under the circumstances such device calibration could not be performed in the IR-range. Instead another method was used to get a valid absolute wavelength scale. The method involves three steps:

- Absorption spectra are recorded using a heating wire as IR-source with the same experimental setup used for the emission spectra.
• The absorption spectra can be compared with theoretically calculated spectra from the HITRAN database and an absolute wavelength scale can be determined.
• This automatically generates an absolute scale for the emission spectra since they are recorded under the same experimental conditions and with the same setup as the absorption spectra.

In the first step absorption spectra of atmospheric H$_2$O (approximately 0.2 %) and CO$_2$ (approximately 0.04 %) was recorded with the TRIAX320 using a heating wire as IR-source. Figure 3-7(a) and (b) shows the second step where the H$_2$O absorption around 2.8 µm from the measured spectrum and the spectrum from HITRAN are compared. 23 lines were identified and the absolute wavelength for each line was determined with the HITRAN database. From the lines a wavelength scale could be extended for the spectral range.

Figure 3-7(a) and (b). (a) is the spectrum recorded with the TRAIX320 spectrometer. (b) is the spectrum produced by the HITRAN database.

Figure 3-8(a) and (b) displays the second step of the calibration process around 4.5 µm where the CO$_2$ absorption was used for calibration. The two strong peaks at 4.3 µm and 4.25 µm were identified and used when extending the absolute scale.
Figure 3-8(a) and (b). (a) is the spectrum recorded with the TRAIX320 spectrometer. (b) is the spectrum produced by the HITRAN database.

The final step of the procedure was to fit the absorption spectra with the emission spectra and this was done using MATLAB. The method is theoretically valid but there are several practical challenges.

Even though the number of matching lines is sufficiently enough both in Figure 3-7(a) and (b) and Figures 3-8(a) and (b) to fit a wavelength scale there are lines present in the HITRAN spectrum that are missing in the measured absorption spectrum. One explanation to this is that closely spaced lines in the measured spectrum may not be resolvable by the spectrometer and therefore appear in the spectrum as one line when in fact there are several closely spaced lines. Another explanation is that if other species have absorption lines present in the near spectral range the lines of the observed species can be suppressed. The HITRAN database plots all the absorption lines for water as instructed but in the measured spectrum there may be absorption from more species than H$_2$O. The absorption of some species in the spectral range surrounding the missing line could for example cause the absence of the H$_2$O line, which theoretically should be present in the spectrum.

It is quite clear from the spectrum in Figure 3-8(a) that the absorption lines of CO$_2$ are not fully resolvable. One factor of uncertainty is that the broadening of the peak in the measured spectrum makes it difficult to determine where on the spectral scale the actual top value of the peak occurs. The fact that there are only two calibration points also adds to the uncertainty.

The absolute wavelength calibration was only performed for the TRIAX320 spectrometer. The SP150 absorption spectrum covering the whole range was not comparable to a theoretical absorption spectrum from HITRAN and this is the main reason why a wavelength calibration for the SP150 was not performed. In Figure 3-9 a recorded full absorption spectrum from 1 to 5.5 µm is displayed. The signal was too weak and disappeared in the background noise over large spectral ranges. In addition the typical blackbody signature made it impossible to fit the recorded spectrum to the beautiful noise free spectrum from HITRAN over the same range (see Figure 2-9). Another challenge with
the wide range was that it was no longer a linear scale due to the non linear grating dispersion which means Equation 3.6 is no longer valid. Even if a few lines in the spectrum could be identified it would be impossible to linearly interpolate a complete scale of the whole range from these points.

Figure 3-9. A full absorption spectrum from 1 to 5.5 µm recorded with the TRIAX320, 300 g/mm.

Using the TRIAX320 to record high resolved spectra of H₂O and CO₂ it was possible to work with fragments of the full spectral range. In these smaller spectral regions a linear scale could be assumed and an absorption curve was fitted to HITRAN. Still several pictures had to be put together. A problem with this was the possibility of overlapping images which is a source of error for the absolute wavelength scale. To avoid overlapping effects the spectrum was scanned through several times to get the best fit but some overlapping errors probably still exist.
4 Results and analysis
This chapter contains the results and analysis of the recorded emission spectra.

4.1 The SP150 spectra
Using MATLAB the spectra from the SP150 spectrometer was put together to a single emission spectrum from 1 to 6 µm. Since no absolute wavelength calibration was performed for the SP150 the x-axis in all these spectra are given in number of pixels. The results from the H₂/air and the CO/air flames are shown in Figure 4-1 and Figure 4-2.

Figure 4-1. The emission spectrum for H₂/air premixed flame with φ = 0.95 using the SP150 spectrometer. Height over burner was approximately 1 cm and the background signal was subtracted.

Figure 4-2. The emission spectrum for CO/air premixed flame with φ = 1.35 recorded with the SP150 spectrometer. Height over burner was approximately 1 cm and the background signal was subtracted.

The spectra reveal two spectral regions of interest: the H₂O-lines about 3 µm and the CO₂-lines at 4.5 µm. By comparing the spectra it was possible to distinguish CO₂ and H₂O in the CH₄/air flame.

Figure 4-3 shows the emission spectrum from the CH₄/air premixed flame using the SP150. Figure 4-4 is a FT-IR absorption spectrum of a kerosene diffusion flame detected in some
previous IR-measurements made by Ottesen et al. [9]. Despite fundamental differences between the spectra it is possible to identify and compare H$_2$O and CO$_2$ in both spectra.

The strong emission of carbon dioxide is mainly due to the large Einstein coefficient ($A = 420$ s$^{-1}$) which is the probability per unit time for spontaneous emission. This should be compared to the much smaller Einstein coefficient of for example CO ($A = 27$ s$^{-1}$) or CH$_4$ ($A = 30$ s$^{-1}$) which have much weaker emission lines (CH$_4$ is not visible in the spectra recorded in these experiments).

One basic difference between the spectra is that the emission spectrum is more or less an instant image over the spectral range while the absorption spectrum is recorded over a much longer period of time due to the different technique. This is an advantage of using an IR-camera. If a turbulent environment is analyzed it is important to be able to perform instant measurements and an IR-camera is a preferable choice.

The H$_2$O-lines around 3 µm in the emission spectrum are compared with the lines in the absorption spectrum from 3400 cm$^{-1}$(2.9 µm) to 4000 cm$^{-1}$(2.5 µm) identified as H$_2$O. These lines in the work of Ottesen et al. were identified as H$_2$O vibration-rotational lines of $\nu_1$ and $\nu_3$.

The strong CO$_2$ peak in the emission spectrum at around 4.5 µm is related to the intense $\nu_3$ absorption band of CO$_2$ centered at 2330 cm$^{-1}$(4.29 µm) in Figure 4-4 [9].

The water lines around 5.5µm in Figure 4-3 are outside the relevant boundary of the camera and therefore not reliable.

![Figure 4-3. The emission spectrum for CH$_4$/air premixed flame with $\phi = 1.68$ recorded with the SPI50 spectrometer.](image-url)
Figure 4-4. The absorption measurements of D. K Ottesen and D. A Stephenson where transitions were detected in a FT-IR absorption spectrum of a kerosene diffusion flame [9].

Each of these water and carbon dioxide regions in the emission spectrum are now further analyzed with TRIAX320 spectrometer producing high resolution emission spectra.

4.2 The TRIAX320 spectra

4.2.1 H₂O-emission at 2.8 µm

Figure 4-5 and Figure 4-6 show high resolved emission spectra (2.6 µm-3.1 µm) of water from the CH₄/air and H₂/air premixed flames respectively. According to Herzberg [4] an absorption spectrum over the same spectral range contains absorption bands of ν₁ and ν₃. However it seems like the emission lines in this experiment is slightly shifted towards longer wavelengths compared to the theoretically calculated absorption bands.

Changing the height above the burner, the entrance slit width or the equivalence ratio gives no significant changes of the signal. For example a change of the equivalence ratio from 1.16 to 1.86 hardly increases the signal at all. A change of the entrance slit from 100 µm to 150 µm increases the signal with about 1 %.
Figure 4-5. H$_2$O emission from a premixed CH$_4$/air flame with $\phi = 1.16$. The entrance slit width was 150 $\mu$m and the height above the burner was approximately 1 cm.

Figure 4-6. H$_2$O emission from a premixed H$_2$/air flame with $\phi = 1.20$. The entrance slit width is 150 $\mu$m and the height above the burner is approximately 0 cm.

Figure 4-7(a) displays the CO/air flame in the same spectral region as Figure 4-5 and Figure 4-6. Theoretically the premixed CO/air flame only produces CO$_2$ and there should be no signal in this range. However some sort of signal is observed. An explanation for this could be that the water in the surrounding air is also heated by the flame to some extent causing emission as well.

Another interesting phenomenon is displayed when comparing Figure 4-7(a) and Figure 4-7(b). Figure 4-7(b) is a recorded H$_2$O absorption spectrum in air over the interesting spectral range. In the range of 2.65 – 2.80 $\mu$m the lines in both figures are very similar indicating that these lines could very well be arising from absorption in both figures.

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equality of the figures therefore predicts some sort of absorption in the emission spectrum. However this absorption effect in the emission spectrum is much less visible when comparing the other recorded emission spectra with the absorption spectrum in Figure 4-7(b).

Figure 4-7(a) and (b). (a) shows a spectrum of a CO/air flame with $\phi = 1.10$. (b) shows an absorption spectrum in the same spectral range(b).

4.2.2 CO$_2$ emission at 4.4 $\mu$m
In Figure 4-8 and Figure 4-9 high resolved spectra of CO$_2$ emission in a CH$_4$/air flame are plotted with different equivalence ratio.

Figure 4-8. CO$_2$ emission from a CH$_4$/air flame with $\phi = 1.16$. The entrance slit width is 150 $\mu$m and the height above the burner is approximately 1 cm.
Figure 4-9. CO$_2$ emission from a CH$_4$/air flame with $\phi = 1.85$. The entrance slit width is 150 $\mu$m and the height above the burner is approximately 1 cm.

The peak at 4.4 $\mu$m is the strong CO$_2$ emission. Due to limitations of the resolving power the peak can not be resolved further. The steep intensity drop at 4.5 $\mu$m is due to a gap between two images. However this explanation is not true for the intensity variation at 4.2 $\mu$m. It could be some kind of band conversion but no similar phenomena is found in other measurements.

The two smaller peaks in the right part of the figures are probably absorption bands from CO$_2$($\nu_3$). This is also supported by Herzberg [4]. As well as for the water lines around 2.8 $\mu$m a shift towards longer wavelength exists for the emission peak compared to the well known absorption peak.

In Figure 4-9 the equivalence ratio is increased (from 1.16 in Figure 4-8) to 1.85. This results in detection of CO in the range of 4.6-5.0 $\mu$m. In [9] an absorption band is detected as the P and R branches of CO($\nu_1$) in the same spectral range (see Figure 4-4 around 2145 cm$^{-1}$). The small Einstein coefficient ($A = 27$ s$^{-1}$) makes the CO signal relatively weak.

4.2.3 Some notes of the range above 5 $\mu$m

In Figure 4-10 a spectrum of a CH$_4$/air flame is plotted from 4.9 to 5.5 $\mu$m. The range above 5 $\mu$m is beyond the limit of the IR-camera and the results from this range is therefore unreliable.

Additionally a recorded absorption spectrum of this spectral region was impossible to fit with a spectrum from the HITRAN database since the number of mismatching lines was too large. Therefore the uncertainty of the wavelength scale produced is very large and the scale in Figure 4-10 should only be considered as a rough approximation. A possible explanation to the high number of mismatching lines is that there may be lines from higher order of the...
a grating present in the spectrum. In this range far from the centre of the first order (blazing angle) this is a probable effect and could result in a spectrum like Figure 4-10.

Previous absorption measurements indicate some water absorption in this area (see Figure 4-4 around 1900 cm\(^{-1}\)) and this could very well be emission from water. However since no spectrum from the HITRAN database could be exactly fitted to the absorption spectrum measured no conclusions can be drawn.

Figure 4-10. The spectrum from CH\(_4\)/air with \(\phi = 1.85\).
5  Summary and future work

With the IR-camera it is possible to detect instant flame images over a very short period of time. This is one of the first experiments where an IR-camera is used to investigate IR chemiluminescence emission. Using the SP150 spectrometer the IR spectral range from 1 to 5\(\mu\)m has been recorded and water and carbon dioxide were found. With the TRIAX320 spectrometer high resolution spectral images is produced of water and carbon dioxide emission.

The main source of error in this experiment is the calibration of the absolute wavelength scale. The fitting process with the HITRAN-database and the program putting the spectra together are temporary solutions and can be improved or replaced with a more reliable calibration method. To get an absolute wavelength scale for the whole range a calibration of the control device would be preferable.

In the spectra presented H\(_2\)O and CO\(_2\) is dominant as expected. It was also possible to identify some CO emission lines close to the CO\(_2\) peak at 4.41\(\mu\)m. Since almost no emission measurements have been done in the IR-range of chemiluminescence emission before it is hard to identify any species with guidance of previous work. Hopefully the future will provide such opportunities.

An extension of this thesis work contains the study of laser induced fluorescence (LIF-IR). Using a laser to excite molecules the problem with identifying species is avoided. Another work related to this thesis is an ongoing experiment where ratios are taken between the concentrations of different species. These ratios are linear within certain intervals of the equivalence ratio. In this way it is possible within certain boundaries to determine the stoichiometric ratios of a combustion process only by knowing the concentration of the species involved in the ratio. Until now this has only been done in the visible and near UV-range for intermediate species but an interesting project could be to determine concentrations in the IR-range of H\(_2\)O, CO\(_2\) and CO and then calculate the ratios between these species to see if there are similar relations.
References

## Appendix

A table of all the emission measurements including the variable factors.

<table>
<thead>
<tr>
<th>Flame type</th>
<th>Spectrometer (grating)</th>
<th>Slit width</th>
<th>Height above burner, h</th>
<th>$\Phi$ (correction factor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4) - air</td>
<td>SP150 (150g/mm)</td>
<td>Manually ~0</td>
<td>~1 cm</td>
<td>1.68 (1.24)</td>
</tr>
<tr>
<td>CH(_4) - air</td>
<td>TRIAX320 (300g/mm)</td>
<td>150 µm</td>
<td>~1 cm</td>
<td>1.85 (1.24)</td>
</tr>
<tr>
<td>CH(_4) - air</td>
<td>TRIAX320 (300g/mm)</td>
<td>150 µm</td>
<td>~1 cm</td>
<td>1.16 (1.24)</td>
</tr>
<tr>
<td>CH(_4) - air</td>
<td>TRIAX320 (300g/mm)</td>
<td>100 µm</td>
<td>~0 cm</td>
<td>1.85 (1.24)</td>
</tr>
<tr>
<td>CH(_4) - air</td>
<td>TRIAX320 (300g/mm)</td>
<td>150 µm</td>
<td>~0 cm</td>
<td>1.85 (1.24)</td>
</tr>
<tr>
<td>H(_2) - air</td>
<td>SP150 (150g/mm)</td>
<td>Manually ~0</td>
<td>~1 cm</td>
<td>1.35 (1.66)</td>
</tr>
<tr>
<td>H(_2) - air</td>
<td>SP150 (150g/mm)</td>
<td>Manually ~0</td>
<td>~1 cm</td>
<td>0.95 (1.66)</td>
</tr>
<tr>
<td>H(_2) - air</td>
<td>TRIAX320 (300g/mm)</td>
<td>150 µm</td>
<td>~0 cm</td>
<td>1.20 (1.66)</td>
</tr>
<tr>
<td>H(_2) - air</td>
<td>TRIAX320 (300g/mm)</td>
<td>150 µm</td>
<td>~0 cm</td>
<td>0.87 (1.66)</td>
</tr>
<tr>
<td>H(_2) - air</td>
<td>TRIAX320 (300g/mm)</td>
<td>150 µm</td>
<td>~2 cm</td>
<td>1.50 (1.66)</td>
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<tr>
<td>CO - air</td>
<td>SP150 (150g/mm)</td>
<td>Manually ~0</td>
<td>~1 cm</td>
<td>4.50 (1.64)</td>
</tr>
<tr>
<td>CO - air</td>
<td>SP150 (150g/mm)</td>
<td>Manually ~0</td>
<td>~1 cm</td>
<td>1.35 (1.64)</td>
</tr>
<tr>
<td>CO - air</td>
<td>TRIAX320 (300g/mm)</td>
<td>100 µm</td>
<td>~2 cm</td>
<td>1.10 (1.64)</td>
</tr>
</tbody>
</table>