Methane line parameters investigation using FTIR spectroscopy

Supervisors
Prof. Dr. John P. Burrows
Dr. Anna Serdyuchenko

By
Kankot Sreemaka

Postgraduate Programme in Environmental Physics
University of Bremen
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Abstract

Methane is an important constituent of the Earth’s atmosphere, and it contributes to the greenhouse effect. Methane is released from both natural and anthropogenic sources such as wetlands and biomass burning. It has an effective global warming potential 20 times more than carbon dioxide on a 100 year time scale. Nowadays the methane concentration can be monitored globally from space on the long term scale using orbiting instruments. The measurement of methane concentration in the atmosphere requires good knowledge of its spectroscopic line parameters but the line parameters given by spectral database (HITRAN) are not good enough. Therefore, the improvement of uncertainty for line parameters has to be performed.

This project uses the small home-made Matlab routine to create the model spectra of methane in the region of 1.6 μm and in the future plan these spectra will be analyzed by the software from the University of Leicester, UK to investigate the line parameters. The experimental setup is taken under two conditions of pressure which are high and low pressure cases by assuming the Lorentzian profile for high pressure and Doppler profile for low pressure.
**Motivation and thesis outline**

Methane, CH$_4$, is one of the most important atmospheric species, nowadays monitored globally by means of the satellite remote sensing instruments and also using the ground based stations. Demands on the high accuracy information on the atmospheric methane concentration put criteria on the reference data, such as line parameters, used in the retrievals of the absorption spectra, delivered by the remote sensing instruments. The aim of my work is to participate in improvement of uncertainty for line parameters given by the currently used spectral database (HITRAN).

Within this project I will participate in the investigation of line parameters for CH$_4$ spectrum in the infrared spectral region around 1.6 µm, used by the GOSAT TANSO instrument. New experimental spectra obtained in the Molecular Spectroscopy laboratory by means of the Fourier Transform Spectrometer and HITRAN dataset will be used for the analysis.

This thesis paper is divided into 6 chapters. Chapter 1 contains general information on the atmospheric methane, sources, sinks, chemical properties of methane, and the impact of methane on climate system. Chapter 2 is devoted to the background on the absorption spectroscopy. The chapter explains about the molecular structure and symmetry of methane, energy levels and transitions, line shape profiles, and line intensity. The principle of Beer-Lambert law is also included in this chapter. Chapter 3 is general information about HITRAN database, the main parameters from HITRAN used in this project. Chapter 4 describes the principles of Fourier Transform spectroscopy and its advantages and disadvantages. Chapter 5 presents the experimental setup in the Molecular Spectroscopy Laboratory, IUP, University of Bremen. Chapter 6 is the results and discussion part.
Chapter 1. Atmospheric CH$_4$

1.1 Introduction

This chapter contains general information about atmospheric methane, and also the basics of the earth’s atmospheric composition and the causes contributed atmospheric gases to the greenhouse gases. This information was collected using sources like National Aeronautics and Space Administration (NASA) [1], National Oceanic and Atmospheric Administration (NOAA) [2], the United Nations Environment Programme (UNEP) [3], Intergovermental Panel on Climate Change (IPCC) [4] homepages and Lectures on the atmospheric chemistry II, Prof.Dr. Otto Schrems, AWI [5]. The well-known greenhouse effect mechanism is also explained.

The earth’s atmosphere is composed of plethora of gases, major constituents being the following [2];

<table>
<thead>
<tr>
<th>Gas</th>
<th>Chemical formula</th>
<th>Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>N$_2$</td>
<td>78.08</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O$_2$</td>
<td>20.95</td>
</tr>
<tr>
<td>Water vapor</td>
<td>H$_2$O</td>
<td>0-4</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>0.93</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>CO$_2$</td>
<td>0.0370</td>
</tr>
<tr>
<td>Neon</td>
<td>Ne</td>
<td>0.0018</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>0.0005</td>
</tr>
<tr>
<td>Methane</td>
<td>CH$_4$</td>
<td>0.00017</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H$_2$</td>
<td>0.00005</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>N$_2$O</td>
<td>0.00003</td>
</tr>
<tr>
<td>Ozone</td>
<td>O$_3$</td>
<td>0.000014</td>
</tr>
</tbody>
</table>

As you can see from Table 1 the major constituent gases in the earth’s atmosphere are nitrogen, oxygen, and argon. The remaining gases are referred to as trace gases. Some of these trace gases are also known as greenhouse gases such as carbon dioxide, methane, nitrous oxide, ozone, and water vapor.

Greenhouse gas must be able to absorb and emit infrared radio, thus it must have infrared active (i.e. non-symmetric) molecular vibrational transitions. This excludes monoatomic gases as greenhouse gases, that is why argon, the third most abundant atmospheric constituents is transparent to infrared radiation. Homonuclear diatomic molecules such as nitrogen and oxygen only have symmetric vibration; therefore they are not greenhouse gases [5].

The well-known outcome of these greenhouse gases is “Greenhouse effect”. The phases of greenhouse effect are shown in Figure 1 that can be described by following steps [3, 5];

1. Solar radiation passes through the atmosphere in amount of 343 Watt per m$^2$, the earth receives 343 Watt of solar radiation per m$^2$. 
2. About 50% of incoming solar radiation is absorbed at the earth’s surface.
3. The rest of solar radiation is reflected by the atmosphere and the earth’s surface.
4. The greenhouse gases trap solar radiation, therefore the warms the earth’s surface.
5. Some of the infrared is absorbed and re-emitted by the greenhouse gases molecules.
6. Some of the infrared radiation passes through the atmosphere and lost in space. The net outgoing infrared radiation is 240 Watt per m².

Figure 1. The greenhouse effect [3]

There are four apparent greenhouse gases that can be ranked by the % of contribution to greenhouse effect [6];

- Water vapor ~36-70%
- Carbon dioxide ~9-26%
- Methane ~4-9%
- Ozone ~3-7%

There are many factors that contribute gas to greenhouse gases, the comparison shown in Table 2:
Concentrations

H₂O and CO₂ are the two biggest contributors to the atmospheric warming because of their higher concentrations.

- Lifetime

The longer-live a gas is, the higher the contribution e.g. the contribution of N₂O is higher than methane.

- Effectiveness as an infrared absorber

For example, CFC-11 and CFC-12

Table 2. The comparison of different greenhouse gases on the factors that contribute gas to greenhouse gases [5]

<table>
<thead>
<tr>
<th>Concentration</th>
<th>CO₂</th>
<th>CH₄</th>
<th>CFC-11</th>
<th>CFC-12</th>
<th>N₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preindustrial (&lt;1800)</td>
<td>280 ppm</td>
<td>0.8 ppm</td>
<td>0 ppt</td>
<td>0 ppt</td>
<td>288 ppb</td>
</tr>
<tr>
<td>Current</td>
<td>370 ppm</td>
<td>1.74 ppm</td>
<td>268 ppt</td>
<td>484 ppt</td>
<td>314 ppb</td>
</tr>
<tr>
<td>Atmospheric lifetime (year)</td>
<td>50-100</td>
<td>10</td>
<td>45</td>
<td>130</td>
<td>114</td>
</tr>
<tr>
<td>Per molecule of radiative forcing relative to CO₂</td>
<td>1</td>
<td>23</td>
<td>4000</td>
<td>15,800</td>
<td>296</td>
</tr>
</tbody>
</table>

1.2 Methane importance as greenhouse gas

As mentioned above, greenhouse gases in the atmosphere can absorb solar radiation. To quantify the amount of radiation absorbed a special term called Global-warming potential (GWP) is used. GWP is calculated as a ratio of the amount of heat trapped by a certain mass of the gas in question to the amount of heat trapped by a similar mass of carbon dioxide. The commonly specific time intervals of GWP are 20, 100 or 500 years. The GWP is represented in a factor of carbon dioxide, a standard gas which has a value of GWP equal to 1. For instance, the GWP of methane over 100 years is 25, which means that if the same mass of methane and carbon dioxide were introduced into the atmosphere, that methane will trap 25 times more heat than the carbon dioxide over the next 100 years [4].

The GWP depends on three following factors:

- absorption of infrared radiation by given species. The more infrared radiation absorption, the larger GWP;
- spectral location of its absorbing wavelength;
- atmospheric lifetime of the species. The longer atmospheric lifetime, the bigger GWP.

Table 3 shows the example of the global-warming potential of major greenhouse gases

Table 3. The global-warming potential

<p>| GWP values and Lifetimes | GWP time horizon |</p>
<table>
<thead>
<tr>
<th>Lifetimes from 2007 IPCC AR4</th>
<th>(years)</th>
<th>20 years</th>
<th>100 years</th>
<th>500 years</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>12</td>
<td>72</td>
<td>25</td>
<td>7.6</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>114</td>
<td>310</td>
<td>298</td>
<td>153</td>
</tr>
<tr>
<td>HFC-23 (hydrofluorocarbon)</td>
<td>270</td>
<td>1,200</td>
<td>14,800</td>
<td>12,200</td>
</tr>
<tr>
<td>HFC-134a (hydrofluorocarbon)</td>
<td>14</td>
<td>3,830</td>
<td>1,430</td>
<td>435</td>
</tr>
<tr>
<td>Sulfur hexafluoride</td>
<td>3200</td>
<td>16,300</td>
<td>22,800</td>
<td>32,600</td>
</tr>
</tbody>
</table>

1.2.1 History and trends

Historically, the earliest methane was released from the volcanic eruption, but currently we can classify the sources of atmospheric methane into two main categories:

- natural sources such as wetlands, termites, CH4 hydrates and oceans
- anthropogenic sources such as coal and oil mining, rice cultivation, biomass burning, landfills, sewage treatment, and animal waste.

On Figure 2 atmospheric methane concentration changes are shown since 1985 until recent time [7]. The abundance of methane at the earth’s surface in 1998 was 1745 nmol/mol [8]. We can see that the concentration of methane has increased steadily. This increase of methane concentration in the atmosphere is highly correlated to the growth of world population. It is also related to the human activities such as agriculture and industrial practices.
1.2.2 Global methane cycle: sources and sinks, characteristic timescale

*Methane cycle*

Methane is released from various sources both from anthropogenic and natural sources, then it is consumed by methane sinks. The cycle of releasing and consuming of methane is called methane cycle. The methane cycle is a part of the carbon cycle which is important to the Earth’s atmosphere. Further explanation of the carbon cycle will be explained in the section 1.2.3.

*Sources of methane*

As it was mentioned above, we can classify the sources of methane into two main categories which are of natural and anthropogenic origin. Relative contribution of different sources is shown in the Figure 3 [1]. The biggest natural sources are the natural wetlands which cover about 22% of the total sources. For the anthropogenic sources, coal and oil mining and natural gas are the major sources of methane.
Natural sources of methane

Methanogens

The methanogen is microorganism producing methane by the process call methanogenesis. There are two major reactions in a methanogenesis process leading to the methane production.

Acetoclastic methanogenesis: The certain archaea cleave acetate produced during anaerobic fermentation to produce methane and carbon dioxide.

\[ \text{H}_3\text{C-COOH} \rightarrow \text{CH}_4 + \text{CO}_2 \] (1.1)

Hydrogenotrophic methanogenesis: The archaea oxidize hydrogen with carbon dioxide to produce methane and water.

\[ 4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \] (1.2)

Animals

The digestive tract of ruminants such as buffalo, cows or sheeps contains bacteria which help them to digest plant material. Bacteria use acetate from plants to produce methane. Gastrointestinal system of termite also releases methane. The emission of methane from termite is about 4% of total methane emission from natural sources.

Wetlands

About 22% of methane in the atmosphere is emitted by wetlands [1, 10]. The amount of methane emission in wetlands depends on many factors e.g. the amount of nutrients and organic in soil and type of vegetation.

Ocean and methane hydrate

Methane from the ocean comes from the anaerobic digestion of marine zooplankton. Methane hydrates also called methane clathrate \((\text{CH}_4 \cdot 5.75\text{H}_2\text{O})\)[11] are the decomposition of the solid contains water and methane molecule. This solid can be found in the polar region and in the ocean sediments.

Anthropogenic sources of methane

Coal and oil mining/ natural gas system

Methane trapped in coal sediments is released during mining operations like surface and underground mining and coal handling system. Also in the natural gas and petroleum processing, the emission of methane occurs during the oil refinement and transportation.
Rice cultivation

The anaerobic decomposition of organic matter in flooded rice cultivation produces methane. Flooded soil is an ideal area for methane production, due to the abundance of organic substrate, high level of moisture and oxygen-depleted conditions.

Waste water treatment

The aims of the waste water treatment are to remove the organic matter, suspended solid, pathogenic organism, and chemical contaminants in water. During the treatment process, methane is released. Moreover, the biodegradable residual sludge from some processes under anaerobic condition can produce methane.

![Methane Sources](image)

**Figure 3. Sources of methane [1]**

Sink of methane

There are several chemical reactions leading to the methane sink.

- The reaction of methane with OH radicals

  \[ \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3^+ + \text{H}_2\text{O} \]  

Methane is released to the atmosphere, tropospheric layer, reacts with hydroxyl radical to produce methyl radical and water vapor. This chemical reaction is the largest sink of
methane in the atmosphere. The reaction with hydroxyl radicals occurs in the troposphere because hydroxyl radical is formed by photodissociation of tropospheric ozone and water vapor shown in equation (1.4 and 1.5). The methane lifetime in troposphere is 9.6 years. [8]

\[
O_3 + h\nu \rightarrow O_2 + O (^1D) (\lambda \leq 330 \text{ nm}) \quad (1.4)
\]

\[
O (^1D) + H_2O \rightarrow 2OH \quad (1.5)
\]

The destruction rate of methane is \(\frac{d[CH_4]}{dt} = -k_3 [OH][CH_4]\). The limiting factors of methane destruction are the amount of hydroxyl radical in troposphere and the destruction rate of methane.

- The reaction of methane with free chloride

\[
CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \quad (1.6)
\]

The reaction of methane with free chloride produces Chloromethane and hydrochloric acid. This process is called free radical halogenations.

**Methanotrophs in soils**

Methanotroph is the process of digestion of organic matter in soil that can occur in two phases: low affinity oxidation and high affinity oxidation. The low affinity oxidation of methane is performed by methanotrophic bacteria in soil with pH higher than 4.4 in aerobic zones. The limiting factor of this process is the amount of oxygen. For the high affinity oxidation, forest soil is the most effective for methane sink because the moisture in forest soil is optimal for methanotroph activities. The methanotrophic bacteria use methane as a source of carbon oxidation. The oxidation reaction is

\[
CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (1.7)
\]

**Stratospheric oxidation**

Some of methane is transported to stratosphere. The oxidation of methane by hydroxyl radicals in stratosphere occurs in the same manner as in the troposphere (see equation 1.3). The oxidation of methane in stratosphere is a source of stratospheric water vapor. In stratosphere, methane also reacts with chlorine and oxygen atoms.

**Atmospheric lifetime of methane**

The atmospheric lifetime is the time required to turn over the atmospheric burden. The atmospheric lifetime of methane can be calculated by dividing the atmospheric burden by the global sink of methane.

The atmospheric lifetime of methane = \(\frac{\text{atmospheric burden (Tg)}}{\text{global sink (Tg/yr)}}\) = \(\frac{4850 \text{ Tg}}{576 \text{ Tg/yr}}\) = 8.4 years.
The lifetime of methane is varied by its abundance in the atmosphere. The increasing of methane concentration leads to the longer lifetime \cite{12, 13}.

Table 4 shows the estimates of the global methane budget in a unit of Tg(CH₄)/yr. The uncertainties of the global methane budget mainly come from the difficulty in the measurements of the emission rate from the biosphere because the methane emission rate can be varied with time and space \cite{IPCC}.

<table>
<thead>
<tr>
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<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>Natural sources</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wetlands</td>
<td>115</td>
<td>237</td>
<td>225\textsuperscript{c}</td>
<td>145</td>
<td>-</td>
<td>-</td>
<td>92</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Termites</td>
<td>20</td>
<td>-</td>
<td>20</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ocean</td>
<td>10</td>
<td>-</td>
<td>15</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hydrates</td>
<td>5</td>
<td>-</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Anthropogenic sources</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy</td>
<td>75</td>
<td>97</td>
<td>110</td>
<td>89</td>
<td>-</td>
<td>109</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Landfills</td>
<td>40</td>
<td>35</td>
<td>40</td>
<td>73</td>
<td>-</td>
<td>36</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ruminants</td>
<td>80</td>
<td>90\textsuperscript{b}</td>
<td>115</td>
<td>93</td>
<td>80</td>
<td>93\textsuperscript{b}</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Waste treatment</td>
<td>-</td>
<td>b</td>
<td>25</td>
<td>-</td>
<td>14</td>
<td>b</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rice agriculture</td>
<td>100</td>
<td>88</td>
<td>-</td>
<td>25-54</td>
<td>60</td>
<td>53</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>55</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>34</td>
<td>23</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Other</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Total source</strong></td>
<td><strong>500</strong></td>
<td><strong>587</strong></td>
<td><strong>600</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>597</strong></td>
</tr>
<tr>
<td><strong>Sinks</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soils</td>
<td>10</td>
<td>-</td>
<td>30</td>
<td>30</td>
<td>44</td>
<td>-</td>
<td>30</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Tropospheric OH</td>
<td>450</td>
<td>489</td>
<td>510</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>490</td>
<td>506</td>
</tr>
<tr>
<td>Stratospheric loss</td>
<td>-</td>
<td>46</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td><strong>Total sink</strong></td>
<td><strong>460</strong></td>
<td><strong>535</strong></td>
<td><strong>580</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>560</strong></td>
</tr>
<tr>
<td><strong>Difference between source and sink (trend)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>+37</strong></td>
</tr>
</tbody>
</table>

\begin{itemize}
\item a. TAR budget based on 1745 ppb, 278 Tg/ppb, lifetime of 8.4 yr, and an imbalance of +8 ppb/yr
\item b. Waste treatment included under ruminants
\item c. Rice included under wetlands
\end{itemize}

1.2.3 Contribution to the carbon cycle

The carbon cycle is the biogeochemical cycle by which carbon is exchanged between the land surface, atmosphere, and oceans. The global carbon cycle is of a major interest.
because it plays an important role in the earth’s climate system by controlling the concentrations of carbon dioxide and methane, the two major greenhouse gases in the atmosphere.

![Figure 4. The global carbon cycle](image)

In Figure 4 shows the various reservoirs of carbon such as atmosphere, ocean, the earth’s crust, terrestrial ecosystem. These reservoirs behave as both source and sink of the carbon. The amount of carbon is shown in a unit of Petagram of Carbon (PgC) (1 PgC is equal to $10^{15}$ grams of carbon). Projection on the carbon reservoirs are below;

**The atmosphere**

The earth’s atmosphere contains about 750 PgC. Most of carbon in the atmosphere is in form of carbon dioxide CO2 and the rest are the smaller amounts of methane CH4 and other carbon compounds. For those two major carbon compounds, carbon dioxide and methane are very important due to their concentrations is related to the changes in the atmospheric temperature, the climate change.

**The ocean**

The capacity of the ocean to handle carbon is 38,000 PgC. Most of the carbon is stored at a great depth of the ocean in form of dissolved inorganic carbon (DIC) over a long
period of time. Approximately 1,000 PgC is located near the ocean surface. Thermohaline circulation is an exchange process of carbon between ocean surface and deep ocean.

The earth's crust

The earth's crust stores approximately 100,000,000 PgC and it is the largest reservoir of carbon. Most of carbon on earth is stored in sedimentary rocks within the earth’s crust. The sedimentary rocks are formed either by the hardening of mud into shale over geological time or by the sedimentation of calcium carbonate particles from the shells and skeletons of marine organisms. These sedimentations form limestone and other carbon containing sedimentary rock. Another form of carbon under the planet's crust is fossil fuel. Fossil fuel is a hydrocarbon which formed under the condition of very high temperature and pressure over millions of years. In the global carbon cycle contains about 4,000 PgC in form of fossil fuel.

Terrestrial ecosystems

The carbon in terrestrial ecosystem is stored in form of animals, plants, soils, and microorganisms. Looking on the global carbon diagram, plants contain about 560 PgC and soil contains about 1500 PgC.

1.2.4 The carbon exchange processes

Among these several reservoirs of carbon, there is a transfer of carbon by many processes. The process of carbon transfer through each reservoir is called flux. Various carbon fluxes are explained below:

Photosynthesis

Photosynthesis is a very common process in global carbon cycle where light energy is converted to chemical energy, by the reaction of carbon dioxide and water. The carbon dioxide will be removed from the atmosphere and stored in plant leaves. The amount of carbon removed from the atmosphere by photosynthesis process is approximately 120 PgC/year and it stored in the plant about 610 PgC [14]

The chemical reaction for photosynthesis is \[6CO_2 + 6H_2O + \text{light} \rightarrow C_6H_{12}O_6 + 6O_2\] (1.8)

Plant respiration

After uptaking carbon dioxide from the atmosphere by photosynthesis process, carbon dioxide is also released back through the plant respiration. The respiration can occur in two conditions, aerobic and anaerobic respiration. As can be seen from the diagram, about a half of carbon dioxide stored by photosynthesis is released

Litterfall

Litterfall is referred to the dead plants. Since all parts of the plant are made up of carbon, when it dies, carbon stored in plant will be transfer to the soil.
Soil respiration

The release of carbon dioxide to the atmosphere comes not only from the respiration of plants, but also from the soil respiration. The respiration of soil in this case means total carbon dioxide output of all living organism in the soil. After their decomposition of them, carbon dioxide is released.

Ocean-atmosphere exchange

The exchange of carbon dioxide between the atmosphere and the ocean occurs near the water surface by dissolving of gas in the water.

Fossil fuel combustion and land cover change

Fossil fuels are formed by the sedimentation of dead organisms with very high temperature and pressure below the earth’s crust over millions of years. Fossil fuels contain high percentage of carbon which means that during the combustion of fossil fuels, huge amount of carbon is released to the atmosphere. The burning of fossil fuels releases about 21.3 billion tonnes of carbon dioxide, the largest source of carbon dioxide emissions. The flux of carbon dioxide from the combustion to the atmosphere is around 6-8 PgC/year. The changing of land covers e.g. deforestation for agriculture is also one of the sources of carbon emissions. The net flux of carbon to the atmosphere is around 1.5 PgC/year.

Geological processes

The geological process is very important for the global carbon cycle because it acts as a controller of the amount of carbon in the cycle over hundreds of millions of years. The examples of geological processes that release carbon to the atmosphere are the volcanic eruptions, the weathering of rock, and the formation of sedimentary rocks.

1.2.5 Impact on climate

Figure 5 shows the global air temperature trend over the past 1000 years. The steady increase of the concentration of methane [shown in Figure 2] after the industrialization in the atmosphere causes the rising of the atmospheric temperature, this phenomena being called global warming. The impact of global warming will be showed in the next section.
The projection of the rising temperature over the last 100 years is shown in Figure 6
1.2.6 Other greenhouse gases

In the earth’s atmosphere, there are several important greenhouse gases;

**Water vapor (H₂O)**

Water vapor is a gas phase of water. It is produced from the evaporation or boiling of liquid water. It is a significant greenhouse gas even though it has about 0-4% in the earth’s atmosphere. Hydroxyl bond in water vapor molecule strongly absorbs the radiation in the infrared region leads to the increasing of the temperature. Cloud is formed by the condensation of the water vapor. It warms the atmosphere by trapping the heat.

Sources: evaporation process of water from oceans, seas, lakes, rivers, transpiration of plants, volcanic eruptions, and combustion

Sinks: condensation and precipitation process
**Carbon dioxide (CO₂)**

Carbon dioxide is considered as greenhouse gas. In June 2012, the concentration of carbon dioxide in the atmosphere is 395 ppm by volume [Trends in carbon dioxide, NOAA]. During 2000-2009, the concentration of carbon dioxide increased by 2 ppm/yr [16]. Carbon dioxide can absorb the infrared light from the Sun causes the increases of atmospheric temperature. The life time of carbon dioxide in the atmosphere is in the range of 30 to 95 years [17].

Sources:

Natural: volcanic eruption, the degradation of organic materials, respiration of vegetation, oceans (in form of bicarbonate)

Anthropogenic: Fossil fuel combustions, deforestations, agricultures

Sinks:

Photosynthesis process, dissolved in oceans

**Nitrous oxide (N₂O)**

Nitrous oxide is also one of significant greenhouse gases. It has very long atmospheric lifetime about 120 years and it has 310 times more GWP than CO₂. The concentration of nitrous oxide has been increased since the industrial revolution. It is a primary source of nitrogen oxides in stratosphere. The nitrogen oxides control the amount of stratospheric ozone.

Sources:

Natural: Denitrification process by anaerobic bacterial for energy production, agricultural soil management, ocean

Anthropogenic: Biomass burning, adipic acid (nylon) production, nitric acid production, sewage treatment

Sinks:

Photolysis in the stratosphere

**Ozone (O₃)**

Ozone (O₃) is highly reactive gas composed of three oxygen atoms. Ozone has either good or bad effects life on earth, depending on its location in the atmosphere. The stratospheric ozone or good ozone layer extends from approximately 6-30 miles above the earth’s surface and reduces the amount of UV-radiation reaching the Earth’s surface. In troposphere, ground-level or bad ozone is a pollutant that affects human health and environment. This bad ozone can absorb the radiation reflected by the earth’s surface. It
has a life time in the atmosphere about 22 days. Because of a very short of atmospheric life time, the global effect of ozone is not too strong.

Sources:

In troposphere, ozone is formed from the reaction of two major classes of air pollutants which are volatile organic compounds (VOCs) and nitrogen oxides (NOx) with the presence of sunlight.

Sinks:

The reaction of ozone with hydrocarbons such as aldehyde

1.2.7 The impact of global warming

The greenhouse gases lead to global warming effect. There are several impacts of the global warming: [5].

- **Sea level rise**
  - Beach erosion
  - Coastal wetland loss
  - Loss of low-lying territories
- **Water resource change**
  - Precipitation pattern shift
  - Increases instances of heavy precipitation
  - New burdens on water capture, storage and distribution system to be expected.
- **Effects on agriculture**
  - Changes in the length of growing season
  - Growth of undesirable plant species
- **Effects on air quality**
  - Increase in reaction rates and concentrations of certain of atmospheric species e.g. increase in O₃ in urban area
  - Change in how pollutants are dispersed
  - More droughts > wide spread forest fire > worsen air quality
- **Impact on human health**
  - Respiratory problems affected by air quality change
- **Effect on Biodiversity**
  - Some species may grow too quick and overshoot their reproductive period (e.g. reef coral)
  - Forest could be devastated if the rate of climate change outpaced the rate at which forest species could migrate.
- Change in the pattern of ocean current.

1.3 Methane properties: general information

Methane is a simple alkane chemical compound that consists of four atoms of hydrogen and one atom of carbon, with a chemical formula CH₄. It is a tetrahedral molecule which
has four single bonds of C-H. Methane is a lighter gas compared to air. The properties of methane are as follows: [18, 19]

- methane is a colorless and odorless gas;
- the molecular mass of methane is 16.043 g/mol;
- the density is 0.717 kg/m³;
- the boiling point at atm is -161 °C;
- the melting point is -182.5 °C;
- the critical temperature is -82.7 °C;
- the critical pressure is 45.96 bar;
- methane is quite unreactive gas, except with halogen gases e.g. fluorine, chlorine, bromine etc. The mechanism of the reaction between methane and halogens is called free radical halogenation.
- methane is a flammable gas and it undergoes auto ignition at the temperature of 595 °C.

1.4 Methane observation

1.4.1 GOSAT basic information

Methane absorption in the infrared spectral region (IR) is used by the modern remote sensing instruments for its detection in the atmosphere. More details on the methane spectrum will be given later in Chapter 2.

Currently there are several simultaneous methane observation campaigns from land and sea surface sites and aircraft. There are also continuous measurements from baseline observatories and tall tower provided by NOAA [20]. Nowadays, there are a few networks of surface measurements for observation of the greenhouse gases. Satellite observations combined with modeling can add important missing global information on regional methane sources and sinks required for better climate prediction.

Globally, however, the network of surface measurements for the major greenhouse gases is still very sparse with large continental areas remaining poorly monitored. This is especially true for tropical regions, where strong convection transports emissions aloft resulting in generally very low signals at remote marine observation sites. Therefore, satellite measurements with quasi-global coverage provide a very attractive complement to the surface network. The major challenge for long-lived greenhouse gas measurements from space is the demanding requirements on precision and accuracy to detect the small spatial and temporal gradients in the atmosphere. Such space borne measurements have become available for CH₄ from the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) instrument [24] onboard ESA’s environmental satellite ENVISAT, with an estimated relative accuracy on the order of 1 – 2% [21–24 and references therein ]

Methane was observed in the short wave infrared (SWIR) spectral region using SCIAMACHY spectrometer [24]. Since 2009 the methane concentration distribution can be
observed globally from Greenhouse gases Observing SATellite (GOSAT). It was launched on January 23, 2009. The measurement of greenhouse gases are performed with the Thermal-and Near-infrared Sensors for carbon Observation Fourier Transform Spectrometer (TANSO-FTS).

1.5 Retrieval algorithms

The retrieval algorithm of methane on GOSAT has been modified from the NASA Orbiting Carbon Observatory (OCO)-the mission to retrieve dry-air column-averaged mole fraction of CO₂ (XCO₂) of NASA about the global carbon cycle [24].

1.5.1 GOSAT instrument

The two main sensors of GOSAT are the Thermal and Near infrared Sensor for carbon Observation Fourier Transform Spectrometer (TANSO-FTS) and the Cloud and Aerosol Imager (TANSO-CAI) [25]. The TANSO-FTS composed of three narrow bands in SWIR region which are 0.76, 1.6, 2.0 for band 1, 2 and 3 respectively and a wide TIR band in a range of 5.5 to 14.3 μm for band 4. The spectral resolution of TANSO-FTS is 0.2 cm⁻¹ with the full width at half-maximum (FWHM) of 0.27 cm⁻¹. The TANSO-CAI has four narrow bands in the region of near-ultraviolet to near infrared region which are 0.38, 0.674, 0.87, and 1.6. The specification of the two sensors such as polarization, wavenumber, FWHM at ILSF, signal-to-noise ratio (SNR), IFOV/FOV at nadir, data acquisition time, and target species are shown in Table 5 and Table 6. The polarization beam splitter separates the incident light in SWIR band into two orthogonal polarization components called P and S components.

**Table 5. The specifications of GOSAT TANSO-FTS**

<table>
<thead>
<tr>
<th>Band</th>
<th>Band 1</th>
<th>Band 2</th>
<th>Band 3</th>
<th>Band 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polarization</td>
<td>P, S</td>
<td>P, S</td>
<td>P, S</td>
<td>-</td>
</tr>
<tr>
<td>The range of wavenumber (cm⁻¹)</td>
<td>12900-13200</td>
<td>5800-6400</td>
<td>4800-5200</td>
<td>700-1800</td>
</tr>
<tr>
<td>FWHM of the ILSF (cm⁻¹)</td>
<td>0.6 cm⁻¹ or less</td>
<td>0.27 cm⁻¹ or less</td>
<td>0.27 cm⁻¹ or less</td>
<td>0.27 cm⁻¹ or less</td>
</tr>
<tr>
<td>Signal-to-noise ratio (SNR)</td>
<td>&gt; 300¹</td>
<td>&gt; 300¹</td>
<td>&gt; 300¹</td>
<td>&gt; 300²</td>
</tr>
<tr>
<td>Target species</td>
<td>O₂</td>
<td>CO₂, CH₄</td>
<td>CO₂, H₂O</td>
<td>CO₂, CH₄</td>
</tr>
<tr>
<td>IFOV/FOV at Nadir</td>
<td>IFOV: 15.8 mrad, FOV for observation: diameter of app. 10.5 km</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data acquisition time</td>
<td>1.1, 2.0, 4.0 sec. (nominal: 4.0 sec.) for single scan</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 6. The specifications of GOSAT TANSO-CAI**

<table>
<thead>
<tr>
<th>Band</th>
<th>Band 1</th>
<th>Band 2</th>
<th>Band 3</th>
<th>Band 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral coverage (μm)</td>
<td>0.370-0.390</td>
<td>0.664-0.684</td>
<td>0.860-0.880</td>
<td>1.555-1.645</td>
</tr>
</tbody>
</table>
### Signal-to-noise ratio \( (\text{SNR}) \)^3

<table>
<thead>
<tr>
<th></th>
<th>&gt;200</th>
<th>&gt;200</th>
<th>&gt;200</th>
<th>&gt;200</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Swath (km)</strong></td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>750</td>
</tr>
<tr>
<td><strong>Spatial resolution (km)</strong></td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Target substance</strong></td>
<td>Clouds and aerosols</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Notes:

1) In GOSAT TANSO-FTS, the signal-to-noise ratio \( (\text{SNR}) \) of band 1, 2, and 3 is more than 300 for the 0.3 of the Lambertian surface albedo and the 30 degree of the solar zenith angle.

2) The SNR of band 4 is more than 300 at the wavenumber of 700 cm\(^{-1}\) for the incident blackbody radiation corresponding to the temperature of 280K.

3) The SNR of GOSAT TANSO-CAI is more than 200 for the Lambertian surface albedo of 0.3 at a solar zenith angle of 30 degree.

### 1.5.2 TANSO-FTS SWIR retrieval process

Figure 7 illustrates the TANSO-FTS SWIR retrieval process which has three main steps: data screening, optimal estimation, and quality control. The retrieval process starts with the data screening by select the suitable data for the retrieval analysis. The main obstacles in methane observing by GOSAT are clouds and aerosols. They strongly modify the equivalent optical path length \([26-30]\) lead to an error in retrieved column abundances. TAN-CAI can detect the optically thick cloud inside the TANSO-FTS IFOV \([31]\) and correct the effect of aerosols in the TANSO-FTS spectrum data. The detection of cloud by TAN-CAI is based on the algorithm developed by Ishida and Nakajima \([32]\). The cloud-detection method consists of several threshold tests which are single reflectance tests and reflectance ratio tests. Another constraint factor in the TANSO-FTS measurement scenes is the solar zenith angle. The atmosphere is assumed as a plan-parallel atmosphere in the retrieval analysis. When the solar zenith angle is greater than 72 degrees, it leads to the error of air-mass factor more than 1%. Therefore, the solar zenith angle should less than 70 degrees to avoid the error of air mass factor. The undulation of the ground surface around the TANSO-FTS IFOV is also checked because it conflicts with the plane-parallel assumption leads to the problems on the retrieval results.

In the optimal estimation step, the column abundances of methane were received from the 1.67-\(\mu\)m CH\(_4\) absorption band. The gaseous profiles of methane were retrieved first and the column abundances were obtained as a final product \([\text{Rodgers and Connor 2003}]\).

The last step of the retrieval process is the quality checking of the retrieval results. The degree of freedom for a signal \( (\text{DFS}) \) describes the number of the independent quantities obtainable from the observation. When the DFS is less than the unity, the retrieved of methane column abundances are dismissed because the observed TANSO-FTS spectrum does not have enough information to retrieve them. The retrieved results are removed when the mean squares of the residual spectra \( (\text{MSR}) \) is greater than 3 or the \( X^2 \) for the retrieved state is greater than 5. When the aerosol optical depth \( (\text{AOD}) \) at the
wavelength of 1.6-µm is more than 0.5, the retrieved methane column abundance are dismissed because the relative large value of AOD affects the equivalent optical path length.

Figure 7. The retrieval processing of TANSO-FTS SWIR diagram. In quality control step, DFS, MSR, and AOD are degree of freedom for signal, mean squares of the residual spectra for each retrieval sub-band, and aerosol optical depth respectively [33].

1.6 Other instruments for methane measurement

Apart from using GOSAT in the measurement of methane in the atmosphere, there are other instruments relevant in the observation of atmospheric methane gas such as SCIAMACHY and MIPAS.

1.6.1 SCIAMACHY

SCIAMACHY [34] stands for Scanning Imaging Absorption Spectrometer for Atmospheric Chartography. It is one of ten instruments aboard on the ENVIronmental SATellite (ENVISAT). It was launched by European Space Agency (ESA) in March, 2002 from the Guyana Space Centre in Kourou, French Guyana. It is a passive remote sensing spectrometer used to measure the emitted, transmitted and scattered radiation from the atmosphere and the Earth’s surface in the range of wavelength between 240 to 1700 nm [SCIAMACHY homepage, IUP, University of Bremen]. It has a high spectral resolution of 0.2 nm to 1.5 nm. The advantage of the high spectral resolution is the different trace gases can be detect even though they have very low concentrations. The primary goal of SCIAMACHY is to measure the trace gases in the troposphere and stratosphere [34]. Moreover, SCIAMACHY also measures the atmospheric aerosols, polar stratospheric cloud, stratospheric temperature and pressure, and the Earth radiation budget. SCIAMACHY has three different viewing geometries which are nadir mode, limb mode, and sun/moon occultations [ESA]. The total column values of the atmospheric trace gases and aerosols are
observed in nadir mode and the altitude distribution of trace gases is observed in limb mode. The specifications of SCIAMACHY are shown in Table 7.

Table 7. The instrument parameters of SCIAMACHY [ESA]

<table>
<thead>
<tr>
<th>Channel</th>
<th>Spectral range (nm)</th>
<th>Spectral resolution (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>240-314</td>
<td>0.24</td>
</tr>
<tr>
<td>2</td>
<td>309-405</td>
<td>0.26</td>
</tr>
<tr>
<td>3</td>
<td>394-620</td>
<td>0.44</td>
</tr>
<tr>
<td>4</td>
<td>604-905</td>
<td>0.48</td>
</tr>
<tr>
<td>5</td>
<td>785-1050</td>
<td>0.54</td>
</tr>
<tr>
<td>6</td>
<td>1000-1750</td>
<td>1.48</td>
</tr>
<tr>
<td>7</td>
<td>1940-2040</td>
<td>0.22</td>
</tr>
<tr>
<td>8</td>
<td>2265-2390</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Polarization measurement devices (broadband)

<table>
<thead>
<tr>
<th>Altitude range</th>
<th>Vertical resolution</th>
<th>Operation</th>
<th>Data rate</th>
<th>Mass and power</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 km -100 km depending on measurement mode</td>
<td>2.4 km – 3 km depending on measurement mode</td>
<td>Continuously over full orbit</td>
<td>400 kb/s nominate, 1867 kb/s real time mode</td>
<td>198 kg, 122 W</td>
</tr>
</tbody>
</table>

There are four subsystems in the SCIAMACHY [35]:

1. a scanner-mirror system. It determines the observation mode of the instrument.
2. a spectrometer or optical bench. The incoming signal is separated by the spectrometer.
3. a cooling system. The selected temperature of the spectrometer and its detector is maintained to optimise the signal-to-noise ratio in the measured spectra.
4. an electric subsystem. It controls and operates SCIAMACHY and it interfaces to the ENVIsat platform.

1.6.2 MIPAS

Michelson Interferometer for Passive Atmospheric Sounding or MIPAS is a Fourier transform spectrometer for the detection of limb emission spectra in the middle and upper atmosphere [36]. The several missions of MIPAS include to measure stratospheric chemistry e.g. O₃, H₂O, CH₄, N₂O, and HNO₃, to monitor ozone and CFCs in the stratosphere, to study about the chemical composition, dynamics, and radiation budget of the middle atmosphere. The vertical resolution of MIPAS is 3-5 km depending on altitude. The MIPAS performances are shown in Table 8.

Table 8. The performances of MIPAS

<table>
<thead>
<tr>
<th>Spectral coverage</th>
<th>685 cm⁻¹ to 2410 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral resolution</td>
<td>&lt; 0.035 cm⁻¹</td>
</tr>
<tr>
<td>Spectral stability goal</td>
<td>&lt; 0.001 cm⁻¹ over one day</td>
</tr>
<tr>
<td>Elevation scan range</td>
<td>Between 5 km to 150 km tangential height</td>
</tr>
<tr>
<td>Azimuth scan range</td>
<td>Between 80°-110° and 160°-195° with respect to the</td>
</tr>
</tbody>
</table>
1.7 Conclusion

The measurement of methane concentration in the atmosphere is monitored by satellite. The GOSAT is the instrument used to observe methane abundance in the atmosphere in the short wave infrared region. The GOSAT retrieval process consists of three steps which are data screening, optimal estimation, and quality control.
Chapter 2. Absorption spectroscopy

2.1 Introduction

This chapter contains background on the molecular energy levels and transitions and also provides some insight on the line broadening mechanisms. The basics of the absorption spectroscopy are also described.

2.2 Molecular structure and symmetry

Molecular spectroscopy is used to study the physical processes of the atoms or molecules. The molecular spectroscopy techniques are based on the absorption, emission of electromagnetic radiation by the atoms or molecules.

The atoms and molecules can exist in many states that are different with respect to the electron configuration, angular momentum, parity and energy. Transitions between these states are associated with the absorption and emission of electromagnetic radiation. The transition from a lower level to a higher level with transfer of energy from the radiation field to the atom is called absorption. The transition from a higher level to a lower level is called emission.

2.2.1 Symmetry

CH$_4$ (methane) is a tetrahedral molecule, the simplest hydrocarbon, as schematically shown in the Figure 8. There are four three-fold rotation axes and three four-fold rotation-reflection axes. The highly symmetric shape of the methane means that only two of the vibrational modes depicted below interact directly with infrared light ($\nu_3$ and $\nu_4$ -- the ones where the carbon and hydrogen both move), and these modes are the most likely to absorb or scatter infrared heat radiation from the Earth before it can escape to space.

![Figure 8. Chemical structure of methane](image)

2.3 Energy levels and transitions

In quantum mechanical system, atoms and molecules can have discrete energy values. These discrete values are called energy levels. The energy level can be divided into electronic, rotational, and vibrational energy which can be written in form of equation below

$$ E = E_{rot} + E_{vib} + E_{elec} $$

(2.1)
A selection rule, or transition rule, formally constrains the possible transitions of a system from one state to another. Selection rules have been derived for electronic, vibrational, and rotational transitions.

2.3.1 Electronic energy levels

The electronic energy is due to the electron movement in the potential due to the arrangement of protons and neutrons in the nucleus and it is dependent on the distance between the atomic nuclei.

2.3.2 Vibrational energy levels

The simplest model to describe the vibrational motion is a harmonic oscillator, i.e. the nuclei are connected by a spring. The model implies that the potential relation is approximated by a parabola. For the vibrational motion of a harmonic oscillator the vibrational energy term can be written as:

$$E_{vib} = \hbar \omega \left( \nu + \frac{1}{2} \right)$$

(2.2)

where $\hbar$ is $\frac{h}{2\pi}$, $\omega$ is the angular frequency ($\omega = 2\pi \cdot f$), $\nu$ is a vibrational quantum number ($\nu_{sv} = 0, 1, 2, ...$).

The vibrational transitions occur for $\Delta \nu = \pm 1, \pm 2, \pm 3, ...$. For the harmonic oscillator, only transitions with $\Delta \nu = \pm 1$ are allowed. The real potential is not symmetric. This anharmonic oscillator leads to so called overtone bands with $\Delta \nu = \pm 2, \pm 3, \pm 4, ...$ with fast decreasing intensities. Observation of the higher order transitions is difficult because the intensity of absorption lines is very low. The energy of vibrational transition is on the order of 0.1 eV, with the corresponding wavelengths in the IR spectral range.

2.3.3 Rotational energy levels and transitions

For a given electronic configuration and a given vibrational level ($\nu$ value) the nuclei can finally also rotate around the common center of gravity. This yields a further energy contribution $E_{rot}$ in the range of magnitude 0.001 eV. The rotational energy term for rigid rotator can be written as:

$$E_{rot} = B \cdot J \cdot (J + 1)$$

(2.3)

where $B$ is the rotational constant of molecule, $B = \frac{\hbar^2}{2I}$, $J$ is the rotational quantum number ($J = 0, 1, 2, ...$)

The rotational transition, the rotational transition can be observed when $\Delta J = 0, \pm 1$. For $\Delta J = 0$, the observation of rotational transition depends on a symmetry of molecule structure.
The difference in the angular momentum quantum number of initial and final states is given as $\Delta J = \pm 1$, since the photon exchanged with the atom or molecule has a spin of unity.

### 2.3.4 Total energy and transition frequency

Molecular spectra have a complex structure and involve electronic, vibrational-rotational and pure rotational transitions. The energy levels are described by a sum of corresponding terms:

$$ E = E_{\text{elec}} + \hbar \omega \left( \nu + \frac{1}{2} \right) + B J \cdot (J+1) $$  \hspace{1cm} (2.4)

The absorption of radiation occurs when an atom/molecule makes a transition from one state which has energy $E_k$ to the state which has higher energy $E_j$:

$$ E_j - E_k = \hbar \nu $$  \hspace{1cm} (2.5)

where $h$ is the Plank constant $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$, $\nu$ is the frequency which is related to the wavelength and speed of light by $\nu = c/\lambda$.

For linear molecule the scheme of transitions between two vibrational levels $\nu''=0$ and $\nu'=1$ belonging to the same electronic energy level and separated in the rotational levels $J''$ and $J'$ is shown in Figure 9. The photon energy of allowed transitions is given by the difference of energy of two consecutive states:

$$ \Delta E = E(\nu',J') - E(\nu'',J'') $$

$$ = \hbar \omega \left( \nu' + \frac{1}{2} \right) + B' \cdot J' \cdot (J' + 1) - \hbar \omega \left( \nu'' + \frac{1}{2} \right) + B'' \cdot J'' \cdot (J'' + 1) . $$  \hspace{1cm} (2.6)

Assuming $B'=B''=B$, $\Delta \nu = \pm 1$

$$ \Delta E = \frac{\hbar \omega}{2} + B \cdot (J' \cdot (J' + 1) - J'' \cdot (J'' + 1)) . $$  \hspace{1cm} (2.6a)

The transitions are denoted as P-branch ($\Delta J = -1$), and R-branch ($\Delta J = +1$).

- $\Delta J = +1, \quad J' = J'' + 1, \quad \Delta E = \hbar \nu_0 + 2B \cdot (J'' + 1)$;
- $\Delta J = -1, \quad J' = J'' - 1, \quad \Delta E = \hbar \nu_0 - 2B \cdot J''$.  \hspace{1cm} (2.6b)

Q-branch only occurs if the electronic transitions take place at the same time. Schematically, P, Q and R branches are shown on Figure 9.
Figure 9. An energy level diagram showing some of the transitions involved in the IR vibration-rotation spectrum of a linear molecule.
2.4 Line shape profiles

The width and shape of spectroscopic transitions will affect the ability to extract qualitative and quantitative information from a spectrum.

The spectral line width characterizes the width of a spectral line. The line shape depends on the particular broadening process. The contribution of the line-broadening process is usually estimated by its full width at half the maximum (FWHM). For this study three most important processes are natural broadening, Doppler broadening, and pressure broadening.

First, we consider an excited atom or molecule with the energy \( E_0 \) above the ground state (with \( E=0 \)). The energy of the excited electrical dipole will decrease exponentially with time \( t \) due to the emission of electromagnetic radiation.

\[
E(t) = E_0 e^{-\delta t}
\]  

(2.7)

where \( \delta \) is a damping constant, and \( \tau = 1/\delta \) is the time that energy is decayed to 1/e of its initial value.

2.4.1 Natural broadening – Lorentzian line shape

Natural broadening occurs in both the classical and the quantum mechanical theories of radiation. In both cases it is a consequence of the finite life-time of the excited state due to the spontaneous emission.

The line profile of a spectral line at frequency \( \nu_0 \):

\[
g(\gamma, \nu) = \frac{1}{\pi} \frac{\gamma}{(\nu-\nu_0)^2+\gamma^2}
\]

(2.8)

where \( \gamma \) is the half width on the half of maximum (HWHM). The profile function is normalized to the unity area.
2.4.2 Doppler broadening – Gaussian line shape

Doppler broadening is a result of the well-known Doppler effect which is the shift in wavelength of the signal from a source moving toward or away from the observer. In the experiment the shifts arise from the thermal motion of the emitting atoms or molecules. The collision of the emitting atoms or molecule also induces the Dicke-narrowing effect. The line profile due to Doppler broadening:

\[ g_D(\nu) = \sqrt{\frac{\ln 2}{\pi}} \frac{1}{\gamma_D} \exp \left( -\ln 2 \frac{(\nu - \nu_0)^2}{\gamma_D^2} \right) , \]  \hspace{1cm} (2.9)

where

- \( k \) is the Boltzmann’s constant,
- \( m \) - the molecular mass,
- \( \nu \) – the absorbed frequency,
- \( \nu_0 \) – the central frequency of the absorption line,
- \( \gamma_D \) - the Doppler half width at half maximum (HWHM):

\[ \gamma_D = \frac{\nu_0}{c} \sqrt{\frac{2kT}{m}} . \]  \hspace{1cm} (2.10)

The profile function is normalized to the unit area.

Figure 10. Example of the Lorentzian line shape
In some physical situation, we may have to consider not only the thermal motion of the atoms, but also the bulk motions, which may be due to the turbulent motion in the gas. This can be accomplished by adding a velocity term \( v_{turb} \) to the thermal velocity; we can define an effective Doppler width:

\[
\Delta v_D^{eff} = \frac{v_0}{c} \sqrt{\frac{2kT}{m}} + v_{turb}^2
\]  

(2.11)

2.4.3 Pressure broadening

Pressure broadening or collisional broadening is the consequence of the collisions of molecules. Collisions reduce the life-time of the excited state below the life-time given by the radiation transition alone. The line profile resulting from pressure broadening is a Lorentzian as given in (2.8):

\[
g_p(\gamma_p, v) = \frac{1}{\pi} \frac{\gamma_p/4\pi}{(v-v_0)^2+(\gamma_p/4\pi)^2}
\]

The spectral lines are shifted by increasing gas pressure and by the presence of ions and electrons in sample. The amount of pressure broadening depends not only on the molecular species under consideration but also on the surrounding gas. Of particular interest are the self broadening and air broadening. The frequency of the collision is proportional to the speed of the molecule and the density of gas. In summary, the pressure-broadened line width \( \gamma_p \) is given by:

\[
\gamma_p(p, T) = \left[ \gamma_{air}(p_{ref}, T_{ref}) \cdot (p - p_{self}) + \gamma_{self}(p_{ref}, T_{ref}) \cdot p_{self} \right] \cdot \left[ \frac{T_{ref}}{T} \right]^n
\]  

(2.12)
where \( \gamma_{air/self}(\bar{p}_{ref}, T_{ref}) \) is the pressure broadening coefficients at some reference pressure and temperature.

### 2.4.4 Combined natural, Doppler and pressure broadening

Two types of broadening mechanisms which affect the line profiles were mentioned earlier. Voigt profile is a line profile resulting from the convolution of the Doppler and pressure broadening mechanisms:

\[
g_{V}(v) = \int_{-\infty}^{+\infty} G(v', \gamma_D) L(v - v', \gamma_p) dv' \tag{2.13}
\]

Where \( G \) and \( L \) are Gaussian and Lorentzian profiles.

In typical situation, the center is dominated by Doppler profile and the wings are dominated by Lorentzian profile.

### 2.5 Line intensity

The spectral line intensity describes the probability of transition between two energy levels. The intensity is defined here for a single molecule. Radiative transfer theory for the two states \( n, n' \) of a vibrational-rotational system defines the spectral line intensity (in units of \( \text{cm/molecule} \)) at \( T_{ref} = 296 \text{K} \) as \( [37, 38] \)

\[
S_{nn'} = \frac{h \nu_{nn'}}{c N} \left( 1 - \frac{g_n n_{nn'}}{g_{nn'} n_n} \right) B_{nn'} \tag{2.14}
\]

where \( B_{nn'} \) is the Einstein coefficient for absorption, \( n_n \) and \( n_{nn'} \) are the populations of the lower and upper states respectively, \( g_n \) and \( g_{nn'} \) are the state statistical weights, and \( N \) is the molecular number density.

The Einstein coefficient \( B_{nn'} \) is related to the weighted transition-moment squared \( \mathfrak{R} \) (Debye\(^2 = 10^{-36} \text{ ergs cm}^3 \)):

\[
\mathfrak{R}_{nn'} = \frac{3h^2}{8\pi^3} B_{nn'} \times 10^{36} \tag{2.15}
\]

Assuming local thermodynamic equilibrium (LTE), the population distribution between states is governed by Boltzmann statistics at the ambient temperature. This allows us to write

\[
S_{nn'}(T_{ref}) = \frac{g_{nn'}^3}{3hc} \nu_{nn'} \frac{l_a \theta_n \exp \left( \frac{-c_2 E_n}{T_{ref}} \right)}{Q(T_{ref})} \left[ 1 - \exp \left( \frac{-c_2 \nu_{nn'}}{T_{ref}} \right) \right] \mathfrak{R}_{nn'} \times 10^{-36} \tag{2.16}
\]

where \( S_{nn'} \) is weighted according to the natural terrestrial isotopic abundances, \( l_a \) is the natural terrestrial isotopic abundance, \( c_2 \) is the second radiation constant \( c = hc/k = 1.4388 \text{ cm K} \), \( E_n \) is the lower state energy [\( \text{cm}^{-1} \)], and \( Q(T_{ref}) \) is the total internal partition at
reference temperature. This is a definition that appears in HITRAN database (will be discussed below).

Figure 12 is the example of the line intensities of methane in infrared region for two different temperatures. The line intensities of the red and green spectra correspond 193K and 296K, respectively.

![Figure 12. Line intensities for some CH4 transitions in IR for 193K(red) and 296K(green)](image)

### 2.6 Beer-Lambert law

The absorption spectroscopy techniques are based on the absorption of electromagnetic radiation by matter. In the experiment, when a light passes through a cell which contains an absorber, the intensity of light is decreased by absorption that can be described by Lambert-Beer law.

\[
I(\lambda) = I_0(\lambda) \cdot \exp\{-OD\} 
\]  

\[
OD(\lambda) = \sum \{n \cdot S(\lambda_0) \cdot g(\lambda)\} = \ln \frac{I_0}{I} 
\]

where \(I_0\) is the initial intensity of light, \(I\) is the measured intensity of light, \(OD\) is the optical density, \(n\) is the density of absorber in function of temperature and pressure in units of (molecule/cm\(^3\)), \(I\) is the cell length (cm), \(g\) and \(S\) are the line shape function and line intensity respectively (will be discussed below).
From equation (2.2.1), we consider that the intensity of light at particular wavelengths decreases when the light passes through the cell with corresponding absorber. The absorber must be homogeneously distributed and not scatter the radiation.

2.7 Conclusion

It is possible to model experimentally obtained absorption spectra, using Beer Lambert law and line parameters which are measured or calculated in a theoretical study. In the current work the line parameters are initially taken from a spectral database. This world-known HITRAN database is described in the next chapter.
Chapter 3. HITRAN database

3.1 Introduction

HITRAN is the database that collects the spectroscopic parameters for calculation or simulation of the molecular transmission spectra. These data are archived as a multitude of high-resolution line transitions. There are in addition many molecular species collected as cross-section data. [37, 39].

3.2 General description

HITRAN is an acronym for high-resolution transmission molecular absorption database. HITRAN is a compilation of spectroscopic parameters that a variety of computer codes used to predict and simulate the transmission and emission of light in the atmosphere. The database is a long-running project started by the Air Force Cambridge Research Laboratories (AFCRL) in the late 1960’s in response to the need for detailed knowledge of the infrared properties of the atmosphere. The current edition of the HITRAN molecular spectroscopic database and associated compilation (v13.0) is available on an ftp site located at the Smithsonian Astrophysical Observatory in Cambridge, USA.

Figure 13. Schematic of fundamental spectroscopic parameters of a line transition in HITRAN
### 3.3 Parameters of the data

Schematic of fundamental spectroscopic parameters of a line transition in HITRAN is shown in Figure 13. The format of the parameters for each spectral line (equivalent to a record in the database) is given in Table 9. The total length of the record is now 160 characters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Meaning</th>
<th>Field length of the (100/160) character records</th>
<th>Type</th>
<th>Comments or units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>M</strong></td>
<td>Molecule number</td>
<td>2/2</td>
<td>Integer</td>
<td>HITRAN chronological assignment</td>
</tr>
<tr>
<td><strong>I</strong></td>
<td>Isotopologue number</td>
<td>1/1</td>
<td>Integer</td>
<td>Ordering within a molecule by terrestrial abundance</td>
</tr>
<tr>
<td><strong>ν</strong></td>
<td>Vacuum wavenumber</td>
<td>12/12</td>
<td>Real</td>
<td>cm(^{-1})</td>
</tr>
<tr>
<td><strong>S</strong></td>
<td>Intensity</td>
<td>10/10</td>
<td>Real</td>
<td>cm(^{-1})/(molecule cm(^{-2})) at standard 296K</td>
</tr>
<tr>
<td><strong>R</strong></td>
<td>Weighted square of the transition moment</td>
<td>10/0</td>
<td>Real</td>
<td>Debye(^2) (for an electric dipole transition)</td>
</tr>
<tr>
<td><strong>A</strong></td>
<td>Einstein A-coefficient</td>
<td>0/10</td>
<td>Real</td>
<td>s(^{-1})</td>
</tr>
<tr>
<td><strong>γ(_{\text{air}})</strong></td>
<td>Air-broadened half-width</td>
<td>5/5</td>
<td>Real</td>
<td>HWHM @ 296K (in cm(^{-1})atm(^{-1}))</td>
</tr>
<tr>
<td><strong>γ(_{\text{self}})</strong></td>
<td>Self-broadened half-width</td>
<td>5/5</td>
<td>Real</td>
<td>HWHM @ 296K (in cm(^{-1})atm(^{-1}))</td>
</tr>
<tr>
<td><strong>E''</strong></td>
<td>Lower-state energy</td>
<td>10/10</td>
<td>Real</td>
<td>cm(^{-1})</td>
</tr>
<tr>
<td><strong>η(_{\text{air}})</strong></td>
<td>Temperature dependence exponent for γ(_{\text{air}})</td>
<td>4/4</td>
<td>Real</td>
<td>Unitless,</td>
</tr>
<tr>
<td><strong>δ(_{\text{air}})</strong></td>
<td>Air pressure-induced line shift</td>
<td>8/8</td>
<td>Real</td>
<td>cm(^{-1}) atm(^{-1}) at 296K</td>
</tr>
<tr>
<td><strong>V'</strong></td>
<td>Upper-state “global” quanta</td>
<td>3/15</td>
<td>Hollerith</td>
<td></td>
</tr>
<tr>
<td><strong>V''</strong></td>
<td>Lower-state “global” quanta</td>
<td>3/15</td>
<td>Hollerith</td>
<td></td>
</tr>
<tr>
<td><strong>Q'</strong></td>
<td>Upper-state “local” quanta</td>
<td>9/15</td>
<td>Hollerith</td>
<td></td>
</tr>
<tr>
<td><strong>Q''</strong></td>
<td>Lower-state “local” quanta</td>
<td>9/15</td>
<td>Hollerith</td>
<td></td>
</tr>
<tr>
<td><strong>I(_{\text{err}})</strong></td>
<td>Uncertainty indices</td>
<td>3/6</td>
<td>Integer</td>
<td>Accuracy for 3/6 critical</td>
</tr>
<tr>
<td>$I_{\text{ref}}$</td>
<td>Reference indices</td>
<td>6/12</td>
<td>Integer</td>
<td>Parameters</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------</td>
<td>------</td>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>*</td>
<td>Flag</td>
<td>0/1</td>
<td>Character</td>
<td>Availability of program and data for the case of line mixing</td>
</tr>
</tbody>
</table>

### Table 9. HITRAN format for transition parameters

HITRAN provides uncertainties for the following six transition parameters if available: intensity, line position, air pressure induced line shift, air half-width and self half-width and temperature dependence. The codes for these uncertainties as they are given in HITRAN are explained in the Table 10 and Table 11.

#### 3.4 Quality of the data for CH4 in the region 1.6 µm

It was mentioned above that the aim of my work is to participate in improvement of uncertainty for line parameters (pressure broadening coefficient, $\gamma_s$, $\gamma_a$ pressure induced shift, and temperature dependence exponent). Currently, uncertainties for pressure broadening coefficients and temperature dependence exponent are about 5-20%.

<table>
<thead>
<tr>
<th>Line position and Air pressure-induced line shift (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Code</strong></td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
</tbody>
</table>

**Table 10. The uncertainty codes adopted for HITRAN**

<table>
<thead>
<tr>
<th>Intensity, half-width (air-, and self-) and temperature dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Code</strong></td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
</tr>
</tbody>
</table>

**Table 11. The uncertainty codes adopted for HITRAN**
Figure 14 shows the example of the uncertainty codes for broadening coefficients: self- and air-broadening, temperature dependence and pressure shift for CH$_4$ in the interested region 1.6 µm.

![Figure 14. The uncertainty codes: Upper panel-spectral windows of SCIAMACY, OCO, and GOSAT and line intensities of CH$_4$ taken from the HITRAN 2008; Lower panels-HITAN 2008 uncertainty codes for broadening coefficients: self-and air broadening, Temperature dependence and pressure shift for CH$_4$](image)

### 3.5 Conclusion

HITRAN database contains information on the line parameters. Currently, line parameters for methane in the region around 1.6 µm have uncertainty up to 20%, based on the previous experimental studies and models. Next chapters provide information on the experimental setup used in the Molecular Spectroscopy Laboratory to obtain high quality high resolution spectra by means of Fourier Transform spectroscopy.
Chapter 4. Fourier Transform spectroscopy

4.1 Introduction

The Fourier transform spectrometer (FTS) is in principle a Michelson interferometer [40, 41]. The principle components of the Fourier transform spectrometer are shown in Figure 15. The light is separated into two beams by a beam splitter, some is transmitted to a movable mirror and some is reflected to a fixed mirror. Both beams are reflected by mirrors and then recombine at the beam splitter and interfere. Some of the recombined beam is transmitted to the light source and some is reflected to a detector. At the detector, the interference is recorded and converted to a digital signal. The optical path difference (OPD) is varied by moving the movable mirror. The pattern of the interference is called an interferogram which is used to calculate the spectrum of the incident radiation.

4.2 Mathematical background of Fourier Transform

A Fourier transformation of the interferogram, the incident radiation $B(v)$ can be calculated by using the following equation;

$$B_e(v) = \frac{1}{2}(B(v) + B(-v)) = \int_{-\infty}^{\infty} I(x) \cos(2\pi vx) dv$$  \hspace{1cm} (4.1)

where $B_e(v)$ - an even spectrum, $B(v)$ - a physical spectrum, $B(-v)$ - an unphysical spectrum, $v$ - a spectral energy, $v = \frac{k}{2\pi}$

4.3 Optical principles and main components of the Fourier Transform spectrometer (Michelson interferometer)

![Figure 15. The principle components of a Fourier Transform spectrometer](image)
4.4 Advantages and disadvantages

4.4.1 Advantages of Fourier Transform spectroscopy

- FTS has a very large resolving power
- Vastly reduced stray or unwanted flux problem
- Fast scanning time
- Large wave-number ranges per scan
- Possibility of making weak signal measurements at millimeter wavelengths.
- Use of small images in sample compartments without requiring special measures.
- Low cost of basic optical equipment.
- Smaller size and lower weight of interferometers than spectrometers
- Jacquinot (Throughput) advantage: The interferometer has large circular apertures area than the linear slits used in grating spectrometers with no strong limitation on the resolution, Therefore, the ability of interferometers to collect large amounts of energy at high resolution.
- Fellget (Multiplex) advantage: the interferometer receives information about the entire spectral range during an entire scan, while the grating instrument receives information only in a narrow band at a given time.
- Connes (Wavelength) advantage: It arises because FTIR gives very accurate frequencies in the spectrum. This gives the exact position for the movable mirror.

4.4.2 Disadvantage of Fourier Transform spectroscopy

- The interferometer requires access to computer facilities
- The interferogram sometimes cannot be visually interpreted, which make it for an operator to judge quickly whether or not an experiment is satisfactory.
- The high wave-number accuracy and the problem of reduced stray light both result from the interference phenomena inherent in the instrument.

4.5 Conclusion

The Fourier transform spectrometer (FTS) is a technique used to obtain a spectrum. The using of FTS has both advantages and disadvantages. The spectrum of methane in this project is obtained from the Bruker HR 120 Fourier Transform spectrometer.
Chapter 5. Experimental setup

5.1 Introduction

The experimental setup in the Molecular Spectroscopy Laboratory (IUP, University of Bremen) is shown in Figure 16 and Error! Reference source not found..

The experimental equipment includes Bruker 120 HR FTS spectrometer, IR sources, IR enhanced optics for multipass arrangements (White type) and several absorption cells. Also gas flow system and gas cooling system are available with precise control of gas pressure and temperature in broad ranges.

5.2 Main components

The main components of the set up are the following

- Bruker HR 120 Fourier Transform spectrometer (FTS).
- Light source: tungsten lamp (OSRAM);
• Detector: InGaAs photodiode;
• Cell: Double jacket quartz cell, cryogenic cooling, single (130 cm) or double path (260 cm).

5.2.1 Absorption cell

The schematic of the absorption cell is shown in Figure 18

![Figure 18. The schematics of the absorption cell](image)

The light from the FT spectrometer enters the cell after the adjusting optics (telescope). It is possible to arrange single or double pass. After the cell the light is focused on a semiconductor detector.

The absorption cells can be cooled down to 193 K. It is thermo-insulated from the ambient air via double jacket. This cell allows absorption path lengths 130 – 530 cm. Inner volume can be evacuated down to the ground pressure of 0.01 mbar. It is possible to fill the cell with the gas at different flow rates or in a static regime to any pressure up to 1000 mbar. The pressure can be controlled with the accuracy of about 0.04 mbar.

5.3 Experimental conditions

5.3.1. Previous works in line parameters investigations (Literature reviews)

There are two key publications from Frankenberg et al., 2008 [42] and Lyulin et al., 2009 [43] related to our study.

Scaled N₂-broadening coefficients from Frankenberg et al. were inserted in HITRAN from 5860 to 6184 cm⁻¹. Frankenberg et al. applied a multispectrum nonlinear constrained least squares approach based on Optimal Estimation to derive the spectroscopic parameters by simultaneously fitting laboratory spectra at different ambient pressures.
assuming a Voigt line-shape. The high resolution (0.01 cm\(^{-1}\)) data were obtained using Bruker HR Fourier Transform spectrometer (FTS) as part of a preliminary study undertaken at the University of Bremen (more details on these measurements will be given below). Despite all their significance at improving essentially a situation when no information on the broadening coefficients was available, the experimental basis of the data obtained by Frankenberg et al is limited:

- The buffer gas was pure nitrogen. No knowledge of the broadening by oxygen is available; therefore retrieved broadening coefficients need to be converted for atmospheric applications.
- Only two mixing ratios (~1.2 and 2) and only four pressures were investigated.
- The measurements of the spectra were measured at room temperature only.

Frankenberg et al. report several unsolved and open issues. They point out that the temperature dependence of pressure broadening requires further research for most transitions. In HITRAN 2008 the value for the temperature dependence parameter \(n\) was set either to a default constant (0.75 below 5860 cm\(^{-1}\) or 0.85 above 5860 cm\(^{-1}\)) unless direct measurements were available performed by Lyulin et al.

Experimental data obtained by Lyulin et al. [43] using the Bruker IFS 125 HR FTIR spectrometer in the 5550 – 6236 cm\(^{-1}\) region confirm the importance of the temperature dependence. Lyulin et al. extended the temperature range and buffer gases pressure compared to Frankenberg et al. and recorded the absorption spectra of mixtures of methane with N\(_2\) and O\(_2\) at different partial pressures of both CH\(_4\) and buffer gases for three temperatures: 240, 267, and 296K (see Table 13).

<table>
<thead>
<tr>
<th>Table 12. Key parameters of the experimental set up and mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument</td>
</tr>
<tr>
<td>Absorption path</td>
</tr>
<tr>
<td>Resolution</td>
</tr>
<tr>
<td>spectra/background</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 13. Experimental condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lyulin 2009 &amp; Frankenberg 2008</td>
</tr>
<tr>
<td>T, K</td>
</tr>
<tr>
<td>296</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>267</td>
</tr>
</tbody>
</table>
5.3.2. New experimental conditions

List of investigated pressures and temperatures is given in Table 14. Resolution of the FTS was 0.01 cm\(^{-1}\).

In our research, the experiment is conducted under certain sets of pressures and volume mixing rations at five different temperatures. This set of conditions allows us to investigate line broadening depending on different conditions.

Table 14. The new experimental conditions

<table>
<thead>
<tr>
<th>Low pressure</th>
<th>High pressure</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>T, K</td>
<td>CH4, mbar</td>
<td>T, K</td>
<td>CH4, mbar</td>
<td>O2, mbar</td>
<td>N2, mbar</td>
</tr>
<tr>
<td>293</td>
<td>5</td>
<td>293</td>
<td>10</td>
<td>490</td>
<td>-</td>
</tr>
<tr>
<td>263</td>
<td>5</td>
<td>263</td>
<td>10</td>
<td>490</td>
<td>-</td>
</tr>
<tr>
<td>243</td>
<td>5</td>
<td>243</td>
<td>10</td>
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<td>-</td>
</tr>
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<td>223</td>
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<td>495</td>
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<td>263</td>
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<tr>
<td>243</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>195</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.4 Modeling

5.4.1 Algorithm and parameters

Figure 19 presents the principle scheme of computation using a small home-made Matlab routine. The input spectra are the experimental spectra of methane, obtained using Fourier Transform spectrometer in the laboratory. Additional parameters are experimental conditions, such as temperature, pressure and cell length. Currently modeled spectra can be calculated in assumption of Gaussian and Lorentzian line shapes. Needed line parameters such as line position, line intensity, broadening coefficients for self-broadening and air-broadening and pressure shift of line position are taken from the HITRAN database (see below). Routine calculates absorption spectrum and compares it with the experimental spectrum.

![Diagram of computation scheme](image)

**Figure 19.** The principle scheme of computation with Matlab routine. We have two sets of data which are line parameters of methane from HITRAN and experimental data. We then calculate the absorption profile of methane based on HITRAN line parameters for certain experimental conditions like temperature, pressure, and cell length and estimate the difference with the experimental spectrum.

5.4.2 Example

From the principle scheme shown in Figure 19 we can simply write general steps in the routine:

1. Set pressure and temperature in the code as they were in the experiment.
2. Assume Gaussian or Lorentzian profiles to calculate the model spectra.
3. Plot the experimental and modeled spectra.

4. Analyze difference between the experimental and modeled profiles.

5. Correct for offsets or pressure/temperature experimental uncertainty.

Figure 20 presents several plots:
- upper panel – calculated and experimental transmission spectra;
- lower panel – difference between spectra, calculated in percent as

\[ \frac{\text{Spectrum}_{\text{exp}} - \text{Spectrum}_{\text{model}}}{\text{Spectrum}_{\text{model}}} \times 100\% \]

5.5 Conclusions
The setup is capable of producing the high quality high resolution spectra at different experimental conditions. Conditions were chosen based on the literature review to reproduce and extend the range of data obtained by different researches so far.

Figure 20. The example of spectra plots. The range of wave number considered is around 6001-6002 cm\(^{-1}\) at 2 mbar of pressure. After we change the experimental conditions, the graphs will be plotted into two graphs, transmission graph (upper) and difference graph between experimental and modeled spectra (lower)
Chapter 6. Results and discussion

6.1 Introduction

The small home-made Matlab routine (the principle of the computation is shown in Figure 19) is used to create the model spectra. Then the difference between the experimental and model spectra is calculated by adjusts the experimental conditions like temperature, pressure, and cell length until the best fit of between these two spectra is obtained.

6.2 Data overview

The experimental conditions used to create the model spectra were taken under two main conditions which are high pressure and low pressure cases.

### High pressure

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>CH4, mbar</th>
<th>O2, mbar</th>
<th>N2, mbar</th>
<th>Total, mbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>10</td>
<td>490</td>
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<td>500</td>
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<td>5</td>
<td>-</td>
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<td>263</td>
<td>10</td>
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<td>990</td>
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</table>

For the high pressure case, the experiment was done at five different temperatures. The cell was filled with the mixture of methane and oxygen, and the mixture of methane and nitrogen with the total pressure of 500 and 1000 mbar. Lorentzian line profile was assumed for the high pressure spectra.
The experiment in low pressure case was done at five different temperatures same as in the high pressure case. The cell was filled with pure methane with the pressure of 2 and 5 mbar. Doppler line profile was assumed for the low pressure spectra.

### 6.3 Software for extended data analysis

The software is used to investigate line parameter is the software from the University of Leicester. Our group intends to use this software to derive line parameters from our experimental data. Figure 21 shows the principle algorithm of the software. The experimental spectrum and experimental conditions \((P, T, I)\) obtained from the Molecular spectroscopy laboratory will be analyzed by the software and then create the line parameters.

![Diagram](image)

*Figure 21. The principle algorithm of the software from the University of Leicester, UK*
6.4 Results

Below are the examples of comparison of experimental spectra with ones simulated in Matlab using HITRAN line parameters. Two extreme cases are shown: low pressure (2mbar pure methane) and high pressure (5mbar methane in mixture with 995 mbar air). These conditions are best reproduced by our model. More advanced algorithms with Voigt line shapes for intermediate pressures, or taking into account more complicated line broadening mechanisms would produce even better fitting spectra.

6.4.1 Low pressure case

![Graph showing experimental data and model comparison for low pressure case.](image)

Figure 22. Experimental IUP data at 2 mbar CH4 and T=263 K. Upper panel: Home-made model-assuming HITRAN parameters and Doppler line profile for region 5997-6005 cm⁻¹; Lower panel: the difference (%) between experimental and model spectra.
Figure 22 shows the comparison of model and experimental spectra. It was taken under the low pressure condition, 2 mbar of methane and 263 K of temperature. The upper panel is the transmittance spectra and the lower panel is the difference between experimental and model spectra. Zoom on the region around 6002 cm$^{-1}$ (Figure 23), the small differences between experimental and model spectra are more obvious. The differences are in the range between 0.2% and 1.4%.
6.4.2 High pressure case

Figure 24. The experimental IUP data: 5 mbar CH4 + 995 O2 and T =293 K. Upper panel: Home-made model-assuming HITRAN parameters and Lorentz line profile for region 5997-6005 cm⁻¹; Lower panel: the difference (%) between experimental and model spectra.
Figure 25. Experimental IUP data for high pressure condition. Zoom on the region around 6002 cm$^{-1}$.

Figure 24 and Figure 25 illustrate the comparison of model and experimental spectra for high pressure condition (5mbar methane in mixture with 995mbar air).

6.5 Results discussion

As it can be seen from the figures 22 - 25, our simple Matlab model can produce spectra which differ less than 1.5 % from the experimental data. The discrepancy can be attributed to several factors:

1) Model imperfection. We only assume two basic line broadening mechanisms and correspondent line shapes (Doppler/ Lorentzian). Was the model to take into account more factors influencing the line shape (spectral line mixing, speed dependence of collisional width etc.), so the residuals would be smaller.

2) HITRAN database imperfection. It is a known fact that for the region around 6000 cm$^{-1}$ the line broadening coefficients are provided with up to 20% uncertainty, which influences the output of the model and causes greater fit residuals.
6.6 Conclusions and outlook

Methane is one of the greenhouse gases in the earth’s atmosphere, which plays an important role in the Earth’s climate. The global warming is the impact of the increasing of the concentration of methane and other greenhouse gases in the atmosphere. The abundance of methane in the atmosphere is monitored by Greenhouse gases Observing SATellite (GOSAT). The measurements are performed with the Thermal- and Near-infrared Sensors for carbon Observation Fourier Transform Spectrometer (TANSO-FTS).

Within the course of this work I familiarized myself with several most important aspects relevant to the investigation of methane and other atmospheric species:

1. I systemized my knowledge on the greenhouse gases, and their impact on the climate change. For this, I studied information on the greenhouse gases trends and observations using homepages of the world leading agencies and organizations.
2. I got insight in the modern remote sensing instruments and basics of the retrieval algorithms using recent publications of leading groups.
3. I got used to work with the world-wide used HITRAN database, including using the accuracy codes.
4. I deepened my background on the molecular structure and energy levels and transitions on the example of the CH$_4$ molecule. I applied this background, considering spectroscopic information included in the HITRAN database.
5. I extended my background on the different types of the line broadening mechanisms and resulting shape profiles for cases of low and high pressured.
6. I got familiar with the established spectroscopic laboratory methods, based on the absorption spectroscopy and Fourier transform spectroscopy.
7. I got experience of spectra modeling using home-made software and line parameters from the HITRAN dataset, reproducing experimentally obtained data, obtained in the wide range of temperatures and pressures, which were not available in the literature so far.

As a master student working in the Molecular Spectroscopy Laboratory, i was involved in the investigation of methane line parameters using analysis of spectra obtained by means of Fourier Transform Spectroscopy. The software which would be used to analyze our experimental methane spectra from the collaborating group in the University of Leicester was not available by the end of my thesis project. Therefore, in this project I worked only on the first part which was to acquire experimental spectra and compare them with model spectra by using small home-made Matlab routine and line parameters from HITRAN.

The investigation of line parameters using the software from the University of Leicester is somewhat like a reverse process of using our Matlab routine. The software will create line coefficients by analyzing the experimental spectra obtained from Bruker 120 HR FTS.
spectrometer. The output is then to be compared with existing data in HITRAN. It will also be necessary to test the newly obtained data for methane on existing retrieval algorithms to investigate how it influences the methane observations.

Modeled spectra, based on the current parameters from HITRAN dataset reproduced experimental ones within 1.5% accuracy. According to the recent literature, line mixing must be taken into account which was not possible with the available homemade software.
References


[5] Lectures on the atmospheric chemistry II, Prof.Dr. Otto Schrems, AWI


[34] http://www.sciamachy.org/, The online SCIAMACHY book


[38] Herzberg G. Molecular Spectra and Molecular Structure, 1950, Krieger, Florida

[38a] [Gerhard Herzberg, F.R.S.C; Molecular Spectra and Molecular Structure; Volume II Infrared and Raman Spectra of Polyatomic Molecules; Krieger; 1991][39] HITRAN homepage http://www.cfa.harvard.edu/hitran/
[40] Holger Winkler; Fourier Transform Infrared (FTIR) Spectrometry; Measurement Technique Lecture Material; 2012
http://www.msc-ep.uni-bremen.de/services/lectures/practicals/meas_tech_fts_hw_110406.pdf

[41] Holger Winkler; Fourier Transform Infrared (FTIR) Spectrometry; Measurement Technique Practical Material; 2012


Books used in the Chapter 2:

John M. Wallace, Peter V. Hobbs; Atmospheric Science; Elsevier Inc; 2006 A.Thorne, U. Litzen, S. Johansson; Spectrophysics principle and application; Springer-Verlag Berlin Heidelberg; 1999

I.I. Sobel'man, L.A.Vainshtein, E.A.Yukov; Excitation of Atoms and Broadening of Spectral Lines; Springer; 1995

P.V. Elyutin; Natural line shape; Department of Physics, Moscow State University, Russia; 2008
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