Summary

In this thesis absorption spectroscopy measurements on atmospheric gases are presented. To place these measurements in a wider context, it is helpful to start with some background.

A multitude of observations have shown that the earth’s climate is changing. A recent report from the European Environment Agency “Impacts of Europe’s changing climate” (see reference 135) lists some of the consequences in Europe: a decrease in precipitation and desertification in the south of Europe, an increase in precipitation in north- and east-Europe and retreating glaciers in the mountain ranges. The effects on animal life are not entirely clear, but flooding and changes in crop yields are to be expected, while the diversity of plant life has already been reduced. Observations also showed a rapid decrease in the thickness of the ozone layer starting from the early nineteen-eighties. This decrease was clearly caused by anthropogenic emissions; international political agreement led to a ban on the production of the harmful chemicals, but recovery will take at least another century. The climate changes also seem to be caused by anthropogenic emissions, although not all scientists are convinced this can be concluded from the data gathered so far; further measurements are needed to fully determine the causes for the observed changes.

In order to detect changes in the climate, observations on a global scale are needed. Satellites can perform these measurements; changes in glaciers can be readily detected on satellite images. They are also highly suitable for the detection of changes in the atmosphere, not only because of the global coverage, but also because the observation extends over the entire height of the atmosphere. To detect the composition of the atmosphere from an orbiting instrument, a spectrum of reflected sunlight is recorded. This light has travelled a significant distance through the earth’s atmosphere, and the absorption resonances of the gases that are present in the atmosphere can be found in this spectrum. To determine the concentration of specific gases – for example ozone – from these observed spectra, one needs to know the amount of light that is absorbed by the various gases. The measurements in this thesis form a contribution to this set of reference-spectra.

The absorption resonances of a molecule are specific to a particular species, and allow for identification of the molecule. The spectrum itself tells us about the internal structure of the molecule.

Another interaction between light and matter is scattering. A resonance in the molecule is not needed for scattering, it occurs when light falls on a molecule and is emitted in a different direction. Light is an electro-magnetic wave, and this wave causes the electrons in a molecule to vibrate, much like a small boat rolls when a wave passes the boat on water. These vibrating electrons become broadcasters according to classical electrodynamics theory, and emit light, causing part of the incoming energy to be scattered. To continue the boat analogy: the rolling boat itself creates a smaller wave on the water. The intensity of the scattered radiation
Summary

depends on the wavelength of the incident radiation: shorter wavelengths are scattered more efficiently than longer wavelengths.\(^1\) This also explains why we see a blue sky during the day: the wavelength of blue light is much shorter than that of red light, and is therefore a greater portion of it is scattered from the beam. It dominates all the light that comes from another direction than directly from the sun. The same mechanism is also responsible for the red glow at sunset – as shown on the cover: in the long path through the atmosphere the blue part of the spectrum is scattered out of the beam, leaving only the red part of the spectrum. This type of scattering is known as 'Rayleigh scattering', after Lord Rayleigh (1842–1919).

For visible light, the atmosphere is nearly completely transparent: this leads to the conclusion that the absorption-resonances in atmospheric molecules are weak. To detect these resonances despite their weakness, a sensitive measurement technique is required. For the measurements in this thesis, the ‘cavity ring-down’ absorption spectroscopy technique was used. In this technique, a short pulse of laser light is brought between two highly reflective mirrors. This light bounces back and forth between these mirrors several thousand times. At each reflection the largest fraction, typically more than 99.9\%, bounces back to the other mirror. A small fraction of the light leaks through the mirrors, causing the amount of light enclosed between the mirrors to decrease. Because the enclosed amount of light decreases, the amount of light that leaks out also decreases. By measuring the intensity of this leak out as a function of time, a decay time of the cavity is obtained. With a distance between the mirrors of about one metre and the reflectivity mentioned above, the decay time is about 50\,\mu s, equivalent to a distance of about 15\,km. Depending on the exact reflectivity of the mirrors, distances of up to 100\,km can be obtained. If a gas is put in the cell between the mirrors, the decay time is shortened; part of the light is absorbed or scattered by the gas, which causes the amount of light to decrease faster than if the gas would not have been there. From the decrease in the decay time and the density of the gas in the cell, the absorption cross section can be calculated. Because of the large distance the light travels between the mirrors, this method is very sensitive, and allows for the detection of very weak absorptions. Another advantage of this technique over more conventional absorption spectroscopic techniques is the fact that all information is obtained from the time-evolution of the signal; more conventional techniques use the intensity of the light after it has travelled through the gas. Pulsed lasers cannot easily be used in such techniques, because of the large intensity fluctuations between pulses in such lasers.

For the research in this thesis, the cavity ring-down technique is applied to various gasses in several wavelength ranges. In chapter 3 measurements on Rayleigh scattering of light are presented. The principle behind this type of scattering was published already in 1899, but only recently the measurement techniques have become sensitive enough to quantitatively measure the extinction of light due to scattering in a gas. These measurements can be compared to values for the scattering cross section calculated from measurements of the refractive index.

\(^1\) This is where I'll have to stop using the boat analogy.
to verify the the (classical) theory from Lord Rayleigh. Both results are in close agreement, provided a correction for the asymmetry of the molecules is applied. This correction was already formulated in 1923 by Louis King.

In chapter 8 measurements on an isotopomer of water are shown. The most abundant water is \( \text{H}_2^{16}\text{O} \), water based on an oxygen atom with mass 16. In these measurements the oxygen is replaced by a heavy variant, to form \( \text{H}_2^{18}\text{O} \). Chemically both types of water are identical, but the absorption spectra differ. Water vapour is present in the atmosphere in large quantities, and even a relatively rare isotope variant is important for the analysis of satellite measurements. The measurements on an isotopomer also provide an extra reference for calculations on the absorption spectrum of water, not just for \( \text{H}_2^{18}\text{O} \), but for all of them. In performing these measurement it is not only the sensitivity of the measurement technique that is important, the small cell volume is also plays an important role, because isotope enriched water is rather expensive.

In chapter 7 a newly designed laser system is used to produce light at extremely short wavelengths, far into the ultra-violet part of the spectrum. With this laser system cavity ring-down spectroscopy at wavelengths as short as 197 nm was demonstrated, the shortest wavelength at which cavity ring-down spectroscopy has been used so far. At these wavelengths most gases absorb; some demonstration measurements on the extinction in sulphur hexafluoride, carbon dioxide and oxygen. Further measurements were performed on the absorption spectrum of oxygen in this wavelength range, the so-called Schumann–Runge bands. These measurements are important because the strength of the Schumann–Runge bands and the Herzberg continuum, which lies underneath these bands, determine how far radiation with a wavelength of about 200 nm penetrates the atmosphere.

Chapters 5 and 6 deal with measurements on a final class of absorptions: collision-induced absorptions, in this case in oxygen. Oxygen has many low-lying electronically excited states, but transitions between these states are all symmetry forbidden, causing the absorption resonances to be extremely weak. During a collision the symmetry is broken, and the transition is allowed. The truly remarkable situation in oxygen is that the two molecules can absorb a single photon during the collision and that both molecules leave the collision in an excited state. These collision-induced absorptions occur in wavelength regions where a single oxygen molecule does not have absorption resonances.

The collision-induced absorption in oxygen near 477 nm is important for the recently launched OMI (Ozone Monitoring Instrument) instrument. In the analysis of the recorded satellite spectra, it is important to know the cloud coverage, as clouds change the path-length of the light through the atmosphere. The collision-induced absorption in used as a ruler to determine the effective path-length through the atmosphere: the atmosphere has 20% oxygen in it, and this value is constant. Because the temperature of the atmosphere changes with altitude, further measurements at low temperature were performed, to determine the effects of temperature on these collision-induced absorptions.
Colophon

The layout of this thesis was made in \LaTeX{}, the figures were created in MetaPost. The typeface is Lucida Bright, with Lucida Sans as the support font. The layout is created with the aid of the Memoir document-class, using packages (natbib, the NTG classes, hyperref, wrapfig, dcolumn, babel, fnpara) to customise certain parts of it.

The effort put into maintaining and supporting this software by a large group of volunteers is greatly appreciated. Special gratitude goes out to Gerben Wierda for compiling and maintaining \TeX{} on Mac OS X and Peter Wilson for creating Memoir and its manual.

The photograph on the cover was taken on April 24\textsuperscript{th}, 2004. It shows the sunset as seen from Zandvoort aan Zee, the Netherlands. The nice colours are caused by Rayleigh scattering; the blue part of the spectrum is scattered out of the beam, leaving just the red light. Chapter 3 explains the (classical) theory of Rayleigh scattering in full detail.

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