Collision Induced Absorption in Atmospheric Gasses

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Abstract

In this work a study on collision induced absorption (CIA) in Oxygen-Nitrogen mixtures is described. CIA is relevant for atmospheric research, which needs accurate oxygen data for the retrieval of absolute amounts of gases in our atmosphere. In general CIA is extremely small. However, due to special quantum mechanical properties of the oxygen molecule the CIA at the 1060 nm and 1270 nm band of Oxygen are enhanced and have significant influences on atmospheric absorption. Still the CIA is too small to be measured with normal spectroscopy.

In this report a Cavity Ring-Down Spectroscopy (CDRS) setup was used. During the measurements the pressure of pure oxygen or an air mixture was ramped from 0-8 bar. In total 4 CIA spectra were measured at the 1060 nm band of oxygen. One in pure O$_2$ to find the contribution of O$_2$-O$_2$ collisions and three on dried air to find the contribution of O$_2$-N$_2$ collisions. In the last measurement in air a lens was placed in front of the cavity in order to match the incoming laser light to the longitudinal modes of the cavity. This greatly enhanced the sensitivity by stabilizing the cavity-modes that were excited by the laser.

The integrated CIA cross-section from O$_2$-O$_2$ collisions was found to be (2.08±0.15)*10$^{-4}$ cm$^2$mg$^{-2}$. For N$_2$-O$_2$ the integrated CIA cross-section was found to be (8±5)*10$^{-6}$ cm$^2$mg$^{-2}$. The error on this last value is mainly caused by the uncertainty in the gas-concentration. Due to the large concentration of nitrogen in air, the absorption at N$_2$-O$_2$ collisions still contributes for about 11% of the total CIA in air. In terms of the total short wavelength absorption in earth’s atmosphere this is 0.01-0.04%. At the peak of the CIA spectrum 1.86% of the incoming sunlight is absorbed by our atmosphere.
Chapter 1

Introduction

Absorption of solar light by the constituents of our atmosphere is a complex process. The efficiency of absorption depends not only on the quantum nature of the molecules, but also on collisions in our atmosphere, which occur on a rate of about $10^9$ per second for each molecule, play a role. For example, during a collision a short lived or transient complex is formed. The properties of which differ from that of the individual constituents. Due to the short lifetime of these collision complexes, the collision induced absorption is small compared to the normal line-absorption. The number of successful studies is limited [1]. Nevertheless, CIA is relevant. Climate studies often use satellites to measure the local concentration of active molecules in the atmosphere like CO$_2$ [2]. Clouds and aerosols complicate an accurate determination of these concentrations [3]. To solve this problem a well-known constituent (with a well-known spectrum) can be used as a reference. Oxygen is often used as such a reference, since the oxygen is abundant in our atmosphere and the spectrum is well known. Using oxygen as reference gives rise to the need of a very exact oxygen spectrum. Since the oxygen absorption bands are relatively weak (often quantum mechanically forbidden) CIA plays a significant role in the absorption of light under atmospheric pressure conditions.

Other studies in this area use either very high pressures [4] or low temperatures (to 77K) [5] to get values for the CIA. However since no satisfactorily model exists [3] it is uncertain if these values may be extrapolated to atmospheric circumstances. The reason why CIA is studied at high pressure is that the CIA depends quadratic on the density. At low temperatures the CIA is also larger as well. The molecules that collide then have a chance to form long lived van der Waals complexes which greatly enhances and deforms the CIA spectrum. Under atmospheric conditions CIA is very small. Due to the long path length through the entire atmosphere this effect is still noticeable. In the lab such long path lengths only can be reached using a cavity, consisting of 2 parallel high reflective mirrors [6].

The main spectroscopic technique which uses this is Cavity Ring-Down Spectroscopy (CRDS). This will also be the experimental method used in this report.

The goal of this research is to quantitatively find the CIA at the 1060 nm band in air. As will be demonstrated below in more detail, this CIA can be split in a part caused by O$_2$-O$_2$ collisions and a part caused by N$_2$-O$_2$ collisions. Other gasses than oxygen and nitrogen have such small concentrations in our atmosphere that their contribution to the CIA can be neglected [7]. A study of the contribution of CO$_2$-O$_2$ collisions for example found that the contribution to CIA was similar to the O$_2$-O$_2$ contribution [8]. However since the concentration of CO$_2$ in our atmosphere is only 0.04% the net effect is about 500 times smaller.

For the effect of O$_2$-O$_2$ collisions Chagas et al found a value of $(2.3\pm0.7)*10^{-4}$ cm$^2$ amg$^{-2}$ [7]. Others have also successfully determined the O$_2$-O$_2$ collisions at 1060 nm which are collected by Spiering et al [9] with an average value of $(2.49\pm0.28)*10^{-4}$ cm$^2$ amg$^{-2}$. As can be seen from the standard error on this averaged value the spread in the found CIA is quite large. A possible explanation for this might be that water has also has strong absorption in this spectral region. Different pollution levels of water could cause a part of the spread. Also these data are gathered with different methods at different pressures (although most of them use Fourier transform spectroscopy at high pressures). As stated before, no satisfactory model exists and it is uncertain if these different data could be extrapolated to a single value.

Tran et al, quantified the CIA of O$_2$-N$_2$ collisions at the 1060 nm band using Fourier transform spectroscopy at densities from 40-180 amg [10] and report a value of $(1.4 \pm 0.4)*10^{-5}$ cm$^2$ amg$^{-2}$. Although they do not show the spectrum in the paper itself a different paper of the same group shows that the N$_2$O$_2$ spectrum is smaller than the O$_2$-O$_2$ spectrum and seems to have a shoulder close to the peak [8]. A spectrum was reported by Chagas et al. without being able to give a significant absolute value.
There are many reasons why it is still interesting to investigate the CIA at the 1060 nm band in oxygen. It is difficult to check if the spectrum found by Tran et all has no other contributions than N$_2$-O$_2$ collisions (such as water line-absorption). The value they found for the contribution of O$_2$-O$_2$ collisions ($2.74\pm0.03)\times10^{-4}$cm$^2$amu$^{-2}$ seems to lie quite far above the average given before. Furthermore Chagas et all [7] report that collision induced absorptions in the 1060 nm oxygen band contributes to the atmospheric absorption for about 0.22 %. However due to the huge uncertainty in the data they had to conclude that other high-resolution measurements were needed to complement their results. Still they state that the CIA of oxygen could well explain a portion of the gap between the theoretical absorption and measured absorption in our atmosphere. Another reason why the 1060nm band of oxygen is interesting is because this band is present in many satellite instrumentation observing the Earth atmosphere. Therefore a good characterization of this band could improve atmospheric research at this wavelength region.
Chapter 2

Theory

2.1 Collision Induced Absorption

Collision induced absorption (CIA) is the absorption due to the presence of collision complexes in a gas mixture [11]. When two molecules collide their electron densities are disturbed creating temporarily dipoles. This induced dipole may be both magnetic and electric and can hence result in a non-zero interaction with electromagnetic radiation. CIA is less hindered by the selection rules for the transition dipole since collisions reduce the symmetry of the molecules. CIA can thus dominate the absorption under circumstances where the normal absorption process by individual molecules is forbidden.

Similar to the description of thermodynamic properties of real gases, such as pressure, the induced spectra of gases can be expressed as virial expansion:

\[ I = A*N + B*N^2 + C*N^3 + ... \]  

(1)

Here \( I \) is the absorbed intensity and \( N \) the density. The virial coefficients, \( A, B, C, \) etc. represent the absorption of one molecule, two-molecule-collision complexes, three molecules collision complexes and so on. At low pressures, when this expansion is valid, the contribution of the higher order terms is very small, because of the low chance of two or more molecules to form a collision complex. In this report the third and higher terms are therefore neglected.

![Figure 1: A schematic collision induced absorption spectrum](image)

Figure 1 shows a sketch of a typical CIA spectrum. CIA spectra are always diffuse and cover a whole absorption band. This is related to Heisenberg’s uncertainty principle:

\[ \Delta \nu \cdot \Delta t \geq \frac{\pi}{4} \]  

(2)
Since the time of the collisions is very short ($\Delta t \approx 10^{-12}$ s) the uncertainty in the frequency becomes very large. As a result the individual spectral lines are undistinguishable.

In general the high frequency side of the CIA peak drops slower than the low frequency or left hand side in the figure. On the left hand side of the peak, incoming light has two little energy to facilitate the transition. Since energy is conserved, this process needs to take some translational energy from the collision partners. At the right hand side of the peak the energy of the photon is too high and the molecules gain some translational energy. At low temperatures (such as at room temperature) the translation energy is quite limited in most molecules. This limits the absorption on the left side of the peak.

2.1.1 Absorption of oxygen at the 1060 nm band

Oxygen is an unusual molecule. The fact that it has a doubly degenerate ground-state that holds 2 unpaired electrons results in many special properties. According to Hund’s rule the oxygen molecule has a ground triplet state ($^3\Sigma_g^-$) and two singlet states with low energy ($^1\Delta_g$ and $^1\Sigma_g^+$)[12]. Transitions to these lowest excited states lie in the near-infrared and red region respectively. In figure 2 an overview of the potential curves of the oxygen molecule are shown which are obtained from ab initio calculations.

![Figure 2: Potential curves for several quantum states of molecular oxygen from ab initio calculations.][14]

The absorption band that is investigated in this report is the 1060 nm Oxygen band. This band corresponds to a magnetic-dipole transition from the electronic and vibrational ground state to the second electronic excited state and vibrational excited in oxygen. Using term symbols the transition looks like this:
\[ X^3 \Sigma_g^-(v = 0, N') \rightarrow a^1 \Delta_g(v = 1, N') \quad (3) \]

From the selection rules for the magnetic-dipole transitions it follows that this transition is twofold forbidden even for a magnetic dipole transition. It is not allowed to go from a triplet to a singlet state and from a sigma to a delta state [13]. In an isolated molecule the transition is thus extremely weak and made possible only by higher order multipole transitions and mixing of other states (which make the term symbols not exactly true). The transition rate, from one multipole to the next one, decreases by about a factor 1000. This, together with the fact that magnetic-dipole transitions are intrinsically weak to begin with, causes the line absorption to be very small.

There is a small confusion in nomenclature here. The transition described here is said to be a magnetic-dipole transition but in fact forbidden for magnetic-dipoles. The fact that it is forbidden for both electric- and magnetic-dipole transitions causes the smaller terms in the Hamiltonian to become significant and therefore these can no longer be neglected. The approximation used for the term symbols is thus no longer valid. The transition we are left with has a more magnetic character. The transition is thus said to be a magnetic-dipole one because there in no way (yet) of expressing what it really is.

At high oxygen concentrations, where collisions start to play a role, the intensity of the \(X^3 \Sigma_g^- \rightarrow a^1 \Delta_g\) transition is enhanced 1000 times [12]. At the same time the \(X^3 \Sigma_g^- \rightarrow b^3 \Sigma_g^-\) transition does change much less. Theory gives a good qualitative understanding of these selective actions of collisions on these two transitions. In short, spin orbit coupling mixes the \(d^3 \Pi_g\) state character into the ground state[9]. The transition between the \(d^3 \Pi_g\) and \(d^1 \Pi_g\) states is magnetic-dipole allowed and therefore enhances the \(X^3 \Sigma_g^- \rightarrow a^1 \Delta_g\) transition significantly. Interestingly do the transitions to different vibrational levels of the \(d^3 \Pi_g\) vary greatly in strength under collisions. The transition we are looking at, to \(v=1\), is also much stronger than what would be expected from being a intrinsically weak magnetic-dipole transition. Minaev has written a paper on this were he rationalized the surprisingly large \(a^1 \Delta_g\) \((v=1) \rightarrow X^3 \Sigma_g^-\) transition with symmetry arguments in the collision complex[14]. This however falls outside the reach of this more practical orientated internship.

### 2.1.2 CIA at the 1060 nm band in Air

In gas mixtures CIA consists of contributions from all possible collision pairs [15]. However it should be kept in mind that the frequency at which is absorbed is always related to one or multiple transitions in the colliding molecules. At the 1060 nm band of oxygen, a collision pair consisting of 2 nitrogen molecules does not contribute at all. Similarly a collision of a \(N_2\)\(O_2\) collision pair will be 2 times less effective as an \(O_2\)\(O_2\) collision pair, as long as the efficiency of the collision in generating the possibility for CIA is the same. This efficiency however can vary greatly and sometimes the contribution of a heteromolecular collision can even be stronger than from the homomolecular collision. Collision pairs like \(Ar\)\(Ar\), for example, do not support a dipole moment whereas dissimilar pairs such as \(He\)\(Ar\) generally do. In this case the collision complex of two similar atoms lacks the inversion symmetry to support the electric dipole moment. [15] In the transition we are looking at however the homomolecular \(O_2\)\(O_2\) collision is about 10 times as efficient as the \(N_2\)\(O_2\) collision [10].

The Collision induced absorption in an air mixture can thus be described empirically by the following formula [9]:

\[
CIA(v) = N^2 \left( \rho_{O_2}^2 \alpha_{O_2} \rho_{O_2} (v) + \rho_{O_2} \rho_{N_2} \alpha_{O_2} \rho_{N_2} (v) \right) \quad (4)
\]
Here, $N$ is the particle density, $\rho_{O_2}$ the partial pressure of oxygen, $\rho_{N_2}$ the partial pressure of nitrogen and $\alpha$ the collision induced absorption cross-section. These cross-sections are both related to the efficiency of a collision to make a dipole and the amount of molecules in the collision pair that can absorb in that frequency. Note that the second part of formula 4 is the same as the virial coefficient $B$ from formula 1.

### 2.2 Cavity Ring-Down Spectroscopy

Cavity Ring-Down Spectroscopy (CRDS) is a highly sensitive method to measure absorption spectra. According to the Lambert-Beer law the absorption depends linearly on the path length through the sample and it is this relation that causes CRDS to be so sensitive. In normal absorption spectroscopy the minimum absorption that can still be detected is given by the formula [16]:

$$\sigma_{\text{min}}(v) = \frac{(\Delta I/I_0)_{\text{noise}}}{N L}$$  \hspace{1cm} (5)

Here $\sigma_{\text{min}}(v)$ is the minimal detectable absorption cross section (unit is that of an area), $(\Delta I/I_0)_{\text{noise}}$ is the smallest difference in light intensity that can be detected, $N$ is the concentration of the absorber and $L$ the path length. The product $\sigma N$ has an unit per length and is called optical extinction. This quantity is determined in our experiments directly. Increasing the path length will decrease the minimum absorption that can be measured and thus it is said that the sensitivity increases with the path length. In CRDS the sample is placed inside an optical cavity consisting of 2 highly reflective mirrors. Light inside the cavity bounces between these two mirrors and thus obtains a very long effective path length. The effective path length inside an empty cavity only depends on the reflectivity $R$ of the mirrors and the distance $d$ between the mirrors:

$$L_{\text{eff}} = \frac{d}{(1-R)}$$  \hspace{1cm} (6)

Thus with the mirrors 1 meter apart and a reflectivity of 99.99% an effective path length is created of 10 km. However this does not automatically mean a factor $10^4$ increase in sensitivity. Only a limited amount of light is allowed to pass through the first mirror to enter the cavity. In the next sections (2.2.1 and 2.2.2) it will be shown that certain wavelengths will be able to propagate efficiently through the first mirror.

Another advantage of CRDS is that it does not suffer from intensity instabilities of the laser. The absorption coefficient or cross section is namely not determined directly from the intensity. In a CRDS measurement light is in the form of a pulse sent inside the cavity when no light enters the cavity the leakage of light through the second mirror is recorded with a detector. The intensity of the leaked light behaves like a simple first order exponential decay:

$$I(t) = I_0 e^{-t/\tau}$$  \hspace{1cm} (7)

The decay constant $\tau$ is measured and can be translated to the absorption coefficient by using the relation:

$$\frac{1}{\tau(v)} = \frac{c(1-R)}{d} + cN\sigma(v)$$  \hspace{1cm} (8)

Here $c$ is the speed of light. Interestingly this speed plays two different roles in the decay time. A
higher speed will cause photons to reach the mirrors more frequently and thus increase the change that it leaks through. Also a higher light speed will cause the light to pass through more of the sample per second and thus the light will be quicker absorbed. Both processes ultimately cause less light to pass through the mirrors and thus cause a shorter decay. In section 2.2.3 it will be shown how to deduce CIA form this decay constant

### 2.2.1 Coupling of light inside a cavity

Light that wants to enter the cavity first should pass through the first of the two high-reflective mirrors. On first glance it seems that 99.99% of the light is reflected back and lost, making CRDS not profitable. However, due to interference certain wavelengths are allowed with an almost 100% transmission. The way this goes in a CRD cavity is similar to the workings of a Fabry-Perot Etalon. Figure 3 shows a schematic of an ideal etalon consisting of 2 parallel reflecting surfaces.

![Figure 3: A Fabry–Pérot etalon](image)

When a light beam hits the etalon it is split in a reflection \( R_0 \) and a transmitted beam. The transmitted beam travels through the etalon and when it hits the second reflective surface it is split again in a transmitted beam \( T_1 \) outside the etalon and a reflected beam traveling back to the first reflective surface. This process repeats itself until all light that entered the etalon has gone out. Note that the angle \( \theta \) at which the light approaches the etalon is in practice almost zero. The large angle in figure 3 is just to separate the light beams in the drawing.

Inside the etalon the light beam interferes with itself. The phase difference of the light on one round trip through the etalon is given by: [18]

\[
\delta = \frac{4\pi nl \cos \theta}{\lambda}
\]  

(9)

Here \( n \) is the refractive index inside the etalon, \( l \) the length of the etalon and \( \lambda \) the wavelength of the light.
In CRDS the sum of the transmitted light beams (T1, T2, ...) is measured. The amplitudes of the transmitted light beams can be written as:

\[ E_1 = tt'E_0, \ E_2 = tt'r'r'e^{i\delta}E_0, \ E_3 = tt'r'^2e^{i2\delta}E_0, \ldots \] (10)

Here \( E_0 \) is the amplitude of the incoming light, \( t \) and \( t' \) are transmission coefficient of the first and second surfaces and \( r \) and \( r' \) are the corresponding reflectivity coefficients. When going to infinity and assuming that the two surfaces are identical (\( t=t' \) and \( r=r' \)), the sum of the transmitted waves is:

\[ E_T = \sum_{i=1}^{\infty} E_i = \frac{t^2}{1-r^2}e^{i\delta}E_0 \] (11)

The fraction of light intensity that transmits through the etalon is then:

\[ T = \frac{E_TE_T^*}{E_0E_0^*} = \frac{t^4}{(1-r^2)^2 + 4rsin^2(\frac{\delta}{2})} \] (12)

Here it is used that the intensity is the square of the amplitude. Using the relations \( r^2 = R \) and \( t^2+r^2=1 \) function 12 can be rewritten to:

\[ T = \frac{1}{1+Fs\sin^2(\frac{\delta}{2})} \quad \text{with} \quad F = \frac{4R}{(1-R)^2} \] (13)

This function is known as the Airy function with \( F \) the finesse of the etalon. If the reflectivity is very high (close to 1) the finesse becomes very large. This means that the sinus term and the phase within it, starts to play an important role. If the sinus term is zero the transmission goes to 1 and all light is transmitted. If \( \theta = 0 \) the condition when this happens can be easily found from equation (9):

\[ \frac{\delta}{2} = 2q\pi = \frac{2\pi qnl}{\lambda} \] (14)

Here \( q \) is a positive integer. The transmission as function of wavelength has thus a comb-like structure. The width of each tooth of this comb is determined by the finesse. A higher the finesse causes a narrower band of wavelengths that is allowed to travel through the etalon. The range between two close lying wavelength bands that are supported by a cavity is called the free spectral range. It can be easily found that the free spectral range is given by:

\[ \Delta \nu = \frac{c}{2nl} \] (15)

Here \( c \) the speed of light in vacuum and \( \Delta \nu \) the frequency interval of the light.

In theory, the light from a continuous wave laser would almost never overlap with a wavelength supported with the cavity. In practice however it is almost impossible to stabilise the cavity to such extend that the mirrors do not vibrate with amplitudes above 1 nm. Normal vibrations in the system will thus cause the cavity to fit with the wavelength generated by the laser. However these vibrations are, compared to the speed of light and the build-up time of the cavity, slow enough that only 1 wavelength will be triggered at a time.
So far only longitudinal modes were discussed in a parallel plane etalon. However when 2 curved mirrors are used also transverse waves can build up intensity inside the cavity. In the practice of CRDS this is almost always the case, since curved mirrors are used to increase the stability of the cavity. A cavity of 2 curved mirrors supports waves with frequencies given by:

$$v_{qmn} = \frac{c}{2l} \left( q + \left(\frac{n+m+1}{\pi}\right) \arccos \sqrt{g_1 g_2} \right)$$  \hspace{1cm} (16)

Here $q$, $m$ & $n$ are positive integers and $g_i$ the stability parameter of the cavity given by $g_i = \left(1 - \frac{d}{R_{oc,i}}\right)$ with $R_{oc,i}$ the radius of curvature of mirror $i$. In this formula modes with $m=n=0$ are called longitudinal modes. Modes with different $n$ and $m$ are called transverse modes.

An important consequence of the transverse modes is a change in decay time that is not related to the medium inside the cavity. Empty cavity losses depend not only on the reflectivity of the mirrors, but also on the laser beam cross-sectional area within the cavity and at the end mirrors and the associated diffraction losses [20]. The severity of this impact becomes clear when the decay time of an empty cavity is calculated with a variable diffraction loss $\delta_d$. The decay time is than given by:

$$\tau = \frac{t}{c[(1-R)+\delta_d]}$$  \hspace{1cm} (17)

For high reflectivity the diffraction loss, which is very small, still plays a large role. With high reflectivity mirrors, light makes many round trips and at each round trip light will diffract at the mirrors.

Since the transverse modes lie in between the longitudinal modes the free spectral range between them is much smaller so even when using a continuous wave laser it is possible to excite 2 modes at the same time. This may result in a double exponential decay. Due to the different decay times transverse modes can be a major source for “systematic noise” in the gathered data.

### 2.2.2 Mode-matching in Cavity Ring-down Spectroscopy

Cavity ring-down spectroscopy can be made more stable by matching the incoming laser-beam with one of the cavity modes [19]. Mode matching reduces the number of transverse modes that are excited in the cavity. Also it becomes easier to build up light intensity in certain modes and the probability of exciting multiple modes at single or consecutive measurements is reduced. This enhances the sensitivity of the setup noticeably.

In order to match the incoming light with the cavity the waist of the incoming beam must be at the same spot and size as the waist of the cavity. This condition can be matched using some optical elements. If the laser beam is Gaussian to start with, only 1 confocal lens is required. However in practice often 2 lenses are used since the proper position or strength of the single lens is far outside the practical range. Also a “wave-transformer” may be used to change the shape of the incoming light beam to be more like a Gaussian beam.

Calculating the correct position and properties of the optics required for mode matching can be done using classical electrodynamics. A special beam-like solution from Maxwell's equations is called a Gaussian beam[21]. At a Gaussian beam the intensity of the beam goes down from the centre like a characteristic Gaussian-curve. A Gaussian beam is completely parameterized by a complex beam-parameter $q$: 

$$q = \sqrt{\frac{\omega_0^2}{\pi^2}}$$
\[ \frac{1}{q} = \frac{1}{R_{oc}} - i \frac{\lambda}{\pi \omega^2} \]  

(18)

Here \( R_{oc} \) is the Radius of Curvature of the wavefront, \( \lambda \) the wavelength and \( \omega \) the radius of the beam. The wavefront specifies where the beam is in equal phase. For a diverging Gaussian beam, the radiation in a plane perpendicular to the direction of the traveling wave does not have the same phase. Light at the outside of the beam had to travel further to reach the plane and is thus behind in phase. The wavefront connecting positions with constant phase is curved. The beam-waist, \( \omega_0 \), describes focusing of the beam. The magnitude of the waist is normally taken as two times the standard deviation of the Gaussian intensity distribution. At the focal point the beam-waist is at its minimum and the radius of curvature goes to infinite. Here \( q \) is purely imaginary.

In figure 4 a schematics is shown of a mode matching system containing a single lens. In this schematics \( f_1 \) is a lens with focal length \( f_1 \), \( W_i \) is the beam-radius of the laser, \( W_0 \) the beam-waist supported by the cavity, \( d \) the cavity length, \( d_2 \) the distance between the cavity and the lens and \( M_i \) the mirrors with radius of curvature \( R \).

![Figure 4](image)

Figure 4: A schematic representation of a mode-matching system containing a single lens and an optical cavity.

In order to calculate the required position (\( d_2 \)) and magnitude of \( f_1 \) of the lens the beam parameter \( q \) should be known of the beam at the laser and of the beam supported by the cavity. Inside a cavity the beam waist of the TEM\(_{00} \) mode can be calculated with the formula:

\[ \omega_0 = \sqrt{\frac{d \lambda}{\pi} \left[ \frac{g_1 g_2 (1 - g_1 g_2)}{(g_1 + g_2 - 2 g_1 g_2)^2} \right]^{0.25}} \]  

(19)

If the two cavity mirrors have the same radius of curvature Equation 19 can be rewritten as:

\[ \omega_0 = \sqrt{\frac{d \lambda}{\pi} \left( \frac{g^2 - g^4}{(2g^2 - 2g^4)^2} \right)^{0.25}} \]  

(20)

At the position of the beam-waist the complex beam parameter is now completely defined. At the beam-waist inside the cavity \( q \) is given by:

\[ q_0 = id \sqrt{\frac{g^2 - g^4}{(2g^2 - 2g^4)^2}} \]  

(21)

So to calculate the beam supported by the cavity only the \( R_{oc} \) of the mirrors and the distance between them is needed. It is more difficult to describe the beam coming from the laser correctly. The best method would be to measure the radius of the beam at two positions.
When the parameters of the initial and final beam are known a calculation can be made to determine the distance between the mirror and the lens (d2) and the strength of the lens (f1). The easiest way to do this is by using ray transfer matrices. One of these matrices can be used to calculate the change in the q-parameter when light moves through an optical component. When multiplying ray transfer matrices, the laser light can be traced through the whole optical system.

For the system of figure 4, four ray transfer matrices are required. Going from the center of the cavity to the opposite side of the lens the light first propagates to the mirror. Then it goes through the mirror. Third it propagates to the lens and in the end passes through the lens. In ray transfer matrices it looks like this:

\[
\begin{bmatrix}
1 & d2/2 \\
0 & 1
\end{bmatrix} \times \begin{bmatrix}
1 & 0 \\
2/R & 1
\end{bmatrix} \times \begin{bmatrix}
1 & d2 \\
0 & 1
\end{bmatrix} \times \begin{bmatrix}
1 & 0 \\
-f1 & 1
\end{bmatrix} = \begin{bmatrix} A & B \\ C & D \end{bmatrix}
\]  

(22)

Notice here that the mirror acts as a diverging lens with a focus half of the radius of curvature. This factor 2 is because only one side of the mirror is curved. With the generated ABCD-matrix we can now equate qi to q0 like:

\[q_i = \frac{(AQ_0 - B)}{(CQ_0 - D)}\]  

(23)

This equation has solutions for f and d2 when \(\omega_i > \omega_0\).

The same theory can be applied for focusing with 2 lenses. In that case 2 additional matrices have to be used for the propagation between the two lenses and the second lens itself. In paragraph 4.6 I will quantitatively analyze the use of a lens for mode matching and argue the position and focal distance of the used lens.

2.2.3 Determining the collision induced absorption from decay signals

The signal from a CRDS setup is typically a voltage that is proportional to the light intensity behind the cavity. The time between each data point depends on the sampling rate and the amplitude of the signal depends on the light intensity leaking through the second cavity mirror and on the sensitivity of the photon-detector. In order to find the exponential decay in the signal a fit can be made with the following function:

\[I = x1 \times \exp(t \times x2) + x3\]  

(24)

Here x1, x2 and x3 are the parameters to be determined and t is the time between the data points. From this fit x2 is the exponential decay that carries all information about the absorption. x1 and x3 represent properties of the detector. x1 gives the linear relation between the light intensity and voltage. x3 is the signal from the detector at zero light intensity (offset).

After the exponential fit the decay (x2) can be translated into extinction. This step divides equation (8) by the speed of light. What is left is the extinction with the units per meter:

\[\sigma'(N) = \frac{1-R}{a} + \sigma''(N)\]  

(25)

Here R is the effective reflectivity of the mirrors, \(\sigma'\) is the extinction and \(\sigma''\) is the extinction that is depended on the density N. The advantage or the strength of expressing the extinction this way is that the absorptions due to the cavity and due to the sample are separated. The \(\sigma''(N)\) is now equal to the virial expansion of equation (1). The linear component of \(\sigma''(N)\) is caused by absorption and scattering from single molecules. Here we
see another strength of the method. Scattering is linear in density N, whereas the quadratic component is caused by the collision induced absorption. The linear components of the extinction, due to scattering and line absorption, can be theoretically calculated and subtracted from the data. A quadratic fit of $o'(N)$ then results in an offset caused by the cavity and the collision induced absorption cross-section at a fixed wavelength. To make a quadratic the extinction must be determined for different densities. In order to get the CIA-spectrum this whole procedure has to be repeated for different wavelengths.

The last step is to integrate over this spectrum to give the integrated collision induced absorption coefficient which is a measure for the CIA of the whole peak. Ideally it would be to fit the gained spectrum to a general shape. However, since the CIA spectrum is a complex sum of broadened peaks over each spectral line in the absorption band, this is not possible. In some papers the CIA is fitted to a “skewed” Lorentzian [1, 3 & 9]. This is then a Lorentzian with two different widths at both sides of the peak. Whether this is the proper way to integrate the spectrum is questionable. Is it legitimate to force a complex function to a Lorentzian line shape and if so what is the error involved in doing so? Since these questions cannot be answered easily it was chosen in this report to interpolate and extrapolate the spectrum before integrating it. Also the skewed Lorentzian did not follow the curve in the data properly.
Chapter 3

Experimental setup

A schematic of the experimental setup is shown in figure 5. Fig. 5 shows all optical and electronic components, the path of the light (red) and the connections between all components (black). As light source a Toptica DL100 grating stabilized diode laser was used (continuous wave). The diode itself was the LD-1060-0150-AR, an AR coated semiconductor laser diode with an output power of 170mW in the spectral range of 9259-9569 cm\(^{-1}\). Inside the casing of the laser an optical isolator was placed to stop the reflecting light from the cavity mirrors to enter the laser. Just outside the casing ~2% of the beam was split of using a glass plate. The reflected bundle was then guided into a wavelength meter.

Figure 5: A schematic representation of the cavity ring-down spectroscopy setup used in these experiments.

The cavity mirrors were placed inside a pressure cell which was designed to hold pressures from \(10^{-3}\) to 7 bar. The pressure inside the cavity was measured using a diaphragm pressure detector (Pfeiffer Vacuum D-35614). The gas flow to the pressure cell was controlled by a Digital Thermal Mass Flow Controller (El-Flow, Bronkhorst high tech). The outlet for the gas was connected to a membrane pump (Pfeifer Vacuum MVP 055-3) with which it was possible to reach pressures as low as 1 mbar. The cavity mirrors (Layertec) had a reflectivity higher than 99.993\% in the range of 9100-9900 cm\(^{-1}\) and had a radius of curvature of 8000 mm. The mirrors could be aligned with the use of mechanical motors. The mirrors where separated by approximately 350 mm, creating an effective path length of about 5 km. The decay time of an empty cavity should than be about 17 \(\mu\)s. Directly behind the cavity the light signal was captured with an avalanche photo-diode.

The signals from the pressure- and photo-detector were transmitted to an oscilloscope. The signal from the photo-detector was also sent to a SRS signal generator. This generator was triggered when the signal from the photo-detector reached a certain threshold level. Upon reaching this threshold
the signal generator sends out a trigger signal to the oscilloscope and sends a 4V signal of 500 μs to the laser. This shuts the laser off so the light in the cavity could decay exponentially. To types of gasses were used: purified Oxygen (6.0 purity) and dried pressurized air (Linde).

3.1 Measuring
Before starting the real measurements an accurate alignment procedure was finished with establishing the decay-times at low and high pressure. From these times the proper settings for the scope could be determined so that between 3 and 15 decay times would fit in the data range. This ensures a good exponential fit of the data (see paragraph 4.1). The amount of data points per decay signal varied between 2000 and 4000 and total time of the dataset varied between 150 and 300 μs. The flow rate of the gas was set to a fixed value between 200 and 250 ml/min.

After all scope settings were fixed the pressure signal in volts was calibrated to the pressure in mbar. This was done by measuring the pressure on a pressure ramp from 0 to 8 bar every 0.1 bar. The relation between pressure signal and real pressure was then fitted to a linear function and it was checked that the quality of the fit was high enough (R²>0.9999).

For the measurements the routine was as follows. First a wavelength was selected without line-absorption by oxygen and water. This makes the uncertainty due to an unknown water contamination or a faulty calculated absorption very small. Then the pressure was lowered to its minimum (about 2 mbar). The pressure ramp was started together with the data gathering. At each pressure ramp 1500-2000 decay-signals were recorded together with the pressure signal. The measurements were stopped when 2000 signals were recorded or when the pressure had reached 8 bar. During the pressure ramp the rate was kept at about 3 decay signals per second. This rate was maintained by changing the threshold level on the SRS signal generator or when the thresholds was at its boundary, the voltage over the photon-detector was changed increasing its sensitivity. The limits of the threshold were -0.20V which is a minimum for a “good” the exponential fit (see paragraph 4.1) and -2.56 V, the maximum setting of the signal generator. Note that the signal response of the detector is negative. The standard value for the voltage over the detector was 300 V and was changed in the range of 230-320 V.

In total between 30 and 65 pressure ramps were done on different wavelengths to measure the spectrum. This was done once for pure oxygen and trice for air, which proved to be a lot harder (see paragraph 4.4 and 4.5). For the last measurement in air a lens (focus 25 cm) was added at about 13 cm in front of the cavity. Additionally some test measurements were performed on Oxygen, Air and Argon to evaluate the quality and consistency of the set-up to determine very weak absorption signals (paragraph 4.1 and 4.3).

Using a self-made LabVIEW program (CWCRLDsmark.vi) the signal from the scope was captured on the computer. In LabVIEW the light intensity signal and the pressure signal were saved in separate files for each pressure ramp. For utility reasons, the program also displayed a crude exponential fit to the captured decay signals and together with several other important experimental parameters such as the pressure and fit residue. A decay signal with a high residue was immediately filtered out of the resulting data matrix. These were signals at which 2 transverse cavity modes were excited at the same time. The pressure calibration was done in a much smaller (and faster) program that recorded the voltage signal from the pressure meter at the mouse click. The data files from LabVIEW were then analysed using MATLAB. Here also the absorption from oxygen and water was calculated using the data from the HITRAN database and the Rayleigh scattering was calculated based on an article
Chapter 4

Results and Discussion

In paragraph 4.1, I will describe a number of relevant experimental tests that provide a background to appreciate the origin of noise and the sensitivity of the instrument. These tests explain the chosen experimental procedure.

Paragraph 4.2 contains the result and discussion of the measurement on oxygen. These were successful but this experiment is concluded with the statement that more sensitivity is needed for the measurements in air, where CIA will be about 25 times weaker than in oxygen (see Equation 4). In the next paragraph various methods were tested to improve this sensitivity. The main focus here was to reduce the number of transverse cavity modes that were excited (see also paragraph 2.2.1).

After these test an improved measurement method was found that improved the sensitivity enough to measure the lower CIA in Air. After two attempts to measure air (paragraph 4.4 and 4.5), it was concluded that the coupling of light into the cavity was not stable enough to get the desired integrated CIA coefficients.

To improve the stability the theory of mode matching from paragraph 2.2.2 was applied and tested in paragraph 4.6. Due to experimental difficulties and time-constraints it was decided to continue measuring with an imperfect mode-matching. The results are shown and discussed in paragraph 4.7. These results show that even though the mode matching was not perfect still a remarkable improvement was made in comparison to the first 2 measurements on air. Then finally, the last paragraph contains an elaborated discussion of the results, were I go into detail of all systematic and statistical errors. Also some ways to improve future measurements are discussed there.

4.1 Testing on oxygen

There were several things that needed to be tested before the real measurements could start. The results of the testing here do not directly affect the end results of the integrated CIA coefficients. However the results directly influenced how the measurements were performed and greatly enhanced the quality of the final results. For the sake of the length of this report only test that affected the measurement method are discussed here. But also possible effects of flow speed, of the offset found in the light-detector and of the sampling rate of the data acquisition system have been studied.

An important test was doing measurements on different threshold levels on the SRS signal generator, while keeping everything else constant. Lower thresholds mean that less light intensity is required to trigger the scope. This results in an higher trigger rate. A higher threshold on the other hand makes it easier to fit an exponential decay because more data points will lie above the noise line and the data points will generally lie further away from it as well.

The results of this test are shown in table 1. Hundred measurements were done at each trigger level while keeping the pressure constant at 2 mbar. From the results it is clear that increasing the threshold level decreases the spread in the measured decay times significantly. In the measured regime of -0.20 V to -0.45 V the relation to the standard deviation is more or less linear. For higher thresholds this trend will probably saturate before it reaches zero but this was not tested since the
laser was not strong enough at the used wavelength. From this test it was concluded that it was worthwhile to set the threshold as high as possible as long as the measuring rate is kept at a decent level (about 3 Herz). Also it is better to measure with a threshold level of -0.20 or lower since the average decay time for -0.15 V is far below the average of the rest. The fact that the decay time itself was affected points at a systematic error for which higher thresholds at least partially correct (?)

<table>
<thead>
<tr>
<th>Threshold (V)</th>
<th>Average decay time (10⁻⁵ s)</th>
<th>St. dev. decay time (10⁻⁵ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.15</td>
<td>3.13</td>
<td>0.023</td>
</tr>
<tr>
<td>-0.25</td>
<td>3.16</td>
<td>0.019</td>
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<td>0.019</td>
</tr>
<tr>
<td>-0.35</td>
<td>3.18</td>
<td>0.016</td>
</tr>
<tr>
<td>-0.4</td>
<td>3.19</td>
<td>0.017</td>
</tr>
</tbody>
</table>

Table 1: results from test measurements of the decay time in an empty cavity. 100 measurements were done at each threshold setting.

Another important setting in the setup is the time/division on the scope or put differently: the amount of decay times that will be used in the fit. A fit was made through different traces taken at different pressures. From the selected traces a fit was made to different fractions of the total trace. Two results of this are shown in table 2. Here the amount of data points, the calculated decay time (s) and the amount of decay times in this fitting period are shown. Note that these traces were taken at different pressures and thus have different absorptions.

<table>
<thead>
<tr>
<th># datapoints</th>
<th>Decay time (μs)</th>
<th># decay times fitted</th>
<th>Decay time (μs)</th>
<th># decay times fitted</th>
</tr>
</thead>
<tbody>
<tr>
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<td>7.85</td>
<td>0.12</td>
<td>14.8</td>
<td>1.09</td>
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<tr>
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<td>2.51</td>
<td>0.23</td>
<td>15.0</td>
<td>2.20</td>
</tr>
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<td>0.36</td>
<td>15.0</td>
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<td>15.2</td>
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<td>2000</td>
<td>1.69</td>
<td>2.48</td>
<td>15.2</td>
<td>22.23</td>
</tr>
</tbody>
</table>

Table 2: The fitted decay times when fitting over different sections of the whole decay signal. The results of 2 decay-signals are shown. Also the amount of decay times that is within the fitted section is given.

From the results shown in Table 2 the conclusion is that in the range of 4-22 decay times fitted no significant change in decay time occurs. Even when the amount of data points fitted is reduced by a factor of five when going from 22 to 4.4 decay times. This also shows that 2000 data points per trace is more than enough. For data fits from data less than 2.5 decay times the results have much deviation thus the fitting doesn’t seem to work that well. In between the 1.8-4.4 regions there is a grey area were the deviation can be explained also by a lack of data points fitted. This leads to a conclusion that at least 3 or 4 decay times should be used. There seems to be no real maximum but it might be wise not to go over 25 decay times. This in order to assure a significant amount of data points to lie above the noise line.
The last important thing before the real measurements could begin was to determine the effect of the line-absorption compared to the expected CIA. If the line-absorption is high the error that will be made in calculating this effect will be large as well. Also it will be more difficult to get signals if the absorption is too high. If more light is absorbed, the intensity build up in the cavity is reduced and the maximum intensity output from the cavity will be lower.

In figure 6 a plot is shown with the CIA of oxygen from the data of Chagas et al [7] together with the absorption spectra of oxygen and the spectrum of water assuming a contamination of 25 volume per million (vpm). This contamination value is the maximum contamination level of the dried Air from Linde. All data are shown for a pressure of 1 atm. Both absorption spectra were taken from the HITRAN database [22]. The reason why water features were plotted as well is because water is in practice always difficult to remove completely. In fact it might be possible that the actual H$_2$O concentration in the pressure cell is much higher than the 25 vpm of the gas. Also water has many strong absorption lines in the near infrared.

From figure 6 it is clear that the absorption of oxygen is indeed very small compared with the collision induced absorption. This was explained in the theory (paragraph 2.1). The spectrum of water is also very small in figure 6. This is because of its small concentration. Unfortunately the spectral lines of water lie at the edge of the peak, so were the CIA is small as well. Therefore the water spectrum might still interfere with our experiment. However the possible effect from water contamination can be neglected if the measurements are done in between the spectral lines of water. Just to be certain the peaks in the oxygen spectrum were also avoided. In Appendix 1 a list is shown of the wavelengths were measurements could be done together with a list of the most prominent peaks in the oxygen spectra.

![Figure 6](image.png)

Figure 6: The CIA spectrum of air plotted with the absorption spectra of O$_2$ and the spectra of H$_2$O at a contamination level of 25 vpm [7, 22]. The pressure is 1 atm. Note the fact that CIA is much stronger than the line absorption at this pressure.
4.2 Collision Induced absorption of Oxygen

In figure 7 the measured CIA spectrum of pure Oxygen is shown. The spectrum is shifted down so that the lowest absorption (at 9091.9 cm\(^{-1}\)) was zero. This was needed since there was a constant offset of about 5.2 \(\times 10^{-8}\) cm\(^{-1}\) amg\(^{-2}\). In the results for air (paragraph 4.4 and 4.5) it will be shown that this offset is not constant. However the size of the offset change is less relevant for the CIA spectrum of pure oxygen, which is about 25 times higher. Therefore more information about this offset is given at the results of air. For the moment I will only justify the subtraction by the shape of the CIA spectrum. Looking at the lowest point it seems correct that this should be zero. The two next lowest points are only \(10^{-9}\) cm\(^{-1}\) amg\(^{-2}\) higher than the first point so the absorption curve is more or less flat there. The error bars in figure 7 correspond to 4\(\sigma\) error on the quadratic fit and do not include systematic effects.

The total integrated CIA coefficient requires an extrapolation of the recorded spectrum for the higher wavenumbers. This was done with a self-build extrapolation program that assumes the curve can be written as a third degree polynomial. The reason why the program was homemade was twofold. There were some additional bounds set by nature to which the extrapolation should apply and it needed the possibility to do error propagation. The additional bounds that were used are simple: the absorption does not rise when going away from the peak and does not go below zero. Both these bounds and the error propagation are not straightforward to implement in the existing extrapolation algorithm of MATLAB.
A plot of the extrapolation together with the 4 sigma confidence interval is plotted in figure 8. For the extrapolation third degree polynomial fits were made using different amount of data points. From each fit the error was propagated along with each step in the fitting and extrapolation procedure. Fits that did not reach zero absorption at some point were thrown away since the peak is expected to go down to zero [7]. The resulting graph is an average of all these fits over different amount of data points. The error is the maximum and minimum of those individual fits together with their error. This procedure creates quite a reasonable result although the fit might have gone down a little bit slower. The reason for this fast decrease is because the last (and most important) point of the original data was slightly below the imaginary curve.

The resulting integrated collision induced absorption cross-section is then \((2.08\pm0.14)\times10^{-4}\) cm\(^2\)amg\(^{-2}\). The error displayed here is purely statistical 4 sigma. The only significant error left is that from the offset. This error is at least the size of the error in the first data point end that integrated to the highest wavenumber (9683 cm\(^{-1}\)). The first data point at 9092 cm\(^{-1}\) has a measured CIA of \((5.22\pm0.27)\times10^{-8}\) cm\(^{-1}\)amg\(^{-2}\). Integrating this over all wavelengths of the spectrum gives an additional error of \((1.60\times10^{-6}\) cm\(^{-2}\)amg\(^{-2}\).

The final result for the integrated collision induced absorption cross-section is thus \((2.08\pm0.15)\times10^{-4}\) cm\(^2\)amg\(^{-2}\). This is a bit lower than the average of other measurements \((2.49\pm0.28)\times10^{-4}\) cm\(^2\)amg\(^{-2}\)[9]) but still within the error region. This lower value is partly caused by the extrapolation which (although much effort) seems to be a low. Another reason is probably that our measurement was different compared to the others in two ways. This experiment is the only one done at low pressures and we avoid absorption by water pollution by measuring in between the spectral-lines of water. As
stated earlier in the introduction no satisfactory model exists and extrapolation from high pressures to atmospheric pressure may cause errors.

Although these data are of very high quality, the measurements on oxygen are not sensitive enough for the experiments using air mixtures. In air the CIA is namely about 25 times lower (due to the square of the density). This can best be shown when looking at the $R^2$ values of the quadratic fits from the CIA of oxygen. These are displayed in figure 9. Here it can be seen that the $R^2$ parameter of the fit quickly drops for CIA values below $10^{-7}$ cm$^{-1}$amg$^{-2}$. In air the CIA at the peak would be around $0.5 \times 10^{-7}$ cm$^{-1}$amg$^{-2}$. Therefore it is clear some improvements have to be made before the measurements on air can be started.

![Figure 9](image9.png) **Figure 9**: the $R^2$ fit parameter plotted against the magnitude of the collision induced absorption.

![Figure 10](image10.png) **Figure 10**: the extinction plotted against the density for the measurement at 9162 cm$^{-1}$. The red line is the quadratic fit and the black line is the contribution of the Rayleigh scattering and normal absorption. Note the fact that similar parallel results are observed.

### 4.3 Reducing the number of excited modes

In figure 10 the source of an important error can be appreciated. Instead of 1 quadratic line several quadratic trends can be seen forming a broad band. These individual lines do not seem to be completely parallel to each other. Some lines appear and/or disappear during the pressure ramp. These different lines are attributed to exciting different transverse modes. As stated earlier (paragraph 2.2.2) different transverse modes have slightly different extinctions due to different cross-sectional areas inside the cavity and at the cavity mirrors.

The way to improve the quality of the fit and the quality of the experiment is either to reduce the amount of transverse modes that are excited in the cavity or to be able to select from the data the results of single mode excited decay transients. Our first hypothesis was that a narrower beam would trigger less transverse modes since the cross-sectional area of the laser spot on the mirrors was...
reduced. To test this several experiments were done with different diaphragm settings. At each measurement the pressure was kept constant and 1000 traces were taken.

In figure 11 four plots are shown showing the distribution over the different modes. In figure 11a the diaphragm was open and about 10 modes can be distinguished. When the diaphragm was narrowed (figure 11b) a new mode appeared at a lower extinction but still the number of modes halved.

Initially I concluded that the hypothesis above is true. However at a new alignment (figure 11c and d) also a test was done at a lower detector voltage. Here it can be seen that a lower detector voltage, or lower sensitivity of the detector, also lowers the amount of modes.

These results prove that the hypothesis is partly true. Indeed placing a diaphragm in the setup narrows the beam spot on the mirrors and changes the modes that are excited slightly. However the reduction in the amount of modes is not caused by this but by a lack of intensity/sensitivity that allow fewer modes to reach the threshold level.

Moreover in figure 11 it can be easily seen that the extinction when selecting a single mode (by isolating one of the lines) is normally distributed. The error at a single mode is thus just caused by Gaussian noise on the detector. Hence we conclude that if we would manage to excite only a single mode the noise band in the CIA measurements will be reduced by a factor 10.

Later during the internship mode matching was used to achieve single mode excitation but at this point reducing the sensitivity was the best option. Some tests were performed to look for the best way to do this and it turned out that it was the easiest to change the threshold level. At a measurement the negative threshold is set as low as possible so that as few modes as possible would be able to reach the value. Then during the pressure ramp more and more absorption occurs and the negative threshold is raised accordingly, keeping the trigger rate constant.

![Figure 11: four histogram plots from the extinction at constant pressure. a) the diaphragm open, b) narrow diaphragm, c) low detector voltage, d) optimized conditions.](image-url)
the diaphragm at 0.5 cm. Then for a different alignment: c) diaphragm open and d) diaphragm open but lower voltage over the detector (from 300 V to 200V).

4.4 First measurements in Air

In figure 12 the total CIA spectrum of air is shown in black. In this figure also the contributions of O₂-O₂ collisions (red) and N₂-O₂ collisions (blue) are shown. The contribution of O₂-O₂ collisions in the air mixture was found from the spectrum for pure oxygen from figure 8. The spectrum was lowered with a factor 0.21² to account for the oxygen concentration in air. The N₂-O₂ spectrum is just the spectrum of Air minus the O₂-O₂ spectrum and the error displayed is the sum of the statistical errors from the two spectra. Just as with the oxygen spectra an offset was removed by setting the lowest absorption to zero.

![Figure 12: The first measured collision induced absorption spectra of air (black), the contribution of O₂-O₂ collisions (red) and the remaining contribution of N₂-O₂ collisions (blue). The error bars give the statistical 4σ interval on the quadratic fit.](image)

This however poses a question: what is the lowest point in the spectrum? The lowest values for the peak on the left side seem to oscillate due to some systematic error. Moreover many of the lower CIA values had a quadratic fit with a $R^2$ value lower than 0.1. In other words no quadratic relation could be found at those measurements. One of the reasons for this can be seen in the measurement related to this lowest CIA (figure 13). Here a large jump in extinction can be seen at 1.8 amagat. This jump is also present in other measurements in the lower end of the spectrum but the severity of the impact of the fit changes from measurement to measurement. Probably this is the source for the fluctuations at the left side of the spectrum. This jump in extinction is something that was seen quite regular in the test measurements. It
occurred between 1.5 and 2.5 amagat and its cause is still unknown. At the moment the best guess is that due to the increase in pressure a sudden shift is caused in the entrance flange of the of the pressure cell. Such a motion may cause the light to enter the cavity at a slightly different angle, exciting different transverse modes with different effective extinctions.

Figure 13: The CIA measurement at 9137.03 cm⁻¹ which had the lowest absorption. The red line is the quadratic fit and the black line is the contribution of the Rayleigh scattering and normal absorption.

At this point it is clear that the results shown in figure 12 are not sufficiently reliable for determining the contribution of O₂-N₂ collisions to the total CIA in air. In order to still be able to find some value the extinction jump was eliminated by only using extinctions above 2.5 amagat. The results are shown in figure 14. By using this elimination all R² values were increased significantly. The lowest is now 0.3 which is still not good but certainly better than before (where we found values down to 0.0007).

The spectrum itself looks a lot smoother but also jumps in offset become much more evident. Two possible causes for the offset are dust particles in the gas and a pressure effect on the cell that causes different modes to be excited at different pressures. The effect of the possible presence of dust particles must be the same for all measurements and should be linear to the pressure. The effect of little deformations of the cell due to the pressure could go in every direction. The reason for the jumps was not known at this point but after the second measurement on air (see below) it was thought to be related to the turning of the grating of the diode laser. During a series of measurements the grating had to be turned in order to be able to reach a next section of wavelengths. It is not hard to imagine that the turning of the grating causes a shift in alignment and thus due to pressure effects, a shift in offset. An aspect of the data that increases the confidence in
the results is the observation that the O₂-N₂ CIA spectrum is non-zero in a smaller wavenumber range than the O₂-O₂ spectrum. This observation has also been made by Tran et al [8].

Figure 14: the first measured collision induced absorption spectra of air (black), the contribution of oxygen-oxygen collisions (red) and the remaining contribution of nitrogen-oxygen collisions (blue). Only the extinctions of pressures above 2.5 amagat have been taken into account. The error bars give the statistical 4σ interval on the quadratic fit.

4.5 Second measurement in Air
In order to improve the first measurements multiple adjustments were made. The most important was the change in alignment, which was improved to give better quadratic relations. In general it was possible to change the angle of the mirrors for a small range without losing the amount and strength of the decay signals. Within this range of angles an set of angles was chosen that did not show the jumps in extinction during a pressure ramp. Furthermore it was decided to go to higher pressures 8 bar (instead of 7 bar) and to increase the amount of wavelengths to measure at (64 instead of 38).

In figure 15 the results are shown, in order to plot these results the same procedure as for figure 12 was used. Although the fitting parameters are again much better (lowest 0.5) it is still not possible to determine the CIA cross-section from this. The data points seem to lie on a smooth curve that drastically shifts 2 times at 9180 and 9400 wavenumbers. Note that although the shift at 9400 cm⁻¹ is at the same position as a shift in the first measurement the direction is in the opposite direction. This excludes the possibility that it is caused by the nature of the gas.

During the measurement the grating of the laser was turned two times in order to be able to record the full spectrum. Although at the time no record was made of these turnings (since it was not
supposed to matter) it was remembered that one of those turns happened around the peak of the spectrum (about 9400 cm$^{-1}$). This could be a mere coincidence but it could also be the thing that causes the shifts. As said before, turning of the grating may induce a slight change of alignment. At different alignments different modes get excited, possibly changing the offset.

![Figure 15: the second measured collision induced absorption spectra of air (black) the contribution of oxygen-oxygen collisions (red) and the remaining contribution of nitrogen-oxygen collisions (blue). The error bars give the statistical 4σ interval on the quadratic fit.](image)

4.6 The calculated lens positions and strengths for mode-matching

From the above results it was concluded that the best change to improve the results was to eliminate as many modes as possible and align the cavity to give the lowest transverse mode. The simplest way is to use one or two lenses to match the incoming laser beam to the longitudinal modes of the cavity. Using the theory described in paragraph 2.2.2, predictions were made for the optimal position and strength of the lens. Although in theory it is possible to find the optimum mathematically some problems occurred during the optimization. The used program for the calculations was MATLAB which seems to have difficulties in fitting two or more variables at once. Also the complex nature of the beam parameter q which has a real and an imaginary part made the fitting more difficult. When trying to solve equation 23 no values for the focus and position of the lens were found. In order to solve this, a reverse approach was used. Multiple lenses and distances were tried and then the difference between the incoming beam and the beam inside the cavity was minimized. For one lens the results of this minimization are shown in table 3. In the calculations, lens strengths were used of lenses that were already available. The used positions ranged from 1 cm to 1 meter in front of the cavity, the practical limits of the setup. The assumption was made that the incoming laser beam was parallel and had a focus ($w_0$) of 2 mm. In the minimization the real part of the q-parameter
(the position of the focal point) was optimized.

<table>
<thead>
<tr>
<th>Lens (m)</th>
<th>Best position (m)</th>
<th>ΔR(q)</th>
<th>ΔI(q)</th>
</tr>
</thead>
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<td>0.75</td>
<td>0.45</td>
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<td>11.31</td>
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Table 3: the minimisation results for mode-matching with 1 lens. The best position gives the distance between the cavity and the lens. ΔR(q) and ΔI(q) are the differences in the real and imaginary part of the q-parameters for the incoming wave and the wave supported by the cavity.

The calculated best distances show a logical trend. All lenses with a focal length under 15 cm are too strong to have the focus point overlap with the focus within the cavity. This can be seen in the difference of the real part of q: this is larger at stronger lenses. This indicates that the radius of curvature (R_{oc}) of the beam and the wave supported by the cavity do not overlap. Since the real part of q is the inverse of the RoC, q_{0} at the center of the cavity has only an imaginary part. This imaginary part says something about the radius of the beam. Using equation 21 the calculated beam parameter at the center of the cavity was found: q_{0} = 1.085i. This corresponds to a beam waist of 0.605 mm. However the radius of the incoming beam at the center of the cavity depends strongly on the radius at the laser. If the radius of the laser-beam is estimated to be between 1 and 2 mm the resulting q ranges from 2.86i to 11.85i respectively. This is the reason for the value of 11.85i difference in the imaginary part of the q-parameters in table 3. However it can be seen that at the weaker lenses the difference in radius decreases. Thus a weaker lens corresponds to a larger decrease in radius at its focal point. From the trend in table 3 it was estimated that a perfect matched lens would have a focal point of several meters. This is rather impractical since those lenses
are not available/easy to make and the placement would have to be outside the setup. If a perfect match would be required at least 2 lenses are needed. A table with some results for 2 lenses can be found in appendix 1. However in order to match the beam waist exactly the radius of beam at the laser has to be known with high precision as well. To get this radius it can be measured with a power meter and a digital “beam” shutter, this however was not possible in the time span of the internship. Another alternative is to use a pinhole. Unfortunately this would also mean a severe intensity loss, making it impossible to measure the CIA. It was thus concluded that the best option would be to first try it with one lens.

In practice the placement of the first lens was quite difficult since it implemented 5 new free parameters: the x, y, z-position and the rotation of the lens. This, together with the fact that cavity mirrors where rotated using very old and coarse motors, made it very difficult to align everything in the lowest modes. Due to this and the upcoming death-line for the project it was decided to measure with this single lens even if this would mean an imperfect alignment.

### 4.7 Last measurements in Air using a mode-matching lens

With the addition of a 0.25 m lens at about 13 cm in front of the cavity new measurements were performed. In figure 16 the raw results are shown. Again the lowest extinction was said to be zero to account for an offset. The curve looks quite good but displays a few oddities. At the highest 5 wavenumbers there seems to be a shift again and at the lower wavenumbers there seems to be some strange oscillations. That and all those values lie far above the curve of pure oxygen. The part of the spectrum from N₂-O₂ collisions looks reasonable as long as the edges (where this should be almost zero anyway) are ignored.

![Figure 16: the second measured collision induced absorption spectra of air (black) the contribution of](image-url)
The error bars give the statistical 4σ interval on the quadratic fit.

The reason for the behavior at the edges of the spectrum can be found when looking at individual measurements. In figure 17, 6 measurements at different wavelengths are displayed. When looking at the measurements the first thing that strikes the eye is the low amount of modes in comparison with figures 10 and 13. In most measurements only 2 modes can be distinguished. The measurement that gave the lowest absorption (at 9087.43 cm\(^{-1}\)) is more or less a straight line. This means that it is a good candidate to use for the offset. However at the higher pressures this straight line is accompanied by a second line above it which makes the offset a little bit too high.

The second plot in figure 17 displays the measurement at 9185.91 cm\(^{-1}\). This measurement lies in the wobbly area at the left side of the peak. At this measurement a sharp shift occurs in modes at 5.5 amagat that explains the higher values. This shift occurs in all measurements in the lower wavenumbers expect for the lowest one. It is this shift that causes these measurements to lie so far above the oxygen spectrum.

The third measurement shown in figure 17 lies at 9235.11 cm\(^{-1}\) and seems to have a much lower extinction than the oxygen spectra. However on itself the measurement looks fine leading me to conclude that the downwards shift for the offset was indeed a bit too large. At the next measurement (9482.22 cm\(^{-1}\)) also not much can be seen that goes wrong. Only at the lowest pressures the behavior is a bit odd which might be the reason why this point seems to lie a bit lower that the rest of the peak in that area.

The last two measurements in figure 17 are on the sudden shift at the right side of the peak. At 9552.04 cm\(^{-1}\) everything looks fine but at 9572.46 cm\(^{-1}\) and higher a second mode appears halfway the pressure ramp. This causes the quadratic fit to give a lower value than it should be.

![Figure 17: Examples of measurements taken with the lens at 6 different wavenumbers.](image)
selected. This would improve the offset drastically and cause all values to lie more on one curve. In order to focus on one mode of the first 46 measurements, the lowest 3 out of 5 successive points were used. For the last 5 measurements the highest 3 out of 5 successive points were used. However the shift in the measurements at 9100-9230 cm\(^{-1}\) was not solved completely. The result after this data selection is shown in figure 18. In figure 19 the same measurements as in figure 17 are shown for comparison.

![Collision Induced Absorption Spectra](image)

**Figure 18:** the third measured collision induced absorption spectra of air (black) the contribution of oxygen-oxygen collisions (red) and the remaining contribution of nitrogen-oxygen collisions (blue). The error bars give the statistical 4\(\sigma\) interval on the quadratic fit.
Figure 19: the same measurements as in figure 17 but now after a data selection focused on retrieving a single mode.
Comparing figure 19 to figure 17 it appears that the measurements are now a lot clearer. On doing this selection it was discovered that the measurement at 9562.49 cm\(^{-1}\) showed a very weird behaviour. It seemed to have a minimum extinction at 2 amagat which does not make much sense. Therefore this measurement was marked as outlier and deleted from the final results. This mode-selection improved the measurements a lot. The offset now seems to be much better. Even the measurement at 9235.11 cm\(^{-1}\) lies on the oxygen peak. The area at 9100 to 9230 cm\(^{-1}\) has become lower and less chaotic. Lastly the measurements of the highest wavelengths now lie slightly above or at the oxygen spectrum, which is as expected.
For the resulting N\(_2\)-O\(_2\) contribution one last assumption was made. As has been observed earlier, the CIA spectrum of O\(_2\)-N\(_2\) collisions can be narrower than that of O\(_2\)-O\(_2\). As can be seen in the spectrum, indeed on both sides of the maximum the O\(_2\)-O\(_2\) data meets the air data implying a zero contribution from O\(_2\)-N\(_2\) collisions. Assuming the O\(_2\)-N\(_2\) CIA to lie in between these values, the fluctuations at the left side of the peak can be considered to be zero. Also this eliminates the region which we had to extrapolate at the measurements of pure oxygen. We note that the effect of this assumption for the integrated CIA coefficient is small. It is expected that the N\(_2\)-O\(_2\) collisions forms a peak on top of the O\(_2\)-O\(_2\) collision peak. When the air peak starts to equal the Oxygen peak this means that the N\(_2\)-O\(_2\) contribution has reached zero.
In figure 20 the resulting N\(_2\)-O\(_2\) CIA spectrum is shown for the raw data, in figure 21 the same spectrum is shown but now after the mode selection in the data. For the raw data the peak is smaller and the uncertainties are a bit bigger than for the modified spectra. The modified spectrum also contains more points since the whole peak was raised due to the lower (and better) offset. In both spectra (with some good will) a shoulder seems to appear at the right side of the peak. This is similar to what others have found [7, 8].
The improvement due to the mode selecting within the gathered data is not only visible when looking by eye. Also the fitting parameter $R^2$ is much higher. The lowest $R^2$ value for the raw data is 0.163 whereas the lowest value for the mode-selected data is 0.6414. This means that all measurements for the mode-selected data have a reasonable good quadratic behaviour. However the $R^2$ value does not say all. The measurement at 9562.49 cm$^{-1}$ had a good quadratic fit ($R^2=0.811$). This was caused by the fact that at the start this measurement went slightly down and then at 2 amagat it started rising. The fit saw this just as a quadratic behaviour with a weak increase. The calculated CIA was therefore lower than it should be. Since this faulty measurements did not show up in the fitting values all measurements were checked by eye. The conclusion was that all values at 9100 to 9230 cm$^{-1}$ could be marked as outlier. However this would mean that there would be no data-points at all in this large region causing a greater uncertainty than with using those values. Also the final result of this report, the integrated CIA coefficient for N$_2$O$_2$ collisions is not effected since it is (almost) zero in this region.

Using the statistical 4σ errors only the interpolation and integration of the N$_2$O$_2$ spectra results in values of $(1.34\pm0.23)\times10^{-6}$ cm$^2$cm$^{-2}$ (raw data: $(1.02\pm0.31)\times10^{-6}$ cm$^2$cm$^{-2}$). Again on top of this error some systematical errors must be added. The additional error in the offset contains now 2 parts: for the oxygen spectra and for the air spectra. The error in the Air spectra offset is $3.3427\times10^{-10}$ cm$^{-1}$cm$^{-2}$. As in the oxygen spectra this is the error on the lowest data point. The integrated error is than $1.337\times10^{-7}$ cm$^2$cm$^{-2}$. The error on the oxygen spectra offset is $2.723\times10^{-9}$ cm$^{-1}$cm$^{-2}$, this has to be multiplied by the square of the concentration. This results in an additional error of $0.480\times10^{-7}$ cm$^{-1}$cm$^{-2}$. Lastly there is also now a significant effect from the uncertainty in the oxygen concentration in the used air. This uncertainty is $0.21\pm0.5$ and causes an error of $6.344\times10^{-5}$ cm$^2$cm$^{-2}$. This was calculated by doing the whole data-analysis again but now for the minimum and maximum oxygen concentration. This value includes the 4σ statistical error and thus replaces the error on the original results. The reason why this is so big is simple. The contribution of the oxygen spectrum depends quadratic on the oxygen concentration. An error of 0.5% therefore significantly shifts the spectrum of N$_2$O$_2$ CIA up and down.

The final results are than $(1.3\pm0.8)\times10^{-6}$ cm$^2$cm$^{-2}$ for the integrated spectrum. Recalculating this to concentrations of unity this results in an integrated CIA coefficient for N$_2$O$_2$ collisions of $(8\pm5)\times10^{-6}$ cm$^2$cm$^{-2}$. Here again the uncertainty in the concentration has been taken into account. Following
the same procedure for the raw data leads to a value of \((1.0\pm0.8)\times10^{-5}\ cm^2\ amg^{-2}\) for the integrated CIA contribution of \(N_2-O_2\) collisions in air. The Integrated CIA coefficient is than \((6\pm5)\times10^{-6}\ cm^2\ amg^{-2}\) for concentrations of unity. Both of these values lie slightly below the value found by Tran et all [10] but the uncertainty intervals still overlap.

The contributions to CIA at the 1060 nm band of oxygen in our atmosphere is shown in table 4. Here an oxygen concentration of 21% is used. Since our own value might be a bit to low the weighted average of the averaged measurements collected in the report of Spiering et al[9], and our own measurement of the integrated CIA cross-section was used \((2.35\pm0.13)\times10^{-5}\ cm^2\ amg^{-2}\). It was found that in air \(N_2-O_2\) collisions contributes about 11% to the total CIA and is thus clearly significant. Chagas et al [7], have calculated the effect of CIA in the 1060 nm band in the total absorption in our atmosphere. For a mid-latitude summer atmospheric profile, a solar zenith angle of 60%, a surface albedo of 0.1 and a total incoming solar irradiation of 1368 Wm\(^{-2}\), they found that the CIA of \(O_2-O_2\) at 1060 nm contributed for 0.30 Wm\(^{-2}\). This value was recalculated for our CIA contributions of \(O_2-O_2\) and \(N_2-O_2\) collisions and the results are shown in the third row of table 4. To put these numbers into perspective Chagas et al calculated that the total short-wave absorption of ozone and water vapor in our atmosphere (by far the greatest contributions) was 133.55 Wm\(^{-2}\). Using this total absorption we see that the CIA at 1060 nm adds 0.24-0.28% to the shortwave absorption in our atmosphere. 0.01-0.04 % of this is caused by collisions between \(N_2\) and \(O_2\).

<table>
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<tr>
<th>CIA contributors</th>
<th>(O_2-O_2)</th>
<th>(N_2-O_2)</th>
<th>Total</th>
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<tr>
<td>CIA contribution ((10^{-5}\ cm^2\ amg^{-2}))</td>
<td>1.04±0.06</td>
<td>0.13±0.08</td>
<td>1.17±0.10</td>
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<tr>
<td>Sunlight absorption ((W/m^2))</td>
<td>0.31±0.02</td>
<td>0.04±0.02</td>
<td>0.35±0.04</td>
</tr>
<tr>
<td>Short-wave absorption (%)</td>
<td>0.22 to 0.25</td>
<td>0.01 to 0.04</td>
<td>0.24 to 0.28</td>
</tr>
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</table>

Table 4: The effect of CIA on the absorption in our atmosphere using an oxygen concentration of 21%, a mid-latitude summer atmospheric profile, a solar zenith angle of 60%, a surface albedo of 0.1 and a total incoming solar irradiation of 1368 Wm\(^{-2}\). The total shortwave absorption was 133.55 Wm\(^{-2}\)[7].

Lastly, it is interesting to calculate the absorption due to collisions at the center of absorption peak.

This gives insight in how much light of a single wavelength will be absorbed. The highest CIA in air is \((4.73\pm0.01)\times10^{6}\ m^3\ amg^{-2}\) at 9348.55 cm\(^{-1}\) (see figure 18 and note the unit change to meters). The density in our atmosphere decays more or less exponentially with height: \(e^{-\frac{z}{H}}\). Here \(z\) is the height in meters and \(H\) the scale height (The height at which the density from an atmosphere declines by a factor of \(e\)). Using a scale height of 8000 m and assuming that the density at \(z=0\) is 1 amg, we find that the squared density integrated over an infinite high atmosphere is 4000 m\(^4\)amg\(^{-2}\). Multiplying this with the CIA we find that 1.89% of the light is absorbed at this wavelength. Doing the same for the CIA at 9348.55 cm\(^{-1}\) of \(N_2-O_2\) collisions \((6\pm1\times10^{-7}\ m^3\ amg^{-2})\) leads to an absorption of 0.2%. The absorption in our atmosphere is thus indeed quite significant at the CIA peak.

4.8 Discussion

So far in the analysis above some errors have not been discussed properly or have been ignored completely. The statistical error on the quadratic fits is build-up of 3 factors. The largest part is caused by the different extinctions of different modes. However for a part it also consists of an error in the pressure and the calculated extinction. The above values for the errors are correct as long as the pressure and extinction have a Gaussian distribution around the correct value. From test measurements not discussed here it is shown that the pressure readings at constant pressure indeed
show a Gaussian distribution with a sigma of 0.0003 amagat. In figure 11 it can be seen that the extinctions also lie on a Gaussian distribution around the value of the mode. Here the standard deviation is about $10^{-7}$ cm$^2$amg$^{-2}$.

It is difficult to proof that the Gaussian distribution of those two variables is distributed around the correct value. However important is that a constant offset in the extinction does not affect the value for the absorption at all. In equation 25 it can be seen that this off-set only affects the non-pressure depended part of the decay-time, i.e. the effective reflectivity of the mirrors. An offset in the pressure, or even worse an offset increasing linear with pressure, would indeed affect the absorption but it is difficult to say to what extent. However it is certain that such an offset would be very small.

Both at 0.001 bar and 1 atm the detector displayed the correct value. The linearity of the pressure meter was also tested by setting the flow meter on different settings and measuring time and pressure in the cell (with constant volume). No discontinuities were found in that test. This leads to the conclusion that it is reasonable to ignore a possible offset in the pressure detection.

The last error that is not mentioned jet is the error in wavelength. This error is however very small. The wavelength meter was able to measure the wavelength with 0.0001 cm$^{-1}$ precision. However in order to get ring-down signals at a higher frequency the wavelength a slight oscillation of the wavelength. Still the uncertainty in the wavelength is 0.005 cm$^{-1}$. How this can be included in the total error is unclear. However still something can be said about its magnitude. At the steepest area of the oxygen CIA spectrum the spectrum rises $10^{-6}$ cm$^{-1}$amg$^{-2}$ in 100 cm$^{-1}$. A shift of 0.005 cm$^{-1}$ of a data point at the steepest point in the peak then has an effect of $5 \times 10^{-11}$ cm$^{-1}$amg$^{-2}$. Since the errors on those data points are 100 times larger and because the error in the wavelength can be cancelled by integrating over multiple data points, it is safe to say that the error in the wavelength can be ignored. To be certain that these errors where accounted for if they, although this reasoning, would be present, a 4σ used (instead of the common 2σ or 3σ error).

An important analyzing process that needs some discussion is the integration of the spectrum. In the theory it was already briefly mentioned that there are multiple ways to do this. In this report it was chosen to use inter-and extrapolation of the data. The main argument for using this method is that the shape of the spectrum is unknown and complex. Therefore the other option: being fitting the spectrum to a predefined shape is not a priori logic. However due to the large uncertainties in the spectrum the error induced when fitting to the wrong shape might be smaller than by just integrating over all the uncertain values. However since it is impossible give an absolute value of the error of fitting against the wrong curve it was decided to use the extrapolation and integration method. Also the skewed Lorentzian fit was not able to follow the curve of the spectrum. This choice may result in a large error but at least it is known what it is.

The other analyzing process is the quadratic fit of the extinction against the density. As stated before MATLAB has some difficulties with fitting against multiple parameters. This is especially the case when these parameters are very small. Therefore it was chosen to fit the quadratic behavior as a linear fit against the square of the density. In theory this would have the same result as a normal quadratic fit but in practice there are always some difficulties. In these experiments the difficulties are the unknown effects that cause the linear offset. By using the linear fit the linear offset is not filtered out but just distributed among the offset (mirror) and the quadratic component (CIA). This makes the statistical error on the quadratic fit bigger and causes an offset in the CIA itself. It might therefore be better to use a fitting algorithm that is capable to filter the linear component. Some possible explanations for this unknown linear behavior are: Rayleigh scattering on dust particles in
the gas, change in reflectivity of the mirrors due to particles sticking to it and of course changes in modes due to pressure related effects of the cell.

There are several other ways to improve the results above. The easiest way would probably be by reducing the error on the gas concentration. If this concentration would be known at a precision of 0.1% the error would almost be half its original value. Indeed, it has been decided to determine the composition of the gas with this accuracy. Another but more difficult way is to measure the beam waist of the laser and place a second lens. If anyone wants to attempt such thing it would be wise to implement computer controlled mirror holders together with a camera at the back of the cavity. This can make the alignment phase much easier. It goes too far to say that placing and aligning a second lens would be impossible to do without these additions but the time required for it would certainly decrease drastically. There are also many trivial ways to improve the setup, for example: using a laser that covers the full spectrum, using a laser with more lasing power and changing the pressure cell so measurements higher pressures can be done.

**Results After finishing report**

The Callibration results came back way after finishing/marking of this results. The O2 concentration was high 22.316%. That is almost a percent higher than we expected. This shifts the data drastically.

![Figure 21: The N2-O2 spectra after mode-selecting of the data (with negative CIA included)](image)

Using the statistical 3σ errors only the interpolation and integration of the N2-O2 spectra results in values of (2.457±2.803)*10^{-7} cm^{-2}amg^{-2}. Again on top of this error some systematical errors must be added. The additional error in the offset contains now 2 parts: for the oxygen spectra and for the air spectra. The error in the Air spectra offset is 3.3427*10^{-10} cm^{-1}amg^{-2}. As in the oxygen spectra this is
the error on the lowest data point. The integrated error is than $1 \times 10^{-7}$ cm$^2$ amg$^{-2}$. The error on the oxygen spectra offset is $2.723 \times 10^{-9}$ cm$^{-1}$ amg$^{-2}$, this has to be multiplied by the square of the concentration. This results in an additional error of $0.4 \times 10^{-7}$ cm$^2$ amg$^{-2}$.

The final results are than $(2.457 \pm 4.203) \times 10^{-7}$ cm$^2$ amg$^{-2}$ for the integrated spectrum. Recalculating this to concentrations of 1 amg this results in an integrated CIA coefficient for N$_2$-O$_2$ collisions of $(2 \pm 3) \times 10^{-6}$ cm$^2$ amg$^{-2}$. This value lies far below the value found by Tran et all [10].

![Figure 18: the third measured collision induced absorption spectra of air (black) the contribution of oxygen-oxygen collisions (red) and the remaining contribution of nitrogen-oxygen collisions (blue). The error bars give the statistical 4σ interval on the quadratic fit.](image-url)
Using the statistical 4σ errors only the interpolation and integration of the N$_2$-O$_2$ spectra results in values of $(3\pm2)\times10^{-7}$ cm$^2$ amg$^2$. Again on top of this error some systematical errors must be added. The additional error in the offset contains now 2 parts: for the oxygen spectra and for the air spectra. The error in the Air spectra offset is $3.3427\times10^{-10}$ cm$^2$ amg$^2$. As in the oxygen spectra this is the error on the lowest data point. The integrated error is than $1\times10^{-7}$ cm$^2$ amg$^2$. The error on the oxygen spectra offset is $2.723\times10^{-9}$ cm$^2$ amg$^2$, this has to be multiplied by the square of the concentration. This results in an additional error of $0.4\times10^{-7}$ cm$^2$ amg$^2$.

The final results are than $(3\pm3)\times10^{-7}$ cm$^2$ amg$^2$ for the integrated spectrum. Recalculating this to concentrations of unity this results in an integrated CIA coefficient for N$_2$-O$_2$ collisions of $(2\pm2)\times10^{-6}$ cm$^2$ amg$^2$. This value lies far below the value found by Tran et al [10].
Chapter 5

Conclusion
This master project has been quite successful. Not only was the integrated collision induced absorption cross-section of nitrogen-oxygen collision determined at the 1060 nm band in oxygen, also the setup itself and the theoretical knowledge about the setup was improved. This increased the sensitivity and made it possible to accomplish the planned experiments successfully.

The integrated collision induced absorption cross-section of pure oxygen at the 1060 cm$^{-1}$ band was determined to be $(2.08\pm0.15)\times10^{-4}$ cm$^2$amg$^{-2}$. This is a bit lower than found in other reports but the error regions still overlap. Using a lens to enhance the sensitivity of the setup the integrated collision induced absorption cross-section of nitrogen-oxygen collisions was determined in Air. This was found to be $(8.1\pm5.5)\times10^{-6}$ cm$^2$amg$^{-2}$ where the concentrations of both gases is unity. Although the integrated CIA cross-section of N$_2$-O$_2$ is about 25 times smaller than the cross-section of O$_2$-O$_2$ collisions its contribution in the atmosphere is still quite significant due to the high concentration of N$_2$. N$_2$-O$_2$ collisions contribute for about 11% to the collision induced absorption. In terms of the total short wavelength absorption in our atmosphere this is 0.01-0.04%.

This experiment is the first experiment to our knowledge to present a value for the N$_2$-O$_2$ CIA Cross-section that is gathered at low pressures. This report therefore clearly demonstrates the power of a cavity ring-down setup. Even though the mode-matching was not perfect it was still possible to measure CIA cross-sections as low as $10^{-9}$ cm$^2$amg$^{-2}$. The accuracy of the final result was therefore more hindered by the uncertainty of the gas-concentration than by the experimental setup itself. Currently the used gas is being calibrated with which we hope to improve our results.
References


9. Spiering, F. R., & van der Zande, W. J. (2012). Collision induced absorption in the a¹Δ (v= 2)←X¹Σ⁺ (v= 0) band of molecular oxygen. Physical Chemistry Chemical Physics, 14(28), 9923-9928.


17. http://en.wikipedia.org/wiki/Fabry%E2%80%93P%C3%A9rot_interferometer


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*Wim van der Zande*, who, although his limited time, helped me a lot with discussing the theory and evaluating the results. Also he had a key role in finding the right people to help with technical issues.

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*Afric Meijer*, with who I discussed all sorts of things when Wim was unavailable.

*René van Buuren, Cor Sikkens, and Arjan van Vliet*, for their technical support.
## Appendix 1: Tables

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Table 3: wavenumbers that have little absorption from H₂O and O₂

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<th>Peaks oxygen</th>
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<td>9423,36</td>
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</table>

Table 4: wavenumbers of the main peaks in the Oxygen spectrum

<table>
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<tr>
<th>ω_0</th>
<th>Lens 1 (m)</th>
<th>Lens 2 (m)</th>
<th>d2</th>
<th>d3</th>
<th>ΔR(q)</th>
<th>ΔI(q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>0.3</td>
<td>-0.1</td>
<td>0.222828</td>
<td>0.227027</td>
<td>-0.02762</td>
<td>-1.94401</td>
</tr>
<tr>
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<td>-0.1</td>
<td>0.222828</td>
<td>0.227027</td>
<td>-0.02768</td>
<td>-10.8353</td>
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<tr>
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<td>0.3</td>
<td>-0.1</td>
<td>0.099091</td>
<td>0.228018</td>
<td>-0.00924</td>
<td>-4.46338</td>
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<td>-0.1</td>
<td>0.099091</td>
<td>0.228018</td>
<td>-0.00929</td>
<td>-13.3547</td>
</tr>
<tr>
<td>$d_2$</td>
<td>$d_3$</td>
<td>$\omega_i$</td>
<td>$\Delta R(q)$</td>
<td>$\Delta I(q)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
<td>-----------</td>
<td>---------------</td>
<td>-------------</td>
<td></td>
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</tr>
<tr>
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<td>0.15</td>
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<td>0.422252</td>
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<td>0.123838</td>
<td>0.170541</td>
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<tr>
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<td>0.123838</td>
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<td>-0.1</td>
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<td>0.000265</td>
<td>3.090505</td>
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<tr>
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<td>-0.1</td>
<td>0.30697</td>
<td>0.16955</td>
<td>0.000838</td>
<td>-5.80076</td>
</tr>
</tbody>
</table>

Table 5: the minimisation results for mode-matching with 2 lenses. $d_2$ is the distance between the cavity and the second lens, $d_3$ is the distance between the two lenses and $\omega_i$ is the beam-waist at the laser. $\Delta R(q)$ and $\Delta I(q)$ are the differences in the real and imaginary part of the q-parameters for the incoming wave and the wave supported by the cavity.