CAVITY RING-DOWN SPECTROSCOPY ON ATMOSPHERIC MOLECULES

Hans Naus

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"Nothing can be noticed without previous knowledge"

Fyodor Dostoyevsky, Crime and Punishment

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Chapter 1 Introduction and summary

1.1 Preface

Molecular gases in the atmosphere influence the climate on Earth in different ways. The effect of greenhouse warming, considered to be induced by enhanced absorption by atmospheric molecules, is well known, also beyond the scientific community. The underlying physics of the Earth's radiation budget is still not fully understood. Particularly on the absorption side not all contributions are known, and it was speculated that a missing part might be ascribed to water vapor, including water-containing Van der Waals clusters, as well as to collisionally induced absorptions, such as $(O_2)_2$ dimers [1]. Apart from greenhouse warming the observed decay of the ozone layer, predominantly over the Antarctic, but recently also over major regions on the Northern hemisphere, has become a topic of public concern and, hence, of increased scientific study.



Figure 1.1: The GOME instrument measures the total radiance of the Earth and Earth's atmosphere (62° Northern latitude, Solar Zenith Angle of 73°). Normalization with respect to the sun's spectrum results in a transmittance spectrum. Clearly visible are the A, B, and γ bands of O₂ and absorption features due to water vapor. The broad feature at 578 nm is due to collisionally induced absorption by $(O_2)_2$.



Figure 1.2: Detail of the GOME spectrum showing absorptions due to H_2O and $(O_2)_2$. The dotted line represents the spectrum as measured by the GOME instrument, while the solid line is a modeled spectrum in which data from experiments presented in this thesis are incorporated.

Science aims at understanding the origin of these problems with contributions from different fields. One important contribution is in the monitoring and measuring of the effects with the aid of a variety of instruments, often satellite based, because that allows for measurements with global coverage. Spectroscopic measurements, using the characteristic fingerprint of each molecule, are ideally suited for this purpose. Laboratory spectroscopic measurements deliver the means to quantitatively interprete these fingerprints, and it is in this area that this thesis work contributes.

One of the satellite instruments that monitors the Earth's atmosphere is the 'Global Ozone Monitoring Experiment' (GOME) aboard the second European Remote Sensing (ERS-2) satellite of the European Space Agency (ESA) [2]. The GOME instrument continuously measures the radiance of the light I, which is reflected by the Earth and the Earth's atmosphere in the wavelength range 240–790 nm. Normalization with respect to the incoming sunlight (I_0) results in a spectrum, the transmittance, with absorption features of the Earth and Earth's atmosphere. From these spectra the amounts and distribution of atmospheric gases can be retrieved.

A (normalized) spectrum as measured by the GOME instrument is shown in Fig. 1.1. Clearly visible are absorption bands of O_2 that originate from $b^1 \Sigma_g^+ - X^3 \Sigma_g^-$ electronic transitions; the A band at 760 nm, the B band at 689 nm, and the γ band at 630 nm. Furthermore absorptions due to H₂O vapor are present. Less prominent but still discernable is a broad structure at 578 nm which is due to collisionally induced absorption by $(O_2)_2$. The background of the GOME spectrum is determined by a combination of Rayleigh and Mie scattering, and the ground surface albedo. The spectrum shown in Fig. 1.1 is a typical example of a spectrum recorded over a water surface (a low background level around 600 nm which increases at longer wavelengths). Due to bad detector pixels a small part of the spectrum is missing at 600 nm. To retrieve reliable information from these satellite spectra it is not only necessary to understand the radiation transport through the atmosphere but it is also important to understand the molecular physics that determines the scattering and absorption properties of atmospheric gases.

The wavelength-dependent absorption of light by molecules can be investigated in a laboratory environment under controlled circumstances. Based on these laboratory data it is possible to retrieve the concentration of gases in the atmosphere from spectra recorded with the GOME instrument. In Fig. 1.2 part of the GOME spectrum from Fig. 1.1 is shown. The absorptions in the spectrum (Fig. 1.2) are due to collisionally induced absorption by $(O_2)_2$ and water vapor. Data from experiments presented in chapter 4 and 6 of this thesis are used in the complex calculations to model the spectrum [3]. One ongoing project is to provide improved data for the modelling of GOME data to retrieve water vapor column densities with a global coverage. The spectroscopic window 585–600 nm appears to be a suitable range because atmospheric saturation effects play a minor role [3, 4].

Although the absorptions are clearly visible in Fig. 1.1 they originate from weak absorptions; it is the large amount of gas in the Earth's atmosphere and/or the long absorption path lengths achieved in the satellite measurements which make the absorptions visible in the spectra. Because of the weakness of the absorption, accurate determination of absorption cross sections in a laboratory is not trivial. It requires a highly sensitive measurement technique because long absorption path lengths (>1 km) under controlled circumstances are not easy to achieve. In this thesis the sensitive Cavity Ring-Down (CRD) technique is applied to study the molecular spectroscopy of the atmospheric gases O_2 and H_2O and to measure absolute absorption cross sections of $(O_2)_2$.

Isotopic effects seem to play an important role in the photodynamics and/or the chemistry of atmospheric ozone. From spectroscopic measurements on atmospheric ozone isotopic ratios in O₃ were found to deviate from the terrestrial abundance of oxygen isotopes [5,6]. For a deeper understanding of this process it is of importance to identify transitions by which the isotopic constitution of oxygen bearing molecules can be determined. The $b^1\Sigma_g^+-X^3\Sigma_g^-$ electronic system is such a tool, as was demonstrated by Osterbrock *et al.* [7] and by Slanger *et al.* [8]. The spectrum of this electronic system has been investigated for various isotopomers by taking advantage of the CRD method to perform sensitive measurements on small gas samples.

1.2 Absorption spectroscopy

Molecules (and atoms) absorb electromagnetic radiation of specific frequencies. The rate of absorption depends on the nature of the species, the frequency of the light, and external conditions such as temperature and pressure. The frequency dependence of the absorption is unique; each species possesses a unique 'spectrum' of frequency dependent absorptions. Measurement of a spectrum can be used to determine the nature of an unknown species or conditions of known species, such as concentration and temperature. The absorption of light is, under conditions where saturation does not occur, described by Beer's law:

$$I_{(\nu)}^{l} = I_{(\nu)}^{0} \cdot e^{-\sigma_{(\nu)} nl}, \qquad (1.1)$$

where $I_{(\nu)}^0$ is the intensity of an incident light beam at frequency ν , $I_{(\nu)}^l$ is the intensity of that beam after a distance l through the absorbing medium, n is the number density of the species, and $\sigma_{(\nu)}$ is the frequency-dependent absorption cross section. The product $\sigma_{(\nu)}n$ is the absorption coefficient $\alpha_{(\nu)}$ which follows directly from Eq. 1.1,

$$\alpha_{(\nu)} = \frac{1}{l} \ln \left(\frac{I_{(\nu)}^0}{I_{(\nu)}^l} \right).$$
(1.2)

The lowest amount of absorption detectable by conventional direct absorption techniques is limited by the minimum intensity change that can be measured and the absorption path length. A first-order Taylor expansion of Beer's law,

$$e^{-\alpha_{(\nu)}l} = 1 - \alpha_{(\nu)}l \quad (\alpha_{(\nu)}l \ll 1),$$
 (1.3)

reveals the limitations. Substituting Eq. 1.3 in Eq. 1.1 simplifies Eq. 1.2:

$$\alpha_{(\nu)} = \frac{I_{(\nu)}^{0} - I_{(\nu)}^{l}}{I_{(\nu)}^{0}l}
= \frac{\Delta I_{(\nu)}}{I_{(\nu)}^{0}l}.$$
(1.4)

It is evident from Eq. 1.4 that the detection limit is governed by intensity fluctuations. The sensitivity of conventional direct absorption techniques can be improved by increasing the absorption path length l. Very long absorption path lengths are achieved in sunset spectra of the Earth's atmosphere [9], with reported absorption sensitivities of $\approx 10^{-11}$ cm⁻¹ [10]. In a laboratory, multi-pass absorption cells can be used to increase the effective absorption path length. Commonly used are the White cell [11] and the Herriot configuration [12].

Non-laser absorption spectroscopic techniques use broad-band light sources (lamp, sun). The absorption spectrum can be obtained through the use of a dispersive element

(grating, prism) that unravels the light in its frequency components before the light reaches the detector. This can be a diode array, a CCD camera, or a photographic plate [13]. The resolution and sensitivity achieved are remarkable. The pivotal study of Babcock and Herzberg [9] in 1948, using data from the sunset spectrum of the Earth's atmosphere of the $b^1\Sigma_g^+-X^3\Sigma_g^-$ atmospheric system of O₂, can still compete with recent spectroscopic studies of O₂ isotopomers [14,15], performed with the technique of Fourier Transform (FT) Spectroscopy [16].

These techniques benefit greatly from the multiplex advantage of detecting a wide frequency range at all times. Fourier Transform spectroscopy possesses the additional advantage of a high light intensity; there is no narrow entrance slit which severely restricts the radiation throughput in a prism or grating spectrometer [13].

Tunable laser sources enable recording of an absorption spectrum by detecting the transmitted intensity of the laser beam while the frequency is scanned. The sensitivity is limited by the minimum detectable intensity change, but normalization of the transmitted intensity with respect to the incoming intensity can yield a Signal-to-Noise-Ratio (SNR) in a spectrum of better than $\approx 10^{-6}$ cm⁻¹. More sensitive techniques (up to $\approx 10^{-10}$ cm⁻¹) use absorption-induced effects, such as IntraCavity Laser Absorption Spectroscopy (ICLAS) and Frequency Modulated (FM) spectroscopy. Although these techniques do not measure direct absorption the obtained signals are directly correlated to the absorption coefficient $\alpha_{(\nu)}$, unlike in techniques as PhotoAcoustic (PA) spectroscopy, Laser Induced Fluorescence (LIF), and Resonance Enhanced MultiPhoton Ionisation (REMPI). The latter three techniques need calibration against signals from known absorptions for quantitative absorption measurements. Discussion of these techniques is beyond the scope of this thesis; the reader is referred to, for example, Demtröder [13].

The above mentioned techniques are often more sensitive than direct absorption techniques, but do not measure absorption directly. The Cavity Ring-Down (CRD) technique, however, does measure direct absorption and is some orders of magnitude more sensitive than all other direct absorption techniques.

1.3 Pulsed cavity ring-down

While the first paper on the cavity ring-down technique in relation to measurements of molecular absorptions appeared in 1988 [17], the principle of CRD was already proposed in 1980 by Herbelin *et al.* [18] to determine mirror reflectivities. The transmission T of mirrors can be measured by sensitive power meters. Accurate determination of the reflectivity R, however, is difficult because the measured transmittance also includes losses L due to absorption and scattering (T = 1 - (R + L)). In 1984 Anderson *et al.* [19] were the first to use the decay rate of light leaking out of an optical resonator to determine mirror reflectivities but did not use the 'ring-down' technique as a spectroscopic tool. O'Keefe and Deacon [17] were the first to apply the 'ring-down' technique as a laser based direct-absorption measurement technique. Where standard (laser) absorption techniques detect intensity changes, CRD measures the intensity of light leaking out of an optical cavity as a function of time. The decay rate of the light intensity contains information about losses in the cavity. The ring-down cavity is an optical resonator of which the theory will be discussed briefly. Detailed studies can be found in several textbooks [13, 20] and in papers which discuss specific CRD-related aspects of this theory [21–24].

The first CRD experiments were performed with pulsed lasers [17, 25]: Pulsed-CRD (P-CRD). Since then CRD has been developed into a versatile and sensitive technique with new and innovating variants. The group of Meijer at the University of Nijmegen introduced four variants of the CRD technique: Phase Shift CRD (PS-CRD) [26], Fourier Transform CRD (FT-CRD) [27], Polarization Dependent CRD (PD-CRD) [28], and Cavity Enhanced Absorption Spectroscopy¹ (CEAS) [30]. Pipino *et al.* at NIST introduced Evanescent Wave CRD (EW-CRD) [31] to study solid/gas and solid/liquid interfaces. The groups of Lehmann (Princeton) and Zare (Stanford) developed Continuous Wave CRD (CW-CRD) [32, 33]. Recently the group of Orr added another variant of CW-CRD detection [34]. P-CRD remains, however, the most commonly used CRD technique.

1.3.1 The principle of pulsed cavity ring-down

A (short) laser pulse of light with intensity I_{in} is 'coupled' into a stable cavity of length d, consisting of two highly reflecting curved mirrors with a reflectivity R, loss L, and transmittance T (R + L + T = 1). At each mirror a small part, T, of the trapped light leaks out while the remaining part is reflected, as is schematically shown in Fig. 1.3. The first pulse of light leaking out of the cavity will have an intensity $I_0 = T^2 \cdot I_{in}$. The n^{th} pulse with intensity

$$I_n = I_0 R^{2(n-1)}$$

= $I_0 e^{2(n-1)\ln(R)}$ (1.5)

will leak out (2d(n-1)/c) seconds after the first pulse, where c is the speed of light; the exponent is negative because R < 1. When the cavity is shorter than the light pulse and due to limited response times of the detection circuit, the pulses leaking out of the cavity will overlap and smear out to a continuously decaying signal as a function of time t,

$$I_{(t)} = I_0 e^{-\left(\frac{c}{d}\right) |\ln(R)| t}.$$
(1.6)

¹Not to be confused with 'Noise-Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy' (NICE-OHMS) [29] which is also referred to as 'cavity enhanced absorption spectroscopy'.



Figure 1.3: Principle of the CRD technique. A pulse of light (I_{in}) is trapped in a stable optical resonator. The intensity of the light leaking out of the resonator will decay exponentially in time. Imbedded in the decay rate of the intensity is information on optical losses inside the cavity.

The decay rate of an empty cavity β_0 , or the decay time $\tau_0 = 1/\beta_0$, is the background signal of a spectrum recorded with the CRD technique. This decay rate β_0 is determined by the reflectivity R of the mirrors and the cavity length d:

$$\beta_0 = \frac{c \left| \ln(R) \right|}{d}.$$
(1.7)

Additional losses in the cavity will result in a faster decay. These losses can be due to species in the cavity (absorption, Rayleigh scattering). To distinguish between the, frequency dependent, absorption coefficient $\alpha_{(\nu)}$ and species-induced extinction in general, the extinction coefficient is represented by $\kappa_{(\nu)}$. If the extra losses are only due to absorption then $\kappa_{(\nu)} = \alpha_{(\nu)}$.

When the additional losses satisfy Beer's law, the decay remains exponential:

$$I_n = I_0 R^{2(n-1)} e^{-2(n-1)\kappa_{(\nu)}l}$$

= $I_0 e^{2(n-1)\ln(R) - 2(n-1)\kappa_{(\nu)}l}$

hence

$$I_{(t)} = I_0 e^{-(\frac{c}{d})(|\ln(R)| + \kappa_{(\nu)}l)t}, \qquad (1.8)$$

where $\kappa_{(\nu)}$ is the extinction coefficient of a species inside the cavity, ν is the frequency, and l is the single pass absorption path length. The decay rate β in case of additional extinction is larger than β_0 , as schematically shown in Fig. 1.4, and is given by

$$\beta_{(\nu)} = \frac{c}{d} (|\ln(R)| + \kappa_{(\nu)}l). \qquad (1.9)$$



Figure 1.4: Extra losses $\kappa_{(\nu)}$ owing to a species in the cavity (left figure) result in a faster decay (β_0 vs. β_{\max}) of the light leaking out of the cavity (right figure).

From Eq. 1.7 and 1.9 the extra loss in the cavity follows:

$$\beta - \beta_0 = \frac{c}{d} \kappa_{(\nu)}, \qquad (1.10)$$

hence

$$\kappa_{(\nu)} = \frac{d}{l} \frac{(\beta - \beta_0)}{c}.$$
 (1.11)

When the cavity is completely filled with the medium of interest d and l cancel and Eq. 1.11 becomes

$$\kappa_{(\nu)} = \frac{(\beta - \beta_0)}{c}.$$
 (1.12)

The coefficients $\kappa_{(\nu)}$ measured as a function of frequency constitute, in case of absorption, an absorption spectrum in which β_0/c is the background level.

The CRD technique has two marked advantages. First, information on absorption is embedded in the decay rate of the light intensity leaking out of the cavity, and is thus independent of intensity fluctuations. Second, the use of low-loss optical resonators enhances the absorption path length; up to 100 km in a 1 m long cell can be achieved. The combination of both features results in a high detection sensitivity $(10^{-9} \text{ cm}^{-1})$ with a relatively simple experimental setup and pulsed laser sources.

Some remarks must be added to this explanation of the principle of the CRD technique. Since no two mirrors are equal, R used in the previous equations is a geometric

average $\sqrt{R_1R_2}$ of the reflectivities R_1 and R_2 of the two mirrors. Furthermore, not only the transmission T and the reflectivity R of the mirrors are involved. Additional species independent losses L have to be taken into account, i.e., diffraction, scattering, and absorption of light by the substrate of the mirrors. In an experiment the background signal is the equivalent of an 'effective reflectivity': $R_{\text{eff}} = 1 - (T + L)$. In the following R_{eff} is assumed for simplicity, unless stated otherwise. The reflectivity R may be frequency dependent, which can result in a slope in the background of a frequency scan, but often the effect is negligibly small and the background is constant.

Whereas these effects are easily accounted for, effects due to the finite line width of the exciting laser pulses are not. Both the laser and the absorption cross sections possess a spectral distribution. If $(d\kappa_{(\nu)}/d\nu) \approx 0$ within the laser bandwidth Eq. 1.8 should be replaced by

$$I_{(t)} = \int_{\nu} I_{(\nu)} e^{-\beta_{(\nu)} t} \, \mathrm{d}\nu, \qquad (1.13)$$

which does not result in a mono-exponential decay. A mono-exponential fit of Eq. 1.13 leads to an underestimation of the decay rate, which in turn gives an underestimation of $\kappa_{(\nu)}$ [21, 35, 36]. This effect is comparable to the 'slit function problem' of other spectroscopic techniques. However, correction for these effects in CRD spectroscopy is not trivial, since each frequency component within the laser bandwidth profile will give rise to a different decay time, thus producing multi-exponential decay.

1.3.2 The CRD cavity

A typical CRD cavity is a stable, linear resonator (although three- and four-mirror cavities are also used [37, 38]) with identical mirrors. To form a stable resonator with identical mirrors the geometry of the cavity has to obey the stability criterion [13, 20]

$$0 < g^2 < 1, (1.14)$$

where $g = 1 - d/r_c$, d is the cavity length, and r_c is the radius of curvature. For a given radius of curvature of the mirrors the cavity length of a stable resonator is restricted to values in between 0 and $2r_c$. Due to boundary conditions only light with frequencies that match resonator modes can be coupled into an optical resonator and will propagate unchanged (neglecting losses) inside the resonator. The trapped light in the resonator can be described as a superposition of longitudinal and transverse modes [13,22].

The mode spectrum of a stable confocal resonator $(d = r_c)$ is given by [13, 20]

$$\nu = \frac{c}{2d}(q + \frac{1}{2}(m + n + 1)), \qquad (1.15)$$

where q is the longitudinal-mode index, and m and n are the transverse-mode indices. A mode is represented by TEM_{qmn} , where the longitudinal mode index q is often omitted



Frequency

Figure 1.5: (a) Frequency spectrum of a confocal cavity, the longitudinal and transversal modes are degenerate and the frequency spectrum is discrete. (b) In a nonconfocal cavity the degeneracy is lifted, the frequency spectrum is quasi-continuous.

for simplicity. From Eq. 1.15 it follows that transverse modes $(q = q_1, m + n = 2q_2)$ are degenerate with axial modes $(q = q_1 + q_2, m = n = 0)$.

The frequency difference between two successive transverse modes TEM_{qmn} and $\text{TEM}_{qm(n+1)}$ or $\text{TEM}_{q(m+1)n}$, the Free Spectral Range (FSR), is

$$\delta\nu_{\rm trans} = \frac{c}{4d},\tag{1.16}$$

while the distance between two longitudinal modes TEM_{qmn} and $\text{TEM}_{(q+1)mn}$ is

$$\delta\nu_{\rm long} = \frac{c}{2d}.\tag{1.17}$$

So in a confocal cavity geometry only certain frequencies can be coupled into the resonator and the frequency spectrum of the resonator is discrete, as depicted in Fig 1.5a.

The mode structure of the resonator can have considerable effects on CRD measurements. When the bandwidth of the probing laser is much narrower than the FSR of a confocal cavity a continuous scan is not possible; an absorption can be missed if the FSR is larger than the width of the absorption. The Doppler width of a resonance in the oxygen A band for example is $\approx 0.03 \text{ cm}^{-1}$, Full Width at Half Maximum (FWHM). The absorption could remain unnoticed in a 10 cm long confocal cavity with an FSR of 0.05 cm⁻¹ because the absorption line may fall exactly in between two successive cavity modes.

The frequency spectrum of the resonator can be made quasi-continuous by changing the geometry from confocal to a stable, nonconfocal geometry. When the distance dbetween the mirrors is not equal to r_c and the resonator geometry satisfies the stability criterion (Eq. 1.14), the degeneracy of the modes is lifted and the frequency spectrum becomes [13, 20] (Fig 1.5b):

$$\nu = \frac{c}{2d} \left[q + \frac{1}{2} (m + n + 1) \left(1 + \frac{4}{\pi} \arctan(\frac{d - r_{\rm c}}{d + r_{\rm c}}) \right) \right].$$
(1.18)

The advantage of this geometry is the very dense mode pattern of the resonator; the mode spectrum is quasi continuous, as demonstrated by Meijer *et al.* [39].

Multiple-mode excitation, however, can result in mode beating effects and/or nonexponential decay of the light intensity. Beating between different frequency components (modes) can result in a periodic signal superimposed on the decay transient if for example the output of the cavity is not completely collected with equal efficiency [40]. This beat signal can influence the determination of the decay rate. Nonexponential decay can occur when the loss in the cavity is not equal for each mode, even if no absorption is present. The empty cavity loss β_0 is then not 'mode independent' because different transverse modes TEM_{mn} experience different Fresnel losses [41, 42]. As a result the decay of the light intensity in the cavity is a superposition of decays with slightly different decay rates:

$$I_{(t)} = I \sum_{mn} e^{-\beta_0^{mn} t}.$$
 (1.19)

To minimize this effect a method has been developed to optimize the cavity alignment towards effective mono-exponential decay (chapter 7).

1.4 Continuous wave cavity ring-down

The intrinsic bandwidth of pulsed lasers not only limits the spectral resolution but also complicates the data analysis due to the possibility of mode beating and nonexponential decay. Another limitation of pulsed lasers are the often limited repetition rates, thus hampering fast data acquisition. Continuous Wave Cavity Ring-Down (CW-CRD) can eliminate this limitation.

The first CW-CRD experiments were performed with CW-dye lasers [26, 43], but these were soon replaced by cheaper, smaller, and 'turn-key', single mode diode lasers [32, 33]. A decay can be recorded if the CW laser beam is rapidly interrupted when a certain intensity level of the light leaking out of the cavity is reached. The spectral resolution of a typical CW diode laser is 2 orders of magnitude better than the resolution of pulsed lasers with typical bandwidths of 1.5 GHz (0.05 cm^{-1}). The narrow bandwidth of a diode laser also enables the excitation of a single resonator mode; then mode beating and nonexponential decay are avoided.

Mode matching a CW laser with (TEM_{00}) cavity modes can increase the efficiency with which the light is coupled into the resonator. The intensity of the light leaking out of the cavity is thus increased, which simplifies the detection of the decay transient and reduces the shot noise. This can be achieved by locking the CRD cavity to the laser: Cavity Locked CW-CRD (CLCW-CRD) [37]. State-of-the-art CLCW-CRD setups achieve repetition rates of 80 kHz, a resolution of 75 kHz, and use analog detection schemes to determine the decay rate [44]; the sensitivity of the method is better than 10^{-11} cm⁻¹. Closely related to the CLCW-CRD technique is Noise-Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS) [29] with an even higher sensitivity; discussion of this technique however is beyond the scope of this thesis.

Although the achievements of CW-CRD are impressive, there are also some drawbacks. Diode lasers often have a limited scan range compared to pulsed lasers. To record spectra as presented in chapter 2 multiple short scans of $\approx 3 \text{ cm}^{-1}$ would be required, where a single scan of a pulsed dye laser is sufficient. A diode laser can cover a frequency range of 400 cm⁻¹, but controlled single mode scans are only possible over a limited frequency range. Pulsed dye-laser systems can cover the frequency range 11000–20000 cm⁻¹ without wavelength conversion. The development of all-solid-state narrow bandwidth Optical Parametric Oscillators (OPO) extends the wavelength range of pulsed systems. Not only is the scan range of a diode laser limited, more important is that they are not yet available at every desired wavelength. CW-CRD lacks the simplicity of P-CRD because it requires delicate electronics and optical devices. Nevertheless CW-CRD is a very powerful and sensitive technique.

For comprehensive discussions of the CRD technique the reader is referred to Scherer *et al.* [45], Wheeler *et al.* [46], Berden *et al.* [47], and Busch and Busch [48]

1.5 The experimental setup

The setup used for the experiments described in this thesis is a typical pulsed cavity ring-down configuration [45,46], as schematically shown in Fig. 1.6. Pulsed laser light is coupled into a stable, nonconfocal cavity. The decay is monitored by a photomultiplier tube, and the transient is fitted online to estimate the decay rate. Iodine spectra for absolute wavelength calibration as well as the pressure in the CRD cell are recorded simultaneously with the CRD spectrum.



Figure 1.6: Scheme of the experimental setup. Optical components are explained in the legend. Other components: IGP, Integrating Gated Photodiode unit; ADC, Analog-to-Digital-Converter; PMT, PhotoMultiplier Tube.

1.5.1 Laser system and wavelength calibration

Tunable pulsed laser radiation is generated by a Nd:YAG pumped Quanta-Ray PDL-3 dye laser. Several Nd:YAG lasers were used: Spectra Physics GCR-190, GCR-3, and GCR-4. The GCR-190 with a repetition rate of 50 Hz enabled faster data acquisition, but the output of the dye laser turned out to be less stable. Therefore the GCR-190 was replaced by a GCR-3 or GCR-4, both with a repetition rate of 10 Hz. The Quanta-Ray PDL-3 dye laser was used without pre-amplifier; the CRD technique does not require high pulse energies. The advantage is that Amplified Spontaneous

Emission (ASE) from the laser was reduced to a minimum.

An iris diaphragm and the built-in telescope of the PDL-3 were used to shape the beam profile and to adjust the divergence of the beam. Spectral properties of the laser were investigated with a Burleigh WA-3500 'Pulsed Laser Spectrum Analyzer' (PLSA). The bandwidth of the system was typically 0.05 cm^{-1} (1.5 GHz) at low output energies ($\approx 15 \text{ mJ}$). The iris diaphragm ID-1 (Fig. 1.6), placed in the beam to select and shape the beam profile, reduces the net power of the used part of the beam to several mJ.

For the purpose of wavelength calibration an I₂ spectrum [49] was recorded simultaneously with the CRD spectrum. The front side reflection of a suprasil disc placed behind iris diaphragm ID-1 is divided into two beams, one beam to monitor the pulse energy, while the second beam is directed through a 40 cm long iodine cell to record an I₂-absorption spectrum. Reflections from the front and back of the suprasil disc are separated to prevent possible interference effects. To record I₂ spectra at wavelengths longer than 630 nm the I₂ cell is placed inside an oven. Normalization of the iodine spectrum to the pulse energy increases the signal-to-noise ratio of the recorded spectrum and enables absolute wavelength calibration with a typical accuracy of ≈ 0.01 cm⁻¹.

1.5.2 Cavity ring-down cell

The CRD cell consists of several stainless steel parts: mirror mounts, tubes, and gas in- and outlets. Due to this modular design the experimental setup is very flexible. The mirror mounts are designed in such a way that the mirrors act as windows of the cell if the mirror diameter is 1 inch. Mirrors with a diameter smaller than 1 inch (d =7.75 mm) are mounted in adapters and do not act as windows. In that case additional suprasil windows seal the cell. A flexible bellow welded between the rigid part and adjustable part of the mirror mount allows for accurate alignment of the mirror with micrometer screws. To ensure mechanical stability, and to spare the bellows, the two parts of the mirror mounts are pressed together by six springs.

Tubes of varying lengths and diameter are used to build up a CRD cell to customize the setup to specific requirements. For example a small size cell is employed in the measurements of isotopically enriched samples. Stainless steel cubes are used to assemble the CRD cell, to connect the gas in- and outlets, and to mount pressure gauges. The cell is evacuated via a liquid nitrogen trap to prevent pump oil to reach the CRD cell.

1.5.3 Data acquisition

The light leaking out of the CRD cell, the decay transient, is detected with a PhotoMultiplier Tube (PMT) (Thorn EMI 9658 RA, socket 9658-81-81) which is directly connected to a digital oscilloscope (LeCroy 9450, 350 MHz, 8-bit resolution) without any amplification or bandwidth-limiting devices; the full bandwidth of the oscilloscope is used. A recorded trace typically consists of 4000–5000 points. The first $\approx 10\%$ of the trace prior to the decay is used to estimate the baseline of the transient. The decay transient is recorded over about 10 decay times to ensure total capture of the decay transient. A summed average of typically 5 shots is stored in the onboard memory of the oscilloscope. Summation, or averaging, of the 8-bit signal not only reduces the (shot) noise, but also enhances the resolution of the final signal due to the 16-bit memory of the oscilloscope. The data is transferred to a computer for online fitting of the transient and/or storage of the trace.

Other relevant data are simultaneously recorded via an Analog-to-Digital-Converter (ADC) (Stanford Research System 'SR 245 Computer Interface'). The pressure in the CRD cell is measured with two capacitance manometers (Edwards 600 AB, 0.00–100.00 Torr and/or 0.0–1000.0 Torr) with an absolute accuracy of 0.15% of the reading. The 0–10 V output signal of the manometers, proportional to the pressure, is monitored via the ADC with a resolution of 2.5 mV. With the aid of a home-built 'Integrating Gated Photodiode' (IGP) unit the photodiode signals for wavelength calibration are recorded with the ADC and together with the pressure data transferred to the computer.

1.5.4 Experimental details

As mentioned in the previous section the beam profile is shaped, and the divergence adjusted, with the aid of the built-in telescope of the PDL-3 dye laser and iris diaphragm ID-1 (Fig. 1.6). Beyond ID-1 no further beam shaping is performed by telescopes and pinholes. The typical energies, 1–2 mJ per pulse, are still too high for the sensitive PMT. To prevent saturation of the PMT a continuously variable Neutral Density (ND) filter mounted on a translation stage is placed in the beam to adjust the pulse energy. The variable ND filter enables adjustments of the light intensity without cumbersome replacement of ND filters, with the advantage that the alignment does not change.

Iris diaphragm ID-2, placed just before the entrance mirror of the CRD cell, not only prevents background light to enter the cavity, but is also of great importance for the alignment of the CRD cavity. The diameter of the aperture and the alignment of ID-2 with respect to the beam and the CRD cavity both influence the coupling of light into the cavity. Misalignment of ID-2 will result in mode beatings and/or overall nonexponential decay. For accurate alignment ID-2 is placed on a y - z translation stage, where x is the direction of the laser beam.

An appropriate (bandpass) filter or combination of filters in front of the PMT prevents the detection of surrounding light that passes unhampered through the CRD mirrors. The high reflectivity of the CRD mirrors is limited to a range of $\approx 10\%$ around a center wavelength, for example 500–600 nm; the mirrors are transparant for other wavelengths.

1.6 Summary

In this thesis cavity ring-down experiments on the atmospherically relevant gases O_2 and H_2O are presented. The sensitivity of the CRD technique, in combination with the relatively simple experimental setup, enables the investigation of weak absorptions under controlled circumstances. In a generic CRD experiment pulsed laser light is coupled into a stable optical resonator which contains the gaseous species of interest. The information on absorptions or other species-induced losses are embedded in the decay rate of the light leaking out of the cavity and not in intensity changes of the transmitted light. This feature and the enhancement of the absorption path length due to the highly reflecting mirrors results in a sensitivity which can be more than two orders of magnitude larger than the sensitivity of 'conventional' absorption spectroscopy techniques.

Chapter 2 deals with the determination of frequency positions and molecular constants for the oxygen A band for all isotopomers. A positive signal on a line with an absorption coefficient of 2×10^{-9} cm⁻¹ could be recorded, demonstrating the sensitivity of the cavity ring-down setup. The spectroscopic information on isotopomers provided insight in the occurrence of coincidences at search positions for symmetry-forbidden lines with weakly allowed resonances.

Transition frequencies and molecular constants of the $b^1\Sigma_g^+-X^3\Sigma_g^-$ ((3,2,1),0) bands of oxygen isotopomers are presented in chapter 3. The frequency positions of over 750 lines are determined with an accuracy of 0.01 cm⁻¹. These values may help to identify emission bands from excited vibrational levels of $O_2(b^1\Sigma_g^+)$, including minority isotopomers, as observed in the Earth's atmosphere [7,8]. Pressure shifts of the frequencies are discussed and an estimate of the band intensity of the δ -band is given.

In chapter 4 improved band parameters of the collisionally induced $a^1\Delta_g + a^1\Delta_g$ $(v=1) \leftarrow X^3\Sigma_g^- + X^3\Sigma_g^-$ and $a^1\Delta_g + a^1\Delta_g \leftarrow X^3\Sigma_g^- + X^3\Sigma_g^-$ transitions in O₂ dimers are presented. Measurements in a pressure range from 0 to 730 Torr confirm that the collision-induced absorption of oxygen is a quadratic function of the pressure throughout the entire pressure range for all wavelengths. Contributions of the overlapping γ and δ band of O₂ have been evaded, and Rayleigh extinction has been taken into account.

A quantitative verification of Rayleigh scattering cross sections for Ar and N_2 is presented in chapter 5. The work represents, to the best of our knowledge, the first laboratory verification of a Rayleigh scattering cross section.

In chapter 6 the water vapor absorption spectrum in the wavelength range 555–604 nm is investigated. The spectrum consists of 1830 lines, of which eight hundred are not included in the HITRAN-96 (HIgh resolution TRansmission molecular AbsorptioN, edition 1996) database [50]. Of the set of hitherto unobserved lines 112 could be given an assignment in terms of rovibrational quantum numbers. Additionally, seven lines could be assigned to transitions in $H_2^{18}O$.

Finally chapter 7 deals with a quantitative analysis of the noise properties of decay

transients. The transients are analyzed experimentally and theoretically. Weighted nonlinear least-squares analysis of decay transients is shown to provide the most reliable results. An online method has been developed to aid in aligning the CRD cavity.

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Chapter 2

The $b^1 \Sigma_g^+ - X^3 \Sigma_g^-$ (0,0) band of oxygen isotopomers in relation to tests of the symmetrization postulate in ${}^{16}O_2$

Abstract

The $b^1\Sigma_g^+-X^3\Sigma_g^-(0,0)$ band of the ¹⁶O¹⁸O, ¹⁶O¹⁷O, ¹⁸O₂, ¹⁷O¹⁸O, and ¹⁷O₂ isotopomers of oxygen was investigated. The positions of over 400 lines are presented together with (re)analyses of the rotational constants. The importance of these data in view of tests of the symmetrization postulate in ¹⁶O₂ is discussed and a sensitivity scale of 13 orders of magnitude which could be practical for future test experiments is presented.

2.1 Introduction

The so-called 'A band' of oxygen, corresponding to the $b^1\Sigma_g^+-X^3\Sigma_g^-$ (0,0) band at 760 nm, is the most prominent near-infrared absorption feature in the Earth's atmosphere. This A band is highly forbidden, since it is a gerade-gerade, $\Sigma^+-\Sigma^-$ and a singlet-triplet transition. With an Einstein A₀₀ coefficient of 0.0887 s⁻¹ [1] the four allowed branches in the magnetic dipole transition are $\approx 10^9$ times weaker than typical electric-dipole-allowed transitions.

This oxygen A band has been used for a test of the symmetrization postulate of quantum mechanics in the ${}^{16}O_2$ molecule [2,3]. Since the early observations of the spectra of molecular oxygen it was recognized that transitions starting from even rotational quantum states of ${}^{16}O_2$ were missing [5]. This phenomenon was explained by Heisenberg [6] to be a consequence of the symmetrization postulate for identical spin-0 nuclei. The ¹⁶O nuclei in this homonuclear molecule are spin-0 particles and quantum statistics rules that its molecular wave function must be totally symmetric under permutation of the nuclei. As a consequence, states with an even rotational angular momentum cannot exist, or cannot be populated. For a detailed explanation the reader is referred to Herzberg [7] and Bunker [8]. This well known phenomenon may be used for a test of the symmetrization postulate, in search of weak signals on transitions originating from such symmetry-forbidden states. In two experiments, upper limits for a violation of the postulate have been set to 5×10^{-7} [2] and 8×10^{-7} [3], using techniques of frequency-modulated absorption with tunable diode lasers¹. In one of these studies [2] transitions in ¹⁶O¹⁸O and ¹⁶O¹⁷O were explicitly studied. Magnetic dipole transitions in ${}^{18}O_2$ or electric quadrupole transitions in ${}^{16}O_2$ [9], which should be observable at the 5×10^{-7} sensitivity level were not included in these studies.

In this work observations on the oxygen A band are reported, using cavity ringdown spectroscopy. This technique has been developed into a versatile and sensitive spectroscopic tool for measuring weak absorptions or low concentrations [10–15]. The A band of the isotopomers ¹⁶O¹⁸O, ¹⁶O¹⁷O, ¹⁸O₂, ¹⁷O¹⁸O, and ¹⁷O₂ was studied in isotopically enriched samples, resulting in line positions with an accuracy of 0.03 cm⁻¹. Knowledge of the spectral positions of all isotopomer lines will ascertain that no coincidences occur between weak signals from isotopomer lines and the position of lines in ¹⁶O₂ selected for procedures to test the symmetrization postulate. Furthermore an electric quadrupole line in ¹⁶O₂ was observed, which is known to have a line strength 3×10^{-6} times weaker than the magnetic dipole transitions [9], setting the present sensitivity limit at 1.5×10^{-6} . Based on the known natural abundances of the rare oxygen isotopomers in conjunction with the electric quadrupole transitions a sensitivity scale is established which may be of use in future work testing a possible violation of the symmetrization postulate in ¹⁶O₂.

¹During the writing of this thesis NICE-OHMS experiments by Gianfrani *et al.* [4] have set the upper limit for a violation of the symmetrization postulate to 5×10^{-8} .



Figure 2.1: Schematic display of the experimental setup. PD, photodiodes; RC, Raman cell; DM, dichroic mirrors for seperation of the Raman-shifted wavelength from the fundamental, and PMT; photomultiplier tube.

2.2 Experiment

The experimental setup is displayed schematically in Fig. 2.1. Wavelength tunable pulsed laser radiation (5 ns) near 760 nm is used in a typical Cavity Ring-Down (CRD) configuration. For the principles of CRD the reader is referred to the literature [10–15] and chapter 1 of this thesis. With highly reflecting mirrors, R > 99.998% (Research Electro Optics), a stable cavity (radius of curvature 45 cm, mirror separation 42 cm) is formed. Ring-down decay times of typically 100 μ s (empty cavity) could be obtained. Decay transients were detected with a photomultiplier tube (Thorn EMI 9658 RA) and stored on a 350 MHz oscilloscope (LeCroy 9450). After averaging signals from 10–30 laser pulses the decay transients were evaluated online by computer. The resulting decay transient, measured as a function of wavelength setting, is an accurate and sensitive measure of the absorption in the cavity. The ring-down decay times obtained in the setup correspond to effective absorption path lengths of over 100 km (3τ). As an example, a spectrum of the ^RR and ^RQ branches of ¹⁸O₂ is shown in Fig. 2.2, with adjacent parts recorded at different pressures. Spectra of O₂ isotopomers were



Figure 2.2: CRD spectrum of both R branches of ${}^{18}O_2$. The two parts displayed here were recorded at different pressures, as indicated.

recorded, either from natural O₂-gas samples, a ¹⁸O₂-enriched sample (EurisoTop, 95% ¹⁸O₂) also containing ¹⁷O¹⁸O and ¹⁶O¹⁸O, or a ¹⁷O-enriched sample (Campro Scientific, 50% ¹⁷O-atom) also containing ¹⁶O¹⁷O and ¹⁶O₂. A spectrum of the A band for ¹⁷O₂ is shown in Fig. 2.3. Lines pertaining to ¹⁶O¹⁷O and ¹⁶O₂ are also present.

Since absolute frequency calibration of pulsed near-infrared lasers is not straightforward a dye laser running in the range 577–587 nm and subsequent Raman shifting in H₂ is used to cover the wavelength range 759–775 nm. The visible output of the dye laser can easily be calibrated against the I₂-reference standard [16]. For this purpose the I₂-absorption spectrum (in linear absorption) and the dye laser power are measured simultaneously with the CRD spectrum of O₂ isotopomers. Before further analysis the I₂ spectrum is normalized to the power spectrum of the dye laser. Absolute frequency positions of O₂ lines are obtained from computerized fitting of both spectra and subsequent interpolation.

The Raman shift Ω , which slightly depends on the H₂-gas density in the Raman cell, is evaluated with $\Omega_{(p)} = \Omega_0 + \alpha p + \beta p^2$, where $\Omega_0 = 4155.2547 \text{ cm}^{-1}$, $\alpha = -3.38 \times 10^{-3} \text{ cm}^{-1}$ amagat⁻¹, $\beta = 4.1 \times 10^{-6} \text{ cm}^{-1}$ amagat⁻² and p is the H₂ density in amagat [17]. Various densities of 10–25 amagat were used in the Raman shifter.


Figure 2.3: Part of the A band of ${}^{17}O_2$ at a pressure of 2.25 Torr of the ${}^{17}O$ -enriched sample. Lines of ${}^{16}O{}^{17}O$ are indicated by '*', three absorptions owing to ${}^{16}O_2$ are indicated by '•' (a fourth ${}^{16}O_2$ transition is obscured by the ${}^{P}P(27)$ line of ${}^{17}O_2$).

The linewidth of the laser source is 0.06 cm^{-1} and the bandwidth of the Raman shifted frequency was found to be the same. Under the chosen pressure conditions in the CRD cell of 0.1-20 Torr, collisional broadening ($\approx 0.08 \times 10^{-3} \text{ cm}^{-1} \text{ Torr}^{-1}$) [18], and pressure shifts ($\approx -0.015 \times 10^{-3} \text{ cm}^{-1} \text{ Torr}^{-1}$) [19] can be neglected. The I₂ calibrations were performed in low-pressure samples, where typical linewidths of 0.07 cm^{-1} were obtained. The estimated uncertainty in our frequency determination is $0.02-0.03 \text{ cm}^{-1}$ and up to 0.05 cm^{-1} for overlapping and very weak lines.

2.3 Spectroscopic results on ${}^{16}O^{18}O$, ${}^{16}O^{17}O$, ${}^{18}O_2$, ${}^{17}O^{18}O$, and ${}^{17}O_2$

From series of CRD recordings, using low- and high-pressure samples of natural O_2 and ${}^{18}O_2$ - and ${}^{17}O$ -enriched samples data was derived on the transition frequencies of the $b^1\Sigma_g^+-X^3\Sigma_g^-$ (0,0) band. The results for ${}^{16}O^{18}O$, ${}^{16}O^{17}O$, ${}^{18}O_2$, ${}^{17}O^{18}O$, and ${}^{17}O_2$ are collected in Tables 2.6–2.10 (appendix A).



Figure 2.4: Energy-level scheme of molecular oxygen with the $X^{3}\Sigma_{g}^{-}, v = 0$ ground and $b^{1}\Sigma_{g}^{+}, v = 0$ excited state. On the left side the symmetry-allowed levels in ${}^{16}O_{2}$ and ${}^{18}O_{2}$ are shown with the four magnetic dipole branches (^PP, ^PQ, ^RR, and^RQ) as well as the four electric quadrupole branches (^PO, ^NO, ^RS, and ^TS). On the right side the symmetry-forbidden levels and transitions are shown; note that these are allowed for isotopomers other than ${}^{16}O_{2}$ and ${}^{18}O_{2}$.

Since the resolution in the present experiment does not make an improvement over existing data for ${}^{16}O_2$ [9,20] this data is not included. During the final analysis of the measurements, highly accurate data on the A band of ${}^{18}O_2$ were reported [21]. Since the data of Ref. [21] were limited to 15 transitions it was decided to report the extended analysis of 72 lines for ${}^{18}O_2$. Transitions in the four magnetic-dipole-allowed branches (see Fig. 2.4 for an energy-level scheme) were determined. For ${}^{18}O_2$, similar to ${}^{16}O_2$, transitions originating in the even rotational states are forbidden. This is not the case for ${}^{17}O_2$, where a 7:5 ratio is found between odd and even N due to the nuclear spin of 5/2 for the ${}^{17}O$ nucleus, nor for the heteronuclear isotopomers.

For each isotopomer the data were incorporated in a least-squares minimization routine to derive molecular constants. For the $X^{3}\Sigma_{g}^{-}(v=0,N,J)$ state the effective

Table 2.1: Molecular constants for the $b^1 \Sigma_g^+$, v = 0 excited state of molecular oxygen. The constants for ${}^{16}O_2$ were derived from a reanalysis of the data of Refs. [9,20]. All values are in cm⁻¹. The value in parentheses represents the estimated error (1σ) from the fit in units of the last digits.

	$^{16}O_{2}$	$^{16}{\rm O}^{17}{\rm O}$	$^{16}{ m O}^{18}{ m O}$
$egin{array}{c} u_{00} \ B' \ D' \end{array}$	$\begin{array}{c} 13122.2401 \ (7) \\ 1.39125183 \ (10) \\ 5.360 \ (1) \times 10^{-6} \end{array}$	$\begin{array}{c} 13123.344 \ (3) \\ 1.350232 \ (15) \\ 5.07 \ (2) \times 10^{-6} \end{array}$	13124.319 (7) 1.31392 (9) 4.4 (2) $\times 10^{-6}$
	$^{17}O^{18}O$	$^{18}O_{2}$	$^{17}{ m O}_2$
$egin{array}{c} u_{00} \ B' \ D' \end{array}$	13125.430 (8) 1.27319 (8) 4.8 (1) $\times 10^{-6}$	$\begin{array}{c} 13126.4237\ (8)\\ 1.236833\ (6)\\ 4.255\ (8)\times 10^{-6}\end{array}$	$\begin{array}{c} 13124.451 \ (8) \\ 1.30916 \ (3) \\ 4.68 \ (8) \times 10^{-6} \end{array}$

Hamiltonian of Rouillé et al. [22] was adopted, while for the excited states

$$E_{(N)} = \nu_{00} + B'N(N+1) - D'N^2(N+1)^2, \qquad (2.1)$$

was used, where ν_{00} is the band origin, B' is the rotational constant, and D' is the centrifugal distortion parameter. Accurate spectroscopic studies on the $X^{3}\Sigma_{g}^{-}, v = 0$ state have been performed for all isotopomers except ${}^{17}O_2$. The results from microwave, far-infrared, laser magnetic resonance (LMR), and Raman spectroscopic studies yield a better accuracy for the ground-state molecular constants than the present study. Therefore these constants were kept fixed in the fitting routines at accurate values from the literature. These ground-state constants are listed in Table 2.11 (appendix B). The data on the $b^1\Sigma_g^+-X^3\Sigma_g^-$ (0,0) band of ${}^{16}O_2$ from Babcock and Herzberg [20] and Brault [9] were reanalyzed with updated constants for the ground state. These were obtained from the study of Rouillé et al. [22], in which data from the LMR study of Mizushima et al. [23] and the far-infrared study of Zink and Mizushima [24] were included. For ¹⁶O¹⁸O and ¹⁸O₂ the constants of Steinbach and Gordy [25] were used, while for ¹⁶O¹⁷O and ¹⁷O¹⁸O the constants of Cazolli *et al.* [26] were adopted. In the fit for ${}^{18}O_2$ the data of Gagliardi *et al.* [21] with an accuracy of 10^{-3} cm⁻¹ were included. For the ${}^{17}O_2$ isotopomer no data were available, and therefore also the ground-state constants were varied in the minimization routine. The spin coupling constants λ_0 , λ_0' , μ_0 , and μ'_0 for ¹⁷O₂ were estimated from the values for ¹⁶O¹⁸O; the mass and reduced mass of these isotopomers only differ by 0.3%. These values are listed in Table 2.11

Table 2.2: The offset of the N = 0, J = 1 level (in cm⁻¹) with respect to the zero-energy level as defined by the trace of the Hamiltonian of Rouillé *et al.* [22] The offset for ¹⁶O₂ was derived from a reanalysis of the data of Babcock and Herzberg [20] and Brault [9].

	$^{16}\mathrm{O}_2$	$^{16}\mathrm{O}^{17}\mathrm{O}$	$^{16}\mathrm{O}^{18}\mathrm{O}$	$^{17}\mathrm{O}^{18}\mathrm{O}$	$^{18}\mathrm{O}_2$	$^{17}\mathrm{O}_2$
Offset	-0.450	-0.465	-0.478	-0.494	-0.509	-0.480

(appendix B) as well.

Resulting molecular constants for the $b^1\Sigma_g^+$, v = 0 excited state are presented in Table 2.1 for all isotopomers. In all cases an unperturbed molecular band structure was found. The deviations from the least-squares fit for each line are included in Tables 2.6–2.10 (appendix A). Consistency is found with the estimated uncertainty of 0.03 cm^{-1} for the transition frequencies, resulting in a reduced χ^2 of one. The band origin ν_{00} is for all isotopomers chosen as the difference between the N = 0, J = 0level in the $b^1\Sigma_g^+, v = 0$ state and the energy given by the Hamiltonian of Rouillé *et al.* [22] without spin and rotation, i.e., not a specific level. With this definition the N = 0, J = 1 level is $\approx 0.45 \text{ cm}^{-1}$ below zero, slightly dependent on isotopomer. For clarity the values for the offset between N = 0, J = 1 levels and the zero energy as defined here are given for each isotopomer in Table 2.2.

2.4 Relevance for tests of the symmetrization postulate in ${ m ^{16}O_2}$

In their search for a possible violation of the symmetrization postulate, de Angelis *et al.* [2] probed the expected position for the ^RR(4) line of the A band, while Hilborn and Yuca [3] searched for the ^PQ(22) [27] line. Upper limits, with respect to the 'allowed' transitions in ¹⁶O₂, were determined at 5×10^{-7} [2] and 8×10^{-7} [3] respectively.

Study of the less abundant isotopomers of oxygen is of importance for tests of the symmetrization postulate in ${}^{16}\text{O}_2$. First of all, the weak line intensities of the rare isotopomers can provide a sensitivity scale. The dynamic range of many detectors is limited to a few orders of magnitude and Beer's law for direct absorption is only linear in the limit of weak absorption. Searches for violation of the symmetrization postulate at the intensity level of 10^{-8} and beyond require an intensity scale over many orders of magnitude. Weak resonances pertaining to rare isotopomers in a gas sample can be used for this purpose. The line strengths of the various isotopomers can in first order be considered equal, the abundances themselves reflect the intensity levels to be obtained in measurements on natural gas. The natural abundances of atomic ${}^{18}\text{O}$ and

Isotopomer	Transition	Relative strength
$^{16}O_{2}$	magnetic dipole	1
$^{16}\mathrm{O}^{18}\mathrm{O}$	magnetic dipole	2×10^{-3}
$^{16}\mathrm{O}^{17}\mathrm{O}$	magnetic dipole	4×10^{-4}
$^{18}\mathrm{O}_2$	magnetic dipole	4×10^{-6}
$^{16}\mathrm{O}_2$	electric quadrupole	3×10^{-6}
$^{17}\mathrm{O}^{18}\mathrm{O}$	magnetic dipole	7×10^{-7}
$^{17}\mathrm{O}_2$	magnetic dipole	1×10^{-7}
$^{16}\mathrm{O}^{18}\mathrm{O}$	electric quadrupole	6×10^{-9}
$^{16}\mathrm{O}^{17}\mathrm{O}$	electric quadrupole	1×10^{-9}
$^{18}\mathrm{O}_2$	electric quadrupole	1×10^{-11}
$^{17}\mathrm{O}^{18}\mathrm{O}$	electric quadrupole	2×10^{-12}
$^{17}\mathrm{O}_2$	electric quadrupole	3×10^{-13}

Table 2.3: Relative intensity scale of transitions in O_2 isotopomers.

¹⁷O are 0.20% and 0.037% respectively [28]. From these values the natural abundances of all isotopomer molecules can be calculated. Resulting values are listed in Table 2.3. It is taken into account that the symmetry-allowed states in ¹⁶O₂ and ¹⁸O₂ have double occupancy, because half of the states are symmetry forbidden. In ¹⁷O₂ there is a 7:5 ratio between odd and even rotational states.

The sensitivity scale can be extended to lower values if electric quadrupole transitions are considered. Brault succeeded in recording several quadrupole transitions in ${}^{16}O_2$ from long path-length spectroscopic studies of the Earth's atmosphere and determined their relative intensity, with respect to magnetic dipole transitions, at 3×10^{-6} [9]. The combination of natural isotopic abundances and quadrupole or dipole line strengths provides a sensitivity scale of 13 orders of magnitude as given in Table 2.3. Fine tuning between the gaps on this scale is possible via calculable relative populations of rotational states in a room temperature gas sample. From such calculations it follows that the ${}^{P}Q(22)$ line, sought by Hilborn and Yuca [3, 27], is a factor of 5 weaker than the ${}^{P}Q(8)$ line in the same branch.

In this work spectra of the A band for the ${}^{17}O{}^{18}O$ and ${}^{17}O{}_2$ isotopomers were recorded, while improved analysis has been presented for the other isotopomers. Knowledge of the spectral positions of the isotopomer lines prevents erroneous interpretation of weak signals. From the analysis in this work it follows that the ${}^{R}R(3)$ line of ${}^{17}O{}^{18}O$ lies at 13133.78 cm⁻¹, while the ${}^{R}R(4)$ line of ${}^{16}O{}_2$ is expected at 13133.89 cm⁻¹. The separation is only 3 GHz, while the linewidth in the absorption spectrum of de Angelis *et al.* [2] equals this value when the side lobes occurring in frequency-modulated spectra

N	PO	$^{\mathrm{N}}\mathrm{O}$	^R S	тS
1	13119.91		13 129.26	13 147.73
3	13113.95	13105.74	13133.56	13164.03
5	$13\ 107.59$	13088.14	13138.22	13179.91
7	13100.85	13070.21	13142.53	$13\ 195.40$
9	13093.74	13051.93	13146.48	$13\ 210.50$
11	13086.25	13033.28	13150.05	13225.21
13	13078.40	13014.28	13153.24	$13\ 239.52$
15	13070.17	12994.93	13156.05	$13\ 253.43$
17	13061.58	12975.22	13158.47	$13\ 266.93$
19	13052.61	12955.16	13160.51	$13\ 280.03$
21	13043.27	12934.74	13162.16	$13\ 292.71$
23	13033.56	12913.97	13163.41	13304.98
25	13023.48	12892.85	13164.27	13316.82
27	13013.02	12871.38	13164.72	13328.23
29	13002.18	12849.56	$13\ 164.77$	13339.21

Table 2.4: Calculated transition frequencies (cm^{-1}) for electric quadrupole transitions in ${}^{16}O_2$.

are included. Note that the relative abundance of ${}^{17}O^{18}O$ in natural O_2 is 7×10^{-7} , just at the detection limit claimed by de Angelis *et al.* [2]. Near the symmetry-forbidden magnetic dipole ${}^{R}R(4)$ line of ${}^{16}O_2$ is a ${}^{R}S(3)$ electric quadrupole line. These electric quadrupole transitions, calculated from the molecular constants of Tables 2.1 and 2.11, are presented in Table 2.4. The ${}^{R}S(3)$ line, separated by 10 GHz from the ${}^{R}R(4)$ line, should be observable at the 3×10^{-6} level, which is a factor of 6 above the detection limit in the experiment of de Angelis *et al.* [2].

The ${}^{P}Q(22)$ line sought by Hilborn and Yuca [3,27] is not overlapped by any of the isotopomer lines. The ${}^{P}Q(20)$ line, initially referred to as the searched line in ref. [3], coincides with the ${}^{P}P(21)$ line of ${}^{16}O^{18}O$. At a sensitivity level of 8×10^{-7} this ${}^{16}O^{18}O$ isotopomer line should appear with a Signal-to-Noise Ratio (SNR) of 5000 at the search position of the symmetry-forbidden ${}^{16}O_{2} {}^{P}Q(20)$ line!

For convenience of future use, the symmetry-forbidden lines of ${}^{16}O_2$ are listed in Table 2.5. The fact that these frequencies are accurately known makes the ${}^{16}O_2$ diatomic homonuclear molecule a suitable candidate to study fundamental physics. Symmetryforbidden lines can be searched at a well-established frequency position.

N	$^{\mathrm{P}}\mathrm{Q}$	$^{\mathrm{P}}\mathrm{P}$	RR	$^{\mathrm{R}}\mathrm{Q}$
0				13125.47
2	13117.24	$13\ 115.07$	13128.98	$13\ 130.90$
4	$13\ 110.89$	$13\ 108.85$	$13\ 133.89^{\ a}$	13135.86
6	$13\ 104.26$	$13\ 102.27$	13138.43	13140.43
8	13097.27	13095.31	13142.59	13144.62
10	13089.93	13087.99	13146.37	$13\ 148.43$
12	13082.21	13080.30	$13\ 149.78$	$13\ 151.85$
14	13074.13	13072.24	13152.80	$13\ 154.89$
16	13065.68	13063.81	13155.44	13157.55
18	13056.86	13055.01	13157.69	13159.82
20	13047.67	13045.84	13159.55	$13\ 161.70$
22	13038.11^{b}	13036.30	13161.02	13163.19
24	13028.18	13026.38	13162.09	13164.28
26	13017.87	13016.09	13162.77	13164.97
28	13007.19	13005.43	13163.04	13165.26
30	12996.13	12994.39	13162.90	13165.14

Table 2.5: Calculated transition frequencies (cm^{-1}) for symmetry-forbidden magnetic dipole transitions in ${}^{16}O_2$.

^a Line sought by de Angelis *et al.* [2].

^b Line sought by Hilborn and Yuca [3, 27].

2.5 Experimental sensitivity

The noise equivalent detection limit in the CRD setup was determined from a measurement of a quadrupole line in the ^TS branch. The electric quadrupole lines are well suited for a sensitivity determination, since they lie at the blue side of all magnetic dipole lines. Also no interference with the (1,1) band [20] occurs at these frequencies. For the spectroscopic measurements aiming at a high sensitivity the average of 12 decay times (after signal summation over 10 laser shots for each decay) was determined at each wavelength position in search of the ^TS(9) electric quadrupole transition, at 600 Torr pressure. The result of this procedure is shown in Fig. 2.5.

By interpolation with a simultaneously recorded I_2 spectrum a weak resonance is observed at a frequency of 13210.51 cm⁻¹, determined by a computerized fit of a Voigt profile with an oscillatory background. The background level is mainly due to the reflectivity of the mirrors, while at 600 Torr gas pressure extinction due to Rayleigh scattering is also observed. The oscillation at an absorption level of 3×10^{-9} cm⁻¹ corresponds to an effective variation of 10^{-7} in the mirror reflectivity. Oscillations of



Figure 2.5: Upper panel: observed absorption of the ${}^{T}S(9)$ electric quadrupole line of ${}^{16}O_2$ superimposed on an oscillatory background. The solid line represents the fit of a Voigt profile with an oscillatory background. The bottom panel shows a simultaneously recorded I₂-absorption spectrum with the fundamental output of the dye laser. The O₂ spectrum is Ramanshifted by 4155.24 cm⁻¹ with respect to the calibration spectrum.

the background are also observed in other CRD studies, their origin however is not understood yet. It is verified that the weak resonance is reproducible and disappears in an empty cavity, while the oscillatory background remains.

According to the molecular constants of ${}^{16}O_2$ an electric quadrupole transition can be expected at 13210.50 cm⁻¹, Table 2.4. In view of the 0.05 cm⁻¹ error margin for this weak and pressure-broadened line, the observed resonance perfectly coincides with ^TS(9), a possible pressure shift of ≈ -0.01 cm⁻¹ at 600 Torr is neglected. Also the width (FWHM = 0.1 cm⁻¹) and intensity (2×10^{-9} cm⁻¹) are in good agreement with the expected values. From the observation of this quadrupole line, at an SNR of 2, the sensitivity to perform a test on the symmetrization postulate with the presented experimental setup is estimated at 1.5×10^{-6} with respect to a magnetic dipole transition of ${}^{16}O_2$. Compared to previous tests the sensitivity for a test of the symmetrization postulate is only slightly lower than in Ref. [2] and [3]. Attempts were made to observe ^RR lines at N = 9-13 of ¹⁸O₂ in natural O₂ gas. Although the lines should have intensities at the 4×10^{-6} level, they were obscured by the strong Lorentzian wings of the nearby ¹⁶O₂ lines, and were therefore not observed.

In fact the work of Brault [9] represents the highest sensitivity study of molecular oxygen. Quadrupole lines were recorded from 43 atm·km oxygen samples in the sunset spectrum of the Earth's atmosphere, with an SNR of 100. This corresponds to a 3×10^{-8} sensitivity, which is more than an order of magnitude better than the laboratory studies of molecular oxygen using lasers, including this study, the study of de Angelis *et al* [2], and the study of Hilborn and Yuca [3]. In a recent laboratory study by Gianfrani *et al.* [4] a sensitivity of 5×10^{-8} is reported, only a factor of 2 above the sensitivity of Brault [9]. However, the method of Fourier-transform spectroscopy in the Earth's atmosphere was not used to search for symmetry-forbidden lines.

2.6 Conclusions

In this work, frequency positions and molecular constants for the oxygen A band were determined for all isotopomers. A positive signal on a line at the 3×10^{-6} sensitivity level $(2 \times 10^{-9} \text{ cm}^{-1})$ was recorded, thus demonstrating the sensitivity of the cavity ring-down setup. The use of a sensitivity scale of 13 orders of magnitude is presented, which is practical for future test experiments. This scale, based on isotopic abundancies, electric quadrupole line strengths, and Boltzmann populations, gives the possibility to record a positive signal (resonance line) at each desired intensity level. The spectroscopic information on isotopomers and also the electric quadrupole lines presented here, provides insight in the occurrence of coincidences at search positions for symmetry-forbidden lines with weak allowed resonances.

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2.7 Appendix A: Transition frequencies

In this appendix the transition frequencies (in cm⁻¹) of the investigated isotopomers are listed. Transitions denoted by an asterisk (*) do not exist due to constraints of angular-momentum coupling. Δ_{o-c} refers to the difference between the observed value and the calculated value of the transition frequency determined by a least-squares fit of the molecular constants.

	$^{\mathrm{P}}\mathrm{Q}$		PР		R		$^{\mathrm{R}}\mathrm{Q}$	
N	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$
0	*	*	*	*	*	*	$13\ 127.467$	0.042
1	*	*	$13\ 120.278$	0.006	$13\ 128.192$	0.036		
2	$13\ 119.616$	-0.005	$13\ 117.419$	-0.050	$13\ 130.608$	0.000	$13\ 132.549$	0.010
3	$13\ 116.589$	-0.058	$13\ 114.522$	-0.056	$13\ 132.994$	0.023	$13\ 134.932$	0.004
4					$13\ 135.249$	0.003	$13\ 137.238$	0.016
5	$13\ 110.530$	-0.008	$13\ 108.507$	0.037	$13\ 137.446$	0.013	$13\ 139.423$	-0.001
6					$13\ 139.525$	-0.007		
7	$13\ 104.104$	-0.005	$13\ 102.141$	0.002			$13\ 143.532$	-0.026
8	$13\ 100.756$	-0.012	13098.836	0.025	$13\ 143.447$	-0.015	$13\ 145.482$	-0.008
9	$13\ 097.380$	0.040	13095.444	0.049	$13\ 145.295$	0.001	$13\ 147.331$	-0.002
10	$13\ 093.853$	0.026	13091.865	-0.028	$13\ 147.043$	0.006	$13\ 149.069$	-0.017
11	13090.178	-0.049	13088.249	-0.055	$13\ 148.716$	0.026	$13\ 150.803$	0.054
12	13086.510	-0.031	13084.598	-0.030	$13\ 150.281$	0.027		
13	$13\ 082.792$	0.024	13080.833	-0.032	$13\ 151.786$	0.057	$13\ 153.835$	0.028
14	13078.897	-0.012	$13\ 077.003$	-0.012	$13\ 153.147$	0.033	$13\ 155.202$	0.001
15	$13\ 074.949$	-0.014	13073.080	0.001	$13\ 154.409$	0.000	$13\ 156.499$	-0.006
16	13070.947	0.016	13069.064	0.008	$13\ 155.614$	0.000		
17	13066.844	0.032						
18			13060.759	0.009				
19	13058.275	-0.040	13056.425	-0.042				
20	13053.885	-0.053	13052.052	-0.046	$13\ 159.519$	-0.014		
21	$13\ 049.491$	0.018	13047.666	0.024				
22	13044.945	0.022	13043.127	0.027				

Table 2.6: Transition frequencies of ¹⁶O¹⁸O.

Table 2.7: Transition frequencies of ¹⁶O¹⁷O.

	^{P}Q		PP		R	,	RQ	
N	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	Δ_{o-c}
0	*	*	*	*	*	*	$13\ 126.493$	-0.015
1	*	*	$13\ 119.231$	0.010	$13\ 127.328$	0.005	$13\ 129.221$	0.014
2	$13\ 118.510$	0.004	$13\ 116.336$	-0.005	$13\ 129.871$	0.029	$13\ 131.798$	0.029
3	$13\ 115.444$	-0.003	$13\ 113.361$	-0.009	$13\ 132.290$	0.019	$13\ 134.213$	-0.012
4	$13\ 112.298$	-0.046	$13\ 110.298$	-0.011	$13\ 134.591$	-0.019	$13\ 136.574$	-0.009
5	$13\ 109.180$	0.013	$13\ 107.177$	0.018	$13\ 136.849$	-0.008	$13\ 138.867$	0.020
6	$13\ 105.906$	-0.001	$13\ 103.928$	0.009	$13\ 139.035$	0.021	$13\ 141.051$	0.034
7	$13\ 102.549$	-0.012	$13\ 100.571$	-0.018	$13\ 141.051$	-0.028	$13\ 143.120$	0.025
8	$13\ 099.113$	-0.015	13097.160	-0.010	$13\ 143.120$	0.068	$13\ 145.108$	0.027
9	$13\ 095.605$	-0.001	13093.672	0.011	$13\ 144.968$	0.033	$13\ 146.996$	0.022
10	13092.010	0.014	13090.069	0.007	$13\ 146.746$	0.021	$13\ 148.766$	-0.009
11	13088.291	-0.006	13086.345	-0.029	$13\ 148.424$	0.001	$13\ 150.464$	-0.019
12	13084.501	-0.007	13082.582	-0.015	$13\ 149.999$	-0.029	$13\ 152.061$	-0.037
13	13080.641	0.010	13078.737	0.008	$13\ 151.510$	-0.031	$13\ 153.595$	-0.026
14	13076.649	-0.015	13074.770	-0.002	$13\ 152.941$	-0.021	$13\ 155.067$	0.016
15	13072.609	0.001	13070.704	-0.022	$13\ 154.286$	-0.003	$13\ 156.408$	0.021
16	13068.451	-0.012	13066.603	0.013	$13\ 155.541$	0.019		
17	13064.215	-0.013	13062.356	-0.008				
18	13059.892	-0.011	13058.021	-0.028				
19	13055.486	-0.003	13053.638	-0.005				
20	$13\ 050.995$	0.010	13049.166	0.018				
21	13046.400	0.010	13044.588	0.025				
22	13041.716	0.010	13039.889	0.002				
23	13036.933	0.001	13035.126	0.004				
24	13032.057	-0.010	13030.261	-0.005				
25	$13\ 027.142$	0.030	13025.328	0.009				
26	13022.075	0.009	13020.289	0.007				
27	$13\ 016.919$	-0.011	13015.149	-0.005				
28	$13\ 011.700$	-0.002	13009.921	-0.014				
29	$13\ 006.392$	0.008	13004.624	-0.001				
30	13000.977	0.003	12999.243	0.020				
31	12995.473	0.001	12993.726	-0.004				
32	12989.888	0.009	12988.156	0.011				
33	12984.172	-0.022	12982.427	-0.042				

	$^{\mathrm{P}}\mathrm{Q}$		PP		RR		$^{\mathrm{R}}\mathrm{Q}$	
N	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$
1	*	*	$13\ 122.536$	-0.001	$13\ 129.957$	-0.001	$13\ 131.869$	0.002
3	$13\ 119.341$	0.110	$13\ 117.228$	0.050	$13\ 134.491$	-0.001	$13\ 136.458$	0.001
5	$13\ 113.514$	0.026	$13\ 111.473$	-0.018	$13\ 138.697$	0.001	$13\ 140.692$	0.002
7	$13\ 107.497$	0.054	$13\ 105.536$	0.060	$13\ 142.565$	-0.002	$13\ 144.588$	0.003
9	$13\ 101.116$	0.039	13099.160	0.027	$13\ 146.100$	-0.004	$13\ 148.139$	-0.002
11	13094.455	0.069	13092.524	0.061	$13\ 149.303$	-0.002	$13\ 151.362$	0.001
13	13087.401	0.031	13085.498	0.033	$13\ 152.170$	0.001	$13\ 154.244$	0.001
15	13080.057	0.030	13078.165	0.026	$13\ 154.725$	0.030	$13\ 156.821$	0.034
17	13072.386	0.030	13070.511	0.026	$13\ 156.909$	0.029	$13\ 159.010$	0.022
19	13064.397	0.040	13062.549	0.047	$13\ 158.746$	0.024	$13\ 160.860$	0.014
21	13055.977	-0.052	13054.178	-0.012	$13\ 160.245$	0.026	$13\ 162.377$	0.018
23	13047.406	0.035	13045.580	0.032	$13\ 161.394$	0.026	$13\ 163.548$	0.024
25	13038.441	0.059	13036.628	0.053	$13\ 162.185$	0.018	$13\ 164.374$	0.035
27	13029.114	0.053	13027.230	-0.039	$13\ 162.622$	0.010	$13\ 164.822$	0.022
29	13019.417	0.011	13017.655	0.025			$13\ 164.917$	0.012
31	13009.462	0.045	13007.692	0.036				
33	12999.085	-0.005	12997.369	0.025				
35	12988.422	-0.003	12986.698	0.003				
37	12977.423	0.003	12975.706	0.001				
39	12966.097	0.025	12964.361	-0.011				
41	12654.359	-0.020	12952.659	-0.035				
43	12942.170	-0.169	12940.603	-0.066				

Table 2.8: Transition frequencies of ${}^{18}O_2$.

 ^{R}Q PР ^{P}O ^RR Nobserved observed Δ_{o-c} observed $\Delta_{\rm o-c}$ observed Δ_{o-c} Δ_{o-c} * * * * * * 0 $13\ 128.512$ 0.042 * * 1 $13\ 121.536$ 0.029 $13\ 131.029$ 0.0210.068 $13\ 129.136$ $\mathbf{2}$ 13 133.445 0.024 $13\ 120.932$ 0.043 13 118.723 -0.030 $13\ 131.507$ 0.023 $\mathbf{3}$ 13 117.986 -0.027 $13\ 115.901$ -0.052 $13\ 133.785$ 0.009 $13\ 135.737$ 0.0014 $13\ 115.033$ -0.059 $13\ 113.002$ -0.066 $13\ 135.978$ -0.004 $13\ 137.967$ 0.007513 112.035 -0.065 $13\ 110.112$ 0.012 $13\ 138.102 - 0.001$ 6 $13\ 109.046$ 0.016 $13\ 107.099$ 0.0527 $13\ 105.921$ 0.043 $13\ 103.953$ 0.043 $13\ 144.088 - 0.018$ 8 $13\ 102.667$ 0.023 $13\ 143.930\ -0.023$ $13\ 145.971\ -0.010$ 9 $13\ 099.333$ 0.006 $13\ 145.711\ -0.019$ $13\ 147.764 - 0.004$ 10 $13\ 095.943$ 0.017 $13\ 147.402$ -0.019 $13\,094.008$ 0.01611 $13\,090.460 - 0.058$ $13\ 151.124$ 0.04112 $13\,088.811 -0.061$ $13\,086.904 - 0.055$ $13\ 150.577$ 0.035 $13\ 152.644$ 0.03513 $13\,085.207 - 0.012$ $13\,083.307 - 0.008$ $13\ 152.003$ 0.031 $13\ 154.062$ 0.01514 $13\ 081.445\ -0.037$ $13\,079.575 - 0.012$ $13\ 153.316$ 0.003 $13\,077.636 - 0.024$ $13\,075.761 - 0.013$ $13\ 154.591$ 0.02415-0.013 $13\,073.740$ 16 $13\,071.876$ 0.000 $13\ 155.733$ 0.001170.000 13 069.763 0.002 $13\,067.892$ 18 0.067 $13\,065.686$ 0.002 $13\,063.891$ 19 $13\ 061.523$ 0.002 $13\,059.635$ -0.03520-0.06013 057.241 -0.032 $13\,055.370$ 21 $13\,052.901$ -0.038 $13\,051.108$ 0.00422 $13\,048.562$ 0.043 $13\,046.741$ 0.049 23 $13\,044.087$ 0.0650.075 $13\,042.258$ 24 $13\ 039.456$ 0.03713 037.628 -0.02025 $13\,034.671$ -0.067 $13\,032.868 - 0.068$ 26 $13\ 029.914$ -0.057 $13\,028.153 - 0.023$ 27 $13\ 025.164$ 0.049

Table 2.9: Transition frequencies of ${}^{17}O{}^{18}O$.

	$^{\mathrm{P}}\mathrm{Q}$		PР		RR		^{R}Q	
N	observed	Δ_{o-c}	observed	Δ_{o-c}	observed	$\Delta_{\rm o-c}$	observed	Δ_{o-c}
0	*	*	*	*	*	*	$13\ 127.558$	0.010
1	*	*	$13\ 120.421$	0.008	$13\ 128.300$	0.032	$13\ 130.191$	0.030
2	$13\ 119.760$	-0.010	$13\ 117.591$	-0.028	$13\ 130.729$	0.018	$13\ 132.656$	0.013
3	$13\ 116.796$	-0.011	$13\ 114.745$	0.006	$13\ 133.084$	0.018	$13\ 134.998$	-0.025
4	$13\ 113.794$	-0.007	$13\ 111.734$	-0.037	$13\ 135.324$	-0.010	$13\ 137.325$	0.015
5	$13\ 110.714$	-0.007	$13\ 108.736$	0.019	$13\ 137.520$	0.007	$13\ 139.512$	0.008
6	$13\ 107.569$	0.008	$13\ 105.596$	0.021	$13\ 139.610$	0.006	$13\ 141.612$	0.003
7	$13\ 104.317$	0.000	$13\ 102.337$	-0.009	$13\ 141.612$	0.006	$13\ 143.654$	0.031
8	$13\ 100.973$	-0.015	13099.016	-0.015	$13\ 143.553$	0.033	$13\ 145.577$	0.029
9	$13\ 097.555$	-0.018	13095.605	-0.023	$13\ 145.373$	0.028	$13\ 147.401$	0.017
10	13094.071	-0.002	13092.158	0.019	$13\ 147.110$	0.029	$13\ 149.126$	-0.004
11	13090.502	0.016	13088.560	-0.003	$13\ 148.766$	0.038	$13\ 150.755$	-0.032
12	13086.796	-0.017	13084.885	-0.015	$13\ 150.244$	-0.041	$13\ 152.327$	-0.026
13	13083.053	0.000	13081.165	0.015	$13\ 151.732$	-0.020	$13\ 153.797$	-0.033
14	13079.215	0.008	13077.304	-0.009	$13\ 153.108$	-0.022	$13\ 155.232$	0.016
15	13075.269	-0.005	13073.385	-0.005	$13\ 154.420$	0.003		
16	$13\ 071.239$	-0.016	13069.358	-0.022	$13\ 155.630$	0.017		
17	$13\ 067.145$	-0.004	13065.282	0.000				
18	13062.950	-0.006	13061.101	0.003				
19	13058.668	-0.008	13056.819	-0.008				
20	13054.295	-0.013	13052.494	0.026				
21	13049.871	0.017	13048.020	-0.002				
22	13045.345	0.032	13043.522	0.033				
23	$13\ 040.693$	0.009	13038.868	-0.001				
24	13035.959	-0.008	13034.165	0.004				
25	13031.156	-0.007	13029.349	-0.016				
26	13026.280	0.008	13024.477	-0.005				
27	$13\ 021.323$	0.031	$13\ 019.509$	-0.001				
28	$13\ 016.229$	0.005	13014.452	0.001				
29	$13\ 011.059$	-0.010	13009.298	-0.005				
30	$13\ 005.835$	0.011	13004.052	-0.015				
31	$13\ 000.482$	-0.009	12998.773	0.031				
32	$12\ 995.053$	-0.017	12993.328	-0.001				

Table 2.10: Transition frequencies of ${}^{17}O_2$.

2.8 Appendix B: Molecular constants

Table 2.11: Molecular constants for the $X^3 \Sigma_g^-$, v = 0 ground state of molecular oxygen, which were kept fixed in the analysis, obtained from the literature. For ¹⁷O₂ the rotational and centrifugal distortion constants were derived in the present study. Values for the spin-coupling parameters of ¹⁷O₂ were estimated (*in italics*). All values are in cm⁻¹. The value in parentheses represents the uncertainty (1 σ) in units of the last digits.

	$^{16}\mathrm{O}_2$	$^{16}O^{17}O$	$^{16}O^{18}O$
B_0	1.437676476 (77)	1.395319 (3)	1.3578530(3)
D_0	$4.84256~(63) \times 10^{-6}$	4.623×10^{-6}	4.302×10^{-6}
${H}_0$	$2.8~(2) \times 10^{-12}$		
λ_0	$1.984751322\ (72)$	1.9847094 (3)	1.9846762(14)
λ_0'	$1.94521~(50) \times 10^{-6}$	$1.917~(6) \times 10^{-6}$	$1.771~(26) \times 10^{-6}$
λ_0''	$1.103~(41) \times 10^{-11}$		
μ_0	$-8.425390(13) \times 10^{-3}$	$-8.17612(13) \times 10^{-3}$	$-7.9551(23) \times 10^{-3}$
μ_0'	$-8.106~(32) \times 10^{-9}$	$-8.0~(1) \times 10^{-9}$	$-8.06(38) \times 10^{-9}$
μ_0''	$-4.7(2) \times 10^{-14}$		
Ref.	[22]	[26]	[25]

	¹⁷ O ¹⁸ O	$^{18}O_{2}$	$^{17}{ m O}_2$
B_0	1.315490(3)	1.27800847(23)	1.35289(2)
D_0	4.102×10^{-6}	3.835×10^{-6}	$4.29~(5) \times 10^{-6}$
${H}_0$			
λ_0	1.9846329 (13)	1.98459622 (37)	1.9846762
λ_0'	$1.801~(10) \times 10^{-6}$	$1.738~(14) \times 10^{-6}$	1.8×10^{-6}
λ_0''			
μ_0	$-7.70696~(23) \times 10^{-3}$	$-7.48648~(10) \times 10^{-3}$	-7.9×10^{-3}
μ_0'	$-9.0(2) \times 10^{-9}$	$-11.7(2) \times 10^{-9}$	-8.0×10^{-9}
μ_0''			
Ref.	[26]	[25]	[This work]

Chapter 3

The $b^1\Sigma_g^+-X^3\Sigma_g^-$ ((3,2,1),0) bands of oxygen isotopomers

Abstract

The $b^1\Sigma_g^+-X^3\Sigma_g^-$ ((3,2,1),0) bands of oxygen isotopomers were investigated and line positions of the four branches in each band of the weak magnetic dipole transitions were determined with an accuracy of 0.01 cm⁻¹. The positions of over 750 lines are presented together with (re)analyses of the rotational constants, resulting in improved or new molecular constants for the excited states.

3.1 Introduction

The $b^1\Sigma_g^+-X^3\Sigma_g^-$ electronic system of the O₂ molecule is, despite its small oscillator strength, a prominent feature in the absorption spectrum of the terrestrial atmosphere. For this reason the system is of importance for light scattering and extinction studies of the Earth's atmosphere and has, after a pivotal study of Babcock and Herzberg [1], been subjected to numerous investigations aimed at the determination of the line positions [2, 3], intensities [4], and pressure-induced effects [2, 5]. The majority of these studies focus on the most abundant isotope, ¹⁶O₂ [2, 3, 6]. The small oscillator strength originates from the strongly forbidden character of the gerade–gerade and Σ^+ – Σ^- transitions. The b–X system can only be observed via a magnetic-dipole transitionmoment.

From spectroscopic measurements on atmospheric ozone, isotopic ratios in O₃ were found to deviate from the terrestrial abundance of oxygen isotopes [7,8]. This phenomenon is ascribed to dynamical processes occurring in the atmosphere. To gain deeper understanding of these processes it is of importance to identify transitions by which the isotopic constitution of oxygen bearing molecules can be determined. The $b^1\Sigma_g^+-X^3\Sigma_g^-$ electronic system is such a tool to probe O₂ isotopomers in the earth's atmosphere, as was demonstrated by Osterbrock *et al.* [9] and by Slanger *et al.* [10].

The oxygen A band [11] is the most prominent absorption feature of this electronic system, followed by the (1,0) band near 688 nm, usually referred to as the B band. This B band has an experimentally determined radiative rate A_{10} ranging from 0.0069 s^{-1} [4] to 0.00724 s^{-1} [12, 13]. These values correspond to an oscillator strength of $f_{10} \approx 1.6 \times 10^{-11}$. The B band is 10 orders of magnitude weaker than ordinary electricdipole-allowed transitions, and ≈ 10 times weaker than the A band. In this study all isotopomers of this absorption band were investigated, except ${}^{16}O_2$; the resolution in the present experiment would not have contributed to an improvement of the existing data.

Next in line is the γ band, corresponding to the (2,0) band with an oscillator strength $f_{20} \approx 0.63 \times 10^{-12}$. The Franck-Condon factor for this band is very small: 0.00264 [4]. Nevertheless it can be readily observed in the Earth's atmosphere. The weakness of this band in combination with the reflectivity of the used mirrors limited the study to the ${}^{16}O_2$, ${}^{16}O^{17}O$, ${}^{18}O_2$, and ${}^{17}O_2$ isotopomers. The weakest band discussed is the (3,0) band, which is 10^4 times weaker than the A band. Known as the δ band, this weak absorption band was investigated by Babcock and Herzberg [1] and Biennier and Campargue [5]. Results of the ${}^{16}O_2$ and ${}^{18}O_2$ isotopomers will be presented.



Figure 3.1: The experimental setup. PD, photodiodes; PMT, photomultiplier tube.

3.2 Experiment

3.2.1 General

The experimental setup is similar to the setup used for the study of the A band [11], with exception of the wavelength calibration part, see Fig. 3.1. Wavelength tunable pulsed laser radiation (5 ns) at the necessary wavelengths is obtained from a Nd:YAG pumped dye laser system running on various dyes. With highly reflecting mirrors (R > 99.98%) a stable nonconfocal cavity is formed. The light leaking out of the cavity is detected with a photomultiplier tube (Thorn EMI 9658 RA) and stored on a 350 MHz oscilloscope (LeCroy 9450). The decay transient, measured as a function of wavelength setting, is an accurate and sensitive measure of the absorption in the cavity. After a summation of 5 decay transients the resulting decay curve was evaluated online by computer.

Accurate frequency determination of oxygen resonances is the central issue of this study. For this purpose I₂-absorption spectra and the dye laser power were recorded simultaneously with the O₂ spectra. Spectra of ${}^{16}O_2$ were obtained from a natural gas sample (99.999% pure O₂), while spectral recordings of the other isotopomers were obtained from enriched oxygen samples. Spectra of ${}^{16}O{}^{17}O$ and ${}^{17}O_2$ were obtained



Figure 3.2: CRD recording of the B band from the ¹⁸O₂-enriched sample at 31.6 Torr. This recording was used to determine line positions of ¹⁷O¹⁸O and ¹⁶O¹⁸O (marked with '•'). The bottom panel shows a simultaneously recorded I₂-absorption spectrum (after intensity normalization).

from a 50% ¹⁷O-enriched sample (Campro Scientific), also containing ¹⁶O₂. The 3 different isotopes in this sample appeared to have equal densities. To record spectra of ¹⁶O¹⁸O, ¹⁸O₂, and ¹⁷O¹⁸O, a ¹⁸O₂-enriched sample (Eurisotop, 95% ¹⁸O₂) was used. The ¹⁶O¹⁸O and ¹⁷O¹⁸O isotopes were minority species in the enriched sample, see Fig 3.2, and could therefore not always be detected.

3.2.2 B band

Tunable pulsed laser radiation near 688 nm is obtained from the dye laser system running on Pyridine-1 dye. With highly reflecting mirrors ($R \approx 99.998\%$, Research Electro Optics) transients with decay times τ of 50–60 μ s were established in a 42 cm long cell, corresponding to an effective absorption path of 50 km (3τ). Spectra of the ¹⁷O¹⁸O and ¹⁶O¹⁸O isotopomers were recorded in ≈ 30 Torr of the ¹⁸O₂-enriched sample, an example is shown in Fig 3.2. Under this condition the signals on the ¹⁸O₂ lines were saturated and reliable determination of the line position is not possible. Line



Figure 3.3: CRD recording of the γ -band bandhead of ${}^{16}O_2$ at 60 Torr. This spectrum is recorded in an 86.5 cm long cell. The noise is 5.3×10^{-9} cm⁻¹ at five shots averaging. This is less than 0.25% of the baseline.

positions of ¹⁸O₂ were determined from a sample at ≈ 1 Torr. The ¹⁷O-enriched sample was investigated at 16–17 Torr. At pressures below 30 Torr the pressure-induced shift is $<0.001 \text{ cm}^{-1}$ [2,6], negligibly small for the accuracy of the present experiment. Doppler broadening, FWHM $\approx 0.031 \text{ cm}^{-1}$ for the B band at room temperature, contributes to the observed line width of 0.07–0.08 cm⁻¹, which is dominated by the laser bandwidth of 0.06 cm⁻¹.

For the purpose of wavelength calibration an I₂-absorption spectrum was recorded at a temperature of 430 K. An example of such an I₂-absorption spectrum is shown in the bottom panel of Fig 3.2. In the wavelength range near 690 nm I₂ has strong transitions in the B–X system for (v', v'' = 6) bands. To reach sufficient population of v'' = 6 levels the I₂ sample was heated to 430 K. From the weight of solid iodine evaporated in the cell an operation pressure of 60 Torr I₂ gas is estimated at which the absorption measurements are performed. At these pressures collisional broadening of I₂ lines occur, but not in an amount to affect the width of the observed resonances (0.07 cm^{-1}) . Pressure-induced shifts at 60 Torr in I₂ are on the order of 0.002 cm⁻¹. Three passes through the heated I₂ cell creates a total absorption length of 1.2 m.



Figure 3.4: CRD recording of the R branches of the δ band of ¹⁸O₂ at 223 Torr. The descending baseline represents the wavelength dependence of the mirror reflectivity.

3.2.3 γ band

DCM dye is used to obtain pulsed laser radiation in the wavelength range 625–645 nm. Mirrors with reflectivities $R \geq 99.98\%$ (Newport SuperMirrors) and radii of curvature of 1 m formed a stable nonconfocal cavity of 42 cm. Typical ring-down times (τ) of 7.5 μ s could be obtained. Spectra of ¹⁶O₂ and ¹⁸O₂ were recorded using pressures of 60 Torr in the cell, while in case of the ¹⁷O-enriched sample pressures of 200 Torr were applied. Signals of ¹⁶O¹⁸O and ¹⁷O¹⁸O, observed for the A and B bands, were in case of the γ band to weak to be detected. Since the mirrors used at 630 nm have a lower reflectivity than the sets available at 760 and 680 nm, the noise-equivalent detection limit at 630 nm is a factor of 10 higher at $\approx 1 \times 10^{-8}$ cm⁻¹, thus prohibiting observation of weaker features. Fig. 3.3 shows a spectrum of the bandhead of ¹⁶O₂.

To obtain a good SNR on the I_2 spectra, the I_2 sample in a glass cell was heated to 305 K, thus reaching a vapor pressure of 1 Torr. Three passes through the 40 cm long cell were sufficient to record a reliable I_2 spectrum. In the I_2 atlas the frequency range 15789–15806 cm⁻¹ is missing due to interference with the HeNe-laser line during the

3.2.4 δ band

Rhodamine B dye is used to obtain laser radiation in the wavelength range 578–590 nm. Mirrors with reflectivities of $R \geq 99.99\%$ (Research Electro Optics) and radii of curvature of 1 m formed a stable nonconfocal cavity of 86.5 cm. With a summation over 5 shots a noise equivalent detection limit of 2.0×10^{-9} was achieved, which allowed recording spectra of the δ band at moderate pressures. An example of an ¹⁸O₂ spectrum is shown in Fig. 3.4. The intensities of the individual lines are in the order of 20×10^{-9} cm⁻¹ at pressures of 223 Torr.

Wavelength calibration is straightforward in this wavelength region. A single pass through the 40 cm long I_2 cell is sufficient to record a clear I_2 -absorption spectrum at room temperature.

3.3 Data analysis

3.3.1 Spectroscopic analysis

Determination of transition frequencies and rotational constants requires an accurate absolute frequency scale. Simultaneously recorded I₂-absorption spectra, as shown in the bottom panel of Fig. 3.2, are used for absolute wavelength calibration. The Signalto-Noise Ratio (SNR) of the I₂-absorption spectra are improved by normalizing them to the laser power, measured for each pulse on a separate photodiode. With computerized fitting routines the I₂ resonances were detected and fitted to Gaussian curves. After assignment with the I_2 -reference atlas [14], including a recalibration of the atlas involving a shift of -0.0056 cm⁻¹ [15], an interpolation between the assigned I₂ lines establishes an accurate frequency scale which, in turn, was employed to calibrate the O_2 spectra. The O_2 resonances in the frequency-calibrated spectra were then fitted to Voigt profiles to determine the frequency positions of these resonances. With line widths in the I_2 - and O_2 -spectra of 0.06–0.07 cm⁻¹, predominantly caused by the laser bandwidth, this results in an absolute accuracy for strong and nonoverlapped O_2 lines of 0.01 cm⁻¹. In some O_2 spectra an oscillatory background occurred. Oscillations in the background signal of CRD are well known, the exact origin of this phenomenon is not yet understood. Shifts in the maximum of an absorption due to the oscillating background, and thus errors in the determination of transition frequencies, are circumvented by taking into account the oscillating background while fitting Voigt profiles to determine the frequency positions.

	$^{16}O_{2}$	$^{16}{\rm O}^{17}{\rm O}$	$^{16}{ m O}^{18}{ m O}$
$egin{array}{c} u_{10} \ B' \ D' \end{array}$	$\begin{array}{c} 14526.9976 \ (12) \\ 1.372951 \ (18) \\ 5.40 \ (5) \times 10^{-6} \end{array}$	14507.583 (2) 1.332761 (15) $5.11 (2) \times 10^{-6}$	$\begin{array}{c} 14490.145 \ (3) \\ 1.29727 \ (3) \\ 4.80 \ (8) \times 10^{-6} \end{array}$
	$^{17}{ m O}^{18}{ m O}$	$^{18}O_{2}$	$^{17}{ m O}_2$
$\nu_{10} \\ B' \\ D'$	$\begin{array}{c} 14470.146 \ (3) \\ 1.25710 \ (3) \\ 4.77 \ (8) \times 10^{-6} \end{array}$	$\begin{array}{c} 14452.164 \ (2) \\ 1.221495 \ (15) \\ 4.28 \ (2) \times 10^{-6} \end{array}$	$\begin{array}{c} 14487.858 (3) \\ 1.292776 (14) \\ 4.95 (2) \times 10^{-6} \end{array}$

Table 3.1: Molecular constants for the $b^1 \Sigma_g^+$, v = 1 excited state of molecular oxygen. The constants for ${}^{16}O_2$ were derived from a reanalysis of the data of Ref. [1]. All values are in cm⁻¹. The values in parentheses represent the estimated error (1σ) from the fit in units of the last digits.

The transition frequencies as determined by the above described procedure, presented in appendix A, B, and C, were included on the input deck of a least-squares fitting routine for each isotopomer. The excited state is represented by

$$E_{(N)} = \nu_{v0} + B'_{v0}N(N+1) - D'_{v0}N^2(N+1)^2, \qquad (3.1)$$

while the $X^{3}\Sigma_{g}^{-}$, v = 0 ground state energies were represented by an effective Hamiltonian as given by Rouillé *et al.* [16]. Except for ¹⁷O₂ the molecular constants for the ground state were kept fixed at accurate values obtained from far-infrared and microwave spectroscopy. In chapter 2, appendix B, a detailed listing of all relevant ground state constants and references are given.

The data were included in the weighted least squares fits with an uncertainty of 0.01 cm^{-1} for intense and nonoverlapped lines, and $0.02-0.03 \text{ cm}^{-1}$ for the weak or partially overlapped lines. These estimated uncertainties resulted in a reduced χ^2 of one, confirming the estimated experimental uncertainty of the spectroscopic method. For each resonance line the deviation between measured transition frequency and calculated value is given in Tables 3.5–3.15, appendix A, B, and C. Molecular constants, resulting from the fitting procedures, for the $b^1\Sigma_g^+$, v = (3, 2, 1) excited states are presented in Table 3.1, 3.2, and 3.3. The listed value of the band origin ν_{v0} is dependent on the definition of the zero energy level. Usually the lowest energy state is chosen at zero energy, but in case of ${}^{16}O_2$ and ${}^{18}O_2$ the N = 0, J = 1 level does not exist for symmetry reasons; the lowest energy state for these isotopomers is the N = 1, J = 0

	$^{16}O_{2}$	$^{16}{ m O}^{17}{ m O}$
$egin{array}{c} u_{20} \ B' \ D' \end{array}$	$\begin{array}{c} 15903.748 \ (3) \\ 1.35463 \ (2) \\ 5.49 \ (3) \times 10^{-6} \end{array}$	$\begin{array}{c} 15864.681 \ (2) \\ 1.31523 \ (2) \\ 5.16 \ (4) \times 10^{-6} \end{array}$
	$^{18}O_{2}$	$^{17}O_{2}$
$egin{array}{c} u_{20} \ B' \ D' \end{array}$	$\begin{array}{c} 15753.033 \ (2) \\ 1.20614 \ (2) \\ 4.32 \ (2) \times 10^{-6} \end{array}$	$\begin{array}{c} 15824.969 \ (3) \\ 1.27587 \ (3) \\ 4.69 \ (5) \times 10^{-6} \end{array}$

Table 3.2: Molecular constants for the $b^1 \Sigma_g^+$, v = 2 excited state of molecular oxygen. All values are in cm⁻¹. The values in parentheses represent the estimated error (1σ) from the fit in units of the last digit.

level. Here zero is defined at the energy given by the Rouillé Hamiltonian without spin and rotation, i.e., not at a specific level. The offset between N = 0, J = 1 levels and the zero energy as defined here are given for each isotopomer in chapter 2, Table 2.2.

For ${}^{17}\text{O}_2$ no accurate ground state constants are available from microwave or farinfrared spectroscopy. Therefore the data on the A, B, and γ band are included in a combined fit. In the fit to 276 points the rotational constants of the ground state as well as 3 constants for each vibrational level in $b^1\Sigma_g^+$ were varied, resulting in updated values for the ground state of ${}^{17}\text{O}_2$, listed in Table 3.4. The spin coupling constants of the ground state were kept fixed in the fit at values as estimated from the values for ${}^{16}\text{O}{}^{18}\text{O}$.

3.3.2 Band intensities of the $b^1 \Sigma_g^+ - X^3 \Sigma_g^-$ (3,0) band

The data on the $b^1\Sigma_g^+-X^3\Sigma_g^-$ (3,0) band allowed for an estimate of the absorption strength of this band. Signal integration over all measured lines up to J = 21 yields a value of $9.3 \pm 0.4 \times 10^{-27}$ cm/molecule. However this value needs correction for the effect of laser bandwidth. The laser bandwidth of 0.05 cm⁻¹ is approximately equal to the combined effects of Doppler and collisional broadening (≈ 0.04 cm⁻¹). In combination with the low absorption per line with respect to the background this leads to a correction factor of 1.4 [17]. Hence, a band intensity of $1.3 \pm 0.1 \times 10^{-26}$ cm molecule⁻¹ is obtained for the (3,0) band of ${}^{16}O_2$. This value is somewhat smaller than the one obtained in Ref. [5]. When comparing with the band intensity of the

	$^{16}O_2$ [this work]	${}^{16}O_2$ [1]
$egin{array}{c} u_{30} \ B' \ D' \end{array}$	$\begin{array}{c} 17252.452 \ (3) \\ 1.33611 \ (3) \\ 5.43 \ (5) \times 10^{-6} \end{array}$	$\begin{array}{c} 17252.428 \ (8) \\ 1.3363 \ (5) \\ 5.63 \ (47) \times 10^{-6} \end{array}$
	${}^{16}O_2$ [5]	$^{18}O_2$ [this work]
$egin{array}{c} u_{30} \ B' \ D' \end{array}$	$\begin{array}{c} 17252.464 \ (4) \\ 1.3361 \ (3) \\ 5.5 \ (2) \times 10^{-6} \end{array}$	$\begin{array}{c} 17028.978 \ (4) \\ 1.19063 \ (5) \\ 4.23 \ (9) \times 10^{-6} \end{array}$

Table 3.3: Molecular constants for the $b^1 \Sigma_g^+$, v = 3 excited state of molecular oxygen. All values are in cm⁻¹. The values in parentheses represent the estimated error (1σ) from the fit in units of the last digit.

(2,0) band [18], we find that the (3,0) band is 35 times weaker than the (2,0) band, in accordance with the calculated Franck-Condon factors [19]. Following a similar procedure, we derive a band intensity of $1.6 \pm 0.1 \times 10^{-26}$ cm molecule⁻¹ for the (3,0) band of ¹⁸O₂. From the fact that the v = 3 wavefunction lies lower in the b¹ Σ_g^+ potential for the heavier isotope, a larger overlap with the $X^3\Sigma_g^-$ (v = 0) wavefunction, and hence a larger band intensity, may be expected.

3.4 Discussion and conclusions

Transition frequencies of the $b^1 \Sigma_g^+ - X^3 \Sigma_g^-$ (1,0) band were measured for ¹⁶O¹⁸O, ¹⁶O¹⁷O, ¹⁸O₂, ¹⁷O¹⁸O, and ¹⁷O₂, with an accuracy of 0.01 cm⁻¹, under pressure conditions where pressure shifts are negligible with respect to the achieved accuracy of the absolute frequency determination. Combined with previous work [1,3,11] spectral positions of the A and B bands are known with high accuracy for all isotopomers of oxygen.

In case of the γ and δ band the decreasing transition probability prevented the investigation of all isotopomers. Accurate line positions of the γ band were determined for four oxygen isotopomers (¹⁶O₂, ¹⁶O¹⁷O, ¹⁸O₂ and ¹⁷O₂), and molecular constants were derived. The δ band was investigated for ¹⁶O₂ and ¹⁸O₂. The obtained information may help to identify emission bands from excited vibrational levels of O₂(b¹ $\Sigma_{\rm g}^+$), including minority isotopomers, as observed in the Earth's atmosphere.

All recordings were taken in a laboratory environment at well-defined pressures, that were constant over the absorption path. Phillips and Hamilton [2] have determined

Table 3.4: Molecular constants for the X ${}^{3}\Sigma_{g}^{-}$, v = 0 ground state of ${}^{17}O_{2}$ as obtained from a combined fit to the b–X ((2, 1, 0), 0) bands. B_{0} and D_{0} are obtained from the fit, spin-coupling parameters were estimated (see text). All values are in cm⁻¹. The values in parentheses represent the estimated error (1 σ) from the fit in units of the last digit.

$egin{array}{c} B_0 \ D_0 \end{array}$	$\begin{array}{c} 1.35300 \ (2) \\ 4.272 \ (16) \times 10^{-6} \end{array}$
$egin{array}{l} \lambda_0 \ \lambda_0' \ \mu_0 \ \mu_0' \end{array}$	$\begin{array}{c} 1.9846762 \\ 1.8 \times 10^{-6} \\ -7.9 \times 10^{-3} \\ -8.0 \times 10^{-9} \end{array}$

pressure shifts, amounting to -14.5×10^{-6} cm⁻¹ Torr⁻¹ for the A band and -18.4×10^{-6} cm⁻¹ Torr⁻¹ for the B band. In a simple extrapolation a pressure shift of -22.4×10^{-6} cm⁻¹ Torr⁻¹ would follow for the γ band, and -26.3×10^{-6} cm⁻¹ Torr⁻¹ for the δ band.

For the measurements on the γ band of ${}^{16}O_2$, conducted at 60 Torr, this implies a pressure shift of -0.0013 cm^{-1} , while for the ${}^{16}O^{17}O$, ${}^{18}O_2$ and ${}^{17}O_2$ spectra a pressure shift of -0.005 cm^{-1} may be expected assuming that the pressure shift is isotope independent. The values in Table 3.2 are not corrected for these pressure shifts. For ${}^{16}O^{17}O$ and ${}^{17}O_2$ the presented data are the first reported for the γ band. The γ band of the ${}^{18}O_2$ isotopomer was previously studied by Hill and Schawlow [20], however without an absolute calibration. Relative frequency measurements yielded rotational constants B = 1.2067 (5) cm⁻¹ and D = 4.7 (5) $\times 10^{-6}$ cm⁻¹, in agreement with the present findings. Engeln *et al.* [21] did not perform a rotational analysis on their data for the γ band of ${}^{18}O_2$.

The old data of Babcock and Herzberg [1] are still considered the most accurate for the γ band of ${}^{16}\text{O}_2$. It should be noted that the value for ν_{20} given in Ref. [1] relates to the lowest N = 1, J = 0 level which is offset by 1.3316 cm⁻¹ from the zero level contained in the Hamiltonian of Rouillé *et al.* [16]. When corrected for this offset a value of 15903.747 cm⁻¹ results for the band origin in the work of Babcock and Herzberg, exactly coinciding with the present value for ν_{20} .

Also in case of the δ band pressure-induced shifts have to be considered. In this study, pressures of 183 Torr (¹⁶O₂) and 223 (¹⁸O₂) Torr of pure oxygen were used for the spectral recordings. The values in Table 3.3 are not corrected for pressure shifts. The spectra of Babcock and Herzberg [1] were recorded through a large air mass, where the absorption is integrated over a range of altitude-dependent pressures, the dominant contribution originating from ambient atmospheric conditions.

The ICLAS data of Biennier and Campargue [5] were recorded with a cell filled with 600 Torr pure oxygen, surrounded by ambient air, conditions for which a similar pressure shift as in Ref. [1] was expected. Biennier and Campargue have commented that the data of Ref. [1] may possess a systematic measurement shift of 0.02 cm^{-1} . We find, from a study at lower pressure, a value for ν_{30} which is smaller by 0.012 ± 0.005 cm⁻¹ compared to Ref. [5]. From the simple extrapolation of the pressure shifts as determined by Phillips and Hamilton [2] a pressure shift of $-26.3 \times 10^{-6} \text{ cm}^{-1}$ Torr⁻¹ follows for the δ band. This would bring the present value in accordance with the value of Ref. [1] rather than Ref. [5]. A final resolution of this issue will await measurements of pressure shifts in the (3,0) band, including shifts induced by N₂.

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3.5 Appendix A: Transition frequencies of the B band

In this appendix the transition frequencies (in cm⁻¹) of the B band of the investigated isotopomers are listed. Transitions denoted by an asterisk (*) do not exist due to constraints of angular-momentum coupling. Δ_{o-c} refers to the difference between the observed value and the calculated value of the transition frequency determined by a least-squares fit of the molecular constants.

	$^{\mathrm{P}}\mathrm{Q}$)	Р		RR		RQ	
Ν	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$
0	*	*	*	*	*	*	$14\ 493.211$	0.000
1	*	*	14486.104	0.005	14493.857	-0.025	14496.758	-0.016
2	14485.410	-0.004	14483.263	0.001	$14\ 496.241$	0.007	14498.149	-0.016
3	14482.376	0.002			14498.453	-0.011	14500.385	-0.036
4			14477.233	0.007	14500.535	-0.038	14502.518^\dagger	-0.030
5	14476.042	0.011	14474.026	0.000	14502.518^{\dagger}	-0.042	14504.543	-0.008
6			14470.704	-0.002	14504.411	-0.013	14506.429	0.000
7			14467.267	0.002	14506.166	-0.001	14508.195	0.011
8	14465.670	0.009	14463.716	0.013	14507.794	0.007	14509.833	0.018
9	14461.976	0.010	14460.018	-0.003	14509.294	0.010	14511.336	0.013
10	14458.156	0.004	14456.234	0.016	14510.660	0.001	14512.711	0.003
11	14454.238	0.020	14452.290	-0.005	14511.902	-0.008	14513.958	-0.011
12	14450.152	-0.011			14513.040	0.001	14515.094	-0.013
13	14445.982	-0.006	14444.082	-0.003	14514.031	-0.012	14516.117	-0.004
14	14441.690	-0.003	14439.799	0.000	14514.916	-0.008	14516.996	-0.015
15	14437.267	-0.010	14435.394	0.001	14515.661	-0.019	14517.786	0.010
16	14432.759	0.018	14430.877	0.012	14516.310	-0.002	14518.426	0.008
17	14428.093	0.010	14426.217	0.000	14516.814	-0.006	14518.940	0.006
18	14423.299	-0.006			14517.193	-0.009	14519.352^{\dagger}	0.027
19					14517.458^{\dagger}	-0.001	14519.625^{\dagger}	0.035
20	14413.369	-0.016	$14\ 411.542$	-0.003	14517.595^\dagger	0.005	14519.758^\dagger	0.028
21	$14\ 408.246$	0.003			14517.595^{\dagger}	0.000	14519.758^{\dagger}	-0.006

Table 3.5: Transition frequencies of ¹⁶O¹⁸O.

Table 3.6: Transition frequencies of ${}^{16}O{}^{17}O$.

	^{P}Q		PP		RR		RQ	
Ν	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$
0	*	*	*	*	*	*		
1	*	*	14503.454	-0.008	14511.453	-0.005	14513.337	-0.006
2	14502.707	-0.005	14500.526	-0.020	14513.873	0.000	14515.793	-0.007
3	14499.575	-0.007	$14\ 497.495$	-0.011	14516.166	0.003	14518.111	-0.005
4	$14\ 496.369$	-0.006	$14\ 495.339$	-0.001	14518.321	-0.005	14520.309	0.010
5	14493.057	-0.001	$14\ 491.058$	0.008	14520.362	-0.002	14522.360	0.007
6	14489.633	0.009	14487.656	0.021	14522.275	-0.001	14524.281	0.002
7	14486.087	0.019	14484.103	0.007	14524.057	-0.004	14526.080	0.002
8	14482.383	-0.007	$14\ 480.426$	-0.006	14525.707	-0.014	14527.746	-0.003
9	14478.589	-0.000	14476.646	0.003	14527.238	-0.015	14529.292	0.000
10	14474.674	0.010	$14\ 472.745$	0.015	14528.653	-0.006	14530.709	0.000
11	14470.623	0.008	14468.690	-0.003	14529.948	0.011	14531.994	-0.003
12	14466.444	0.002	14464.537	0.006	14531.097	0.009	14533.171	0.013
13	$14\ 462.148$	0.002	14460.248	0.004	14532.112	0.000	14534.193	0.001
14	14457.733	0.009	14455.843	0.011	14533.023	0.015	14535.095	-0.002
15	14453.178	-0.001	14451.309	0.013	14533.774	-0.001	14535.861	-0.013
16	14448.506	-0.003	$14\ 446.619$	-0.017	14534.420	0.006	14536.521	-0.001
17	14443.717	0.003	14441.854	0.004	14534.930	0.006	14537.032	-0.009
18	14438.790	-0.005	14436.932	-0.008	14535.286	-0.019	14537.427	-0.004
19	14433.764	0.013	$14\ 431.917$	0.012	14535.540	-0.017	14537.691	-0.001
20	14428.586	0.004	14426.737	-0.008	14535.672	-0.007	14537.816^{\dagger}	-0.007
21	14423.274	-0.014	$14\ 421.445$	-0.015			14537.816^{\dagger}	-0.007
22	14417.878	0.010	14416.061	0.012				
23	14412.319	-0.005	$14\ 410.498$	-0.015				
24	$14\ 406.648$	-0.006	$14\ 404.848$	-0.004				
25	14400.877	0.019	14399.083	0.018				
26	14394.944	0.007	14393.154	0.002				
27	14388.880	-0.009	14387.104	-0.009				
28	14382.770^{\dagger}	-0.054	14380.956	0.008				
29	14376.409	-0.007	14374.663	0.006				

	$^{\mathrm{P}}\mathrm{Q}$		РР		^R R		^{R}Q	
Ν	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	Δ_{o-c}	observed	$\Delta_{\rm o-c}$
1	*	*	14448.277	0.000	14455.607	0.001	14457.515	0.000
3	14444.865	-0.014	14442.828	0.002	$14\ 459.928$	0.002	14461.893	0.002
5	14438.930	0.008	14436.922	-0.003	$14\ 463.786$	-0.006	14465.788	0.001
7	14432.550	0.011	14430.581	0.009	14467.204	0.002	14469.218	-0.002
9	14425.708	-0.005	14423.760	-0.009	14470.143	-0.013	14472.188	-0.006
11	14418.443	0.004	14416.514	-0.001	14472.650	-0.002	14474.697^{\dagger}	-0.012
13	14410.713	-0.004	14408.806	-0.006	$14\ 474.697^{\dagger}$	0.009	14476.770	0.008
15	$14\ 402.559$	0.014	14400.655	-0.002	14476.259	-0.003	14478.350	-0.003
17	14393.924	0.001	14392.054	0.003	$14\ 477.376$	0.004	14479.488	0.008
19	14384.844	-0.005	14382.975	-0.019	14478.017	0.001	14480.137	-0.003
21	14375.339	0.016	14373.526	0.042	14478.190	-0.002	14480.330	-0.002
23	14365.328	-0.016	14363.524	0.003	14477.897	0.001	14480.051	-0.002
25	14354.891	-0.020	14353.089	-0.014	$14\ 477.132$	0.005	14479.313	0.014
27	14344.012	-0.009	14342.227	-0.003	14475.893	0.012		
29	14332.665	-0.010	14330.888	-0.011	$14\ 474.169$	0.014		
31	14320.868	-0.003	14319.119	0.009	$14\ 471.934$	-0.014		
33	14308.607	0.000	14306.863	0.002				
35			14294.160	0.011				

Table 3.7: Transition frequencies of ${}^{18}O_2$.

	$^{\mathrm{P}}\mathrm{Q}$		РЧ		R		RQ	
Ν	observed	$\Delta_{\rm o-c}$	observed	Δ_{o-c}	observed	Δ_{o-c}	observed	$\Delta_{\rm o-c}$
0	*	*	*	*	*	*		
1	*	*	14466.203	0.019			14475.620	-0.007
2	14465.588	0.015	14463.422	-0.015				
3	14462.633	0.000	14460.567	-0.006				
4	14459.629	0.013					14482.194	0.000
5	14456.496	0.001	14454.512	0.018	14482.141	-0.003	14484.133	-0.004
6	14453.272	0.008	14451.275	-0.006	$14\ 483.952$	-0.003	14485.967	0.007
7	14449.909	-0.010	14447.943	-0.008	14485.644	-0.003	14487.668	0.004
8	14446.442	-0.017	14444.500	-0.004	$14\ 487.208$	-0.014	14489.253	0.003
9			14440.948	0.007	$14\ 488.669$	-0.009	14490.716	0.000
10	14439.201	0.006	14437.267	0.006	$14\ 490.008$	-0.007	14492.054	-0.009
11	14435.394	0.006	14433.469	0.004	$14\ 491.238$	0.005	14493.290^{\dagger}	-0.001
12	14431.473	0.007	14429.571	0.018	$14\ 492.329$	-0.004	14494.395	-0.004
13	14427.439	0.012	14425.514	-0.009	$14\ 493.290^{\dagger}$	-0.022	14495.365	-0.023
14	14423.299^\dagger	0.027	14421.391	0.014	$14\ 494.170$	-0.002	14496.241	-0.016
15	14419.012	0.012	14417.130	0.016	$14\ 494.900$	-0.012	14496.985	-0.020
16	14414.640	0.029	14412.739	0.005	14495.520	-0.011	14497.624	-0.009
17	14410.102	-0.004	14408.246	0.009	$14\ 496.036$	0.007	14498.149	0.010
18	$14\ 405.482$	-0.001	$14\ 403.622$	-0.001	$14\ 496.409$	0.003	14498.520	-0.005
19	$14\ 400.781^\dagger$	0.038	14398.882	-0.009	$14\ 496.671$	0.010	14498.780	-0.008
20					14496.807^{\dagger}	0.013	14498.933^{\dagger}	0.003
21					$14\ 496.807^{\dagger}$	0.003	14498.933^{\dagger}	-0.015

Table 3.8: Transition frequencies of ${}^{17}O{}^{18}O$.

	^{P}Q		PP	PP		R		$^{\mathrm{R}}\mathrm{Q}$	
Ν	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	
0	*	*	*	*	*	*	14490.945	0.021	
1	*	*	14483.824	0.003	$14\ 491.583$	0.005	14493.462	-0.009	
2	14483.144	-0.002	14481.009	0.014	$14\ 493.917$	-0.005	14495.858	0.004	
3	14480.109	-0.008	14478.072	0.024	$14\ 496.148$	0.003	14498.103	0.001	
4	14477.022	0.011	14474.982	0.001	14498.249	0.002	14500.203	-0.020	
5	14473.797	-0.001	14471.792	-0.002	14500.203	-0.025	14502.212	-0.007	
6	14470.477	0.005	14468.487	0.001	14502.074	-0.013	14504.090	-0.001	
$\overline{7}$	14467.035	0.006	14465.053	-0.006	14503.816	-0.009	14505.848	0.007	
8	14463.461	-0.007	14461.513	0.002	14505.436	-0.004	14507.467	-0.001	
9	14459.795	0.007	14457.851	0.008	14506.942	0.008	14508.963	-0.010	
10	14455.994	0.005	14454.055	0.000	14508.302	-0.003	14510.342	-0.012	
11	14452.079	0.008	14450.151	0.004	14509.558	0.004	14511.612	-0.001	
12	14448.035	0.003	14446.114	-0.005	14510.674	-0.006	14512.744	-0.004	
13	14443.875	0.001	14441.971	0.000	14511.673	-0.010	14513.751	-0.009	
14	14439.579	-0.017	14437.694	-0.008	14512.555	-0.007	14514.659	0.011	
15	14435.192	-0.006	14433.313	0.000	14513.325	0.008	14515.412	-0.001	
16	14430.692	0.013	14428.802	-0.001	14513.938	-0.011	14516.063	0.010	
17	14426.035	-0.005	14424.170	-0.003	14514.465	0.010	14516.580	0.011	
18	14421.270	-0.010	14419.426	0.004	14514.848	0.011	14516.965	0.006	
19	14416.387	-0.012	14414.552	0.002	14515.104^{\dagger}	0.010	14517.239^{\dagger}	0.014	
20	14411.377	-0.021	$14\ 409.549$	-0.008	14515.225^{\dagger}	0.000	14517.374^{\dagger}	0.010	
21	14406.276	0.001	$14\ 404.446$	0.003	14515.225^{\dagger}	-0.005	14517.374^{\dagger}	-0.004	
22	$14\ 401.040$	0.009	14399.219	0.012	14515.104^{\dagger}	-0.005	14517.239^{\dagger}	-0.026	
23	14395.689	0.023	14393.856	0.006					
24	14390.157	-0.022	14388.356	-0.016					
25	14384.593	0.023	14382.770	-0.001					
26	14378.828	-0.011	14377.072	0.024					
27	14372.989	0.004	14371.187	-0.015					
28	14367.007	-0.001	14365.235	0.001					

Table 3.9: Transition frequencies of ${}^{17}O_2$.
3.6 Appendix C: Transition frequencies of the γ band

In this appendix the transition frequencies (in cm⁻¹) of the γ band of the investigated isotopomers are listed. Transitions denoted by an asterisk (*) do not exist due to constraints of angular-momentum coupling. Δ_{o-c} refers to the difference between the observed value and the calculated value of the transition frequency determined by a least-squares fit of the molecular constants.

	^{P}Q		Р		^R R		RQ	
Ν	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$
1	*	*	15899.534	-0.007	15907.660	-0.009	15909.549	0.004
3	15895.372	-0.005	15893.311	0.019	$15\ 912.259$	0.004	15914.206	0.001
5	15888.392	0.000	15886.376	-0.005	15916.179	0.004	15918.167	0.004
7	15880.784	0.004	15878.814	0.008	$15\ 919.432$	0.005	15921.446	0.004
9	15872.514	-0.001	15870.570	0.000	$15\ 922.005$	-0.003	15924.037	-0.010
11	15863.601	0.009	15861.658	-0.012	$15\ 923.911$	-0.005	15925.975	-0.003
13	15853.985	-0.023	15852.102	-0.006	$15\ 925.144$	-0.006	$15\ 927.234$	0.002
15	15843.768	0.005	15841.871	-0.012	$15\ 925.705$	-0.001	15927.828	0.020
17	15832.853	-0.002	15831.011	0.017	$15\ 925.579$	-0.003	$15\ 927.719$	0.016
19	15821.282	0.000	15819.438	-0.002	$15\ 924.761$	-0.014	15926.916	0.002
21	15809.036	-0.007	15807.218	-0.001	$15\ 923.282^{\dagger}$	0.001	15925.442	0.004
23	$15\ 796.060^{\ddagger}$	-0.077	$15\ 794.279^{\ddagger}$	-0.052	15921.101	0.005	15923.282^{\dagger}	0.010
25	$15\ 782.560$	-0.002	$15\ 780.785$	0.011			15920.436	0.025
27	$15\ 768.324$	0.009	$15\ 766.526$	-0.019	15914.646	0.006	15916.904	0.052

Table 3.10: Transition frequencies of ${}^{16}O_2$.

[†] Blended line.

[‡] Possible calibration inaccuracy due to missing part in the I_2 atlas.

	PO		РР		RB		RO	
	<u>ــــــــــــــــــــــــــــــــــــ</u>		1		I		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	
Ν	observed	Δ_{o-c}	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$
0	*	*	*	*	*	*		
1	*	*	15860.545	-0.015	15868.443	-0.008	15870.348	0.013
2	15859.762	-0.012	15857.628	0.019	15870.762^{\dagger}	0.002	15872.693	0.006
3	15856.602	0.027	15854.480	-0.018	15872.942	0.033	15874.870^{\dagger}	0.007
4	15853.262	0.000	15851.211	-0.017	15874.870^{\dagger}	-0.028	15876.871	0.000
5	15849.798	-0.007	15847.798	0.001	15876.726	0.001	15878.720	0.005
6	15846.187	-0.008	15844.214	0.007	15878.393	0.001	15880.401	0.006
7	15842.425	-0.004	15840.454	-0.003	15879.903	0.007	15881.908	-0.005
8	15838.496	-0.010	15836.542	-0.006	15881.241	0.001	15883.254	-0.014
9	15834.427	0.003	15832.481	0.002	15882.425	0.003	15884.466	0.005
10	15830.185	0.002	15828.247	-0.003	15883.423	-0.018	15885.508^{\dagger}	0.017
11	15825.781	-0.003	15823.860	-0.001	15884.293	-0.006	15886.371^\dagger	0.012
12	15821.232	0.007	15819.309	-0.004	15884.999	0.005	15887.067	0.003
13	15816.504	-0.003	15814.611	0.006	15885.508^\dagger	-0.018	15887.602	-0.003
14	15811.624	-0.006	15809.738	0.000	15885.893	-0.002	15887.974	-0.010
15	15806.589	-0.004	15804.712^{\ddagger}	0.002	15886.114^\dagger	0.014	15888.230^\dagger	0.031
16	15801.413^{\ddagger}	0.017	$15\ 799.527^{\ddagger}$	0.004	15886.114^\dagger	-0.028	15888.230^\dagger	-0.020
17	$15\ 796.033^{\dagger \ddagger}$	$^{\ddagger}-0.006$	$15\ 794.168^{\ddagger}$	-0.008	15886.022	0.002	15888.143	0.006
18	$15\ 790.521$	-0.002	$15\ 788.651^\dagger$	-0.017	15885.734	0.001	15887.858	-0.001
19	$15\ 784.843$	-0.003	$15\ 783.003$	0.002	15885.302	0.020	15887.426	0.009
20	$15\ 779.013$	0.003	$15\ 777.173$	0.000	15884.678	0.013	15886.818	0.009
21	$15\ 773.041$	0.028	$15\ 771.211$	0.026			15886.022^\dagger	-0.014
22	$15\ 766.886^{\dagger}$	0.031	$15\ 765.021$	-0.015	15882.939	0.003	15885.084	-0.013
23	$15\ 760.527$	-0.010			15881.812	-0.009		
24					15880.540	0.000		

Table 3.11: Transition frequencies of ${}^{16}O{}^{17}O$.

[†] Blended line. [‡] Possible calibration inaccuracy due to missing part in the I_2 atlas.

	$^{\mathrm{P}}\mathrm{Q}$		^P P		RR		RQ	
Ν	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$
1	*	*	$15\ 749.142$	-0.004	$15\ 756.377$	-0.006	$15\ 758.292$	0.000
3	$15\ 745.650$	-0.006	$15\ 743.610$	0.006	$15\ 760.490$	0.002	$15\ 762.442$	-0.011
5	$15\ 739.489$	0.005	$15\ 734.477$	-0.010	$15\ 764.017$	0.001	$15\ 766.006$	-0.005
7	$15\ 732.771$	0.008	$15\ 730.797$	0.001	$15\ 766.969$	0.004	$15\ 768.986$	0.002
9	$15\ 725.478$	0.002	$15\ 723.536$	0.004	$15\ 769.335$	0.000	$15\ 771.377$	0.003
11	$15\ 717.616$	-0.003	$15\ 715.708$	0.013	$15\ 771.133$	0.009	$15\ 773.190$	0.009
13	$15\ 709.190$	0.001	$15\ 707.279$	-0.005	$15\ 772.335$	0.005	$15\ 774.408$	0.004
15	$15\ 700.183$	-0.004	$15\ 698.298$	-0.001	$15\ 772.957$	0.006	$15\ 775.035$	-0.007
17	$15\ 690.604$	-0.008	15688.727	-0.013	$15\ 772.990$	0.006	$15\ 775.080$	-0.012
19	15680.457	-0.004	15678.606	-0.001	$15\ 772.436$	0.007	$15\ 774.555$	0.002
21	15669.734	-0.001	15667.886	-0.011	$15\ 771.283$	0.003	$15\ 773.432$	0.011
23	15658.424	-0.009	15656.610	0.000	$15\ 769.551$	0.014	$15\ 771.698$	0.004
25	$15\ 646.569$	0.017	$15\ 644.737$	-0.008	$15\ 767.184$	-0.013		
27	15634.086	-0.005	$15\ 632.290$	-0.009	$15\ 764.265$	0.010	$15\ 766.441$	-0.002

Table 3.12: Transition frequencies of ${}^{18}O_2$.

	^{P}Q		PР		RR		$^{\mathrm{R}}\mathrm{Q}$	
Ν	observed	Δ_{o-c}	observed	$\Delta_{\rm o-c}$	observed	Δ_{o-c}	observed	Δ_{o-c}
0	*	*	*	*	*	*	15827.999	-0.001
1	*	*	15820.928	-0.004			15830.491	0.011
2	15820.230	0.008	15818.068	-0.003	15830.848	0.018	15832.780	0.019
3	15817.132	-0.003	15815.065	0.008	15832.911	-0.007	15834.877^{\dagger}	0.002
4	15813.908	-0.011	15811.884	-0.005	15834.877^\dagger	0.026	15836.830	0.003
5	15810.575	0.003	15808.564	-0.003	15836.633	0.003	15838.623	0.002
6	15807.077	0.000	15805.100^{\ddagger}	0.009	15838.239	-0.014	15840.257	-0.001
7	15803.424^{\ddagger}	-0.008	$15801.413^{\dagger 3}$	$^{\ddagger}-0.048$	15839.711	-0.011	15841.726	-0.012
8	$15\ 799.608^{\ddagger}$	-0.027	$15\ 797.665^{\ddagger}$	-0.013	15841.033	-0.001	15843.083	0.021
9	$15\ 795.674^{\ddagger}$	-0.012	$15\ 793.736^{\ddagger}$	-0.005	15842.184	-0.008	15844.231^{\dagger}	0.001
10	$15\ 791.578^{\ddagger}$	-0.006	$15\ 789.648^{\ddagger}$	-0.002	15843.216	0.023	15845.245^{\dagger}	0.003
11	$15\ 787.323$	-0.006	$15\ 785.410$	0.004	15844.044	0.006	15846.093	-0.004
12	$15\ 783.958^\dagger$	0.037	$15\ 781.013$	0.006	15844.729	0.001	15846.814	0.018
13	$15\ 778.366$	0.007	$15\ 776.475$	0.019	15845.245^{\dagger}	-0.015	15847.342^{\dagger}	0.004
14	$15\ 773.659$	0.015	$15\ 771.749$	-0.001	15845.621	-0.015	15847.701^{\dagger}	-0.022
15	$15\ 768.771$	-0.005	$15\ 766.886$	-0.005	15845.840^{\dagger}	-0.015	15847.939^{\dagger}	-0.012
16	$15\ 763.756$	0.002	$15\ 761.887$	0.009	15845.916	-0.001	15848.012	-0.009
17	$15\ 758.564$	-0.015	$15\ 756.706$	-0.006	15845.840^{\dagger}	0.019	15847.939^{\dagger}	0.005
18	$15\ 753.276$	0.027	$15\ 751.394$	0.003	15845.536^\dagger	-0.032	15847.701^\dagger	0.011
19	$15\ 747.761$	-0.005	$15\ 745.919$	0.002	15845.126^{\dagger}	-0.030	15847.342^{\dagger}	0.055
20	$15\ 742.128$	-0.001	$15\ 740.271$	-0.018	15844.571	-0.015	15846.730	0.005
21	$15\ 736.352$	0.013			15843.860	0.002		
22								
23					15841.926	0.003		

Table 3.13: Transition frequencies of ${}^{17}O_2$.

 $\begin{tabular}{ll} † Blended line. \\ $^\sharp$ Possible calibration inaccuracy due to missing part in the I_2 atlas. \\ \end{tabular} \end{tabular}$

3.7 Appendix D: Transition frequencies of the δ band

In this appendix the transition frequencies (in cm⁻¹) of the δ band of the investigated isotopomers are listed. Transitions denoted by an asterisk (*) do not exist due to constraints of angular-momentum coupling. Δ_{o-c} refers to the difference between the observed value and the calculated value of the transition frequency determined by a least-squares fit of the molecular constants.

	PQ		PР		RR		$^{\mathrm{R}}\mathrm{Q}$	
Ν	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$	observed	$\Delta_{\rm o-c}$
1	*	*	17248.241	-0.004			17258.136	-0.002
3	17243.972	0.002	17241.887	0.002	17260.592	0.003	17262.541	0.003
5	17236.723	-0.003	17234.713	-0.001	17264.100	-0.001	17266.086	-0.003
7	17228.704	-0.002	17226.743	0.010	17266.798	0.001	17268.807	-0.006
9	17219.880	-0.006	17217.934	-0.006	17268.673	-0.002	17270.705	-0.009
11	17210.268	0.009	17208.349	0.012	17269.731	-0.001	17271.796	0.003
13	17199.825	0.001	17197.922	-0.002	17269.969	0.003	17272.053	0.005
15	17188.582	0.003	17186.697	-0.002	17269.365	-0.011	17271.482	0.005
17	$14\ 176.533$	0.009	14174.673	0.010	17267.950	-0.007	17270.080	0.002
19	14163.666	0.009	$14\ 161.804$	-0.011	17265.715	0.006	17267.841	-0.007
21	$14\ 149.966$	-0.011	14148.138	-0.015	17262.626	0.000	17264.799	0.016

Table 3.14: Transition frequencies of ${}^{16}O_2$.

	^{P}Q		PР	R	$^{\mathrm{R}}\mathrm{Q}$
Ν	observed	$\Delta_{\rm o-c}$	observed Δ_{o-c}	observed Δ_{o-c}	observed Δ_{o-c}
1	*	*	17025.088 - 0.003	17 032.275 0.040	17 034.148 0.004
3	17021.505	-0.003	17019.464 0.009	17036.146 0.023	17038.070 - 0.017
5	17015.118	-0.001	17013.115 - 0.007	17039.305 - 0.005	17041.278 - 0.027
7	17008.051	-0.006	17006.086 - 0.004	17041.768 - 0.027	17043.806 - 0.007
9	17000.334	0.029	$16\ 998.370$ 0.009	17043.563 - 0.013	17045.610 - 0.005
11	16991.847	-0.012	$16\ 989.903\ -0.033$	17044.654^\dagger 0.001	17046.719 0.009
13	16982.732	0.014	$16\ 980.818 0.005$	17045.035 0.012	17047.084 - 0.014
15	16972.890	0.009	$16\ 971.008 0.015$	17044.699^{\dagger} 0.013	17046.785 0.008
17	16962.355	0.009	$16\ 960.471\ -0.004$	17043.612 - 0.026	17045.750 0.004
19	16951.124	0.009	$16\ 949.261$ 0.001	17041.880 0.002	17043.998 - 0.004
21				17039.403 0.000	17041.519 - 0.025
23					17038.382 0.014

Table 3.15: Transition frequencies of ${}^{18}O_2$.

 † Blended line.

Chapter 4

The 580 and 630 nm absorption bands of the $(O_2)_2$ collision complex at pressures below 760 Torr

Abstract

The collision-induced absorption of oxygen in the 540–650 nm wavelength region has been measured at a pressure range from 0 to 730 Torr at T = 294 K. Pressuredependent cross sections of the $a^1\Delta_g(v=0) + a^1\Delta_g(v=1) \leftarrow X^3\Sigma_g^- + X^3\Sigma_g^-$ and $a^1\Delta_g(v=0) + a^1\Delta_g(v=0) \leftarrow X^3\Sigma_g^- + X^3\Sigma_g^-$ transitions have been determined. Contributions of the overlapping γ and δ band of O₂ have been evaded, and Rayleigh extinction has been taken into account.

4.1 Introduction

Observations of weak and broad absorption resonances in the oxygen spectrum were reported as early as 1885 [1]. Through further detailed studies in the 1930s it was established [2,3] that these absorption features originate from the oxygen collision complex, and even at that early stage it was understood that both collision partners undergo an electronic transition during the collision process. Subsequently the O₂ complex was studied at lower temperatures [4], while also some weak absorption phenomena in the 200–280 nm UV range were observed [5]. By now the $(O_2)_2$ absorptions are well characterized, and pressure dependent cross sections have been derived through the work of Dianov-Klokov [6], Greenblatt *et al.* [7], and Newnham and Ballard [8].

The collisional complexes relate to an O_2-O_2 interaction potential, and the broad absorption features observed at room temperature correspond to continuum states at positive energies. In the negative energy region of the electronic ground state of the dimer, with a well depth of some 150 cm⁻¹ due to Van der Waals interactions [9], there exist bound states that were investigated in a liquid-nitrogen-cooled cell by Long and Ewing [10] and in jet experiments [11, 12]. These $(O_2)_2$ Van der Waals complexes should not be confused with covalently bound O_4 molecules that were observed in an electronically excited state [13]. An important result of previous work is that at room temperature no significant structure exists in the broad collisionally induced absorption bands; these features can be considered as essentially continuous even at the highest resolution.

The oxygen collision complex was first observed in the Earth's atmosphere by Perner and Platt [14]. The amount of solar radiation absorbed by $(O_2)_2$ was discussed by Pfeilsticker *et al.* [15]. In a review Solomon *et al.* [16] have estimated the globally averaged all-sky radiation budget of oxygen complexes, including O_2-N_2 , at 1 Wm⁻². Accurate data on the oxygen complexes may be of practical interest for atmospheric research. Erle *et al.* [17] suggested that the broad (>300 cm⁻¹) absorptions of $(O_2)_2$ may be used to determine the path length of photons through clouds. Since water vapor absorptions near 580 nm are minimal, the yellow band of the oxygen complex, which has the largest intensity, is likely to be most suitable for such purpose.

Here a laboratory reexamination of the 580 nm and 630 nm collisionally induced oxygen bands is presented. These bands can be assigned as $a^1\Delta_g + a^1\Delta_g(v=1) \leftarrow X^3\Sigma_g^- + X^3\Sigma_g^-$ and $a^1\Delta_g + a^1\Delta_g \leftarrow X^3\Sigma_g^- + X^3\Sigma_g^-$ respectively. Here and below $X^3\Sigma_g^-(v=0)$ and $a^1\Delta_g(v=0)$ are assumed if the vibrational assignment is not specified. The sensitivity of the CRD setup enabled examination of the collisionally induced absorption of oxygen throughout the entire atmospheric relevant pressure range of 0– 730 Torr at room temperature. Previous measurements were done at pressures of 760 Torr [8] or higher [6,7]. By taking discrete steps on the frequency scale, the collisionally induced absorption was unraveled from the absorption of the γ and δ band [18] of the oxygen monomer. Moreover, the problem of Rayleigh scattering was addressed.

4.2 Experiment

The experimental setup used in this experiment is a typical CRD setup [19] and is similar to the one used for studies of the oxygen monomer bands of O₂ isotopomers [20]. A pulse of laser light is coupled into an optical resonator; the extinction κ (in cm⁻¹) due to a species inside the CRD cavity can be estimated from the decay rate β of the light leaking out of the CRD cavity;

$$\kappa = \frac{\beta - \beta_0}{c}, \tag{4.1}$$

where β_0 is the decay rate of the empty cavity, and c is the speed of light. For details on the principle of the CRD technique, the experimental setup, and data treatment the reader is referred to chapter 1 and 7 of this thesis.

Tunable pulsed-laser radiation from a Nd:YAG pumped dye laser system running on various dyes is used to cover the frequency range from 15300 to 18400 cm⁻¹ with a bandwidth of <0.05 cm⁻¹. To select a frequency that does not coincide with an O₂ absorption feature, the laser was scanned over a few wavenumbers to record an I₂-absorption spectrum. This spectrum was calibrated against the I₂-reference standard [21]. The frequency at the end of the scan can thus be determined. The (O₂)₂-absorption measurement is performed at that frequency. Afterwards the laser is scanned further to check for possible drifts in the frequency position. The calibration was performed at every position, resulting in an accuracy better than 0.1 cm⁻¹.

Two mirror sets were used. One set for the region 15300–16600 cm⁻¹ (NewPort SuperMirrors, $R_{\text{max}} = 99.983\%$) and a set for the region 16850–18400 cm⁻¹ (Research Electro Optics, $R_{\text{max}} = 99.998\%$). The noise-equivalent detection limit is 10^{-8} cm⁻¹ for the red range (>600 nm) and 10^{-9} cm⁻¹ for the yellow range (<600 nm), after a summation of five decay transients to reduce the shot noise.

The oxygen pressure in a 86.5 cm long CRD cell was gradually increased from 0 to 730 Torr via a needle-valve tap. The pressure was simultaneously recorded with the decay transients via a capacitance manometer (Edwards 600 AB, 1000 Torr) connected to an analog-to-digital converter (ADC). The pressure change in the cell during a measurement cycle of ≈ 0.5 s is comparable to the uncertainty of the recorded pressure (0.1 Torr or 0.15% of the reading), while the increase of the loss rate is negligible. Commercial gas samples (oxygen and nitrogen with 99.999% purity) were used without further purification.

Derived absorption strengths are only correct if the bandwidth of the laser pulse is much smaller than the width of the absorption resonance, otherwise the absorption strength will be systematically underestimated [22, 23]. Because of the broad $((\Delta_{abs}/\Delta_{laser}) = 6000)$ and structureless absorption bands of $(O_2)_2$ the absorption strengths determined here will represent the true values.



Figure 4.1: N₂ extinction versus pressure at 570 and 650 nm. The lower panels show the residuals of an unweighted linear regression of the extinction curves ($\sigma_{570 \text{ nm}} = 1.8 \times 10^{-9} \text{ cm}^{-1}$ (lower panel), $\sigma_{650 \text{ nm}} = 6.3 \times 10^{-9} \text{ cm}^{-1}$ (middle panel)).

4.3 Data analyses and results

At pressures below 760 Torr, Rayleigh scattering gives rise to losses at a rate comparable to absorption by the oxygen complex. To address this issue the extinction due to Rayleigh scattering by nitrogen was measured at 8 calibrated positions between 570 and 650 nm. Fig. 4.1 shows the measured extinction κ as a function of the pressure at 2 wavelengths. These pressure-dependent extinction curves typically consist of 900 data points. The residuals of the unweighted linear fit (Fig. 4.1, lower panels) show that the extinction is indeed linear and give an impression of the achieved sensitivity. The larger noise in the data at 650 nm is due to the lower reflectivity of the mirrors. At each of the 8 frequencies a Rayleigh extinction rate is determined.

The total Rayleigh scattering cross section per molecule $\sigma_{(\nu)}$ (cm² molecule⁻¹) is given by [24]

$$\sigma_{(\nu)} = \frac{24\pi^3 \nu^4}{N^2} \frac{(n_{(\nu)}^2 - 1)^2}{(n_{(\nu)}^2 + 2)^2} \left(\frac{3 + 6\rho_v}{3 - 4\rho_v}\right),\tag{4.2}$$



Figure 4.2: The O₂-extinction $\kappa_{O_2(P)}$ at three different frequency positions; 17401.1 cm⁻¹ (I), 17206.1 cm⁻¹ (II), and 16887.7 cm⁻¹ (III). The insets show the weighted residues of a second-order polynomial fit.

where ν is the frequency (cm⁻¹), $n_{(\nu)}$ is the refractive index, N is the molecular number density (cm⁻³), and ρ_v is the depolarization ratio for polarized light. Rayleigh extinction is, to a good approximation, linear with pressure [24, 25], so only a linear pressure dependence of the extinction is expected, $\kappa_{(P)} = \kappa' P$, where κ' is the extinction rate and P is the pressure. With the approximations that the refractive index ($n_{590 \text{ nm},273.15 \text{ K}} = 1.000279$ [25]) and depolarization ($\rho_{633 \text{ nm}} = 0.01018$ [26]) are constant over the 80 nm wavelength range [24] substitution of these values in Eq. 4.2 gives the expected extinction rate $\kappa'_{N_2(\nu)}$ for nitrogen (at 294 K):

$$\kappa'_{N_2(\nu)} = 1.37 \ (0.02) \times 10^{-27} \ \nu^4 \ (cm^{-1} \ Torr^{-1}),$$
(4.3)

with the frequency ν in cm⁻¹. A ν^4 fit through the 8 measured extinction rates gives

$$\kappa'_{\exp(\nu)} = 1.36 \ (0.02) \times 10^{-27} \ \nu^4 \ (\text{cm}^{-1} \ \text{Torr}^{-1}),$$
(4.4)

with the estimated errors (1σ) in parentheses, in good agreement with the expected extinction rate (Eq. 4.3).



Figure 4.3: The uncertainty in the estimate of the $(O_2)_2$ collision-induced absorption cross sections is largely reduced in the far wing of the absorption if κ'_{lin} in Eq. 4.5 is kept fixed (2-parameter fit) at the estimated value from Eq. 4.6.

The clearly visible linear pressure dependence of κ (Fig. 4.1) not only confirms that Rayleigh extinction cannot be neglected at the sensitivity level of the present measurements, it also shows, together with the good agreement between the extinction rates, that the background (β_0/c) is constant during the measurements.

Since the Rayleigh cross sections for N₂ and O₂ are comparable, the linear Rayleigh contribution to the measured extinction $\kappa_{O_2(P)}$ should be accounted for. Because two, and only two, oxygen molecules are involved in the collision-induced absorption process the absorption due to oxygen will be quadratic in pressure [3,4]. Hence the extinction owing to oxygen as a function of the pressure should be a second-order polynomial:

$$\kappa_{\mathcal{O}_2(P)} = \kappa_{\mathrm{lin}}' P + \kappa_{\mathrm{sq}}'' P^2, \qquad (4.5)$$

where $\kappa'_{\rm lin}$ is the extinction rate due to the Rayleigh extinction, and $\kappa''_{\rm sq}$ is the absorption rate owing to the collision-induced absorption. Fig. 4.2 shows three extinction curves of O₂, from which the absorption cross section can be deduced, measured at three different frequency positions. A nonlinear behavior is clearly visible in curves I and II,



Figure 4.4: $(O_2)_2$ collision-induced absorption cross section. The solid curve represents the skewed Voigt profiles fitted to the data.

but curve III also contains a nonlinear term. The insets show the weighted residuals of a second-order polynomial fit. All three curves are very well described by Eq. 4.5. A pressure-dependent extinction curve was measured for over 200 frequencies in the range 15300–18400 cm⁻¹. A 3-parameter fit to the measured curves reveals the background β_0/c (subtracted in Fig 4.1 and 4.2) and the two extinction rates $\kappa'_{\rm lin}$, and $\kappa''_{\rm sq}$.

The extinction rate κ'_{lin} represents the Rayleigh extinction and should thus have a ν^4 dependence. A ν^4 function fitted to these extinction rates results in a frequency dependent functional form of $\kappa'_{\text{lin}(\nu)}$:

$$\kappa'_{\text{lin}(\nu)} = 1.25 \ (0.03) \times 10^{-27} \ \nu^4 \ (\text{cm}^{-1} \ \text{Torr}^{-1}).$$
 (4.6)

According to Eq. 4.2 the extinction rate $\kappa'_{O_2(\nu)}$ for oxygen, at 294 K ($n_{590 \text{ nm},273.15 \text{ K}} = 1.0002715$ [25], $\rho_{633 \text{ nm}} = 0.0302$ [26]), is¹

$$\kappa'_{O_2(\nu)} = 1.26 \ (0.03) \times 10^{-27} \ \nu^4 \ (\text{cm}^{-1} \ \text{Torr}^{-1}).$$
 (4.7)

¹In the original paper the depolarization ratios for polarized and unpolarized light were interchanged (see chapter 5). Here the correct depolarization ratio is substituted in Eq. 4.2.



Figure 4.5: Absorption cross sections of $(O_2)_2$ from the works of Greenblatt *et al.* [7] and Newnham and Ballard [8], whose data is fitted to a functional form for better comparison (see text), and this work.

The extinction rate $\kappa'_{\text{lin}(\nu)}$ as determined from the measurements is well represented by a ν^4 dependence, as expected for Rayleigh scattering, and agrees with the extinction as calculated according to Eq. 4.7. A source of uncertainty in the calculated extinction rates, especially in the case of oxygen, is the substantial spread in values for the depolarization ratios reported in the literature [27].

Subsequently the extinction rate $\kappa'_{\rm lin}$ in Eq. 4.5 is equated to the expected value obtained from the experimental data (Eq. 4.6) and implemented in a 2-parameter fit $(\vartheta_0, \kappa''_{\rm sq})$ for a reanalysis of the data. This results in reduced noise for the absorption rate $\kappa''_{\rm sq}$ because the correlation between the quadratic and linear term in Eq. 4.5 disappears. Particularly in case of low (O₂)₂ absorptions $\kappa'_{\rm lin}$ and $\kappa''_{\rm sq}$ are strongly correlated in the 3-parameter fit. In Fig. 4.3 the result of this procedure is shown for the frequency range 18000–18400 cm⁻¹, corresponding to the blue wing of the $\Delta v = 1$ resonance. To check the reproducibility of the data, measurements at one frequency (17315.1 cm⁻¹) were done on different days. Six measurements give an average absorption cross section of 11.40 × 10⁻⁴⁶ cm⁵ molecule⁻² with a standard deviation of 0.65%.

Table 4.1: Band parameters of the $a^1\Delta_g + a^1\Delta_g \leftarrow X^3\Sigma_g^- + X^3\Sigma_g^-$ resonance. The position is defined as the maximum of the absorption, and the width is defined as the bandwidth at half the band absorbance. The numbers in parentheses are the 1σ uncertainty in the last digit.

	Greenblatt [7]	Newnham [8]	This work
Position (cm ⁻¹)	15869~(5)	15862~(5)	15880(1)
Width (cm^{-1})	$368\ (5)$	369~(5)	367(1)
Peak Abs. $(10^{-46} \text{ cm}^5 \text{ molecule}^{-2})$	7.2(2)	7.1(2)	7.55(5)
Band Int. $(10^{-43} \text{ cm}^4 \text{ molecule}^{-2})$	3.1(1)	2.8(1)	3.19(3)

The I₂ calibrations and the narrow laser bandwidth made it possible to omit frequencies coinciding with an absorption of the γ or δ band of O₂. Effects of absorptions due to these O₂ bands are therefore absent in the presented measurements. A margin of a few wavenumbers between an O₂ absorption and the position at which the (O₂)₂ measurement is performed is necessary because the absorption in the wing of a resonance will not be linear with the pressure (because of pressure broadening and laser bandwidth effects) and would thus contribute to the nonlinear behavior of the total loss.

The results of the data analyses are shown in Fig. 4.4 in which the final values of the absorption cross sections of $(O_2)_2$, pertaining to the effect of collision-induced absorption, are plotted as functions of wavelength. The two absorption bands are fitted to skewed Voigt profiles. These profiles have no physical meaning, but a function format of the absorption envelopes enables easier determination of relevant band parameters (Table 4.1 and Table 4.2) and comparison with existing data [7,8].

The noise near 16400 cm⁻¹ is due to the lower reflectivity (R < 99.97%) of the mirrors at these frequencies and the low absorption cross section. At frequencies >18000 cm⁻¹ the fitted line profile slightly deviates from the data. This small deviation may be attributed to the far wing of another weak collision-induced absorption resonance at 18800 cm⁻¹ [7,8] which is not included in the present analyses. Data of Ref. [7], Ref. [8], and of this work are shown in Fig. 4.5. The original data of Newnham and Ballard [8] is also fitted to skewed Voigt profiles for better comparison.

The absorption cross section for the $(O_2)_2$ collision complex as determined by Newnham and Ballard is zero to the left and right of each absorption band. This can be explained by the fact that Newnham and Ballard used an empty cell spectrum to determine the background and corrected the transmittance to 1 at 'nonabsorbing' points [8].

	Greenblatt [7]	Newnham [8]	This work
Position (cm ⁻¹)	17320(5)	17314~(5)	17308(1)
Width (cm^{-1})	348~(5)	$339\ (5)$	340(1)
Peak Abs. $(10^{-46} \text{ cm}^5 \text{ molecule}^{-2})$	11.0(3)	11.7(3)	11.41(5)
Band Int. $(10^{-43} \text{ cm}^4 \text{ molecule}^{-2})$	4.8(1)	4.7(1)	4.66(3)

Table 4.2: Band parameters of the $a^1\Delta_g + a^1\Delta_g(v=1) \leftarrow X^3\Sigma_g^- + X^3\Sigma_g^-$ resonance. The position is defined as the maximum of the absorption, and the width is defined as the bandwidth at half the band absorbance. The numbers in parentheses are the 1σ uncertainty in the last digit.

Hence the background was explicitly set to zero. Greenblatt *et al.* [7] performed their experiments at much higher pressures and used a cell pressurized with nitrogen at 90% of the oxygen pressure to record a background spectrum.

The band parameters of the $(O_2)_2$ absorption bands as determined in this experiment are in good agreement with the studies of Greenblatt *et al.* [7] and Newnham and Ballard [8]; see Table 4.1 and Table 4.2. The only deviation is the band intensity of the $a^1\Delta_g + a^1\Delta_g \leftarrow X^3\Sigma_g^- + X^3\Sigma_g^-$ absorption band of the measurements of Newnham and Ballard. This may be caused by the fact that Newnham and Ballard had to correct their data for the background and the absorption because of the γ band of the oxygen monomer. Greenblatt *et al.* performed their measurements at high pressures, up to 55 atm, at which the relative effect of the absorption due to the γ band is negligible. The effect of this contribution is totally evaded in the present experiment by choosing discrete measurement positions in between the monomer resonances in combination with a narrow-band light source.

4.4 Conclusions

By means of CRD the band parameters of the $a^1\Delta_g + a^1\Delta_g(v=1) \leftarrow X^3\Sigma_g^- + X^3\Sigma_g^-$ and $a^1\Delta_g + a^1\Delta_g \leftarrow X^3\Sigma_g^- + X^3\Sigma_g^-$ transitions have been determined from measurements in a pressure range from 0 to 730 Torr. Contributions of the overlapping γ and δ band of O_2 have been omitted, and Rayleigh extinction has been taken into account. The accuracy of the band parameters is improved. It is confirmed that the collision-induced absorption of oxygen is a quadratic function of the pressure throughout the entire pressure range for all wavelengths. The determined Rayleigh extinction rates are in good agreement with the expected values, verifying the data analyses.

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Chapter 5

Experimental verification of Rayleigh scattering cross sections

Abstract

The cavity ring-down technique is applied to measure Rayleigh extinctions of Ar, N_2 , and SF_6 in the 560–650 nm region at 294 K. It is shown that experimental and calculated Rayleigh scattering cross sections agree within the experimental uncertainty of 1% for Ar and N_2 , and 3% for SF_6 .

5.1 Introduction

A century ago Lord Rayleigh formulated a theory of light scattering by ideal gases that not only explained the molecular origin of atmospheric scattering and the blue color of the clear sky, but also provided a quantitative expression for the amount of light scattered [1]. In modern formulation the Rayleigh scattering cross section $\sigma_{(\nu)}$ (cm²) is given by [2–4]:

$$\sigma_{(\nu)} = \frac{24\pi^3 \nu^4}{N^2} \frac{(n_{(\nu)}^2 - 1)^2}{(n_{(\nu)}^2 + 2)^2} F_{k(\nu)}, \qquad (5.1)$$

where ν is the frequency (cm⁻¹), N is the molecular density (cm⁻³), $n_{(\nu)}$ is the refractive index, and is $F_{k(\nu)}$ the King correction factor.

The factor $(n_{(\nu)}^2 - 1)/(n_{(\nu)}^2 + 2)$, an effect of the local electrostatic field that is known as the Clausius–Mossotti or Lorentz–Lorenz factor, is proportional to N. Because of this proportionality one must be consistent in choosing the values of $n_{(\nu)}$ and N. The King correction factor is defined as $F_{k(\nu)} = (6 + 3\rho_n)/(6 - 7\rho_n)$, where ρ_n is the depolarization ratio of natural or unpolarized light, and accounts for the anisotropy of nonspherical molecules [5].

Eq. (5.1) includes effects of nonresonant scattering that where unknown to Rayleigh; the fine structure on the Rayleigh line is related to vibrational and rotational Raman scattering, the influence of the modes of hypersound is known as Brillouin scattering, and the effects of collisional redistribution give rise to Rayleigh wing scattering.

Hence Rayleigh scattering cross sections follow directly from the theory of electromagnetism, with N, $n_{(\nu)}$, and ρ_n as relevant parameters. N involves knowledge of Avogadro's number, and values of $(n_{(\nu)} - 1)$ can be measured to high accuracy by interferometric techniques [6] or can be calculated in terms of a molecular polarizability. The depolarization ratio ρ_n can be determined from studies of the rotational Raman effect [7,8]. With known parameters the Rayleigh scattering cross section $\sigma_{(\nu)}$ can be calculated with accuracies of 1% for N₂ and 0.3% for Ar. The uncertainties originate from the accuracy of $n_{(\nu)}$ and, in case of N₂, $F_{k(\nu)}$.

In the present experiment a linearly polarized laser was used. Although for polarized light the depolarization ratio ρ_v is different [8,9], i.e., $\rho_n = 2\rho_v/(1+\rho_v)$, the King factor that enters the equation for the cross section is not dependent on the polarization state of the incident beam, as is clear from symmetry.

Accurate tabulations of frequency-dependent Rayleigh scattering coefficients for air have been produced based on electromagnetic theory and measurements of $n_{(\nu)}$ and ρ_n . The tables by Buchholtz [2], Bates [3], and Penndorf [10] are often used in atmospheric physics. It is probably for this reason that calculations of these coefficients have to the best of our knowledge never been subjected to a laboratory test; moreover, a measurement of scattered intensity requires accurate knowledge of both optical-collection and quantum efficiencies of a detector. Hence a direct quantitative measurement of the scattered light is impractical. However, in the absence of absorption, scattering is equal to extinction. Based on this assumption, measurements of the Rayleigh scattering cross section by monitoring extinction with the Cavity Ring-Down (CRD) technique were performed.

5.2 Experiment

The CRD setup has been described in detail before [11]. A laser pulse is coupled into a stable nonconfocal cavity consisting of two highly reflecting curved mirrors. The intensity of the light leaking out of the cavity will decrease exponentially in time [12] with a decay rate $\beta_{(\nu)}$. The decay rate is determined by the reflectivity of the mirrors and losses in the cavity that are due to absorption or scattering. Under the condition that the additional losses obey Beer's law, the decay rate $\beta_{(\nu)}$ is described by

$$\beta_{(\nu)} = \frac{c}{d} \mid \ln(\mathbf{R}) \mid + \frac{c}{d} \sigma_{(\nu)} l N, \qquad (5.2)$$

where c is the speed of light, d is the cavity length, R is the reflectivity of the mirrors, and l is the length of the scattering medium. If the medium fills the cavity (d = l) the slope of the decay rate $\beta_{(\nu)}$ as a function of pressure yields the scattering cross section, independent of the cavity length. This is a marked advantage of the CRD technique.

Light emerging from the cavity is detected with a photomultiplier tube; transients are stored on a digital oscilloscope and fitted on-line to an exponential function by computer. Reliable determination of the cavity loss requires mono-exponential decay. The cavity is aligned by on-line monitoring fit parameters and residuals to achieve mono-exponential behavior over the total decay (chapter 7). Decay rates $\beta_{(\nu)}$ are determined by use of a summation over 3 laser pulses. Decay times $\tau (= 1/\beta_{(\nu)})$ of 15–85 μ s fitted over $\approx 5\tau$ correspond to path lengths of 20–125 km in the 80 cm long cell. This is another advantage of CRD; long path lengths can be obtained in a short cell, yielding high sensitivities, on average 5×10^{-9} cm⁻¹ for this setup.

While transients are recorded at a fixed laser frequency the gas pressure in the CRD cell is gradually increased from 0 to 750 Torr by means of a needle-valve tap. Two buffer chambers with multiple outlets welded to the tube over the total length of the CRD cell ensure a homogeneous gas pressure. Before gas (Ar, N₂, and SF₆ with 99.999% purity) enters the cell it is purged through a 0.5 μ m sintered stainless steel filter. The pressure, measured by a capacitance manometer (Edwards 600 AB; 0.15% accuracy), is simultaneously recorded with the decay transients. Calibration of the laser frequency against the I₂-reference standard results in an absolute frequency accuracy better than 0.1 cm⁻¹ [11].

Fig. 5.1 shows the measured cavity loss $(\beta_{(\nu)}/c)$ in Ar, N₂, and SF₆ as a function of pressure at 579.82 nm. The curves typically consist of 1500 data points. The difference between the extinction of Ar and N₂ is clearly visible. The extinction of SF₆ is an order of magnitude larger, reflecting the large refractive index of SF₆. A linear regression reveals the slope or Rayleigh extinction rate (in cm⁻¹ Torr⁻¹), from which



Figure 5.1: Upper panel: loss due to Ar, N₂, and SF₆ at 579.82 nm as a function of pressure. Bottom panel: the residuals of an unweighted linear regression of the Ar-extinction curve (rmse = 3×10^{-9} cm⁻¹).

the scattering cross section can be determined. The intercept represents the loss of the empty cavity. The residue of an unweighted linear regression (Fig. 5.1, bottom panel) of the Ar-extinction curve confirms the linear behavior of the extinction as a function of the pressure and gives an impression of the achieved sensitivity.

5.3 Data analysis and results

The Rayleigh scattering cross sections for Ar and N₂, determined from the extinction rates, are plotted in Fig. 5.2 as a function of frequency. The experimentally determined cross sections are compared with calculations based on Eq. 5.1. The well-known refractive indices for Ar and N₂ are used [3,6]. Ar is a spherical particle, but N₂ is a diatom for which depolarization has to be taken into account [3]:

$$F_{k(\nu)} = 1.034 + 3.17 \times 10^{-12} \,\nu^2. \tag{5.3}$$

The calculated cross sections $\sigma_{(\nu)}$ are displayed as solid curves in Fig. 5.2.



Figure 5.2: Experimentally determined Rayleigh scattering cross sections for Ar and N_2 compared with calculations.

Scattered light in the backward direction does not give rise to extinction in the CRD experiment, resulting in an underestimation of the true scattering cross section. However, with effective reflection surfaces of 5 mm diameter and mirrors separated by 80 cm, imposing the stability criterion for the cavity, and accounting for the non-isotropic scattering distribution the underestimate is less than 0.03%. These effects are therefore neglected.

For quantitative verification the obtained data on the cross section $\sigma_{(\nu)}$ are fitted to a functional form. Since the Rayleigh scattering cross section deviates from a ν^4 behavior, due to the frequency dependence of the refractive index and the depolarization, it is usually expressed as [13]

$$\sigma_{(\nu)} = \overline{\sigma} \, \nu^{4+\epsilon}. \tag{5.4}$$

The measurements span a relatively small frequency domain, which results in a strong correlation between the experimentally determined value $\overline{\sigma}_{exp}$ and ϵ in a 2-parameter fit. To determine reliable values for $\overline{\sigma}_{exp}$ it was decided to keep ϵ fixed at values following from calculations according to Eq. 5.1. Values of $\overline{\sigma}_{exp}$ as well as calculated values for $\overline{\sigma}_{th}$ and ϵ (from Eq. 5.1) are listed in Table 5.1. The dashed curves

parameter	Ar	N_2	${ m SF}_6$
$\epsilon imes10^3$	61.5	62.4	41
$\overline{\sigma}_{th} \times 10^{45}$	$20.04 \ (0.05)$	23.00(0.23)	183~(6)
$\overline{\sigma}_{exp} \times 10^{45}$	19.89(0.14)	22.94(0.12)	180(6)

Table 5.1: Deduced Rayleigh-scattering parameters $\overline{\sigma}_{th}$ and ϵ from calculations and experimentally determined values for $\overline{\sigma}_{exp}$. The numbers in parentheses are the 1σ uncertainties.

in Fig. 5.2 represent $\sigma_{(\nu)}$ as derived from the measurements.

In addition to the most-abundant atmospheric species, N₂, and a noble gas, Ar, SF₆, chosen for its extremely large Rayleigh scattering cross section resulting from its high refractive index, was also investigated. Very little is known about the refractive index of SF₆; in the literature only refractivities at 633 and 1300 nm have been reported [14]. Since SF₆ is a highly symmetric molecule, zero depolarization is assumed. From the obtained data $\overline{\sigma}_{th} = 180$ (6) $\times 10^{-45}$ and $\epsilon = 0.041$ were extrapolated. The error in $\overline{\sigma}_{th}$ was estimated by taking into account the extrapolation error in ϵ . In Table 5.1 the value $\overline{\sigma}_{exp}$ as determined from the measured data is compared with the value following from the extrapolation.

5.4 Discussion and conclusion

The values for $\overline{\sigma}_{exp}$, obtained after several (weighted) fitting and data-analyzing procedures, allow for a comparison between observed and calculated values of the Rayleigh scattering cross section. Only then is a quantitative assessment of the small Rayleigh scattering phenomenon feasible. Finally, values for $\overline{\sigma}_{exp}$ are deduced with an accuracy of $\approx 1\%$ for Ar and N₂, and 3% for SF₆.

Some remarks must be made about the assumption that in the present measurement a scattering cross section is determined. This assumption is only valid if absorption can be ruled out. In the Ar atom the first electronically excited state is in the vacuumultraviolet range and cannot give rise to absorption in the visible. In N₂, overtones of very weak quadrupole transitions will in principle occur in the visible, but these are too weak to cause observable absorption in the visible range or to affect the refractive index. In SF₆, with several active vibrational modes, visible absorption in electricdipole-allowed overtone transitions could well be possible; however in the present study no such features are observed, and the Rayleigh scattering cross section is found to be consistent with predictions from the reported index of refraction [14]. Nonexponential decay of the observed CRD transients owing to laser bandwidth effects has hampered the application of pulsed-laser CRD to cross-section measurements of narrow features. The decay transient will only remain exponential if the bandwidth of the laser is much smaller than the width of the investigated extinction feature [15], or if only a single cavity mode is excited [16]. Since Rayleigh extinction is smooth and structureless, the 0.05 cm^{-1} bandwidth of the laser does not affect the results in this study.

The major result of this work is a quantitative verification of Rayleigh scattering cross sections for Ar and N_2 within the experimental uncertainty. The present work represents, to the best of our knowledge, the first laboratory verification of a Rayleigh scattering cross section.

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Chapter 6

Spectroscopy on water vapor in the wavelength range 555–604 nm

Abstract

The method of pulsed cavity ring-down spectroscopy was employed to record the water vapor absorption spectrum in the wavelength range 555–604 nm. The spectrum consists of 1830 lines, calibrated against the iodine standard with an accuracy of 0.01 $\rm cm^{-1}$. Eight hundred of these lines are not included in the HITRAN-96 database, while 243 are not included in the newly recorded Fourier-Transform spectrum of the Reims group. Of the set of hitherto unobserved lines, 112 could be given an assignment in terms of rovibrational quantum numbers from comparison with updated first-principles calculations.

6.1 Introduction

The absorption spectrum of water in the gas phase is important and complicated. Purely rotational and rovibrational absorptions within the ground electronic configuration extend from the far-infrared to the near ultraviolet part of the spectrum, with a spectral density of many lines per wavenumber (cm⁻¹). From an atmospheric physics perspective water vapor is the most important greenhouse-gas absorber. The Earth's radiation budget is still not fully understood and a missing part on the absorption side might be ascribed to water vapor, either to the monomeric form or to clusters involving H₂O molecules. Here the motivation for recording part of the visible absorption spectrum of H₂O is also related to an atmospheric issue: the retrieval of water-vapor column densities from satellite data, such as recorded by the Global Ozone Monitoring Experiment (GOME) aboard the ERS-2 satellite. In the range covered by the GOME instrument (240–800 nm) there exist three spectral windows of pronounced spectral features related to water vapor, centered at 590 nm, 650 nm and 720 nm. The final goal is to provide improved data for the weakest of these spectral ranges (585–600 nm) where atmospheric saturation effects play a minor role [1].

Also from an astrophysics perspective water and water vapor, after H_2 and CO the third most abundant gaseous species in the universe, have recently gained interest. Observation of water vapor in sunspots [2,3] has driven most of the theoretical efforts to bring the calculational methods to the level of spectroscopic accuracy [4–10]. The water molecule, as a light triatomic true asymmetric rotor system, is a benchmark system for testing theoretical methods. Studies on H_2O have served to bring about an essential shift in the theoretical perspective from perturbative expansions of effective Hamiltonians to first principles, variational formulations of the problem (including a relativistic treatment of the electronic motion [6,7]), and allowance for non-Born-Oppenheimer effects [5].

In the last decade the water spectrum collected in the HITRAN-96 database [11], which was based on a number of publications [12–16], has served as a reference in atmospheric modeling. In view of inconsistencies and inaccuracies [17] the need for improved data has become apparent. A collaboration between the Brussels/Waterloo/Reims groups [18] have reinvestigated the water-vapor spectrum in the near infrared, visible, and ultraviolet range (467–763 nm) by means of Fourier-transform spectroscopy. Some groups have applied modern laser spectroscopic techniques to study the H₂O spectrum in a limited wavelength range; intracavity laser measurements [19] and cavity ring-down spectroscopy [20] were applied. Here we present a recording of the water vapor spectrum in the range 555–604 nm, measured by pulsed cavity ring-down spectroscopy. In this range 243 new transitions were found that do not appear in HITRAN-96, nor in the new Fourier-transform spectrum [18]. By comparison with the calculated line lists, based on the recently developed variational methods, a total of 112 of these transitions could be assigned to transitions in H₂¹⁸O.



Figure 6.1: H₂O absorption spectrum recorded in the wavelength range 555–604 nm at a pressure of ≈ 16 mbar and T = 295 K. The slope in the background is due to the wavelength dependent reflectivity of the mirrors. Two different mirror sets (M1 and M2) were used at the red and blue side of 16860 cm⁻¹.

6.2 Experimental results

The experimental arrangement used in this study is a typical pulsed laser Cavity Ring-Down (CRD) setup, that has been described previously in detail [21]. Tunable pulsed laser radiation with a bandwidth of $\approx 0.05 \text{ cm}^{-1}$ was obtained from a Nd:YAG pumped dye laser system (Quanta-Ray PDL-3). The ring-down cell was 86.5 cm long and two mirror sets (M1, M2) with reflectivities of R > 99.99% and a radius of curvature of 1 m were used to cover the range 555–604 nm. After evacuation of the cell, water vapor was leaked into the cell and the pressure was given time to stabilize. During the spectral measurements the pressure was online recorded by means of a capacitance manometer (Edwards 600 AB baratron, 0.00–100.00 Torr) with an absolute accuracy of 0.15%; spectra were taken at a pressure of ≈ 16 mbar and a temperature of 295 K. Data points were taken at a step size of 0.01 cm^{-1} with averaging of 5 laser pulses per frequency position. The cavity decay constants $\beta_{(\nu)}$ were estimated from an online fit, a plot of the estimated values of decay rates constitutes the spectrum; the baseline represents the decay rate of the cavity if no absorption is present. An overview of the entire set of recordings is shown in Fig. 6.1 with the loss (β/c) , where c is the speed of light) of the ring-down cavity plotted vertically, including both the effects of mirror



Figure 6.2: Recording of a detail spectrum in the range $17100-17122 \text{ cm}^{-1}$ of the weakest detectable resonances; lines marked with a dot are not contained in the HITRAN-96 database. The lower spectrum is an online recording of the I₂-absorption spectrum which is used for wavelength calibration.

reflectivity and molecular absorption. The baseline jump at 16700 cm^{-1} signifies the difference in reflectivity between the two mirror sets M1 and M2.

Simultaneously with the recording of the water-vapor spectrum an absorption spectrum of molecular iodine was measured for wavelength calibration. In Fig. 6.2 such a simultaneous recording of a part of the spectrum is displayed. After converting the cavity decay-constants into a water-vapor absorption spectrum the H₂O resonances were calibrated, using well known interpolation techniques [21] and the I₂-reference at-las [22]. This results in an absolute accuracy for the transition frequencies of 0.01 cm⁻¹ for each individual line. By this means a total number of 1830 lines were clearly distinguishable from the background noise level. It should be noted that the noise-equivalent detection limit, on the order of 10^{-8} - 10^{-9} cm⁻¹, is dependent on the specific reflectivity of the mirrors and hence varies over the range under study.

A comparison between the frequency positions of 1183 previously obtained and assigned lines (HITRAN-96 and Reims data [18]) and the present data reveals an average redshift of the present data of -0.0036 cm^{-1} with a standard deviation of 0.009 cm⁻¹. In view of the standard deviation, which is twice the mean deviation $(-0.0036 \text{ cm}^{-1})$, and the accuracy of the CRD experiment (0.01 cm^{-1}) the redshift is negligibly small.

This work	Rheims [18]	$J^{'}K^{'}_{\rm a}K^{'}_{\rm c}$	$J^{''}K^{''}_{\rm a}K^{''}_{\rm c}$	$v^{'}$
16 761.672	$16\ 761.6749$	$3\ 1\ 3$	$4 \ 1 \ 4$	401
$16\ 769.400$	$16\ 769.3977$	$4 \ 4 \ 0$	$4 \ 4 \ 1$	401
$16\ 769.400$	$16\ 769.3977$	$2\ 1\ 1$	$3\ 1\ 2$	401
$16\ 780.344$		$2\ 2\ 0$	$2\ 2\ 1$	321
$16\ 783.584$	$16\ 783.5735$	$2 \ 0 \ 2$	$3 \ 0 \ 3$	401
16843.473	16843.4709	$2\ 2\ 0$	$2\ 2\ 1$	401
16845.943	16845.9774	$4 \ 0 \ 4$	$3 \ 0 \ 3$	321

Table 6.1: Assigned $H_2^{18}O$ lines in the range 555–604 nm. The line at 16780.344 cm⁻¹ is newly observed.

6.3 Line assignments

Line assignments were performed using techniques developed to analyze other short wavelength water spectra [18, 23]. This technique relies on comparisons with line lists of water transitions calculated using variational techniques. In the present work the analysis was performed with line lists computed using a spectroscopically determined potential energy surface and completely ab initio procedures [5, 23]. As has been discussed elsewhere [23], these line lists provide complimentary information. However it should be noted that the frequencies analyzed here are near the limits of reliability of Partridge and Schwenke's spectroscopically determined potential [10] and, in particular, the vibrational labels given by this line list were in generally not correct.

Linelists, combined where appropriate with an allowance for systematic errors associated with a particular vibrational band, were used to identify candidate line assignments based on both frequency and intensity considerations. These assignments were then used to predict other lines using combination differences; the presence of these predicted lines allows a further assignment to be made as well as confirming the original assignment. In some cases it is not possible to use combination differences to confirm line assignments. This does not invalidate the original assignment if the predicted line lies outside the frequency range of the spectrum, or under another stronger line, or is too weak to be observed.

The 1830 observed lines can be distinguished in several subsets. About a thousand were already contained in the HITRAN-96 database, nearly 1600 were observed in the recent Fourier-transform spectrum [18], but 243 lines were not previously reported in either the HITRAN-96 database or the Reims spectra [18]. Table 6.2 presents 111 newly observed transitions that have been positively assigned to H_2^{16} O transitions belonging to the 5ν polyad. All transitions originate in the (0,0,0) ground vibrational level. Table 6.2 distinguishes between assignments which have been confirmed by combination

differences, which can be regarded as secure, and those for which only a single transition involving the upper energy level has been observed, for which occasional misassignments are possible. The extra information available in the new spectrum and the new ab initio line list [23] which is much more reliable for states with high K_a means that further assignments are possible. More than 195 previously unassigned lines seen both here and in the spectrum of Carleer *et al.* [18] have been assigned; hence the analysis of the present data have aided in the assignment of previously obtained sets of data.

Besides the $H_2^{16}O$ lines discussed above, we have been able to assign 7 of the observed lines to transitions of $H_2^{18}O$. These lines, listed in Table 6.1, belong to the (401) and (321) vibrational transitions and are the first $H_2^{18}O$ lines that have been assigned to the 5ν polyad. The 5ν polyad is already weak for $H_2^{16}O$ transitions and $H_2^{18}O$ is only present in natural abundance of 0.02% in the spectrum. The observation of these $H_2^{18}O$ transitions are an additional illustration of the sensitivity of the cavity ring-down technique.

Observation of new short wavelength transitions of $H_2^{16}O$ yields new information about the energy levels of this important molecule. The data reported here will be included in a comprehensive new compilation of water energy levels [24].

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6.4 Appendix: Newly observed and assigned $H_2^{16}O$ lines

In this appendix the transition frequencies (in cm⁻¹) and the assignments of the newly observed and assigned $H_2^{16}O$ lines are listed. All transitions originate in the (0,0,0) ground vibrational level. Assignments which have been confirmed by combination differences, which can be regarded as secure, are commented with 'c'. Those for which only a single transition involving the upper energy level has been observed, for which occasional misassignments are possible, are commented with 'n'. For convenience unassigned newly observed and previously known transitions are not listed here; the reader is referred to Ref. [24] and [25].

This work	$J^{'}K^{'}_{ m a}K^{'}_{ m c}$	$J^{''}K^{''}_{\rm a}K^{''}_{\rm c}$	$v^{'}$	comment
16692.054	$6\ 1\ 6$	$6\ 1\ 5$	321	n
$16\ 706.331$	8 6 3	$8 \ 6 \ 2$	401	n
$16\ 707.782$	$6\ 3\ 4$	$7\ 1\ 7$	241	n
$16\ 710.320$	$1 \ 1 \ 1$	$2 \ 2 \ 0$	142	n
$16\ 722.708$	$7\ 6\ 1$	$7 \ 6 \ 2$	401	n
$16\ 731.137$	$8\ 5\ 3$	$8 \ 5 \ 4$	401	n
$16\ 762.938$	$4\ 3\ 2$	$4\ 1\ 3$	241	n
$16\ 779.478$	$3\ 2\ 2$	$3 \ 3 \ 1$	142	n
$16\ 781.742$	$5\ 1\ 5$	$5\ 2\ 4$	500	n
$16\ 790.505$	$6\ 3\ 3$	$5 \ 3 \ 2$	241	с
16800.786	$7\ 5\ 3$	$7 \ 5 \ 2$	321	n
16808.955	$5\ 3\ 3$	$5\ 4\ 2$	142	n
16823.485	$2\ 2\ 1$	$2 \ 2 \ 0$	321	n
16836.923	8 4 4	$7 \ 5 \ 3$	500	n
16842.177	$5\ 4\ 2$	$4 \ 4 \ 1$	241	n
16846.013	$6\ 2\ 4$	$5\ 1\ 5$	340	n
16852.026	$6\ 3\ 3$	$6\ 1\ 6$	241	n
16863.662	$5\ 3\ 3$	$5 \ 3 \ 2$	321	n
16876.272	$2\ 1\ 2$	$2\ 1\ 1$	401	n
16887.282	$6\ 5\ 1$	$6\ 4\ 2$	500	n
16889.540	$2\ 2\ 1$	$2 \ 0 \ 2$	321	n
16891.468	$4\ 1\ 3$	$3\ 2\ 2$	142	n
16898.751	$5\ 5\ 1$	$5\ 4\ 2$	500	с
16900.443	8 4 4	$7 \ 4 \ 3$	241	n
16911.802	$9\ 2\ 8$	$9\ 1\ 9$	500	n

Table 6.2: Newly observed and assigned $H_2^{16}O$ lines in the range 555–604 nm.

This work	$J^{'}K_{ m a}^{'}K_{ m c}^{'}$	$J^{''}K^{''}_{\mathrm{a}}K^{''}_{\mathrm{c}}$	$v^{'}$	comment
16912.225	8 2 7	8 0 8	321	n
16915.142	$7\ 5\ 3$	$6\ 5\ 2$	401	n
16917.548	$5\ 5\ 1$	$5 \ 5 \ 0$	241	n
16947.563	$10\ 2\ 8$	$9\ 1\ 8$	420	n
16960.802	$7\ 2\ 6$	$7\ 1\ 7$	142	n
16966.545	$9\ 2\ 7$	8 3 6	500	n
16969.152	$9 \ 3 \ 6$	$8 \ 4 \ 5$	500	n
16973.240	$1 \ 1 \ 1$	$1 \ 1 \ 0$	043	n
16974.785	$8\ 4\ 5$	$7 \ 3 \ 4$	340	n
16977.143	$10\ 2\ 8$	$9\ 2\ 7$	401	n
16985.090	$9\ 2\ 7$	$8\ 2\ 6$	401	n
16989.330	7 0 7	$6\ 1\ 6$	500	n
16994.280	8 3 6	$7\ 2\ 5$	500	n
16996.102	$2\ 1\ 1$	$2 \ 1 \ 2$	043	n
17003.441	$7\ 3\ 5$	$6 \ 0 \ 6$	340	n
17009.339	$7\ 1\ 6$	$6\ 1\ 5$	401	n
17021.680	$6\ 4\ 3$	$5\ 4\ 2$	321	n
17025.000	9 1 8	$8\ 2\ 7$	142	n
17026.585	$4\ 2\ 2$	$3\ 1\ 3$	142	n
17035.195	$3\ 1\ 3$	$2 \ 1 \ 2$	043	n
17039.610	$7 \ 7 \ 0$	$6 \ 6 \ 1$	500	n
17045.013	$8\ 7\ 2$	$7 \ 6 \ 1$	500	n
17052.726	$8\ 5\ 4$	$7 \ 4 \ 3$	500	n
17063.164	8 3 6	$7\ 2\ 5$	420	n
17070.876	$6\ 2\ 4$	$5\ 1\ 5$	420	n
17075.750	$6\ 1\ 6$	$5\ 1\ 5$	043	n
17085.313	$5\ 1\ 5$	$6 \ 0 \ 6$	222	n
17117.694	$6\ 2\ 5$	$6\ 3\ 4$	222	n
17125.776	$6\ 2\ 4$	$7\ 2\ 5$	123	n
17136.913	$5\ 3\ 2$	$5\ 4\ 1$	222	n
17137.497	$6\ 2\ 5$	$7\ 2\ 6$	123	n
17137.638	8 4 5	$7 \ 3 \ 4$	420	n
17153.243	$4 \ 3 \ 2$	$3 \ 3 \ 1$	043	n
17164.023	$3\ 1\ 3$	$3 \ 3 \ 0$	123	с
17170.484	$5\ 5\ 1$	$5 \ 5 \ 0$	043	n
17176.666	8 3 5	$7\ 2\ 6$	420	n
17183.690	$7\ 5\ 2$	$8 \ 5 \ 3$	203	n
17189.735	8 4 5	$7\ 1\ 6$	500	n
17190.909	$6\ 5\ 1$	$5\ 4\ 2$	420	n
17197.182	$4\ 3\ 2$	$5 \ 3 \ 3$	123	n

This work	$J^{'}K^{'}_{ m a}K^{'}_{ m c}$	$J^{''}K^{''}_{\rm a}K^{''}_{\rm c}$	v^{\prime}	comment
17 207.299	$6\ 5\ 1$	6 6 0	302	с
17221.505	$7\ 2\ 6$	$8\ 1\ 7$	302	n
17242.404	$4\ 2\ 2$	$5 \ 3 \ 3$	302	с
17246.503	$6\ 1\ 5$	$7\ 2\ 6$	302	n
17271.415	$3\ 1\ 3$	$4\ 2\ 2$	302	с
17272.780	$4\ 1\ 3$	$4 \ 0 \ 4$	222	n
17282.102	$9\ 2\ 8$	$9\ 2\ 7$	203	n
17283.153	$6\ 3\ 4$	$6\ 4\ 3$	302	n
17284.521	$5\ 1\ 5$	$5 \ 3 \ 2$	203	n
17288.544	$4\ 1\ 3$	$3\ 2\ 2$	222	n
17288.928	$7 \ 0 \ 7$	$7\ 1\ 6$	302	n
17291.992	$2\ 2\ 1$	$2 \ 1 \ 2$	222	с
17292.136	$3\ 1\ 3$	$2 \ 0 \ 2$	222	n
17296.439	$8\ 1\ 7$	$8 \ 3 \ 6$	203	n
17302.437	$4\ 3\ 1$	$5\ 1\ 4$	123	с
17305.753	$3 \ 0 \ 3$	$4\ 2\ 2$	203	n
17322.300	$7 \ 0 \ 7$	$6\ 1\ 6$	222	n
17362.560	$4\ 2\ 2$	$4 \ 3 \ 1$	302	n
17367.241	$6\ 2\ 5$	$5\ 1\ 4$	222	n
17398.949	$3 \ 3 \ 1$	$2 \ 2 \ 0$	222	n
17401.893	$4\ 2\ 2$	$3\ 1\ 3$	222	с
17402.203	$6\ 3\ 4$	$7 \ 4 \ 3$	104	с
17431.226	$6\ 3\ 4$	$5\ 2\ 3$	222	n
17447.988	$6 \ 6 \ 1$	$6\ 5\ 2$	302	n
17471.944	$6\ 2\ 4$	$6\ 1\ 5$	302	n
17487.863	$5\ 4\ 1$	$4 \ 3 \ 2$	222	с
17501.383	$8\ 5\ 4$	$7 \ 5 \ 3$	203	n
17502.183	$8\ 5\ 3$	7 5 2	203	n
17509.585	$4\ 2\ 3$	$5\ 3\ 2$	104	n
17510.858	$6\ 2\ 4$	$5 \ 3 \ 3$	302	n
17517.943	$7\ 2\ 6$	$7\ 1\ 7$	302	n
17534.105	$5\ 5\ 1$	$4 \ 4 \ 0$	222	n
17541.145	$3\ 2\ 2$	$3 \ 0 \ 3$	203	с
17546.251	$3\ 2\ 2$	$2\ 1\ 1$	302	n
17580.380	$2\ 2\ 0$	$3 \ 3 \ 1$	104	n
17581.469	$8\ 5\ 3$	$7 \ 4 \ 4$	302	n
17600.082	$5\ 1\ 5$	$6 \ 0 \ 6$	104	n
17604.353	$6 \ 1 \ 6$	$6\ 2\ 5$	104	с
17609.096	$6\ 4\ 3$	$5 \ 1 \ 4$	222	n
17600 440	131	4 1 4	203	n
This work	$J^{'}K_{\rm a}^{'}K_{\rm c}^{'}$	$J^{''}K^{''}_{\rm a}K^{''}_{\rm c}$	v^{\prime}	comment
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17618.883	$9\ 2\ 7$	8 2 6	203	n
17625.389	$4 \ 0 \ 4$	$5\ 1\ 5$	104	n
17628.687	$2\ 1\ 1$	$3\ 2\ 2$	104	n
17628.961	$5\ 1\ 4$	$4 \ 4 \ 1$	104	\mathbf{c}
17632.410	$5\ 4\ 2$	$4\ 2\ 3$	123	n
17658.343	$6 \ 6 \ 1$	$5 \ 5 \ 0$	222	n
17665.018	8 5 4	$7 \ 4 \ 3$	302	n

Chapter 7

Quantitative analysis of decay transients applied to a multimode pulsed cavity ring-down experiment

Abstract

The intensity and noise properties of decay transients obtained in a generic pulsed cavity ring-down experiment are analyzed experimentally and theoretically. A weighted nonlinear least-squares analysis of digitized decay transients is shown to avoid baseline offset effects, which induce systematic deviations in the estimation of decay rates. As follows from simulations it is the only method that provides correct estimates of the fit parameters and their precision. It is shown experimentally that a properly aligned stable optical resonator can effectively yield mono-exponential decays under multimode excitation. An online method has been developed, based on a statistical analysis of the noise properties of the decay transients, to aid in aligning a stable resonator towards mono-exponential decay.

7.1 Introduction

Since the invention of the Cavity Ring-Down Spectroscopy (CRDS) technique [1] a large number of applications have been described. Also a number of variants of this versatile and sensitive technique for measuring absorption resonances have been proposed, that all exhibit the major advantages of CRDS: long effective absorption path lengths combined with independence of the shot-to-shot fluctuations in the laser output. While the suggestion to use Fabry-Perot cavities for the enhancement of absorption sensitivity dates back to Kastler [2], and methods for intracavity laser absorption were demonstrated in the early days of the tunable laser [3], cavity-enhanced techniques were initially only used for the measurement of mirror reflectivities [4]. But the mere realization by O'Keefe and Deacon [1], that a conceptually simple setup, using two mirrors forming a stable resonator and a commonly available pulsed laser, could detect molecular absorption features with extreme sensitivity, initiated a new branch of research. Widespread applications of CRDS in molecular spectroscopy have been reviewed [5,6].

In the past decade the physical details of cavity enhanced spectroscopic techniques and the problems associated with the measurement and interpretation of decay transients obtained from a stable resonator have been elaborated. Here a few studies are named that have given insight in the physics of the optical decay transients and their analysis.

Lehmann and Romanini [7] analyzed in detail the effects of mode structure on the optical transients obtained from a cavity. Van Zee *et al.* [8] studied the experimental conditions in which a single cavity mode is excited with a pulsed OPO system, using short cavities and transverse mode suppression; their rather complex setup requires control of the cavity length. From a statistical analysis of the observed transients the relative standard deviation in the obtained ring-down time could be extracted, although they use a linear fit to the logarithmic of the decay transients. The drawbacks of this fit approach will be discussed in this chapter. Even the perspective of using CDRS for establishing an absolute pressure standard was considered by Van Zee *et al.* [8].

Martin *et al.* [9] discussed the implications of using single mode Fourier-Transform (FT) limited pulses in analyzing the interference effects in the resonator producing mode-beating oscillations in the CRDS transient. Lee *et al.* [10] performed a time-domain study on CRD signals from a resonator under pulsed laser excitation, focusing on the idealized case of an FT-limited Gaussian laser pulse with complete mode match to the lowest cavity mode, including the subtle effects of carrier frequency detuning from this cavity mode.

The problems associated with the nonzero bandwidth of the laser source, in particular in the regime where it is nonnegligible with respect to the width of the molecular absorption features, have been discussed by Jongma *et al.* [11], Zalicki and Zare [12] and by Hodges *et al.* [13]. These problems are similar to the 'slit-function' problem encountered in classical linear absorption spectroscopy. However, correction for these effects in CRD spectroscopy is not trivial, since each frequency component within the laser bandwidth profile gives rise to a different decay rate, thus producing multi-exponential decay.

In recent years several cavity-enhanced techniques have been developed exhibiting elegant features and employing continuous wave lasers [14–16]. Extreme sensitivity of 10^{-14} cm⁻¹ was obtained by combining these cavity-enhanced techniques with Frequency Modulation (FM) spectroscopic techniques [17]. But at the same time the simple version of CRD with multimode excitation of a cavity by a standard laser, with typical features of 0.1 cm⁻¹ bandwidth and a pulse duration of 5 ns, remains a powerful technique and is implemented in a growing number of laboratories. If the length of the resonator is chosen at $\approx 80\%$ of the radial curvature of the mirror substrates and transverse mode suppression is deliberately omitted, the cavity can be considered as essentially white as was shown experimentally by Meijer *et al.* [18]: the transmission through the cavity is independent of wavelength.

Here we present an analysis and description of the noise properties of decay transients in a generic pulsed CRD experiment. We show that the transmission of a typical CRD cavity in terms of the photon number and its variance can be understood quantitatively. It is demonstrated that a nonlinear least-squares analysis of the decay transient can avoid baseline offset effects, which can be responsible for systematic deviations in the decay rates. A parameter α_p can be defined, characterizing the noise originating from a Poisson-distributed counting process on a decay transient. This parameter can be employed to implement an online alignment procedure for the resonator; it is experimentally demonstrated that the alignment of a CRD cavity can be optimized, towards a setting of mono-exponential decay, even when a large number of cavity-modes are excited by the incident laser pulse. Under this condition effects due to mode structure of the resonator may be ignored; this is the condition of a white CRD cavity.

7.2 Estimating the rate of mono-exponential decay

Excitation of multiple modes in an optical resonator will in principle result in a multiexponential decay of the exiting flux of photons. The multi-exponentiality is caused by increasing diffraction losses for higher order transversal TEM_{mn} modes in the optical resonator [19]. Because pulsed dye lasers will in general excite multiple modes of an optical resonator the decay is in principle not mono-exponential.

The multi-exponential character of the decay in case of a multiple-modes-excited resonator can be so minimal that it is not discernible by any means in the recorded experimental decay, or the cavity alignment can be such that the losses are equal for each excited transversal mode. Experimental decays are considered to be mono-exponential if the results of a mono-exponential fit over $\approx 10\tau$ ($\tau = 1/\beta$) do not indicate non- or multi-exponential behavior.

A purely mono-exponential character of the decay is important for the reliable

retrieval of the absorption properties of a species contained in the resonator. Only under this condition the absorption coefficient $\alpha_{(\nu)}$ can be estimated from the decay rate β via

$$\beta = \frac{c}{l} (|\ln(R)| + \alpha_{(\nu)} l).$$
(7.1)

with l the cavity length, c the speed of light, and R the mirror reflectivity. It is this relation that makes the CRD technique a suitable tool for measuring direct absorption.

7.2.1 Methods to estimate the decay rate

The principles of methods to estimate the decay rate of an experimental transient are best explained by considering a perfect mono-exponential decay in its most general form:

$$I_{(t)} = I_{\text{off}} + I_0 e^{-\beta t}, \tag{7.2}$$

where I_{off} accounts for an offset which may be introduced by the detection system, I_0 is the initial intensity, and β is the decay rate.

The decay rate can be determined with the aid of two boxcars by integrating part of the decay inside two successive time windows of equal width, $t_{\rm g}^{(1,2)}$, and a time delay $\Delta_{\rm g}$ ($\Delta_{\rm g} \ge t_{\rm g}^{(1)}$) with respect to each other [20], as depicted in Fig. 7.1. With

$$A = \int_{t_{g}^{(1)}} I_{(t)} dt,$$

$$B = \int_{t_{g}^{(2)}} I_{(t)} dt,$$
(7.3)

the decay rate β , or decay time $\tau = 1/\beta$, follows from the relation:

$$\beta = \frac{1}{\Delta_{\rm g}} \cdot \ln(\frac{A}{B}). \tag{7.4}$$

Certain 2-channel boxcars can process Eq. 7.4 internally at repetition rates up to 20 kHz, with the advantage that the output signal is directly correlated to β . This detection scheme however requires $I_{\text{off}} = 0$, otherwise Eq. 7.4 is not valid. The signal can be biased to eliminate I_{off} , or a third boxcar is used to determine the offset prior to, or after, the actual ring-down signal; with $C = \int_{t_x} I_{(t)} dt$ (width of $t_g^{(3)} = t_g^{(1,2)}$),

$$\beta = \frac{1}{\Delta_{\rm g}} \cdot \ln(\frac{A-C}{B-C}). \tag{7.5}$$

The output signals of the boxcars have to be recorded and processed to determine β since commercially available boxcar devices cannot perform this operation directly.



Figure 7.1: The decay rate of an exponential decay can be estimated by integrating the decay signal in two successive time windows. The situation shown in this figure represents the settings as used by Romanini and Lehmann [20] (see text). A possible third time window to estimate the baseline (see text) is not shown in this picture.

A scheme very similar to the above described method to determine the decay rate, introduced by O'Keefe [21] and O'Keefe *et al.* [22], uses integration of the total decay,

$$\int_0^\infty I_0 e^{-\beta t} dt = \frac{I_0}{\beta}.$$
(7.6)

The intensity independence of the signal, one of the main advantages of the CRD technique, is however lost. Normalization with respect to the initial intensity I_0 , probed separately by setting a narrow second time window, increases the sensitivity to a level similar to the more generally applied detection schemes.

Another analog detection scheme has been introduced by Spence *et al.* [16]. In this scheme the output of the detector is logarithmically amplified to convert the exponential decay to a linearly decaying signal. The output of the logarithmic amplifier is subsequently differentiated by an analog differentiating circuit, generating a potential that is proportional to the decay rate β . This scheme is particularly suitable when continuous wave lasers or high-repetition rate pulsed lasers are employed.

As an alternative to methods where the signal is processed via analog electronics, the entire decay transient can be recorded, digitized, and transferred to a computer for analysis, which estimates the decay rate β . Often a linear fit is used to determine the decay rate because it is easy to implement and fast. After subtraction of the baseline the logarithm of the decay is fitted to a straight line [8,18]. The slope of the logarithm of the baseline-corrected decay then directly reveals the decay rate:

$$\ln(I_{(t)}) = \ln(I_0) - \beta t.$$
(7.7)

7.2.2 Considerations concerning the estimation of the decay rate

The decay rate of the light exiting from the cavity can only be determined reliably if the detection circuit does not deform the signal. Careful selection of the hardware and experimental settings can minimize nonlinear responses in the detection scheme. A fast photodetector with a linear response to the incident light intensity over several orders of magnitude is required, for example a photomultiplier tube (PMT). But even in the case of state-of-the-art instrumentation, experimental conditions can influence the data analysis and thus the estimation of the decay rate and other parameters.

In case of the analog method as used by Romanini and Lehmann [20] timing is important; the gate widths t_g should be equal and the time separation Δ_g between the gates accurately known and stable. The gate settings, or fit domain in case of the digitization of the signal, are fixed and often optimized for the decay signal of an empty cavity [20]. If the laser frequency is scanned over an absorption line the decay rate will increase and the (fixed) settings are no longer optimal. Variation in the timing settings can introduce additional noise in the measured spectrum [20]. For accurate digitization of the signal the relative accuracy and differential nonlinearity are of importance [16].

Another point of concern is that all methods discussed require a zero offset, or a known offset to be able to correct for the offset. The requirement of a zero offset may seem trivial since the offset can be estimated from the baseline prior to the ring-down signal. This offset, however, has to be determined accurately because a small deviation from a zero offset will result in a substantial error in the estimated decay rate. Consider an exponential decay with an offset of 0.5% of the initial intensity I_0 and $\beta = 1$:

$$I_{(t)} = (0.005 + e^{-t}) \cdot I_0.$$
(7.8)

The effect of the offset in an analog detection scheme with boxcars is illustrated with settings as used by Romanini and Lehmann [20]; $t_{\rm g}^{(1,2)} \approx 0.5\tau_0$, $\Delta_{\rm g} \approx 2\tau_0$, and the first time window delayed by $0.25\tau_0$ with respect to t_0 (Fig. 7.1). Substitution of these settings in Eq. 7.3 and 7.4 results in $\beta = 0.9748$, a deviation of 2.5%. The effect of the small offset on the logarithm of $I_{(t)}$ is clearly visible in Fig. 7.2. A linear (unweighted) fit over $3\tau_0$, a commonly used fit range, from t_0 to $t = 3\tau_0$ returns a decay rate of 0.9745, similar to the value estimated with the boxcar method. The underlying problem is that the logarithm of a biased exponential decay, $\ln(I_{\rm off} + I_0 e^{-\beta t})$, is not a



Figure 7.2: The effect on the logarithm of a 0.5% biased exponential decay (see text) is shown as the solid line. The dashed line is the logarithm of an exponential decay with no offset, the dotted line shows the difference between the two logarithms.

linear function of time. It is easily verified that the deviations in the obtained decay rates depend on the fit range.

If the offset deviations for consecutive laser pulses are randomly distributed around zero, for example as a result of the standard deviation in the baseline estimation, errors in the estimation of the decay rate as a consequence of an offset will result in additional noise. In case of a typical CRD wavelength scan it will result in noise on the frequency spectrum $\beta(\nu)$. Averaging of ring-down events can reduce this noise because the offset uncertainty will average out. The averaging procedure, however, is only allowed if individual decay transients decay with equal rates. Systematic offsets will result in a systematic error in the decay rate. A source of systematic nonzero offsets is the possible baseline shift due to small charge effects in the detection circuit. The baseline of the output of a PMT for example can shift if a signal is present [23]. Then an offset estimated prior to, or after, the ring-down event is not correct.



Figure 7.3: An experimental single-shot decay transient as recorded with the digital oscilloscope. The signal prior to the ring-down event ('baseline') is used to determine the offset.

7.3 Nonlinear fit of experimental mono-exponential decays

7.3.1 Experimental recording of decay transients

A single-shot decay recorded with a typical CRDS setup is shown in Fig. 7.3. In the experiment a Nd:YAG pumped pulsed dye laser emitting pulses of 5 ns duration, with a bandwidth of 0.05 cm⁻¹ at 630 nm was used in combination with an empty cavity built from two mirrors ($R \approx 99.98\%$; Newport SuperMirrors) with a radius of curvature of 1 m, separated by 86.5 cm. The cavity length corresponds to a cavity round-trip time of 5.7 ns. Before detection the exiting light passes through an optical bandpass filter with transmission $T_{630} = 0.856$. A built-in lens placed in front of the photocathode, with an effective diameter of 42 mm, ensures that all the light is detected by a PhotoMultiplier Tube (PMT, Thorn EMI 9658 RA, socket 9658-81-81). According to the specifications the Quantum Efficiency (QE) of the PMT at 630 nm is 0.12, while the gain at the applied supply voltage of 950 V is $\approx 0.3 \times 10^6$. Samples of the decay transient were taken each 50 ns with an 8-bit LeCroy 9450 digital oscilloscope with a bandwidth of 350 MHz.

	$I_{ m off}$	I_0^{fit}	β \times 10^{6}	rmse of residuals	
unweighted	-25~(25)	44222 (102)	3452 (10)	849	
weighted	-29~(10)	44157 (212)	3444 (16)	0.96	

Table 7.1: Fit results of the unweighted- and weighted-fit of the decay shown in Fig. 7.3. The values in parentheses represent the standard deviation.

The scales in Fig. 7.3 are plotted in dimensionless digital coordinates to make the analysis generally applicable. For convenience the negative signal of the PMT is inverted. Negative 'bit-values' are not unusual, the 0–255 dynamic range of an 8-bits digitizer is represented by '7-bits + sign bit' (-128-127) and via the 16-bits buffer memory of the oscilloscope converted to a 16-bits representation with a minimum step size of 256.

7.3.2 Unweighted nonlinear fit of experimental decays

Although the nonlinear fit does not require a zero baseline the original data is shifted vertically to a zero baseline for easier interpretation of the fitted offset. For this purpose the mean value of the signal prior to the ring-down event is determined over the first 350 points (baseline = -31183 ± 244) and subtracted from the signal. The actual decay starts at $t = t_0 = 393$ (t in channels), but for clarity the decay is shifted along the time axis to $t_0 = 0$. The thus transposed decay, with a zero baseline and $t_0 = 0$, is used as the input deck of the nonlinear fit. To prevent errors due to a possible shift of t_0 , as a result of the discreteness of the time scale, the fit does not start at t_0 but typically at $t_{\rm st} = t_0 + 0.01\tau_0$. The maximum dynamic range of the digitizer is not fully used; in the example $\approx 70\%$. Under experimental conditions shot-to-shot intensity fluctuations hamper the use of the full dynamic range. A margin to prevent 'clipping' of the signal is necessary.

To fit the decay a Levenberg-Marquardt algorithm is used; for a detailed explanation of this algorithm the reader is referred to Press *et al.* [24]. In Table 7.1 the results of the described procedure are summarized (first row). The standard deviation of the baseline is a factor of 10 larger than the estimated uncertainty σ_{off} in the fitted offset I_{off} (244 vs. 25). From the number of points used to estimate the baseline prior to the ring-down event and the number of points in the decay that contain information on the offset a factor of 4 difference is estimated. The origin of this difference is the bit resolution of the digitizer; the step size in the digitized electronic noise is 256. Because the baseline noise spans 3–4 vertical bins, visible in the right hand part of Fig. 7.4, the value of the standard deviation in the baseline is approximately equal to the stepsize



Figure 7.4: Residuals of a mono-exponential fit to the decay shown in Fig. 7.3. Discretization effects due to the 8-bits resolution of the digitizer are visible in the right hand part. In the first part of the decay the noise due to Poisson statistics is dominant.

of the noise.

In this example I_{off} is only 0.05% of I_0^{fit} . If the offset is not accounted for (is kept fixed at zero) the error in the estimation of the decay rate as a result of this small offset is negligible. A larger offset, resulting in a wrong estimation of the decay rate, can however be expected in view of the estimated standard deviation of the baseline $(\sigma_{\text{base}} = 244)$, which is $\approx 0.6\%$ of the fitted intensity I_0^{fit} .

The residuals of the unweighted fit (Fig. 7.4) show a variance which decreases over the decay transient. To test whether a power-law relation is present between the variance and the intensity of the fitted model function, the absolute value of the residuals is plotted against the expected value of the intensity of the model function on a double logarithmic scale, as shown in Fig. 7.5. The data in the scatter-plot are fitted to a straight line with a slope of 0.453 (solid line in Fig. 7.5). This is close to a slope of 0.5 which is expected for a Poisson distributed counting process, where the variance is proportional to the expected value (the residuals are proportional to the square root of the number of counts).

The deviation of the slope from the expected value of 0.5 can be explained by the distribution of the points in the scatter-plot. At lower intensities the electronic noise, with a constant variance, is no longer negligible and the intensity dependence of the variance decreases, resulting in a lower estimate of the slope. In Fig. 7.5 it is clearly visible that the envelope of the absolute values of the residuals is well represented by a $x^{\frac{1}{2}}$ dependence; the two dashed lines represent the functions $y = (3x)^{\frac{1}{2}}$ and $y = (0.03x)^{\frac{1}{2}}$.



Figure 7.5: Scatter-plot of the absolute values of the residuals from the unweighted fit versus the fitted intensity. The slope (0.453) of a straight line fitted to the data (solid line) in the scatter-plot indicates that the intensity dependent noise on the recorded transient originates from a Poisson-distributed counting process.

7.3.3 Poisson noise

The signal which is measured in a CRD experiment is proportional to the number of photons. If no gain or averaging processes are present the variance $var(I_c)$ of a Poisson distributed counting process is equal to the expected value $E[I_c]$:

$$E[I_{\rm c}] = \operatorname{var}(I_{\rm c}). \tag{7.9}$$

If a gain g is present in the detection system, the measured intensity $I_{\rm m}^g = g \cdot I_{\rm c}$, and hence Eq. 7.9 is no longer valid. The relation between the variance var $(I_{\rm m}^g)$ and the expected value $E[I_{\rm m}^g]$ of the measurement can easily be derived, giving [25]

$$\frac{\operatorname{var}(I_{\mathrm{m}}^{g})}{E[I_{\mathrm{m}}^{g}]} = g.$$

$$(7.10)$$

An average over N counting events per data point n will also change the relation between the variance and the expected value. In a CRD experiment this can be accomplished by averaging the decay signals of N laser pulses. The expected value $E[\overline{I}_m]$ will remain the same but the variance will decrease [25]:

$$\operatorname{var}(\overline{I}_{m}) = \frac{1}{N^{2}} \sum_{N} \operatorname{var}(E[I_{c}^{(n)}])$$
$$= \frac{1}{N} \operatorname{var}(I_{c}).$$
(7.11)

Hence:

$$\frac{\operatorname{var}(\overline{I}_{\mathrm{m}})}{E[\overline{I}_{\mathrm{m}}]} = \frac{1}{N}.$$
(7.12)

Under typical experimental conditions a combination of gain and averaging results in:

$$\frac{\operatorname{var}(\overline{I}_{\mathrm{m}}^{g})}{E[\overline{I}_{\mathrm{m}}^{g}]} = \frac{g}{N}$$
$$= \alpha_{\mathrm{p}}^{(N)}, \qquad (7.13)$$

defining a parameter $\alpha_{\rm p}$, which represents the relation between the variance and the expected value of a measurement of a Poisson distributed counting process.

7.3.4 Weighted nonlinear fit of experimental decays

From the residuals of the exponential fit shown in Fig. 7.4 it is clear that the noise during the decay is not constant. If the standard deviations in a measurement vary by a factor of three or more it is necessary to take the probabilistic properties into account in the fitting [26,27]. Only by such a procedure the residuals and the results of the fit can be evaluated reliably. In a weighted least-squares fit [24] the expected variance of a data point is used to weight that point; to perform a correctly weighted fit it is necessary to know the expected variance. A perfectly weighted fit will return weighted residuals that behave randomly around zero with a constant variance of one.

From Fig. 7.4 and 7.5 it follows that the noise on the decay, the variance, originates from two sources: (discretized) electronic noise and intensity dependent Poisson noise. Assuming that the two noise sources are independent the total expected variance var^{t} is equal to:

$$var_{(I)}^{t} = var^{e} + var_{(I)}^{p}, \qquad (7.14)$$

where var^{e} is the expected (constant) variance due to electronic noise, and $var_{(I)}^{p}$ is the expected intensity dependent variance due to the Poisson distributed counting process. The expected electronic variance can easily be determined from the standard deviation of the mean value of the baseline prior to the ring-down event, which is already used to shift the original transient; $var^{e} = \sigma_{base}^{2}$. The 'Poisson variance' var^{p} however is not known beforehand since it is intensity dependent. Nevertheless it is possible to estimate the expected variance over the total decay and to perform a weighted fit.

Eq. 7.13 gives the relation between the expected value of the intensity and the variance in the case of a general Poisson distributed counting process with a systemgain g and an average over N counting events per data point. If the expected value $E[I_{\rm m}]$ for the intensity is time dependent also the variance $var(I_{\rm m})$ is time dependent, but their ratio $\alpha_{\rm p}$ remains constant over the total decay. This relation in combination with an unweighted fit enables the estimation of the expected Poisson variance var^{p} . From the results of the unweighted nonlinear fit (Table 7.1) the expected intensity $E[I_{(k)}]$ can be calculated for each point k on the decay transient. The value of α_{p} can now be estimated with

$$\hat{\alpha}_{p} = \frac{1}{K} \sum_{k=1}^{K} \frac{\operatorname{var}(I_{m}^{(k)})}{E[I_{(k)}]}$$
$$= \frac{1}{K} \sum_{k=1}^{K} \frac{(I_{m}^{(k)} - E[I_{(k)}])^{2}}{E[I_{(k)}]}, \qquad (7.15)$$

where the circumflex indicates 'estimator of'.

Eq. 7.15 will give an unbiased value for $\alpha_{\rm p}$ if no other noise is present, but the additional electronic noise calls for a simple correction term. The term $\operatorname{var}(I_{\rm m}^{(k)})$ in Eq. 7.15 represents the total variance which is the sum of the electronic variance and the Poisson variance. Because the electronic variance $\operatorname{var}^{\rm e}$ is known from the baseline prior to the ring-down event it can be subtracted from $\operatorname{var}(I_{\rm m}^{(k)})$ and a reliable value of $\alpha_{\rm p}$ can be estimated:

$$\hat{\alpha}_{p} = \frac{1}{K} \sum_{k=1}^{K} \frac{\operatorname{var}(I_{m}^{(k)}) - var^{e}}{E[I_{(k)}]}$$
$$= \frac{1}{K} \sum_{k=1}^{K} \frac{(I_{m}^{(k)} - E[I_{(k)}])^{2} - \sigma_{\text{base}}^{2}}{E[I_{(k)}]}.$$
(7.16)

Combining Eq. 7.13, 7.14, and 7.16 we find the expected $var_{(I)}^{t}$ which is needed for the weighted fit.

This procedure to estimate the total expected variance $var_{(I)}^{t}$ is valid because the Poisson noise at low intensities of the signal is negligible with respect to the electronic noise. It is thus not necessary to take the Poisson probability density function of the counting process into account for small count values. It is important to note that the estimation of the weight factors relies on the results of the unweighted fit. An incorrect unweighted fit will result in a wrong estimate of $\alpha_{\rm p}$ and subsequently wrong weight factors. It is therefore important to check the results of the unweighted fit and the determined values for $\alpha_{\rm p}$ before proceeding to the weighted fit. Large differences between the estimated parameters of the unweighted and weighted fit can indicate unreliable weight factors and/or nonexponential decay. An indication for a wrong estimation of the weight factor is the value of $\alpha_{\rm p}$. The value of $\alpha_{\rm p}$ is in principle equal for each decay if the data-acquisition settings are kept constant. Strong deviations from the average value of $\alpha_{\rm p}$ indicate unreliable fit results.

The Levenberg-Marquardt algorithm used for the weighted least-squares fit is very similar to the unweighted fit algorithm and is described in detail by Press *et al.* [24]. The



Figure 7.6: Residuals of a weighted mono-exponential fit to the decay as shown in Fig. 7.3.

weighted residuals resulting from the weighted fit, shown in Fig. 7.6, with weights determined by the above described procedure are satisfactory since they show a constant variance with a standard deviation of 0.96. Results of the weighted fit are summarized in the second row of Table 7.1. Comparison of the estimated parameters from the weighted and unweighted fit reveals only small differences, and the standard deviations of the parameters estimated with the unweighted fit are of the same order of magnitude as those estimated from the weighted fit. Both features indicate that the unweighted fit returns useful results, but a weighted fit is necessary to achieve the most reliable estimate of the fit parameters and their standard deviations [28].

Remarkable is that the weighted fit returns a smaller uncertainty for I_{off} than in the case of the unweighted fit. The standard deviations of the unweighted fit (Table 7.1) are in principle a lower bound because the rmse of the residuals is much larger than one. This paradox can be explained by the intensity dependence of the weight factor. The information on the initial intensity I_0^{fit} and the decay rate β is mainly present in the first part of the decay where the accuracy of the collected data points is the lowest due to the Poisson noise. In the tail of the decay, where the information on the offset is present, only electronic noise is present. The unweighted fit assumes a constant noise level, resulting in nonreliable estimates of the uncertainties; the uncertainties for I_0 and β are estimated too low, whereas the uncertainty for I_{off} is estimated too high.

The residuals of the weighted fit (Fig. 7.6) show a discrete distribution on the right hand part, which can be explained by the intensity dependence of the weight factor. At high intensities of the decay transient the weight factor is not constant and will decrease with intensity because the Poisson contribution is dominant, as a consequence the discrete steps due to the bit resolution will wash out in the weighted residuals.



Figure 7.7: An effect of the 8-bits resolution of the digitizer; the digitized signal will remain constant during a certain time interval (neglecting noise) until the slowly decreasing signal reaches the next 'bit-level'. This effect results in striation in the residuals (Fig 7.6) of the fit. For convenience the fitted decay is shown as a solid, white, line.

The weight factor becomes constant at low intensities because the contribution of the Poisson noise is negligible compared to the constant electronic noise; the discrete steps remain.

Another feature is the striation in the residuals, which is an effect of the limited resolution of the 8-bits digitizer. After several decay times τ (1/ β) the intensity change in time is too small to be detected by the digitizer. The digitized signal will remain constant during a certain time interval (neglecting noise) until the signal reaches the next 'bit-level', as shown in Fig. 7.7. The calculated intensity following from the fit is not discretized and the residual ($I_{\text{meas}} - I_{\text{calc}}$) will show a curved behavior after $\approx 4\tau$. Both effects are a result of the 8-bits resolution of the digitizer used.

7.3.5 Simulation study of the nonlinear fitting method

CRDS decay transients are probabilistic in nature. In fact, while fitting it is necessary to take into account the probabilistic properties consistently. Only by such a procedure the residuals of the fit can be evaluated and the model adequacy established [26, 28]. Carroll and Ruppert [27] have stated that weighting will generally be called for if the standard deviations vary by a factor of 3 or more. It is the purpose of this simulation study to demonstrate quantitatively the advantages of the weighted nonlinear fit with a typical CRDS decay.

For the simulation study a decay of 2048 channels was chosen, with a lifetime τ (reciprocal of the decay rate β) of 250 channels ($\beta = 4 \times 10^{-3}$ channel⁻¹). Poisson



Figure 7.8: Distributions estimated from the weighted fit. (a) Deviation Δ_{β} of the estimated decay rate parameter β . (b) Approximate standard error σ_{β} . (c) Ratio of Δ_{β} and σ_{β} (solid line) and the t_{df} distribution (dotted line).

distributed counts with an exponentially decaying mean were simulated. The amplitude of the decay in the first channel (I_0) was 400, the baseline (I_{off}) was 1, and the standard deviation of the additive electronic noise was 2. These values were chosen in order to mimic a CRDS decay as shown in Fig. 7.3. Digitizing effects were not included in this simulation. Two ways of estimating the unknown parameters will be compared: (a) unweighted nonlinear least-squares, and (b) weighted nonlinear least-squares with weights including the reciprocal of the variance. According to Carroll and Ruppert [27] this weighted least-squares estimate is equal to the maximum likelihood estimate, which is the best possible estimate. For the actual weighted fit we proceed iteratively: first we use for the weighting function the profile estimated from an unweighted fit, second we use the resulting profile to perform a refined weighted fit (so called iteratively reweighted least-squares [27]). This refinement is a safeguard against odd results from the unweighted fit; it turned out not to improve the weighted fit results.

From a single simulation we can already observe that the weighted residuals of a weighted fit are satisfactory, i.e., they behave randomly and show constant variance (comparable to Fig. 7.6), whereas the residuals of an unweighted fit behave as in Fig. 7.4. However, in order to investigate quantitatively the properties of a weighted versus an unweighted fit 1024 simulations were performed. This resulted in 1024 realizations of the estimates ($\hat{\beta}$, \hat{I}_0 , and \hat{I}_{off}) and their standard errors ($\hat{\sigma}_{\beta}$, $\hat{\sigma}_{I_0}$, and $\hat{\sigma}_{I_{off}}$; for the calculation of these standard errors see e.g. [26]). We summarize the resulting esti-



Figure 7.9: Distributions estimated from an unweighted fit. Layout as in Fig. 7.8.

mates for the parameters and their standard errors by estimating smoothed probability densities using the Splus-function ksmooth [29]. Figure 7.8a depicts the distribution of deviations in the decay rate parameter $\Delta_{\beta} = \hat{\beta} - \beta$ (the difference between the estimated and the real value) of a weighted nonlinear least-squares fit. It is symmetric around zero with a root mean square value of 17×10^{-6} channel⁻¹. The distribution of the standard error $\hat{\sigma}_{\beta}$ (Fig. 7.8b) is narrowly peaked around 17×10^{-6} . The ratio of the deviation and the estimated standard error should be distributed approximately as a Student's *t*-variable with the degrees of freedom df equal to the number of data points (N) minus the number of parameters (3) (in this case, df = 2045, the t_{df} distribution is practically identical to the normal distribution). The distribution of this ratio is depicted by the solid line in Fig. 7.8c, whereas the dotted line represents the t_{df} distribution. There is a large similarity. The small differences which are present are attributed to the linear approximation of the standard errors [26], and to the inadequacy of the assumed normal distribution to describe small numbers of Poisson distributed counts.

Let us now make a comparison with the results of an unweighted fit for which the residuals do not behave well (Fig. 7.4). The decay rate parameter summary for this case is shown in Fig. 7.9. Note that the distribution of the deviation in Fig. 7.9a is wider by about a factor of 1.5 compared with Fig. 7.8a. The estimated standard errors are on average smaller (compare Fig. 7.8b and Fig. 7.9b). Most important, the differences between solid and dotted lines are much more pronounced in Fig. 7.9c than in Fig. 7.8c, note the tails in Fig. 7.9c. This means that for large deviations the unweighted fit predicts more precise results than are actually achieved.

	$\Delta_\beta \times 10^6$	$\hat{\sigma}_{eta} imes 10^6$	Δ_{I_0}	$\hat{\sigma}_{I_0}$	$\Delta_{I_{\rm off}}$	$\hat{\sigma}_{I_{\rm off}}$	rmse
unweighted	26	16	2.2	0.9	0.14	0.22	7.3
weighted	17	17	1.9	1.9	0.08	0.08	1.0

Table 7.2: Results (root mean square average) from fitting 1024 simulations, for details see text, of a CRDS decay: the deviations of the estimated parameters $(\Delta_{I_i} = (\hat{I}_i - I_i))$, the estimated standard errors, and the rms error of the fit.

The results shown in Table 7.2 confirm that the weighted fit is superior to the unweighted fit. The root mean square of the deviation Δ_{β} of the unweighted fit is larger than with the weighted fit. Only with the weighted fit the root mean square of the standard error $\hat{\sigma}_{\beta}$ is equal to the rms deviation Δ_{β} , which is necessary for a consistent fit. This consistency is also present with the amplitude and baseline parameters. The weighted rms error was 1.0 (rms average). Comparing Table 7.2 with the fit of the experimental data (Table 7.1) we notice agreement with the standard error of the decay rate parameter, $\hat{\sigma}_{\beta}$. Taking into account the ratio of I_0 in the two cases (44000 versus 400; $\alpha_{\rm p}^{(1)} \approx 110$) the standard errors of the amplitude and offset parameters also agree well. Thus the experimental results of Table 7.1 are well mimicked by the simulation parameters.

We conclude from this direct simulation study that the weighted fit is to be preferred for three reasons: (a) the weighted residuals behave well when the mono-exponential model is adequate; in contrast, systematic deviations of these weighted residuals from randomness or constant variance indicate model inadequacy, (b) the weighted fit is more accurate and results in smaller deviations of the estimated parameters, and (c) the ratio of the deviation and the standard error is closer to the t_{df} distribution, meaning a larger probability that the estimated parameters are correct [26].

7.4 Implications and use of $\alpha_{\rm p}$

In previous sections the noise on the decay signal as a consequence of the Poisson distributed counting process and the related constant α_p were discussed. An inspection of the underlying aspects of α_p reveals unexpected and useful features. The value of α_p for example is a useful parameter for the optimization of the cavity alignment. Another feature is that α_p can be used to estimate the amount of photons in the cavity in the case of a properly aligned cavity.

7.4.1 Optimization of the cavity alignment

The initial alignment of the laser beam with respect to the cavity ring-down cell and the mirror alignment usually results in a decaying signal. Pronounced nonexponential decay and mode beats can often be minimized by monitoring the decay on the oscilloscope while tweaking the cavity alignment. The fine tuning of the alignment, however, is not trivial because nonexponential decay and beat effects are at a certain point no longer discernible by visually monitoring the oscilloscope trace. Online monitoring of fit parameters and the weighted residuals can help to improve the final fine tuning of the setup. An obvious parameter to monitor during the alignment of the CRD cavity seems to be the decay rate, but this can turn into a pitfall. A low decay rate does not imply a good alignment; it can even indicate severe nonexponential decay.

More useful parameters for the fine tuning of the cavity alignment are the mean of the weighted residuals and their standard deviation $\sigma_{\rm res}$. In case of wrongly estimated weight factors, however, the values of the mean of the residuals and their standard deviation may be satisfactory while the weighted residuals are not. It is therefore important to monitor the weighted residuals; only then the values of the mean and $\sigma_{\rm res}$ can be interpreted reliably.

Pronounced nonexponential decay and/or beats with a period comparable to or smaller than one τ (1/ β) will be visible in the residuals of the fit while fast beatings are often obscured by the Poisson noise. A very useful measure for the presence of fast beatings is $\alpha_{\rm p}$, a parameter which is already calculated and used in the fitting routine. Under ideal circumstances the value for $\alpha_{\rm p}$ is inversely proportional with the number (N) of averaged ring-down events per analyzed transient, as follows from Eq. 7.13:

$$\alpha_{\rm p}^{(N)} = \frac{\alpha_{\rm p}^{(1)}}{N}.$$
(7.17)

If stable beatings are present in the decay they will appear in the residuals as the number of averaged ring-down events increases because the magnitude of the Poisson noise decreases. The beatings will remain in the decay and affect the value of $\alpha_{\rm p}^{(N)}$ as determined by Eq. 7.16; the value of $\alpha_{\rm p}^{(N)}$ will not decrease linearly with N but converges to a constant.

To estimate the expected value of $\alpha_{\rm p}^{(N)}$ (N typically 50) of an averaged decay trace, $\alpha_{\rm p}^{(1)}$ of a single-shot trace has to be determined. From this value the expected value of $\alpha_{\rm p}^{(N)}$ can easily be determined with Eq. 7.17. During the fine tuning of the cavity alignment the relevant parameters and the weighted residuals are monitored online until they are satisfactory. Alternatively an autocorrelation function or the Fouriertransformed spectrum of the residuals can be used to monitor the residuals. To check the alignment, $\alpha_{\rm p}^{(1)}$ is again determined. It is possible that due to the fine tuning of the cavity alignment $\alpha_{\rm p}^{(1)}$ is significantly smaller. The alignment procedure should then be repeated in an iterative way. By this procedure the alignment of the setup is optimized towards mono-exponential decay.

7.4.2 Estimation of the amount of photons leaking out of the cavity

A PMT converts the photon flux exiting the cavity into a current. With a rise time of 10 ns and an (Electron) Transit Time Spread (TTS) of 22 ns the time constants of the PMT are negligibly small compared to the decay time of the photon flux ($\tau = 15 \mu$ s). The PMT signal is sampled by a digitizer without any additional amplification or low pass filtering. Sampling of a signal, however, is not instantaneous; from the specifications of the oscilloscope it is estimated that data points as sampled in the present experiment correspond to an integration of the continuous signal over 1–2 ns. Therefore the initial intensity I_0^{fit} estimated from the fit corresponds to the number of photons detected within this binwidth $\Delta t = 1.5 \pm 0.5$ ns.

Substitution of $\alpha_{\rm p}^{(N)}$, determined from the fit, in Eq. 7.16 gives the gain g of the detection system with which the actual number of photons $I_0^{\rm ph}$ can be calculated;

$$I_0^{\rm ph} = \frac{I_0^{\rm fit}}{\eta \cdot \alpha_{\rm p}^{(N)} \cdot N}, \qquad (7.18)$$

where η is the QE of the PMT. The initial flux $\Phi_0^{\rm ph}$ which corresponds to an amount of photons $I_0^{\rm ph}$ in the first 1.5 ns of the decay is used to calculate the total amount of photons by integration of the total decay.

A series of 256 single shot (N = 1) recordings were taken for laser pulses with measured energies of 90 (20) nJ just in front of the entrance mirror; at the wavelength of 630 nm this corresponds to 2.9 (0.6) × 10¹¹ photons/pulse. Subsequent data analysis gives an average fitted intensity $\overline{I}_0^{\text{fit}} = 34.2 (0.2) \times 10^3$, an average $\overline{\alpha}_p^{(1)} = 123 (8)$, and an average decay time $\overline{\tau} = 14.52(0.08) \,\mu\text{s}$, with the estimated precisions in parentheses. To estimate the amount of photons leaking out of the cavity the QE of the PMT and the transmittance of the bandpass filter (see 7.3.1) have to be taken into account, resulting in an average of $2.6(0.9) \times 10^7$ photons exiting at both sides of the cavity.

The photon flux can also be estimated from the output current of the PMT. The initial current at the beginning of a decay is on average 418 (6) μ A, which corresponds to $2.6(0.4) \times 10^6$ electrons per ns. Taking into account the gain of the PMT, the TTS, the QE, and T_{630} a total amount of $2.7(0.5) \times 10^7$ photons in one decay is estimated. The good agreement between the photon numbers derived from the statistical analysis and the PMT output-current verifies the correctness of the data-analysis procedure.

7.5 A white CRD cavity

In many descriptions of the CRD technique, in its application to spectroscopy, the mode structure and the optical interference is neglected [6]. The physical picture of the pulses entering the cavity is then as follows: a laser pulse enters the resonator through the first mirror with an effective transmittance T = (1 - R), where R is the effective reflectivity estimated from the decay rate. The fraction of the pulse captured

in the resonator will then gradually leak out through the mirrors at both ends. In this picture the response of the cavity is indeed white, i.e., the transmission has no frequency dependence. Meijer *et al.* [18] measured the frequency response of a CRDresonator and showed that under the condition of alignment far away from confocal the frequency spectrum of the cavity is continuous. Also Scherer *et al.* [30] and Hodges *et al.* [13] have discussed the issue of a white optical resonator.

The data presented in the previous section can also be interpreted in terms of this picture of a white cavity. From the estimated decay time $\tau = 14.52 \ \mu s$ a transmittance of $181.0 (1.4) \times 10^{-6}$ is derived using T = (1 - R). The number of photons coupled into the resonator is then $5.2 (0.9) \times 10^7$ of which 50% will leak out at the rear side of the cavity: $2.6 (0.5) \times 10^7$. This result is in very good agreement with the previous estimates of the photon number and thus verifies the picture that the frequency spectrum of the cavity can be considered to be white.

The data analyzed in the previous section are taken from measurements at a fixed laser frequency. Data retrieved from a frequency scan (in an empty cavity) with a wellaligned cavity, over several wavenumbers and a step size of 0.01 cm⁻¹, are consistent with the data at a fixed laser frequency and do not show any variation in β_{ν} . This again demonstrates the frequency independent transmission of the resonator. The data resulting from a scan with a poorly aligned setup vary and are not consistent with the data at a fixed laser frequency.

7.6 On oscillations in a CRD spectrum

Characteristic oscillations in the decay rate β as a function of the frequency ν were observed in studies in our laboratory [32] as well as in other reports on CRDS [20, 33], but they never occurred in a CRD spectrum recorded in a setup aligned by the optimization method described in section 7.4.1. The oscillations in $\beta_{(\nu)}$ tend to occur in combination with oscillations in I_0 (proportional to the transmitted energy), and can be up to 40%. Often the oscillations in $\beta_{(\nu)}$ and in I_0^{fit} are out of phase. The amount of photons estimated from the pulse energy is then not consistent with estimates based on α_p . In that case the frequency spectrum of the cavity cannot be treated as white because the amount of transmitted energy through the cavity is frequency dependent. If the oscillations are out of phase they cannot originate from etalon effects in the mirrors, as proposed by Romanini *et al.* [20]; the phase difference should then be zero.

The out-of-phase behavior of these oscillations can be explained by the different losses of different transversal modes [19] in the cavity and the transversal mode structure of the laser beam. Due to the transversal mode structure of the laser beam higher order modes, with higher loss rates, can preferably be excited. It is therefore not necessary that the effective reflectivity, the background spectrum, and the intensity are in phase. A resolution of this issue, often limiting the sensitivity, is not found yet.

7.7 Conclusion and outlook

In this work it has been demonstrated that a correct analysis of CRD decay transients is far from trivial. The probabilistic properties of the decaying signal and an offset have to be taken into account for a reliable estimation of parameters. Even a small nonzero offset in the decay signal can introduce systematic errors in the estimated decay rate if the offset is not accounted for, as for example in a linear fit to the logarithm of the decay transient. A simulation study shows that a weighted nonlinear data analysis procedure, in which all properties of the decay transients are taken into account returns the most accurate results with the smallest deviations of the estimated parameters.

A nonlinear fit of the decays to a biased exponential merit function can account for an offset and allows, in principle, for an unlimited fit domain; fixed time settings are superfluous and will thus not influence the results. A mathematical transformation of the data is not necessary; logarithmic transformation of the decay transient can suppress important and interesting features like noise, oscillations due to mode beating, and nonlinearities in the beginning of the decay.

An alignment procedure for the fine tuning of the CRD setup has been developed, based on an online evaluation of the fit results and statistical properties of the decay transient. The basic principle of the procedure is alignment toward a setting of monoexponential decay. Under certain experimental conditions the frequency spectrum of a CRD cavity is white, a necessary condition for retrieving absolute absorption cross sections with pulsed CRD spectroscopy [13].

In case of a well-aligned setup a reliable estimate of the absolute number of photons in the cavity can be given at any time during the decay. With known amounts of photons in the cavity it is possible to quantitatively investigate intensity dependent absorptions with the CRD technique. From a first analysis the absolute amount of photons can be estimated, preferably with the Poisson constant α_p , and this information can be included in the input deck of a second, more advanced analysis. Intensity dependent decay rates have recently been observed in CRD [34,35].

In this chapter laser bandwidth effects are not discussed. Indeed, in the case when the bandwidth of the laser source exceeds the width of molecular resonances the decay transients will exhibit multi-exponential decay. This phenomenon has been extensively discussed in the literature [11–13]. Work to extend the present analysis to cover this case is in progress. An important ingredient is the analysis of all decay transients obtained at various frequency settings over the line profile, hence performing an ensemble fit over all data to yield absolute absorption cross sections of narrow molecular absorption features.

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Publications

This thesis is based on the following papers:

• Chapter 2:

 $b^1\Sigma_g^+-X\,^3\Sigma_g^-$ (0,0) band of oxygen isotopomers in relation to tests of the symmetrization postulate in $^{16}O_2$

H. Naus, A. de Lange, and W. Ubachs, Phys. Rev. A **56**, 4755 (1997).

- Chapter 3:
 - Cavity ring-down spectroscopy on the $b^1\Sigma_g^+-X^3\Sigma_g^-$ (1,0) band of oxygen isotopomers

H. Naus, S. J. van der Wiel, and W. Ubachs,J. Mol. Spectr. **192**, 162 (1998).

- The γ band of ¹⁶O₂, ¹⁶O¹⁷O, ¹⁷O₂, and ¹⁸O₂
 H. Naus, K. Navaian, and W. Ubachs, Spectrochimica Acta Part A 55, 1255 (1999).
- The b¹Σ⁺_g-X³Σ⁻_g (3,0) Band of ¹⁶O₂ and ¹⁸O₂
 H. Naus and W. Ubachs,
 J. Mol. Spectr. 193, 442 (1999).
- Chapter 4:

Visible absorption bands of the $(O_2)_2$ collision complex at pressures below 760 Torr

H. Naus and W. Ubachs, Appl. Opt. **38**, 3423 (1999).

• Chapter 5:

Experimental verification of Rayleigh scattering cross sections

H. Naus and W. Ubachs, Opt. Lett. **25**, 347 (2000). Accepted for publication:

• Chapter 6:

Cavity ring-down spectroscopy on water vapor in the range 555–604 nm

H. Naus, W. Ubachs, P. F. Levelt, O. L. Polyansky, N. F. Zobov, and J. Tennyson, J. Mol. Spectr.

Submitted:

• Chapter 7:

Quantitative analysis of decay transients applied to a multi-mode pulsed cavity ring-down experiment

H. Naus, I. H. M. van Stokkum, W. Hogervorst, and W. Ubachs, Appl. Opt.

Furthermore the author contributed to:

• O_2 photoabsorption in the 40950-41300 cm⁻¹ region: New Herzberg bands, new absorption lines, and improved spectroscopic data

T. G. Slanger, D. L. Heustis, P. C. Cosby, H. Naus, and G. Meijer, J. Chem. Phys **105**, 9393 (1996).

• Cavity ring-down spectroscopy on $(O_2)_2$ collision-induced absorption

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(WPP-161, volume 2, 465).

• DOAS-OCM retrieval of water vapor from GOME and new CRD spectroscopy

R. Lang, A. N. Maurellis, W. J. van der Zande, I. Aben, P. F. Levelt, H. Naus, and W. Ubachs,
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(WPP-161, volume 1, 391).

Cavity ring-down spectroscopie aan atmosferische moleculen

Moleculaire gassen in de atmosfeer beïnvloeden het klimaat van de aarde op verschillende manieren. Het broeikaseffect is een algemeen bekend verschijnsel. De fysische processen die het klimaat beïnvloeden zijn echter complex en nog niet geheel bekend. Zo is bijvoorbeeld de stralingsbalans van de atmosfeer, d.w.z. de optelsom van invallende en uitgezonden straling, nog niet volledig in kaart gebracht. Vooral aan de absorptiezijde zijn er nog hiaten, die wellicht kunnen worden toegeschreven aan waterdamp en botsingsgeïnduceerde absorpties in bijvoorbeeld zuurstof. Gassen kunnen ook, onder invloed van ultraviolette straling in de hogere regionen van de atmosfeer, chemische reacties ondergaan, die kunnen leiden tot schadelijke verbindingen of een verminderde concentratie van een bepaald gas (het ozongat is daarvan een voorbeeld). Het is belangrijk om informatie te verzamelen over de processen die zich in de atmosfeer afspelen. Dit is onder andere mogelijk met meetinstrumenten aan boord van satellieten. Eén van de vele instrumenten die de atmosfeer observeren is het GOME instrument (Global Ozone Monitoring Experiment), aan boord van de in april 1995 gelanceerde ERS-2 satelliet van ESA (European Space Agency), dat het door de aarde en atmosfeer terugverstrooide zonlicht meet. Doel van GOME is in eerste instantie de bepaling van de hoeveelheid ozon over de gehele aarde, maar daarnaast ook het bepalen van concentraties van andere gassen in de atmosfeer. Uit de plaatselijke verdeling van deze gassen kan informatie verkregen worden over de dynamica van de atmosfeer, van belang voor atmosfeermodellen. Om betrouwbare gegevens uit de gemeten spectra af te leiden moet het complexe stralingstransport door de atmosfeer goed begrepen worden, inclusief de molecuulfysica die de verstrooiings- en absorptie-eigenschappen van de gassen bepaalt.

Absorpties van bijvoorbeeld zuurstof en waterdamp zijn duidelijk zichtbaar in een spectrum zoals gemeten door het GOME instrument. Ook al kan de werkzame doorsnede per molecuul bijzonder klein zijn, door een hoge concentratie van gassen in de atmosfeer, in het geval van zuurstof 20%, in combinatie met een grote absorptieweglengte, worden de absorpties meetbaar. Indien de werkzame doorsneden klein zijn is een nauwkeurige bepaling in een laboratorium echter niet eenvoudig. Hiervoor is een gevoelige meettechniek nodig. De in dit proefschrift beschreven experimenten zijn uitgevoerd met een zeer gevoelige meettechniek die het mogelijk maakt om in een cel van typisch 1 meter lengte effectieve absorptieweglengten te bereiken van enkele tientallen tot meer dan honderd kilometer; deze techniek is bekend als de Cavity Ring-Down (CRD) techniek.

Bij de standaard CRD techniek wordt een (korte laser)lichtpuls in een optisch sta-

biele trilholte ingekoppeld. De trilholte bestaat uit twee hoogreflecterende gekromde spiegels met een reflectiviteit van meer dan 99%. De puls gaat vele duizenden malen op en neer in de trilholte; bij iedere rondgang wordt bijna de totale pulsintensiteit gereflecteerd terwijl een klein deel uit de trilholte 'lekt'. De intensiteit van de uitgekoppelde pulsen zal hierbij exponentieel afnemen. Een foton dat bijvoorbeeld na een 1/e tijd (τ) van 100 μ s uit een 1 meter lange trilholte lekt heeft daarin 30 km afgelegd. Een gas in de trilholte, dat volgens de wet van Beer licht absorbeert, geeft aanleiding tot een snellere intensiteitsafname; de absorptieinformatie zit in het tempo van de afname en niet in de gemeten lichtintensiteit zelf. Naast de lange absorptieweglengte is dit een tweede eigenschap die de CRD techniek veel gevoeliger maakt dan conventionele directe absorptiemeettechnieken: omdat intensiteitsvariaties van de laser geen invloed op de meting hebben is het mogelijk om zeer zwakke absorpties te meten. Een bijkomend voordeel van de CRD techniek is dat zij direct informatie levert over werkzame doorsneden

In hoofdstuk 2 worden metingen aan frequentieposities en moleculaire constanten voor de A band van zuurstof gepresenteerd voor de isotopen ¹⁶O¹⁸O, ¹⁶O¹⁷O, ¹⁸O₂, ¹⁷O¹⁸O en ¹⁷O₂. De overgangen in de A band corresponderen met het $b^1\Sigma_g^+ - X^3\Sigma_g^-$ (0,0) systeem bij 760 nm. De absorptiesterkte van dit systeem is 10⁹ maal zwakker dan bij normale dipoolovergangen ten gevolge van het verboden karakter van 'gerade-gerade' en $\Sigma^+ - \Sigma^-$ overgangen; overgangen zijn slechts toegestaan via een magnetisch dipoolmoment. Voor absolute golflengtekalibratie werd, net als bij alle andere experimenten. een I_2 -absorptiespectrum gebruikt. De spectroscopische informatie van alle isotopen van zuurstof is onder meer van belang voor het onderzoek aan symmetrie-verboden overgangen. De kernspins van het ¹⁶O- en het ¹⁸O-isotoop zijn nul. Uit symmetrieoverwegingen zijn in deze isotopen toestanden met een even rotationeel quantumgetal niet toegestaan. Dit bekende fenomeen kan gebruikt worden voor een test van het symmetrisatiepostulaat van de quantummechanica. Om uit te sluiten dat een eventueel gevonden signaal afkomstig is van een ander zuurstofisotoop is het van belang om de frequentieposities van overgangen in alle isotoopcombinaties nauwkeurig te kennen. De gevoeligheid van de CRD techniek is gedemonstreerd met de observatie van een elektrische quadrupoolovergang in ${}^{16}O_2$. Deze overgang is 3×10^6 maal zwakker dan de magnetische dipoolovergangen van zuurstof; de absorptiesterkte is slechts 2×10^{-9} per cm bij 600 Torr en kamertemperatuur.

De frequentieposities en moleculaire constanten van de b¹ Σ_g^+ -X³ Σ_g^- ((3,2,1),0) banden van zuurstofisotopen worden geanalyseerd in hoofdstuk 3. Als gevolg van afnemende Franck-Condonfactoren zijn deze banden respectievelijk 10, 375 en 10.000 maal zwakker dan de A band. De lijnposities van meer dan 750 overgangen zijn bepaald met een nauwkeurigheid van 0.01 cm⁻¹. Voor het eerst konden onder meer moleculaire constanten van ¹⁷O₂ bepaald worden uit experimentele gegevens. Spectra van zuurstofisotopen kunnen wellicht bijdragen tot het ontrafelen van de dynamische processen in de atmosfeer, die de isotoopverhoudingen in ozon doen afwijken van de natuurlijke abondanties van de zuurstofisotopen.

In hoofdstuk 4 worden de bandparameters van botsingsgeïnduceerde overgangen in zuurstof gepresenteerd. Indien twee zuurstofmoleculen elkaar dicht genoeg naderen kunnen ze gezamenlijk één foton absorberen, in een aangeslagen toestand gebracht worden, zowel elektronisch als vibrationeel, en weer afzonderlijk hun weg vervolgen. Metingen bij een continu toenemende druk van 0 tot 730 Torr bevestigen dat de botsingsgeïnduceerde absorptie van zuurstof kwadratisch verloopt als functie van de druk, over het hele drukbereik en voor alle golflengten. In de data-analyse is het effect van Rayleigh-extinctie meegenomen. Mogelijke interferentie met absorpties van de overlappende γ en δ banden van het zuurstofmonomeer konden worden uitgesloten door de metingen te verrichten op van tevoren geselecteerde frequentieposities.

Een kwantitatieve verificatie van de werkzame doorsnede van Rayleigh-verstrooiing voor Ar, N_2 en SF₆ wordt besproken in hoofdstuk 5. Dit onderzoek kwam rechtstreeks voort uit het onderzoek aan de botsingsgeïnduceerde absorptie van zuurstof. Gedurende dat onderzoek werd het duidelijk dat het mogelijk is om met de CRD techniek extinctie ten gevolge van Rayleigh-scattering te meten. Rayleigh-verstrooiing van licht is een bekend verschijnsel, maar directe metingen van de effectieve werkzame doorsnede van dit proces konden tot nu toe niet worden uitgevoerd in een laboratorium.

In hoofdstuk 6 worden metingen aan waterdamp in het golflengtebereik van 555–604 nm gepresenteerd. Het gemeten spectrum bestaat uit 1830 lijnen waarvan er 800 niet in de HITRAN-96 database opgenomen zijn. Van de 800 nieuwe lijnen konden er 112 worden geïdentificeerd en van rovibrationele quantumgetallen worden voorzien. Informatie over zwakke absorpties is van belang voor geavanceerde data-analyseprocedures die gebruikt worden voor de interpretatie van satellietdata. Het uiteindelijke doel is om absolute werkzame doorsneden te bepalen voor waterdampabsorpties in dit golflengtegebied.

In het laatste hoofdstuk worden de ruiseigenschappen van het exponentieel afvallende signaal, zoals gemeten in een gepulst cavity ring-down experiment, zowel experimenteel als theoretisch geanalyseerd. Aangetoond wordt dat een gewogen niet-lineaire fit van het exponentieel afvallende signaal de meest betrouwbare data geeft; systematische afwijkingen in de vervaltijd ten gevolge van onder andere een achtergrond in het signaal worden voorkomen. Met behulp van een procedure, ontwikkeld op basis van de ruiseigenschappen van het afvallende signaal, is het mogelijk om de uitlijning van het experiment te optimaliseren zodat het intensiteitsverval werkelijk exponentieel is. Verder wordt aangetoond dat het mogelijk is om een golflengte-onafhankelijke transmissie van de optische trilholte te bewerkstelligen. Dit is een vereiste om in de toekomst nauwkeurige en betrouwbare absolute waarden van werkzame doorsneden te kunnen bepalen met behulp van de gepulste cavity ring-down techniek. d'n iene di rent veur zien leave d'n andere wandelt hiel rustig vurbeej heej zuj d'r alles vur geave en heej zet ze moge ut hebbe van meej woar ge ok loept en wat ge ok bint niemand de zeat ow wat good is of slecht niemand de wet wie verluust of wie wint ge komt op ut end beej ow zelf terecht

uit *Blieve Loepe*, Rowwen Hèze.