

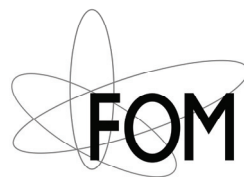


Dmitry Ityaksov

Cavity Ring-Down Optical
Extinction Measurements of
Atmospheric Molecules

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VRIJE UNIVERSITEIT

Cavity Ring-Down Optical Extinction Measurements of
Atmospheric Molecules

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To my family

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Chapter 1:

Optical extinction in the Earth's atmosphere

In this thesis experiments on attenuation of electromagnetic radiation in gases are reported. This subject is of relevance for the extinction of solar radiation in the Earth's atmosphere, either via scattering or absorption. In this introductory chapter some aspects of the extinction phenomena are described, ranging from Rayleigh scattering of molecular particles to scattering of somewhat larger particles (aerosols) and absorption processes where molecular collisions play a role. To put the findings and the underlying questions in perspective of the physics and chemistry of the Earth's atmosphere some aspects of its chemical composition and physical conditions are briefly described. Since a major fraction of the experiments reported in this thesis relate to deep-ultraviolet extinction, the radiation field of the atmosphere at these wavelengths is discussed. Further in this chapter an outline of the thesis is given.

Introduction

The main photoactive molecular species in the Earth's atmosphere below 100 km are ozone, oxygen and nitrogen. Absorption and scattering of solar radiation by these species are responsible for the attenuation of the solar ultraviolet (UV) flux in the atmosphere. Accurate measurements of the intensity and spectral characteristics of the attenuated UV solar radiation in the atmosphere, combined with systematic laboratory studies form a basis for a deeper understanding of the photochemical processes in the atmosphere. Combined results of such investigations provide information on the composition and dynamics of the Earth's atmosphere, and are necessary for the development of radiative transfer models.

Accurate quantitative data on atmospheric absorptions have been accumulated using extensive spectroscopic studies of atmospheric molecules (oxygen, ozone, molecular nitrogen, carbon dioxide, carbon monoxide, nitric oxide, etc) performed under different laboratory conditions and such data are currently available in the scientific literature. In contrast to absorption, only a limited number of accurate scattering measurements have been performed, particularly in the UV and deep-ultraviolet (deep-UV) spectral regions. The general lack of accurate quantitative information on molecular scattering at (deep) UV wavelengths is the main motivation for the Rayleigh scattering studies discussed in this thesis.

1.1. The Earth's atmosphere

The Earth is surrounded by several layers of gas that together make up the *atmosphere*. It stretches from the surface of the Earth towards outer space, becoming thinner and gradually fading at high altitudes. The altitude of about 100 km above the sea level is sometimes used in atmospheric physics to mark the boundary of the atmosphere. In addition there is the dynamic nature of the atmosphere: at very high altitude (~ 1000 km) the density of the atmosphere may vary by a factor of five, depending on the time of the day, time of year, recent solar flux etc.

The major molecular constituents of the Earth's atmosphere (for dry air) are nitrogen N_2 (78.084%), oxygen O_2 (20.946%), argon Ar (0.934%) and CO_2

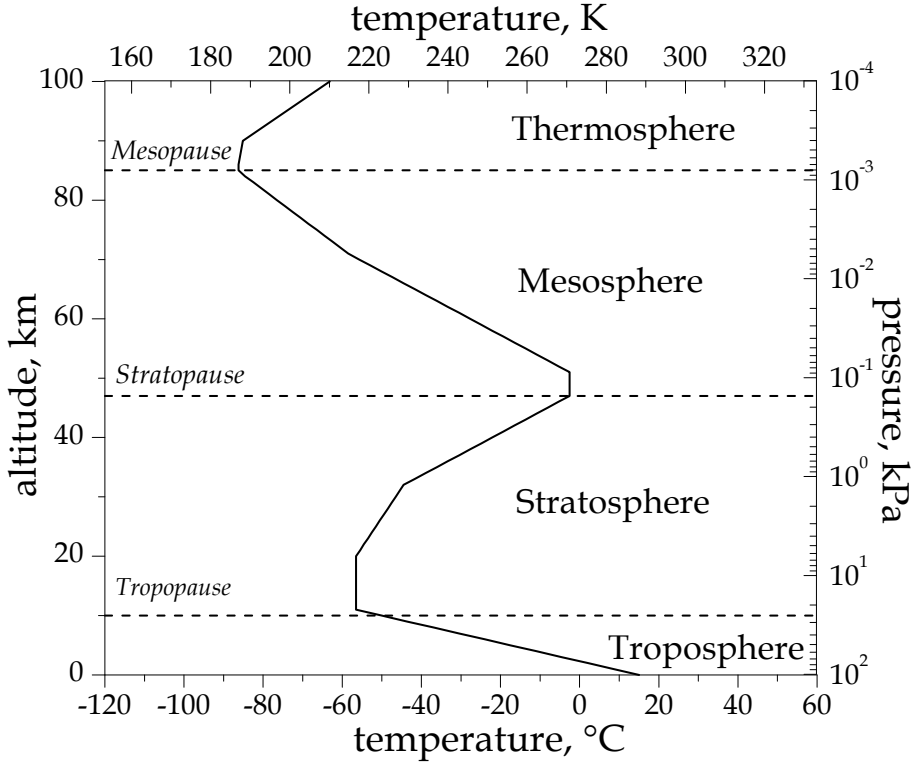


Figure 1.1: Altitude-dependent temperature and pressure profiles in the Earth's atmosphere. The boundaries of four atmospheric layers are indicated. This figure is adapted from [1] and represents the model of the U.S. Standard Atmosphere.

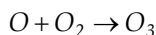
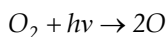
(0.0383%). These values refer to so-called *standard model* of the atmosphere [1, 2]. Air also contains a variable amount of water vapour, on average around ~1%. There are minute portions of other gases (Ne, He, CH₄, H₂ and Kr). Carbon dioxide, methane and water, known as *greenhouse gases* warm the atmosphere by absorbing thermal infrared energy; part of the thermal energy is converted into kinetic energy, which leads to increasing of the temperature of the Earth's surface and its atmosphere.

The Earth's atmosphere is divided into four layers based on altitude, temperature and pressure variations [1], as shown in Fig. 1.1 for a model of the U.S. Standard Atmosphere [2]: the *troposphere* layer (from the ground to 6–10 km height) with temperature steadily decreasing from 17°C on the surface of

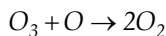
the Earth and reaching about -55°C at an altitude of about 10 km; the *stratosphere* layer with temperature changing from -55°C to almost 0°C at an altitude of about 50 km; the *mesosphere* layer with the temperature dropping from -5°C to almost -85°C at an altitude of about 85 km, and finally the *thermosphere* layer, where the temperature increases to -60°C at the altitude of about 100 km.

Relatively thin isothermal areas of *tropopause*, *stratopause* and *mesopause* characterized by nearly constant temperature values are also discerned. Although the tropopause forms a pronounced barrier between the troposphere and the stratosphere, it is highly variable in height and depending on latitude (and season) may stretch from ~ 16 km on the equator to ~ 6 km on the poles.

The stratosphere contains about 20% of the total mass of the atmosphere and it is a region of pronounced stability [1]. In this layer UV irradiation and short wavelength solar radiation is intensively absorbed, triggering an active photochemistry and resulting in a temperature increase with altitude. Through photodissociation free radicals are produced, that interact with less photoactive species. Formation of *ozone* from ultraviolet radiation (at wavelengths shorter than 240 nm) reacting with oxygen in the stratosphere is a typical example of a photo-induced chemical reaction:



Although ozone is present only at very low concentrations throughout the atmosphere ($\sim 6 \times 10^{-5} \%$), it plays a vital role for life on Earth. Most of the ozone (about 90%) exists in the stratosphere, in a layer between 10 and 50 km above the surface of the Earth, which is also known as the *ozone layer*. Ozone effectively absorbs short wavelengths (shorter than 320 nm) from the solar radiation, that otherwise would have been harmful to many forms of life. At the same time it is destroyed by the reaction with atomic oxygen:



The latter reaction is catalyzed by the presence of certain free radicals, of which the most important are hydroxyl (OH), nitric oxide (NO), atomic chlorine (Cl) and bromine (Br).

1.2. Solar radiation in the Earth's atmosphere

About 31% of the solar radiation reaching the Earth's atmosphere is scattered back into space by air, aerosols, clouds and reflections from the Earth's surface, whilst another 43% is absorbed by the Earth's surface and only about 26% is absorbed by atmosphere itself [3]. Most of the solar radiation resides in the visible and infrared regime, whereas only 7.5% is present at shorter wavelengths below 400 nm and about 1 % below 300 nm [3]. Despite this very low intensity, UV radiation is responsible for most of the photochemical processes in the lower layers of the atmospheric environment.

Transmittance of solar radiation through the atmosphere depends on the absorption and scattering properties of its constituents, i.e. molecules and aerosols. In the UV and particularly in the deep-UV the solar flux is mainly attenuated by *molecular absorption* and *scattering*. The attenuation of the solar radiation in the atmosphere exhibits a complicated altitude- and wavelength-dependent behaviour [3], as shown in Fig. 1.2.

As can be seen from the graph, solar radiation at wavelengths shorter than 310 nm is strongly attenuated in the middle atmosphere due to absorption by ozone, molecular oxygen and nitrogen.

1.3. Absorption of deep-UV light in the atmosphere

1.3.1. Deep-UV absorption of molecular O₃, O₂ and N₂

The absorption of sunlight by ozone that occurs in the stratosphere at altitudes between 20 and 40 km is found to determine the opacity of the atmosphere between 200 and 310 nm. The primary absorption of UV light by ozone is in the so-called *Hartley bands* at wavelengths of 180 to 310 nm, merging with the *Huggins bands* at 310 to 370 nm.

The atmospheric opacity between 100–200 nm (vacuum ultraviolet spectral region) is dominated by the absorption of molecular oxygen through the strong *Schumann-Runge bands* between 175 and 200 nm and a relatively weak *Herzberg absorption continuum* stretching from 185 to 265 nm. While the Herzberg continuum absorption is small compared to that of the Schumann-Runge bands in O₂ and the Hartley bands in O₃ it nevertheless determines the

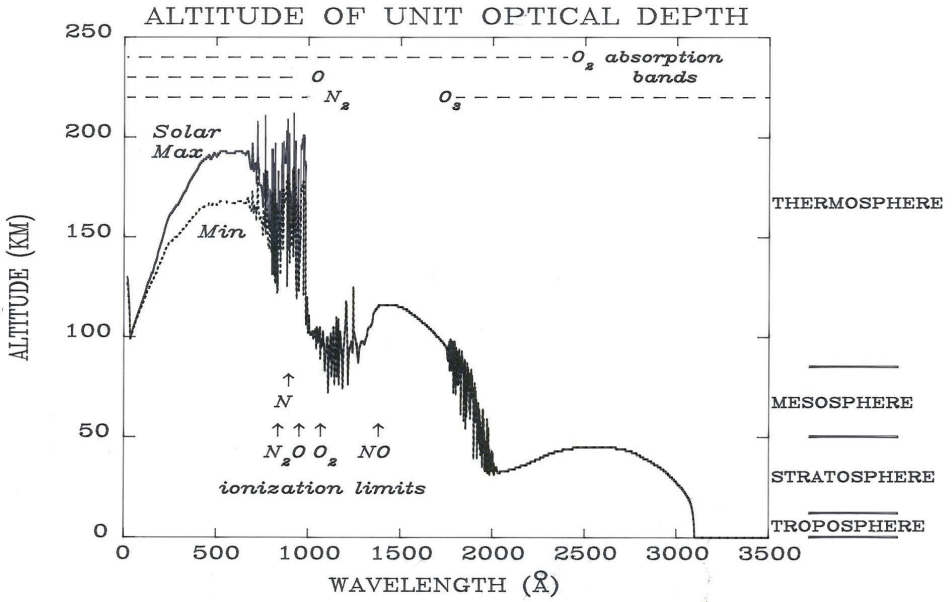


Figure 1.2: Altitudes in the Earth's atmosphere, at which solar radiation is attenuated to the e^{-1} level [3].

penetration of radiation in the wavelength window in between these strong systems. The opacity of the atmosphere at altitudes above 60 km is therefore determined by Schumann-Runge bands appearing as a progression of bands, ranging from the (0,0) band near 203 nm to the (22,0) band near 175 nm [3]. Spectral windows between these bands are occupied by hot bands that are highly temperature-dependent.

Radiation at wavelengths between 140 and 175 nm is absorbed by the *Schumann-Runge continuum*, in which O_2 is dissociated into two metastable oxygen atoms. This process plays a prominent role in the photochemistry of the atmosphere. Due to the large cross-section values (from $\sim 10^{-19} \text{ cm}^2$ at 175 nm to 10^{-17} cm^2 at 140 nm) nearly all of the incident solar radiation in this wavelength region is absorbed in the atmosphere between 100 and 150 km. In this altitudes region the atmospheric temperature may vary from -60°C to 330°C and this influences the O_2 absorption strength due to a significant temperature-dependent behaviour of the Schumann-Runge continuum [4]. In the extreme-

ultraviolet (XUV) spectral region, below 100 nm, N₂ dominates the absorption of solar radiation at altitudes near 150 km.

1.3.2. Collision-induced absorption

Collisional phenomena in a gaseous medium affect the appearance of absorption spectra in a number of ways. First, due to collisional *perturbation* of the isolated atoms and molecules spectral lines may broaden and the central frequency may shift. Further, during collisions a dipole moment can be formed due to displacement of electronic charge clouds, or the symmetry of a molecule can be altered; this may result in adding oscillator strength to transitions that were forbidden in the non-perturbed situation. An example of this phenomenon is the one-photon excitation of $a''^1\Sigma_g^+ - X^1\Sigma_g^+$ transition in molecular nitrogen, which is dipole-forbidden by symmetry, but pressure-induced perturbations make this transition allowed [5]. In this example there is an identifiable quantum transition in an isolated molecule, to which the absorption can be assigned. In addition, absorptions exist in short-lived collisional complexes (with typical lifetimes of $\sim 10^{-13}$ s) for which this is not the case. A celebrated example is that of the collision-induced absorption (CIA) spectrum of molecular oxygen, which was already observed in early atmospheric studies [6]; here absorptions occur that cannot be associated with a transition in a single molecule, but rather the absorbed energy becomes distributed over the two molecular fragments, as was explained in the early days of quantum mechanics. One of these prominent CIA systems in O₂, the broad band at 477 nm, has been re-investigated in this thesis.

While traditional spectroscopy applies to *ideal gases*, CIA studies consider *real gases* [7]. This introduces a significant difference between isolated molecules and collision-induced absorption phenomena. In the ideal gas approximation the absorbing particles obey the linear relation between pressure P , temperature T and density N :

$$P = Nk_B T \quad (1.1)$$

The molecules in a real gas attract at distant range and repel at near distances. The theory of real gases accounts for macroscopic thermodynamic quantities via the *virial expansion*:

$$P = AN + BN^2 \quad (1.2)$$

where $A, B \dots$ are virial coefficients, accounting for monomers and interacting pairs, triplets etc. The values of the virial coefficients are derived from an interaction potential $V(R)$, which varies over the distance R between interacting molecules:

$$A = k_B T, \quad B = -2k_B T \int_0^\infty \left[e^{\left(\frac{-V(R)}{k_B T} \right)} - 1 \right] R^2 dR \quad (1.3)$$

The intensity of spectra induced by molecular interaction may also be described by a similar virial expansion [7]:

$$I = \tilde{A}N + \tilde{B}N^2 + \dots \quad (1.4)$$

with the coefficients referring to monomer $\tilde{A}$ and induced binary $\tilde{B}$ contributions. The intensity of absorption by non-interacting molecules therefore varies linearly with the density $I_{allowed} = \tilde{A}N$, while the intensity of collision-induced phenomena varies with the second or higher powers of the density:

$$I_{induced} = \tilde{B}N^2 + \tilde{C}N^3 + \dots \quad (1.5)$$

At low pressures the second and higher terms in Eq. 1.4 are insignificant, whereas at high pressures many-body interactions may be expected to dominate optical properties.

1.4. Scattering of light in the atmosphere

In addition to absorption, atmospheric scattering is an important phenomenon, which influences the penetration depth of solar radiation. On average, about 40% of the radiation flux is scattered at ultraviolet wavelengths, whereas less than 1% is removed in the near infrared region [8].

A dimensionless size parameter is usually used for the description of light scattering:

$$x = \frac{2\pi d}{\lambda} \quad (1.6)$$

where d is the characteristic size of the particle and λ is the wavelength of the

incident light. Rayleigh scattering takes places in regimes where $x \ll 1$, i.e. for small particles. Rayleigh scattering of deep-UV radiation ($200 < \lambda < 300$ nm) originates from particles with a characteristic sizes up to 30–50 nm.

Light scattering by larger atmospheric species ($x > 1$) is described in terms of *Mie scattering* theory [8, 9]. Solid and liquid particles of both natural and anthropogenic origin (aerosols), present in the lower atmospheric layers, vary in size between 0.01 and few microns. When $x < 0.3$ almost no error is introduced by using the Rayleigh approximation, whereas differences of over 10% exist between Rayleigh and Mie theories for $x = 1$. Rayleigh and Mie approximations tend to fully diverge for $x = 3$ [10].

Early measurements of the amount of scattering, produced by the atmosphere from an intense light beam, demonstrated that the scattering observed at altitudes up to 80 km may be treated in terms of Rayleigh scattering by atmospheric molecules [11], whereas an enhancement of scattered light signal due to the concentration of aerosols between 15 and 30 km was observed. The variation of the intensity of scattered light with height was observed in several studies and was found to agree with the predictions based on the standard atmosphere model.

1.4.1. Rayleigh scattering

Molecular (Rayleigh) scattering has been studied in much detail [12, 13]. Rayleigh scattering is an *elastic* process in which the energy and thus the wavelength of light do *not change*. The angular distribution of scattered light intensity is *symmetric*, so scattering in forward and backward directions are equally strong.

A theory of light scattering as an electromagnetic phenomenon was developed by Lord Rayleigh [14]. He considered spherical scattering particles and assumed that these were *isotropic*, *homogeneous* and *small* compared to the wavelength. The latter condition assures that the electromagnetic field is *uniform* over the extent of the spherical scatterer, which becomes polarized in the same direction as the incident electric field. This results in an *electric dipole*, which oscillates synchronously and in the same direction as the incident electromagnetic field. The oscillating dipole radiates energy and it is this secondary emission that accounts for the scattering.

When the scattering medium is a gas of randomly distributed particles, the phase relationships between waves scattered from different particles are not correlated and the resulting intensity of the scattered light can be determined as a sum of all contributions from all particles. Therefore, intensity measurements of scattered light give quantitative information on the density of the scattering media as long as the scattering properties of a single particle are well known. This idea is widely used in experimental applications aimed to determine the gas density and temperature distribution in specific environments, e.g. combustion or flow media [15] via measurements of scattered light performed at UV and deep-UV wavelengths.

The induced electric dipoles have magnitudes proportional to the momentary amplitudes of the applied electric field. The strength of the oscillation of a dipole $\vec{p}$ induced by an electric field $\vec{E}_0$ from the electromagnetic wave of incident natural light [8] is measured as:

$$\vec{p} = \alpha \vec{E}_0 \quad (1.7)$$

where α is the polarizability of the scatterer, which has a dimension of cm^3 in a CGS units system. In the general case α is not a scalar, but a tensor and the particle is characterized by three tensor components α_1 , α_2 and α_3 . In the case of isotropic scattering media the directions of the applied electric field and of the induced dipole moment coincide and the polarizability becomes a scalar:

$$\alpha_1 = \alpha_2 = \alpha_3 = \alpha \quad (1.8)$$

The induced dipole in turn radiates in all directions a scattered wave, which at large distance r at an angle γ from the dipole has amplitude:

$$E = \frac{1}{c^2} \frac{\sin \gamma}{r} \frac{\partial^2 p}{\partial t^2} = -E_0 k^2 \alpha \frac{\sin \gamma}{r} e^{[ik(r-ct)]} \quad (1.9)$$

where c is the speed of light, k is the wave vector, t represents time and E_0 is the amplitude of the incident electric field.

The intensity $I(\Theta, r)$ of light scattered at angle Θ at the distance r from the dipole is proportional to the averaged value of E^2 :

$$I(\Theta, r) = I_0 k^4 \frac{\alpha^2}{2r^2} (1 + \cos^2 \Theta) = I_0 \frac{8\pi^4 \alpha^2}{\lambda^4 r^2} (1 + \cos^2 \Theta) \quad (1.10)$$

where λ is the wavelength. As can be seen from Eq. 1.10, the scattered intensity has a maximum in the forward $\Theta = 0$ (forward scattering) and backward $\Theta = \pi$ (back scattering) directions.

The scattered power P can be found by integrating the intensity $I(\Theta, r)$ over a sphere, yielding:

$$P = F_0 \frac{128\pi^5 \alpha^2}{3\lambda^4} \quad (1.11)$$

where F_0 is the incident flux of the incident radiation. Finally, the scattering cross-section for an individual molecule is:

$$\sigma_s^R = \frac{P}{F_0} = \frac{128\pi^5 \alpha^2}{3\lambda^4} \quad (1.12)$$

Therefore a Rayleigh scattering cross-section is determined by an inverse fourth power of the wavelength and the polarizability of a scattering particle.

Electromagnetic theory relates the polarizability α to the refractive index n via the Lorentz-Lorenz equation. Thus an ensemble of scatterers with number density N has polarizability:

$$\alpha = \frac{3}{4\pi N} \frac{n^2 - 1}{n^2 + 2} \quad (1.13)$$

Consequently, the Rayleigh scattering cross-section of a spherical particle with isotropic optical properties becomes:

$$\sigma_s^R = \frac{24\pi^3}{\lambda^4 N^2} \left(\frac{n^2(\lambda) - 1}{n^2(\lambda) + 2} \right)^2 \quad (1.14)$$

The Rayleigh formula, given by Eq. 1.14, relates the scattering cross-section to two directly measurable quantities, the wavelength-dependent refractive index $n(\lambda)$ and the gas density N . Note that the latter two are macroscopic properties of the gas, related such that σ_s^R represents a *single particle* cross-section.

Rayleigh scattering has certain polarization properties, as illustrated in Fig. 1.3. The light scattered at the directions perpendicular to the incident radiation propagation direction ($\Theta = \pi/2$) is fully polarized with the electric vector oscillating perpendicular to the scattering plane. The figure illustrates the total intensity of scattered light, as well as the intensities, corresponding to the polarized components: $I_\perp$ accounts for the light intensity scattered in a plane

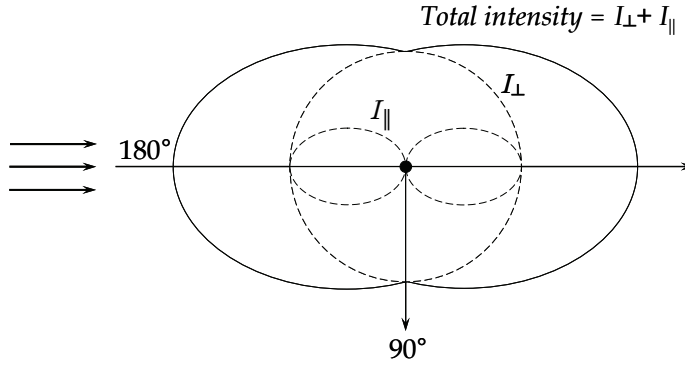


Figure 1.3: Rayleigh scattering of unpolarized light. $I_{\parallel}$ corresponds to the intensity of the scattered light, polarized parallel to the plane of drawing and $I_{\perp}$ - to the intensity of scattered light perpendicular to the plane of drawing whilst the total intensity is a sum of $I_{\parallel} + I_{\perp}$.

perpendicular to the plane of the dipole, and $I_{\parallel}$ – for the intensity of scattered light polarized in the plane parallel to the plane of the dipole. The radius vector to each curve corresponds to the scattered intensity of scattered light.

It has to be noted that the diagram for Rayleigh scattering depicted in Fig. 1.3 [12] holds only if the incident light is natural and the particles are small and isotropic. Light scattered by an isotropic molecule (see Eq. 1.8) from a linearly polarized light beam has a linear polarization, since all the induced dipoles are parallel to the orientation of the electric field vector of the incident light.

In the case of scattering by particles with anisotropic dielectric properties the scattered radiation is *partly polarized*. Polarization of the scattered light depends on the shape and orientation of the molecule with respect to the electric field of the incident light. For example, if the particles are cylindrical, instead of spherical, the polarization of light scattered at 90° is less compared to that for spherical particle.

The effect of partial polarization of light scattered at right angles with respect to the direction of propagation, is known as *depolarization* and was originally studied by King [16], while a comprehensive treatment can be found in [12]. The depolarization of scattered light can be quantitatively represented as intensity ratio of two orthogonal polarization components, *vertical* and

horizontal present in the scattered light. The depolarization ratios for natural ρ_n and polarized light ρ_p are different and connected through:

$$\rho_n = \frac{2\rho_p}{1 + \rho_p} \quad (1.15)$$

The values of the depolarization ratio are determined by the anisotropy K of the molecular polarizability tensor α_{ij} with $(i,j) = 1-3$:

$$K^2 = \frac{(\alpha_{11} - \alpha_{\text{mean}})^2 + (\alpha_{22} - \alpha_{\text{mean}})^2 + (\alpha_{33} - \alpha_{\text{mean}})^2}{6\alpha_{\text{mean}}^2} \quad (1.16)$$

where α_{11} , α_{22} and α_{33} are the principal (diagonal) elements of the polarizability tensor and α_{mean} is the mean value of the polarizability [17]:

$$\alpha_{\text{mean}} = \frac{1}{3}(\alpha_{11} + \alpha_{22} + \alpha_{33}) \quad (1.17)$$

In the case of linear (O_2 , N_2 , CO , NO) or symmetric top molecules (NH_3 , C_6H_6) $\alpha_{11} = \alpha_{//}$ and $\alpha_{22} = \alpha_{33} = \alpha_{\perp}$, leading to the depolarization ratio:

$$k = \frac{(\alpha_{//} - \alpha_{\perp})}{\alpha_{//} + 2\alpha_{\perp}} = \frac{(\alpha_{//} - \alpha_{\perp})}{3\alpha_{\text{mean}}} \quad (1.18)$$

The mean polarizability can be found from the refractive index of the gas and the magnitude of $\alpha_{//} - \alpha_{\perp}$ can be obtained from measurements of the depolarization ratio.

The wavelength dependence of the refractive index of the atmosphere has long been considered in calculations of Rayleigh scattering cross-section values. However, the dispersion of the depolarization has been typically neglected. Bates [18] recalculated the Rayleigh scattering cross-section between 200 and 1000 nm including the wavelength dependence of the depolarization. This dependence was found to be prominent at UV wavelengths and can lead to 3 % difference in the Rayleigh scattering cross-section at 200 nm, whereas at longer wavelengths the depolarization introduces a difference in Rayleigh scattering cross-section of only 0.5%.

An additional correction factor is therefore required for taking into account the anisotropy of molecular polarizability at Rayleigh scattering experiments in UV and deep-UV spectral regions. The proper correction is

attained by introducing a *correction factor* $F_k(\lambda)$, firstly derived by King. In case of non-spherical molecules:

$$F_k(\lambda) = \frac{6 + 3\rho_n(\lambda)}{6 - 7\rho_n(\lambda)} = \frac{3 + 6\rho_p(\lambda)}{3 - 4\rho_p(\lambda)} = 1 + 2\left(\frac{\alpha_{//} - \alpha_{\perp}}{\alpha_{//} + 2\alpha_{\perp}}\right)^2 \quad (1.19)$$

where $\rho_n(\lambda)$ and $\rho_p(\lambda)$ contribute for the wavelength-dependent depolarization of natural and polarized incident light. Consequently, the formula for Rayleigh scattering cross-section modifies to:

$$\sigma_s^R = \frac{24\pi^3}{\lambda^4 N^2} \left(\frac{n^2 - 1}{n^2 + 2} \right)^2 F_k(\lambda) \quad (1.20)$$

A comparison between measurements of the Rayleigh cross-section and the refractive index (for a known density) yields information on the dimensionless King correction factor $F_k(\lambda)$. As it can be seen from Eq. 1.20, the cross-section for non-spherical molecules is *increased* by the King factor.

1.4.2. Aerosol scattering

Scattering of light by spherical particles of arbitrary dimensions was first treated by Mie in 1908 [9]. Mie theory applies to the interaction of electromagnetic radiation with aerosols and cloud droplets and is based on solutions of Maxwell's equations for the electromagnetic field about a dielectric sphere of radius d in the approximation that it is larger than the wavelength of the incident electromagnetic wave.

The heart of the Mie scattering problem is in computation of *scattering matrix elements*, which define a relationship between the magnitudes of incident and scattered electric fields and depend on a complex refractive index of the scattering media and size parameter [12] of scattering particulates. Mie solutions can be found in a form of infinite series, which involve spherical Bessel functions and Legendre polynomials [19].

The efficiency of aerosol scattering Q_s is usually determined as an area of the scattered beam σ_s divided by the geometric area πd^2 of the scattering particle:

$$Q_s = \frac{\sigma_s}{\pi d^2} \quad (1.21)$$

The cross-section σ_s of the aerosol scattering can be significantly larger than the geometrical cross-sections of the particle, leading to the efficiency $Q_s > 1$. Aerosol scattering depends markedly on size distribution, chemical composition and concentration of the aerosol particles.

Radiative characteristics of atmospheric aerosols and quantitative optical data for different types of particles are available in literature, e.g. in [20], from where a scattering coefficient values based on Mie theory computations of scattering efficiencies can be found. Thus, light scattering by dust-like, water-soluble and soot particles with a sizes d of about $0.47\text{ }\mu\text{m}$ [20, 21], $0.03\text{ }\mu\text{m}$ [20, 21] and $0.01\text{ }\mu\text{m}$ [20–22], respectively, exhibits almost no wavelength dependence between 300 and 500 nm and is significantly larger compared to Rayleigh scattering of air.

1.5. Observations of light scattering in the deep-UV spectral region

In the spectral region between 200 and 300 nm the opacity of the Earth's atmosphere is determined by absorption and scattering by atmospheric constituents and a local minimum near 200 nm in the absorption profiles of ozone and molecular oxygen is observed. This notch is responsible for a certain bandwidth of solar radiation to penetrate to lower altitudes. Under these conditions the light scattering becomes a major effect, which governs the attenuation of short wavelength solar radiation. Therefore systematic laboratory and stratospheric measurements of light scattering and its spectral characteristics become very valuable as well as a comparison, made between experimentally measured values and their analytical predictions, based on advanced radiative transfer models.

Despite of the fact that a number of measurements of the solar radiation above the Earth's atmosphere have been reported in literature, quite a limited data on *in situ* measurements of stratospheric ultraviolet irradiance is available and the radiation within the atmosphere cannot be computed with complete confidence [3].

Measurements of diffuse (scattered) radiation field have a great impact on the development of radiative transfer model computations. Such

measurements can be performed with a good precision, using advanced optical techniques between 200 and 300 nm, but few studies have been actually performed, particularly for this spectral region [3]. The results of some of these measurements of diffused light in the atmosphere performed between 200 and 300 nm are discussed below.

1.5.1. Measurements of scattering performed in the stratosphere

Direct and scattered (diffused) components of solar flux between 190 and 320 nm was measured by Herman [23]. Simultaneous measurements of the both scattered and direct components of solar flux were performed using double monochromators, carried on a balloon-borne platform between 40 and 60 km [24]. One of the monochromators pointed directly at the sun, while the other was oriented in six different directions away from the sun to determine the amount of scattered solar flux. Since a multiple light scattering also contributes to entire budget of diffused radiation, a ratio of the scattered flux to the direct one provides a quantitative measure of multiple scattering of light in atmosphere.

A comparison of Herman's observations with radiative transfer model predictions by Kylling *et al.* [25] reveals interesting features, as shown in Fig. 1.4. At shorter wavelengths, between 190 and 210 nm, the results of Herman's measurements are found in a complete disagreement with the predictions of Kylling. Between 210 and 300 nm the model predicts more scattering than the experiment, particularly at longer wavelengths between 280 and 300 nm, where the model yields to a factor of 2 more scattering than concluded from the observations. At longer wavelengths the discrepancy between measured and predicted data becomes smaller. Although the model qualitatively reproduces the general trend of the observations, origins of the indicated discrepancies have not been identified [25]. Furthermore, additional computations of scattering ratio, performed by Lary *et al.* in 1991 [26], yielded a factor of 3 less scattered radiance than it was experimentally observed by Herman and his co-workers.

The next experimental attempt was done in 1983 by Thomas *et al.* [27, 28], who measured scattered solar radiation between 175 and 325 nm with a spectral resolution of 1.5 nm using a balloon-borne spectrometer launched at

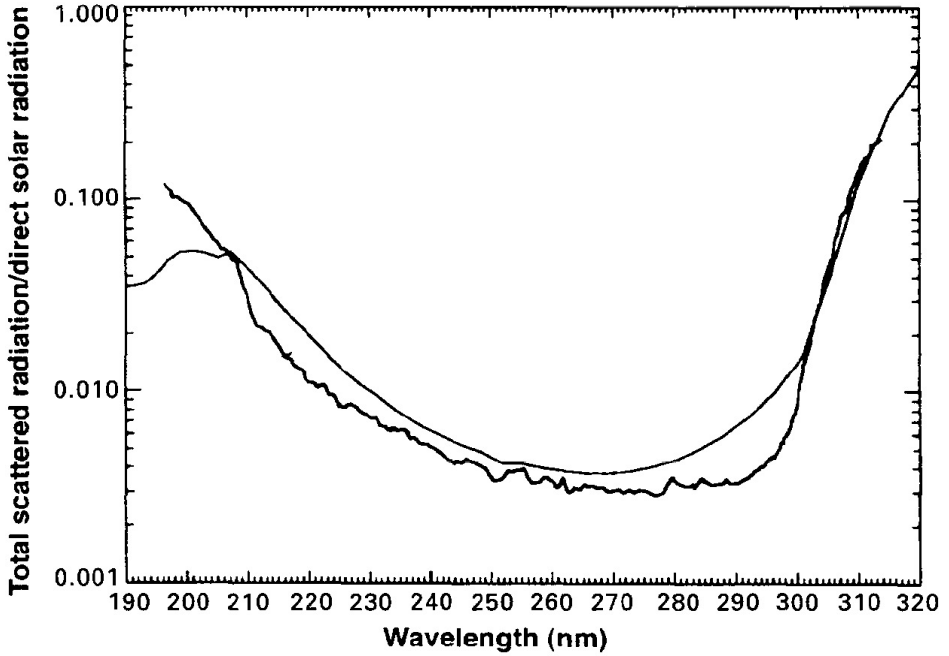


Figure 1.4: The ratio of the scattered to the direct solar radiation at 40 km. The thick line represents the observations of Herman (figure 11 in [23]), whereas the thin line corresponds to the radiative transfer model predictions of Kylling [25].

altitudes of 40–46 km. Atmospheric absorption in the O_3 Hartley band was clearly observed as well as the spectral features, corresponding to the (1,0) through (4,0) absorption Schumann-Runge bands below 200 nm. The scattered radiation was found to fall off rapidly below 210 nm, as predicted by models, in contradiction to the earlier observations by Herman *et al.*

The measurements of direct and scattered sunlight performed at longer wavelengths in the 300–450 nm range on the Earth's surface under cloud free conditions were reported in [29], whereas advanced computational models were developed and discussed in [30]. These models used observation-based profiles of the temperature, pressure and ozone concentrations for vertically inhomogeneous atmosphere in contrast to the radiative transfer model of Kylling [25]. This allowed achieving better agreement between the measured and calculated light scattering over a wide range of observing conditions.

1.5.2. Laboratory measurements of Rayleigh and aerosol scattering

Accurate information on molecular scattering in the deep-UV region based on systematic laboratory measurements of Rayleigh scattering for most atmospherically relevant molecules is not available in the literature. Rayleigh scattering measurements for some atmospheric molecules (Ar, N₂, H₂, O₂, H₂O, CO₂, CH₄) at 193 and 248 nm were reported in [15]. These measurements used imaging techniques of scattered light and aimed for developing Rayleigh scattering diagnostics for temperature and species concentration in flow and combustion environments.

Deep-UV optical extinction cavity ring-down measurements in CO₂ and SF₆ resulted in Rayleigh scattering cross-section values at 198 nm are available from [31], where a close quantitative agreement between the measured and predicted Rayleigh scattering cross-sections was found.

Laboratory measurements of aerosol scattering have been reported mainly for the visible spectral region. Thus, using pulsed cavity ring-down spectroscopy a light attenuation from atmospheric aerosol particulates was measured at 532 and 355 nm [32]. The extinction cross-section measured at 355 nm for 0.1 μ m aerosol particulates was found to be larger than that for 532 nm, but due to low detection sensitivity, achieved at 355 nm, no value of scattering cross-sections of these aerosol particulates were reported.

1.6. Outline of the thesis

Experimental determination of deep-UV Rayleigh scattering and molecular absorption phenomena in atmospheric molecules aid in understanding of the short-wavelength radiation budget of the Earth's atmosphere. The main goals of this thesis are to (1) quantitatively address the optical extinction phenomena in N₂, CO, CO₂, CH₄, SF₆ between 198 and 270 nm, to (2) perform a spectroscopic analysis of the absorption bands of ¹⁵N¹⁸O near 206 nm, and to (3) perform a parameterization of the collision-induced absorption resonances at 477 and 577 nm in O₂-O₂ collision complexes. Due to a very low natural abundance of the ¹⁵N¹⁸O isotopologues, experimental studies of ¹⁵N¹⁸O molecule have limited atmospheric relevance and are merely aimed to pure spectroscopic purposes.

The experimental work has been performed by the sensitive cavity ring-down spectroscopy technique using pulsed dye-laser facilities at the Laser Centre Vrije Universiteit Amsterdam.

Chapter 2 introduces the cavity ring-down spectroscopic (CRDS) technique and describes the setup for experimental studies in the deep-UV, including the operation of the laser system and the method of pressure-ramping. Some results of optical extinction and collision-induced absorption measurements in CO, performed at room temperature at wavelengths 198-220 nm, are presented; these results on CO and their interpretation are not yet conclusive.

Optical extinction measurements, performed in carbon dioxide at room temperature between 197 and 270 nm, providing accurate Rayleigh scattering cross-section values and a quantitative assessment of the absorption onset for CO₂ are presented in *Chapter 3*.

Systematic room-temperature measurements of the Rayleigh scattering in N₂, CH₄ and SF₆ gases and a functional representation of the observed values of Rayleigh scattering cross-section are reported in *Chapter 4*. The values of molecular polarizability and depolarization ratios have been derived from the observations and compared to values available in the literature.

Chapter 5 focuses on the analysis of so far unreported rovibronic transitions of the heaviest chemically stable NO isotopologue – ¹⁵N¹⁸O – in its γ -system in the 205–216 nm region and accurate values of molecular constants for $A^2\Sigma^+(v=1)$ and $A^2\Sigma^+(v=2)$ vibrational levels have been derived for the first time.

Collision-induced absorption resonances in O₂-O₂ molecular complexes have been measured at 477 and 577 nm at temperatures ranging between 184 and 294 K, as is extensively reported in *Chapter 6*. The temperature dependence of peak cross-section, resonance width and band integrated values have been derived from the measurements and compared with data available in literature to establish updated temperature-dependent trends of the shape and strengths of the resonances. The thesis is concluded with a *Summary*.

Chapter 2:

Experimental approach: cavity ring-down spectroscopy

In this chapter a description of the technique of cavity ring-down spectroscopy (CRDS) is given. The CRDS principle and the achievable sensitivity in CRDS measurements are discussed, and a description of the digitizing techniques that are commonly used for a precise determination of the ring-down decay time is given. A comprehensive description of the experimental setup is presented with special emphasis on the method of producing tunable radiation in the deep ultraviolet region (198–220 nm), the analysis of pressure-ramps and decay transient signals and the absolute frequency calibration scheme. The performance of the setup is demonstrated in a room-temperature CRDS study of the $(v',v'')=(0,0)$ absorption band of the $a^3\Pi \leftarrow X^1\Sigma$ system in CO around 206 nm, providing information on absorption, scattering and collision-induced phenomena.

2.1. Cavity ring-down spectroscopy

Cavity ring-down spectroscopy is a direct absorption technique, firstly introduced by O’Keefe in 1988 [33]. Despite of the fact that this method was originally developed for measurements of high reflectivity of mirrors, it has become a widely adopted spectroscopic technique due to its simplicity and high sensitivity, straightforwardly available in rather simple experimental setups.

CRDS can be performed with pulsed or continuous wave light sources in a gas, liquid and solid phase measurements, but this experimental approach is particularly suited for gas phase absorption measurements of weak transitions [34, 35]. A comprehensive historical review of CRDS, as well as discussion on a different CRDS schemes and their applications can be found in literature [36].

2.1.1. CRDS principle and sensitivity

In a conventional cavity ring-down experiment, schematically depicted in Fig. 2.1, a light pulse with a spectral intensity distribution $I(\nu)$ is coupled into a stable optical cavity formed by two highly reflective mirrors $\mathcal{M}_1$ and $\mathcal{M}_2$. The light pulse is reflected back and forth between the mirrors, and at each mirror reflection a minute portion of the light is leaking out of the cavity. This results in a decaying of the output intensity, that can be recorded by fast light detectors (e.g. photomultiplier tubes or photodiodes), placed at the rear side outside the cavity. A typical ring-down event exhibits an exponentially decaying signal.

In an empty cavity the light pulse intensity decays mono-exponentially and the characteristic frequency-dependent decay time $\tau_0(\nu)$ is solely determined by the reflectivity of the mirrors $R(\nu)$ and the optical path length d between the mirrors:

$$\tau_0(\nu) = \frac{d}{c|\ln(R(\nu))|} \quad (2.1)$$

where c is the speed of light. A typical mirror reflectivity in CRDS experiment is close to unity $R(\nu) \approx 1$. Following a Taylor expansion for $\ln(R(\nu))$ it is possible to define $\tau_0(\nu)$:

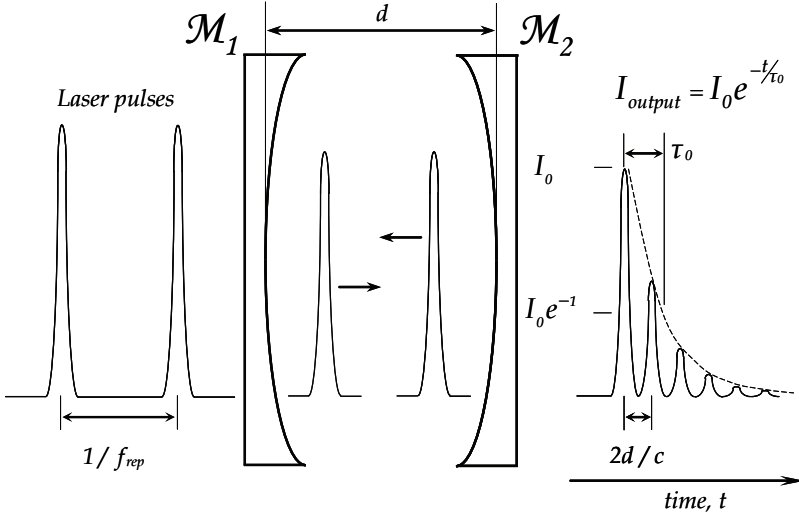


Figure 2.1: The schematic representation of the CRDS method. f_{rep} – repetition frequency of the laser pulses, d – length of the ring-down cavity, c – the speed of light, t – time and τ_0 – the decay time of the output intensity (for the empty cavity). Note that intensity-ratios of the laser pulses entering the cavity, traveling between the mirrors $\mathcal{M}_1$ and $\mathcal{M}_2$ and leaking out the cavity are not drawn to the proper magnitudes.

$$\tau_0(\nu) = \frac{d}{c(1 - R(\nu))} \quad (2.2)$$

Practically, the reflectivity of the used mirrors $\mathcal{M}_1$ and $\mathcal{M}_2$ will not be identical and consequently the reflectivity $R(\nu)$, used in Eq. 2.2, should be regarded as an *effective reflectivity*:

$$R(\nu) = \sqrt{R_1(\nu)R_2(\nu)} \quad (2.3)$$

where $R_1(\nu)$ and $R_2(\nu)$ represent the reflectivity of mirrors $\mathcal{M}_1$ and $\mathcal{M}_2$, respectively.

The appearance of matter inside the ring-down cavity gives rise to additional losses, due to scattering and absorption. Starting from Beer-Lambert's law, the decaying light intensity is given by:

$$I(t) \propto \int_0^\infty I(\nu) \exp\left[-\frac{t}{\tau(\nu)}\right] d\nu \quad (2.4)$$

This results in a shortening of the decay time:

$$\tau(\nu) = \frac{d}{c \left(\left| \ln(R(\nu)) \right| + \sum_i \sigma_i(\nu) \int_0^d N_i(x) dx \right)} \quad (2.5)$$

The sum in the last expression is calculated over all light scattering and absorbing species with frequency-dependent cross-sections $\sigma_i(\nu)$ and a line-integrated number density N_d :

$$N_d = \int_0^d N_i(x) dx \quad (2.6)$$

with the integration taken over the length of the cavity. The product of the absorption and scattering cross-section $\sigma_i(\nu)$ with the number density N_d is commonly expressed as the *extinction coefficient*:

$$k(\nu)d = \sum_i \sigma_i(\nu) \int_0^d N_i(x) dx \quad (2.7)$$

Therefore the frequency-dependent decay time $\tau(\nu)$ can be written as:

$$\tau(\nu) = \frac{d}{c[(1 - R(\nu)) + k(\nu)d]} \quad (2.8)$$

When the losses induced by scattering and absorption by gas in the ring-down cavity have to be considered separately, it is possible to derive the values for the corresponding cross-sections. In this case the extinction coefficient is expressed as:

$$k(\nu) = N(\sigma^{\text{scat}} + \sigma^{\text{abs}}) \quad (2.9)$$

The losses due to the finite reflectivity of the CRD mirrors can be measured for an evacuated ring-down cell and have to be taken into account to determine the extinction coefficient of a sample, yielding its *absolute value* for a known gas density N . In the more general situation with the gas consisting of a mixture with different constituents and partial densities N_i each contribution has to be taken into account, resulting in a sum over all extinction coefficients:

$$k(\nu) = \sum_i N_i(\sigma_i^{\text{scat}} + \sigma_i^{\text{abs}}) \quad (2.10)$$

Cavity ring-down spectroscopy possesses important advantages compared to other spectroscopic techniques. Due to multiple traversals of the light pulse in the ring-down cavity the effective absorption path length is

substantially increased. Thus, in an evacuated 100 cm long ring-down cavity, formed by two mirrors with $R \approx 0.9999$, the path length for a single ring-down time τ_0 can be effectively increased to a few kilometers.

Since CRDS is solely based on measurements of the decay time of a light pulse, CRDS measurements do not depend on the absolute intensity of the transmitted light. Hence the sensitivity does not suffer from *intensity fluctuations* of a light source, which is known to be a common drawback in regular direct absorption experiments.

The sensitivity that is obtained in CRDS measurements can be quantitatively analyzed. When a single shot CRDS measurement is performed and the value of the decay time τ is measured with an uncertainty $\delta\tau$ the *noise equivalent absorption* (detection limit) is determined by [37]:

$$\delta k_{\text{noise}} \propto \frac{\delta\tau}{\tau^2} \quad (2.11)$$

The achieved sensitivity of the averaged value in a series of repeating CRDS measurements with a repetition frequency of f_{rep} is expressed by [38]:

$$S = \sqrt{\frac{2}{f_{\text{rep}} N_{\text{ph}}}} \frac{\delta\tau}{\tau^2} \quad (2.12)$$

where N_{ph} is the number of photons impinging on the photodetector.

Analysis of Eq. 2.12 shows that a sensitivity enhancement can be achieved if the uncertainty $\delta\tau/\tau$ at which an individual decay time is determined decreases. Another way to achieve a higher sensitivity lies in using higher reflectivity ring-down mirrors, resulting in an increasing effective absorption pass length. The latter, however, also leads to a decrease of the number of photons (shot-noise limit) detected by the light detector. Therefore, a realistic compromise has to be found between mirror reflectivity and optical throughput: in this case increasing the laser intensity is an option for improving the sensitivity.

As can be seen from Eq. 2.12, the increase of the repetition frequency f_{rep} can significantly improve the sensitivity. Presently, state-of-the-art electronics, especially light detectors and digitizing techniques, used prior to mathematical processing of the detected transient waveforms, enable

measurements with uncertainties near to shot-noise limit and noise-equivalent absorptions of 10^{-10} – 10^{-12} $\text{cm}^{-1}\text{Hz}^{-1/2}$ [38, 39]. For a comparison: conventional pulsed CRD experiments, performed with commercially available pulsed dye lasers, operating at relatively low repetition frequencies (typically 10–100 Hz) allow for sensitivities at the level of 10^{-7} $\text{cm}^{-1}\text{Hz}^{-1/2}$.

2.1.2. Laser bandwidth and cavity modes effects.

The picture of CRDS as a process of decaying light intensity in a stable optical cavity, given above, involves the assumption that interference effects may be ignored. However, in many CRDS applications interference effects are observed, particularly when laser pulses of long coherence length and narrow bandwidth (as is the case e.g. when using cw laser systems) are used. Laser bandwidth effects in CRDS have been discussed in [40–42].

The transmission spectra of an optical cavity are not continuous and a comb of equidistant resonances exists. The number of modes, simultaneously excited in a ring-down cavity depends on the bandwidth of the exciting laser radiation, the cavity mode spacing and the level of diffraction losses.

The majority of the cavity ring-down measurements described in the present thesis are performed with a deep-UV bandwidth of about 0.5 cm^{-1} or 15 GHz. Under this broadband excitation many higher order cavity modes are excited simultaneously and consequently a laser pulse sees a “white”, i.e. quasi-continuous cavity and all laser frequencies effectively contribute to the ring-down decaying. The measurements on transmission spectra of the ring-down cavity in a non-confocal configuration have been described in [43] and showed a continuous transmission spectrum.

It is important to note that the excitation of multiple modes in an optical cavity will always result in a multi-exponential decay. However, this multi-exponential behaviour is usually hardly discernible in a well aligned ring-down cavity. For practical purposes the measured decay transient may be considered to be mono-exponential, if the results of a mono-exponential fit of the transient waveform do not indicate multi-exponential behaviour over a time span of $\sim 5\tau$. The analysis of residuals from the mono-exponential fit is essential for CRDS experiments, particularly when a white ring-down cavity is used.

2.1.3. Different techniques for retrieving decay time values in CRDS experiments

Different methods for determining the decay times in a CRDS experiment have been discussed in the literature [44]. The decay transient signal $I(t)$ is given by:

$$I(t) = I_{off} + I_0 e^{-t/\tau} \quad (2.13)$$

where I_{off} is the offset of the observed intensity with respect to the zero level, I_0 is the value of the peak intensity prior to its decay and τ is the decay time. Analysis of the transient signal can be performed using either analog integration or fitting techniques. A brief discussion of these approaches, their advantages and disadvantages is given below.

Analog schemes

In analog techniques the value of the decay time is determined using boxcar detection schemes [45], in which two equally broad time windows are selected, as shown in Fig. 2.2. The decay time τ is derived as:

$$\tau = \frac{\delta t}{\ln \left[\frac{A}{B} \right]} \quad (2.14)$$

where δt is the time delay between the integration windows with the same duration Δt and A and B are the integrated signals:

$$A = \int_{\Delta t} I(t) dt, \quad B = \int_{\Delta t} I(t) dt \quad (2.15)$$

This analog technique can be applied only if $I_{off} = 0$. To fulfill this requirement an additional time window C (chosen before the ring-down onset and not shown in Fig. 2.2) with the same duration Δt is used, resulting in:

$$\tau = \frac{\delta t}{\ln \left[\frac{A-C}{B-C} \right]} \quad (2.16)$$

In this analog scheme the timing is evidently important and the width of the integration windows must be accurately known and kept stable, as well as the value of the delay time δt between the integration windows.

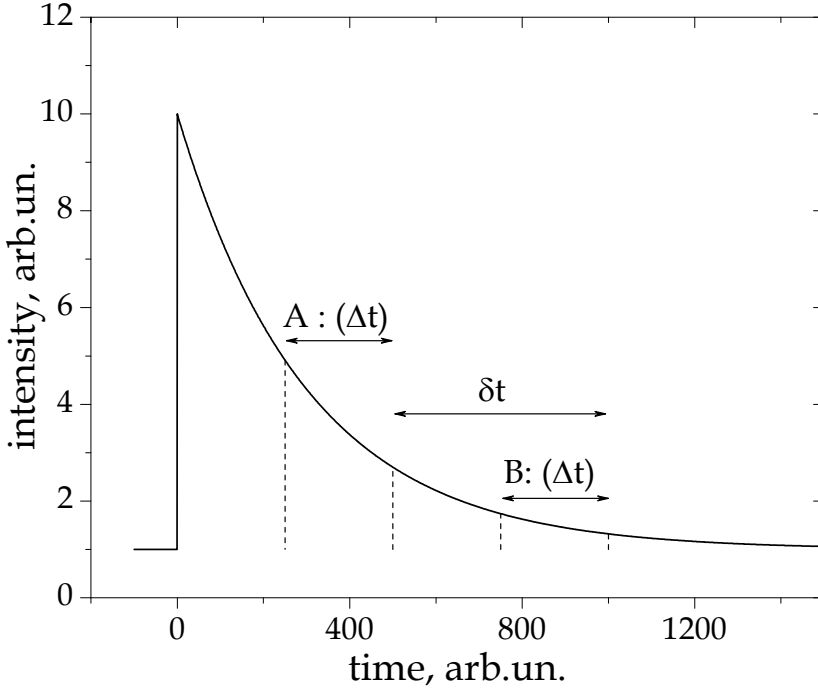


Figure 2.2: Simulated cavity ring-down transient signal and the integrating windows A and B used for the decay time determination in an analog setting.

A similar technique based on integration of the decaying waveform, suggested by O’Keefe [46, 47], yields a representation for the decay time:

$$\tau = \frac{1}{I_0} \int_0^{\infty} I_0 e^{-t/\tau} dt \quad (2.17)$$

Another non-integrating based method for deriving the values of the decay time is suggested in [48]. This method is based upon the logarithmic linearization of the decay transient signal:

$$\ln[I(t)] = \ln[I_{\text{off}}] - \frac{t}{\tau} \quad (2.18)$$

These three methods can be properly used only when the value of the intensity offset is accurately determined. Although the initial intensity offset can be easily determined from the baseline prior to the ring-down signal, it can impede CRDS measurements carried out at a high repetition frequency.

Fitting methods

The most common method to determine a cavity decay time is based on *non-linear least-squares fitting* with a mono-exponential functional form using a numerical Levenberg-Marquardt algorithm. The main advantage of this method lies in its independence to the intensity offset value, which can be independently determined during the fitting process.

A comprehensive evaluation of nonlinear fitting methods of the decay waveforms is given in [44]. A comparison made between *weighted* and *unweighted* fitting methods reveals only small differences in the resulting parameters. CRDS measurements usually require a fast determination of the decay times in the *real time* regime and therefore the unweighted fitting techniques are preferred due to their simplicity and lower CPU-consumption. In this work an unweighted Levenberg-Marquardt nonlinear fitting algorithm has been used.

2.2. The experimental setup for deep-ultraviolet CRDS

Details of the experimental setup used for CRDS measurements are given here. The setup has been used with the aim of performing spectroscopy in the deep-UV. In addition, it has been used in combination with the pressure-ramp method to retrieve quantitative data on molecular scattering and absorption, also in the deep-UV. The generation of tunable deep-UV light and its absolute wavelength calibration is described in below, as well as an assessment of a linewidth and intensity fluctuations of the light source, specifications of the cavity ring-down cells and the analysis of the ring-down decay transient and pressure-ramp signals.

2.2.1. General operation of the experimental setup

In our deep-UV CRDS setup the output of a pulsed dye laser is converted to ultraviolet wavelengths using nonlinear optical crystals. The layout of the optical setup is shown in Fig. 2.3. All measurements performed between 198 and 220 nm, described in the proceeding chapters of this thesis are based on this scheme and the similar approach is used for studies in 215–270 nm range.

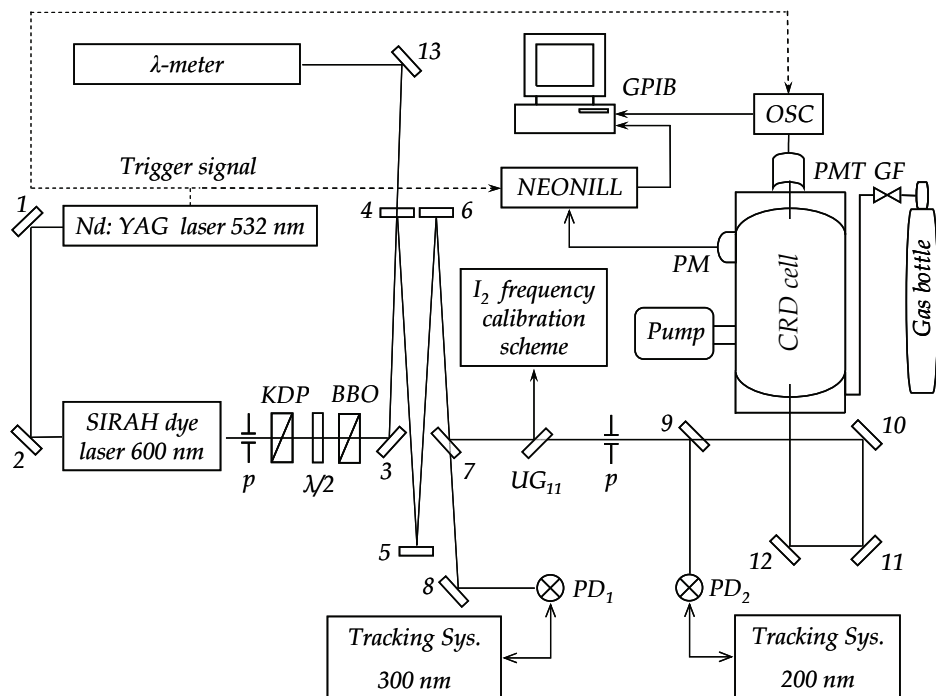


Figure 2.3: CRDS setup used for deep-UV optical extinction measurements. (1–2) - mirrors HR @ 532nm, (3) - HR @ 202–210 nm, (4–8) - mirrors HR @ 208 nm, (9) - mirror HR @ 270–300 nm, (10–12)- mirrors HR @ 193 and 212 nm, UG_{11} - UV filter, p -diaphragm, NEONILL - data acquisition box, Pump - rotary pump, PM - pressure-meter (Edwards 600 AB), PMT - photo-multiplier tube (Hamamatsu H9858), GF - gas filter, OSC - digital oscilloscope (LeCroy LT 372, 500 MHz), λ -meter-(Echelle grating spectrometer with Ne lamp), PD_1 , PD_2 - UV photodiodes, NI - National Instrument data acquisition card, GPIB - data acquisition card.

Pulsed deep-ultraviolet radiation in the 198–220 nm wavelength region is obtained by frequency tripling the red output of a SIRA dye laser operated on *Rhodamine-B*, *Rhodamine-101*, their mixture and *DCM* laser dyes (20 mJ/pulse at 600 nm), pumped by a 532 nm unseeded Nd: YAG laser (Spectra Physics Quanta Ray GCR100) at 10 Hz repetition rate (370 mJ/pulse). The frequency tripling is performed in two subsequent steps: at first red light, shaped beforehand by a pinhole p is doubled in a KDP crystal, resulting in UV light pulses at ~ 300 nm (2 mJ/pulse). A $\lambda/2$ plate is used to rotate the polarization of the UV beam over 90° to match with the polarization of the visible light. Both

visible and ultraviolet light beams are then collinearly mixed (type 1 phase matching) in a second non-linear BBO crystal.

KDP and BBO crystals are mounted on electrically driven rotation stages, providing an accurate alignment of the phase-matching angle. Several dichroic mirrors (mirrors 3–7) are used to separate the short wavelength pulses from the intense red and UV light pulses. The deep-UV radiation in the 198–220 nm region is steered by mirrors 10–12 to the CRDS cell and the ring-down transients are detected by a photomultiplier tube (Hamamatsu 9458) and subsequently digitized by a LeCroy oscilloscope (LT 372, 500 MHz).

Deep-UV radiation at distinct wavelengths between 215 and 270 nm is produced via frequency doubling of the blue and green output of the Quanta-Ray PDL-2 laser, pumped at 355 nm (running on *Coumarine* laser dyes) from an injection-seeded Spectra Physics Nd: YAG laser at 10 Hz. For the separation of the short wavelength deep-UV radiation a Pellin-Broca prism is used.

The laser wavelength calibration is performed either by a wavelength meter or by frequency calibration scheme based on well known absorption spectra of molecular iodine, as discussed below.

2.2.2. Generation of tunable deep-UV radiation between 198 and 220 nm

The setup offers the possibility to measure at fixed wavelengths, as well as in wavelength scanning mode. Additional electronics for tracking the phase matching angles are used when the laser wavelength is scanned. The principle of the operation of the tracking system is depicted in Fig. 2.4.

In the tracking system the angular positions of the KDP and BBO crystals are optimized in a feed-back loop to keep the intensity of the output UV light at optimum level, while the wavelength is scanned. The UV light beam generated in a non-linear crystal (NC) is split into two beams by a quartz prism (QP) and each beam is independently detected by photodiodes PD_1 and PD_2 . The signals from the photodiodes are then compared and an error signal is generated if the photodiodes detect different amounts of UV radiation. An amplified error signal is produced to activate a DC voltage driven step motor (Oriel Motor Mike) tuning and the position of the crystal is changed via a rotational stage.

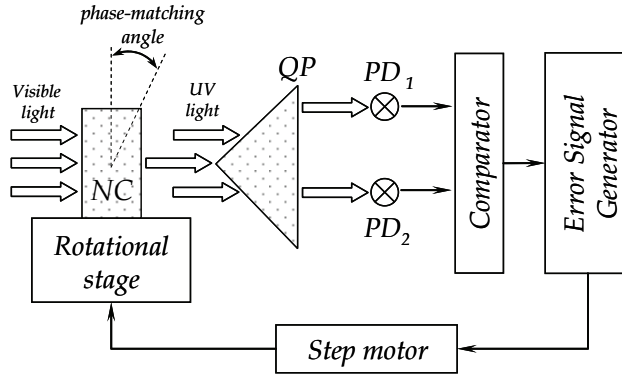


Figure 2.4: The scheme, illustrating the operation of the UV tracking systems (see text for details).

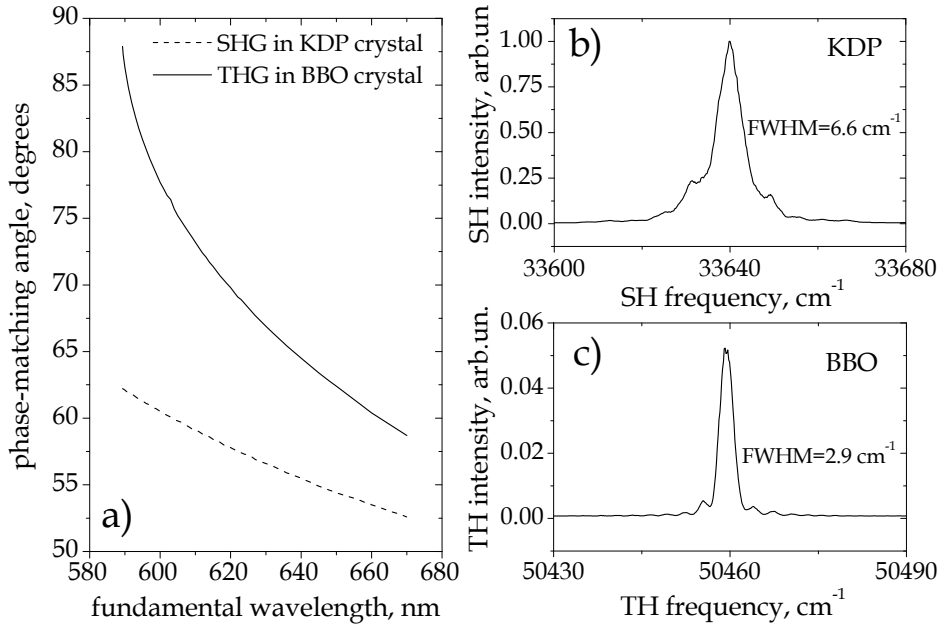


Figure 2.5: Phase matching angles for the second and third harmonic generation in KDP and BBO non-linear crystals (a) as function of wavelength of the fundamental light, the measured opening angle curve for the KDP crystal used in the frequency doubling process (b); similar for the BBO crystal used for the sum frequencies making process (c). The values, plotted in (c) are normalized to the intensity values, plotted in (b).

Calculated values of phase-matching angles for producing the second harmonic (SH) in KDP and the third harmonic (TH) in BBO crystals for the fundamental wavelengths between 590 and 670 nm are shown in Fig. 2.5(a). The values for the phase-matching angles are derived using *SNLO* public domain software, developed at *Sandia National Laboratories* and available from <http://www.as-photonics.com>. Fig. 2.5(b-c) display experimentally determined opening angle curves measured for both non-linear crystals. During the latter measurements the output intensities of the second and the third harmonic, produced in KDP and BBO crystals, are measured as a function of frequency. The opening angle curve for the KDP crystal, plotted in Fig. 2.5(b), is obtained when the second harmonic intensity is measured directly at the output of the KDP crystal, which is kept fixed at an angle of 62.9° . The obtained opening angle for the phase-matching process in KDP corresponds to a frequency bandwidth of 6.6 cm^{-1} (FWHM). The opening angle for the third order process in BBO is measured, while tracking the second harmonic stage. The result, yielding an opening angle corresponding to 2.9 cm^{-1} is shown in Fig. 2.5(c). The sideband oscillations, occurring in Fig. 2.5, originate from the well-known *sinc*-function describing the second harmonic intensity [49].

The efficiency of high harmonic generation in KDP and BBO crystals is estimated from Fig. 2.5. The deep-UV light in the third harmonic is produced at an intensity of about 20 times lower than that of the second harmonic. Under these circumstances only about 0.1 mJ of deep-UV light is available in the CRDS measurements that start with initial powers of 20 mJ and 2 mJ per pulse in the visible and the second harmonic, respectively.

2.2.3. Intensity fluctuations of the laser system

Intensity fluctuations of the laser may negatively influence the functioning of the setup for several reasons, even though CRDS is an intrinsically intensity-insensitive technique. Fluctuations of the power of the visible light introduce noise in the iodine absorption spectra used for absolute wavelength calibration, thus complicating the identification of the iodine transitions. Occasional outbursts of the UV light intensity affect the operation of the electronic tracking systems and may lead to an uncontrolled loss of the phase-matching optimum,

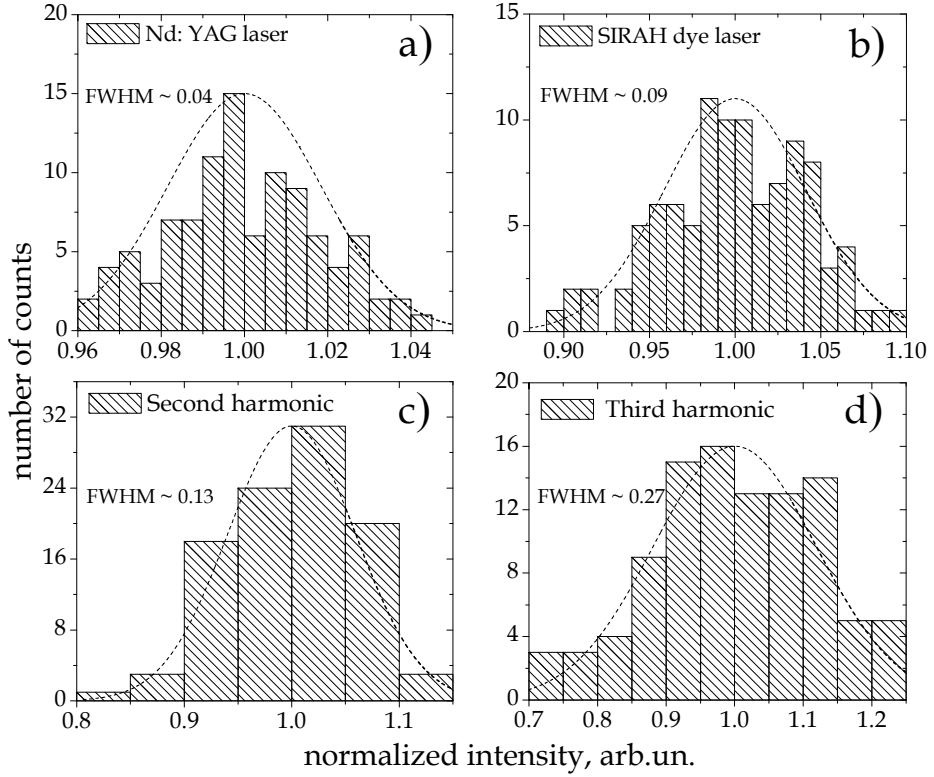


Figure 2.6: Histograms of intensity fluctuations of Nd: YAG (a) and SIRAH dye laser (b), the SH (c) and the TH radiation (d). The overlaying curves corresponding to the normal distribution, plotted as dashed lines are shown as well.

essentially required for the frequency scanning. Moreover, high levels of pulse-to-pulse intensity fluctuations hamper the use of the full dynamic range of the oscilloscope used for digitizing of the cavity ring-down decay transients, and therewith the achievable sensitivity.

Substantial power fluctuations are expected since an unseeded Nd: YAG laser is used to optically pump the SIRAH dye laser. Power fluctuations of the Nd: YAG and SIRAH dye lasers as well as those of the second and the third harmonic are systematically measured. In these measurements, the intensities of 100 laser shots of Nd: YAG and SIRAH lasers are simultaneously measured with two photodiodes, most sensitive in the visible region, whereas the intensities of the generated UV and deep-UV light pulses are measured with

two UV-sensitive photodiodes. Typically observed histograms of the intensity fluctuations and overlaying curves representing Gaussian statistical distributions are shown in Fig. 2.6. From this it can be seen that the output pulses of the frequency-doubled Nd: YAG laser provides a distribution close to normal (with rms-noise of 0.04). The SIRAH dye laser introduces significant additional power fluctuations, doubling the width of the distribution (to an rms of 0.09). These fluctuations, clearly visible in the power of the output radiation of the dye laser, become significantly larger at the second and particularly at the third harmonic, reaching rms-values of 0.13 and 0.27, respectively.

The observed intensity fluctuations of the visible light introduce additional noise to I_2 spectra used for the frequency calibration. In order to minimize this effect signal averaging is used. The measured characteristics of the intensity fluctuations of the UV and deep-UV light have been taken into account to optimize the settings of the phase-matching angles tracking systems, which enable to achieve continuous deep-UV light frequency scanning.

2.2.4. Control of the SIRAH laser linewidth around 600 nm

A narrow linewidth of the visible light is required for providing accurate spectroscopic measurements and is also indispensable for the absolute frequency calibration using iodine absorption. The narrow band operation of a pulsed dye laser is influenced by the portion of *amplified spontaneous emission* (ASE) always present in the output laser light. Since ASE originates from non-coherent processes, it has a broad spectral bandwidth, which obviously impedes some applications of dye lasers. The relatively high output power of the SIRAH dye laser is required to provide sufficient amount of deep-UV power in the third harmonic to perform CRDS measurements. The relative portion of ASE is closely related to the conversion of energy of the laser. The increase of the energy conversion does not only increase the ASE, but also the spectral bandwidth in the laser. Therefore an optimal compromise between maximum energy conversion and minimum portion of ASE in the output of the SIRAH dye laser needs to be found. The latter can be obtained by a proper alignment of the SIRAH dye laser along with a systematic control of the laser linewidth. For this purpose the experimental scheme, depicted in Fig. 2.7 is used.

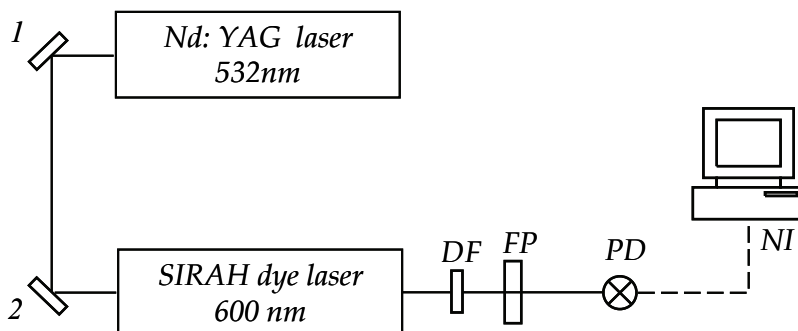


Figure 2.7: The experimental scheme used for SIRA dye laser radiation linewidth control. (1–2) - steering optics, DF - density filter, FP - Fabry-Perot etalon, PD - photodiode, NI - National Instruments data acquisition card.

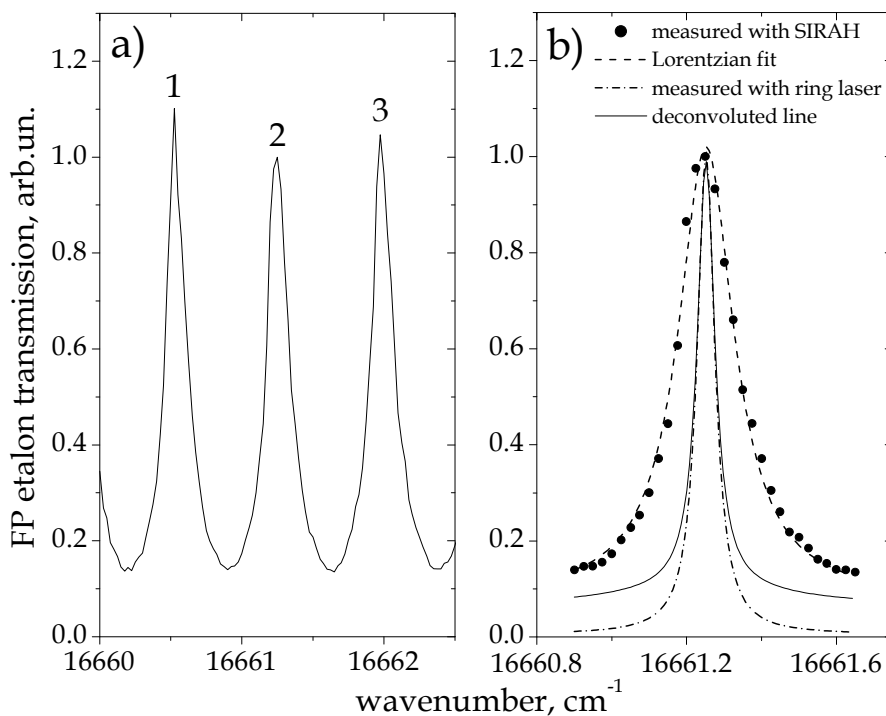


Figure 2.8: Measured Fabry-Perot etalon transmission fringes (a) and deconvolution of the spectral line of the SIRA dye laser (solid line) from the observed FP transmission signal (b). Measured data points (•) are fit to a Lorentzian profile (dashed black line). The FP transmission signal, measured with the ultra-narrow band ring dye laser is shown as dotted line as well.

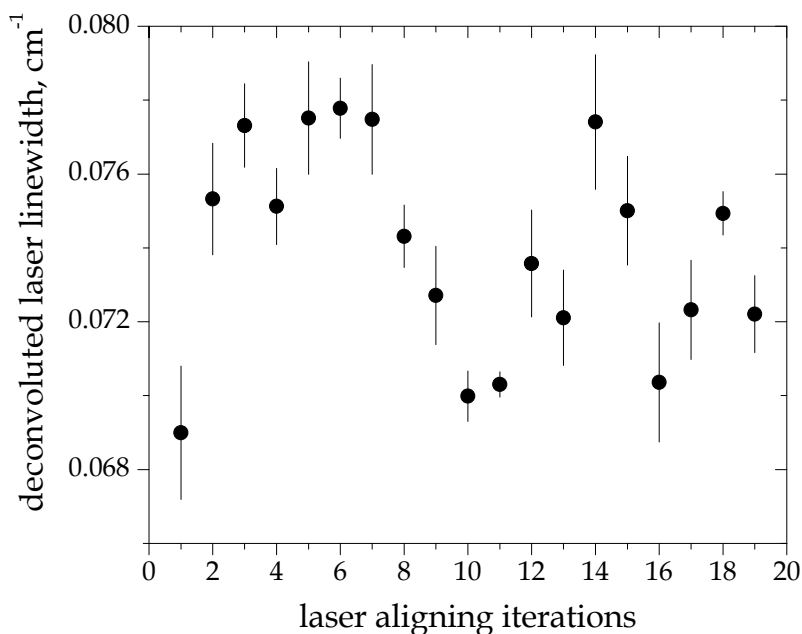


Figure 2.9: Experimentally determined values of the SIRAH dye laser linewidth at 600 nm.

The control of the SIRAH linewidth is based upon the measurement of Fabry-Perot (FP) transmission fringes. While the frequency of the laser is continuously scanned, transmission fringes of the FP etalon are measured with the photodiode and stored to the PC. Typically observed FP transmittance signals are shown in Fig. 2.8(a). These FP transmittance fringes, measured with the SIRAH dye laser, are deconvoluted from their intrinsic width (see Fig. 2.8(b)), which is derived from a measurement with an ultra-narrow band ring dye laser (bandwidth 1 MHz).

A regular careful alignment of the SIRAH dye laser is required to maintain its narrow band operation. Each alignment procedure is usually accompanied with a linewidth determination. Typically observed values of the linewidth of the SIRAH dye laser output at 600 nm are plotted in Fig. 2.9, indicating that the routinely observed linewidth of the SIRAH dye laser amounts to about 0.07 cm^{-1} , which is sufficiently narrow for an accurate absolute wavelength calibration using iodine as a reference gas.

Such a narrow linewidth of the visible light, however, is not directly transferred to shorter wavelengths upon harmonic generation. Generally, the linewidth of the third harmonic may be expected to be $\sim (2 - 3) \times 0.07 \text{ cm}^{-1}$, somewhat depending on the frequency profile of the incident pulse. Experimentally, the deep-UV light produced in the third harmonic is found to have a significantly broader spectral composition. The latter may be caused by the fact that not only the monochromatic constituents of the visible light are involved in the frequency conversion process, but also a broadband ASE-component. As a result, the linewidth of the deep-UV light becomes significantly larger, compared to the spectral linewidth of the fundamental light. The typical linewidth of the deep-UV light between 198 and 220 nm, that was obtained with the SIRAH based laser system, and used in the current CRDS measurements is 0.5 cm^{-1} . The linewidth of the deep-UV radiation in the 215–270 nm region, produced via frequency doubling of the blue and green output PDL-2 laser light (see *Section 2.2.1*) is somewhat narrower and amounts to $\sim 0.2 \text{ cm}^{-1}$.

2.2.5. Analysis of the ring-down transients

The ring-down signal, detected with the PMT is digitized by a LeCroy LT372 oscilloscope. A regular ring-down transient is shown in Fig. 2.10(a). The time base of the oscilloscope is divided into 5000 data points. The voltage scale has a dynamical range of 8 bit, corresponding to 256 data points. To retrieve the best signal to noise ratio in the CRDS experiment the full dynamical range of the oscilloscope needs to be used. Several steps are taken before the final ring-down time value is defined using the non-linear squares fitting procedure.

At first the decay waveform, shown in Fig. 2.10(a) is temporally stored to the PC memory as a two-dimensional array of data (time and voltage). All data points are then multiplied by (-1) , shifted upward for one volt to avoid zero values of the decay transient and first data points, belonging to previous decay transients are averaged and this value is subsequently subtracted from all the data points. This procedure enables one to retrieve baseline corrected decay transients, as plotted in Fig. 2.10(b). The latter waveform is then fitted to a mono-exponential functional form (see Eq. 2.19) via an unweighted non-linear

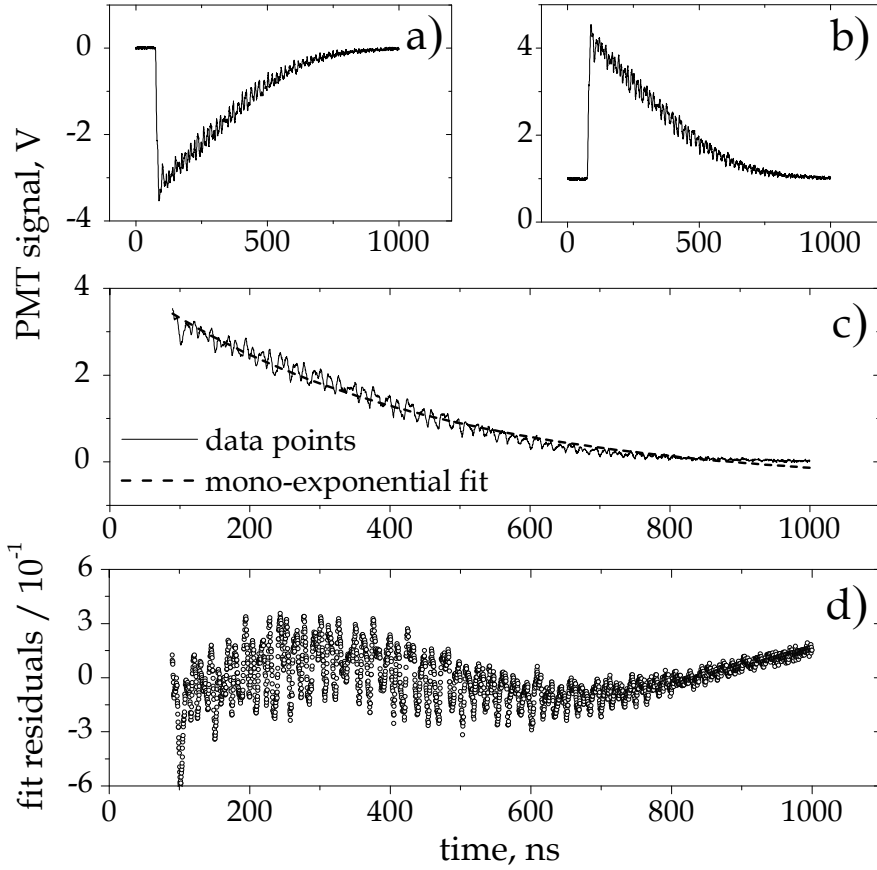


Figure 2.10: Typically measured ring-down transient (a), its modification after reversing (b), upon fitting (c) with fit residuals (d). The fit residuals represent the difference between the measured and fitted values of the decay transient signal.

squares fitting procedure (Fig. 2.10(c)), resulting in the decay time value τ .

$$I(t) = I_0 e^{-t/\tau} \quad (2.19)$$

In order to improve the quality of the fit, when systematic variations are present in the distribution of the fit residuals, an additional fitting option is embedded into the home-written software. For that purpose a fit window is used and the fit procedure is performed only for the data points falling within this window. The width and the time delay (calculated in data points) can be set

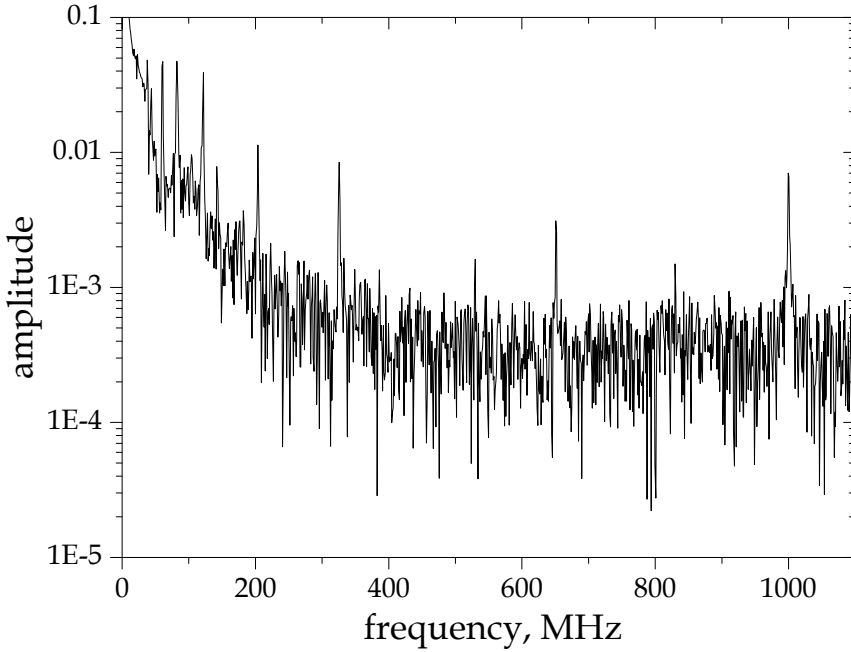


Figure 2.11: *Fourier transform spectrum of the single decay transient signal in 46 cm ring-down cavity detected with the PMT and digitized by LeCroy LT 372 scope. The transform has been performed using the standard fast Fourier transform analysis tool, available from the OriginPro (ver. 8.0) software package.*

independently and usually are kept fixed. The use of this technique, therefore, allows improving the quality of the fit, which is reflected in a decrease of the fit residuals, as shown in Fig. 2.10(d).

Additional noise in the decay transient may be due to interference effects because of cavity mode beating. Mode beating becomes particularly significant when a long ring-down cavity is used. Beatings between neighboring transversal modes in the cavity with $d=46$ cm and $R=25$ cm amount to about 220 MHz, whereas the longitudinal modes beat at a typical frequency of about 325 MHz, as can be calculated using equations in [49]. Some of those frequencies can be discerned in Fig. 2.11, where the Fourier transform of the decay transient signal in a 46 cm long ring-down cavity is plotted. In this case a careful repetitive aligning procedure is required to decrease the mode beating effect and to minimize the fit residuals.

2.2.6. Laser wavelength calibration

The absolute wavelength calibration is performed via two independent methods. A wavelength meter, based on a spectrometer incorporating a Ne discharge lamp with accurately known reference lines is used to determine the wavelength in a non-scanning experiment. The emission of a Ne lamp, as well as the radiation from the laser, are dispersed by a diffraction grating in an *Echelle* configuration and the distance between neighboring lines in different orders of the grating serves as a calibration point. This enables a determination of the absolute wavelength of the laser with an uncertainty of the order of 0.01 nm, resulting in the uncertainty of about 0.28 cm^{-1} at 600 nm. The second calibration scheme is based on iodine absorption spectroscopy as shown in Fig. 2.12.

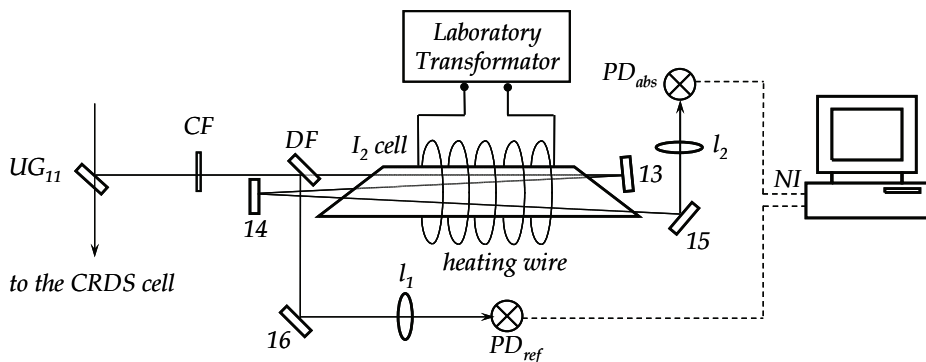


Figure 2.12: The iodine calibration scheme used for frequency calibration of the visible light. CF - colour filter (KC10 series peaked at 600 nm), DF - density filter (4x), (13–16) - flat broadband silver mirrors, l_1 and l_2 focusing lenses, PD_{abs} , PD_{ref} - photodiodes for visible light detection, NI - National Instruments data acquisition card.

Signal averaging is applied to increase the signal-to-noise ratio of the I_2 absorption spectra, as discussed in Section 2.2.3. An improved absorption path length (of about 150 cm in total) is available due to triple-pass geometry of the laser beam. The heating of the sealed iodine cell up to $\sim 50^\circ\text{C}$ provides an increased vapour pressure of iodine of about 100 Pa. In addition, the shot-to-shot power fluctuations in the I_2 absorption spectrum are minimized by

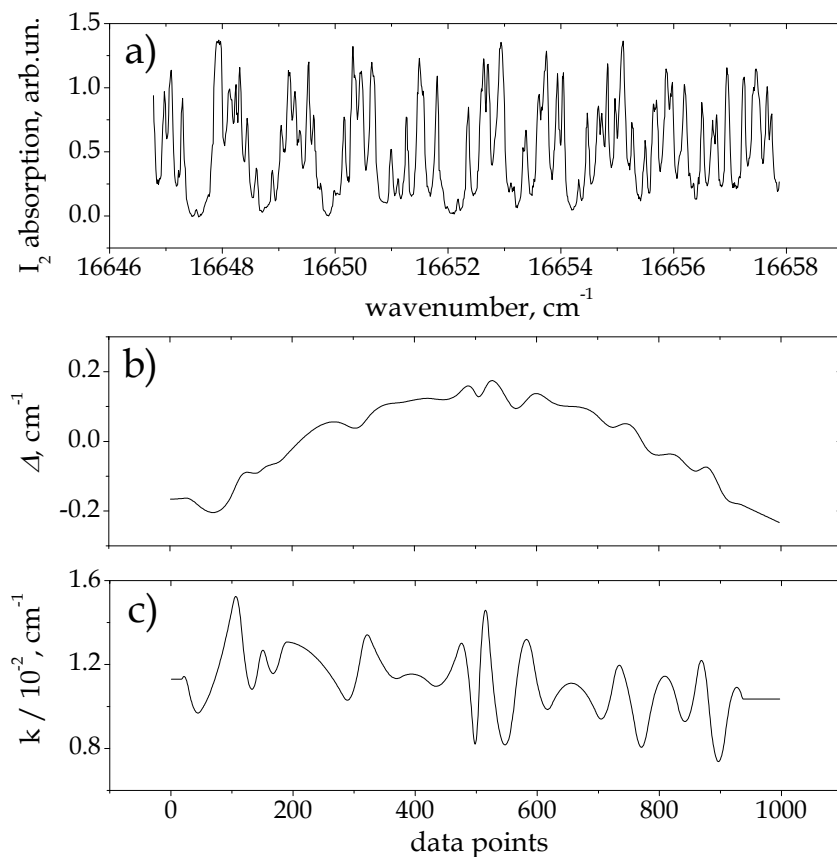


Figure 2.13: Measured iodine absorption signal (a), the deviation of the frequency from linearity (b) and the speed of a frequency scan (c).

dividing through the laser intensity, which is monitored on a second photodiode. An example of an I₂ spectrum measured at 25 laser shots averaging under the conditions, specified above is shown in Fig. 2.13(a).

When the laser linewidth is sufficiently narrow a Doppler limited absorption transition can be measured. The linewidth of the used SIRAH dye laser is ~ 0.07 cm⁻¹, as discussed before, which is about 1.5 times larger than the typical Doppler width of the iodine transitions around 600 nm at 323 K ($\delta\nu_{\text{Doppler}} \sim 1.5$ GHz or 0.05 cm⁻¹). Therefore, the width of individual absorption lines, shown in Fig. 2.13 is predominantly determined by the SIRAH dye laser linewidth.

The SIRAH laser shows a non-linearity in the frequency scanning, as plotted in Fig. 2.13(b). This non-linearity, Δ , is determined as the difference between the actual frequency values ν_{measured} from the linearized frequencies $\nu_{\text{linearized}}$:

$$\Delta = \nu_{\text{measured}} - \nu_{\text{linearized}} \quad (2.20)$$

The scanning speed k can be calculated as the first derivative of the calibrated frequency values:

$$k = \frac{d\nu_{\text{measured}}}{dn} \quad (2.21)$$

where n is the number of data points in the scan (see Fig. 2.13(c)).

The frequency calibration procedure is completed using an *atlas* of well calibrated iodine lines [50]. A home-designed software package (“*AutoFit*”) is used for the fitting. The software performs a fit through peaks in the measured iodine spectra, which can be assigned and matched to reference iodine lines, eventually resulting in accurate frequency calibration of the entire iodine spectra after correcting for the non-linearity in the scan.

2.2.7. Cavity ring-down cells and gas purity precautions

Several sets of high-reflective mirrors, available from Laser Optik are used to cover the entire 198–220 nm wavelength region. CRDS measurements are performed in two different types of ring-down cavities, mainly determined by the curvature radii of the available ring-down mirrors. For the wavelength range 198–210 nm region high reflective mirrors ($R \sim 98.9\%$) with 100 cm curvature radius are available, whereas for longer wavelengths (210–220 nm) mirrors with curvature radius of only 25 cm and reflectivity of about 99.6% are available. For CRDS measurements performed with the short focusing mirrors a shorter ring-down cell (with a total length of about 46 cm) is built. The latter is made of two 20 cm long stainless steel metal tubes with an inner diameter of about 1 cm. The tubes are tightly attached to each other with vacuum sealed clamps and the entire frame is fixed to the optical table, providing a stout and vibration free construction.

The CRDS mirrors with 100 cm curvature radius are mounted onto an

82 cm long cell, specially designed for lower temperature pressure-ramp measurements [51]. Detailed description of the design of the cell and procedures of reaching and maintaining low temperatures will be discussed in *Section 6.1.2* of the thesis. Due to the many inlet holes between the gas distribution chamber and the cavity tube, gas slowly leaks into the ring-down cavity tube, thus avoiding *turbulence effects*, which would disturb the optical beam propagation and consequently the ring-down measurement.

Careful chemical cleaning precautions are taken. Each of the cells has been heated up to $\sim 90^{\circ}\text{C}$ and continuously pumped for about 36 hours down to pressures of $\sim 10^{-6}$ mbar before actual use. This procedure decreases the residual pressure in the cell and cleans it from oil and other contaminating species absorbed by the metal inner surface. The gas under investigation is purified by using a 0.5 micron pore filter.

2.3. CRDS measurements of deep-UV optical extinction in CO

Since carbon monoxide is known to exhibit a rather weak, but well known absorption spectrum in the region of the deep-UV, it was taken as a test molecule for performing cavity ring-down absorption and scattering measurements in this wavelength range. Quantitative information on the absolute value of the optical extinction cross-section of CO in the deep-UV spectral region is lacking and only a few studies of Rayleigh scattering in the visible domain have been reported. Results of optical extinction measurements performed at 632.2 nm are available from [52], where the value of the optical extinction cross-section was found to be close to the dispersion based Rayleigh scattering prediction.

In this section we present, also as a performance check of the setup described here, results of the CRDS work performed for the two lowest CO Cameron bands in absorption: the (0,0) band at 206 nm and the (1,0) band near 199 nm. Attempts are made to assess the quantitative aspects of the absorption and scattering spectrum as well as to address collision-induced effects.

The potential energy curves of the CO molecule, as available from [53] are shown in Fig. 2.14. The CO spectral features are well studied [54]: strong ultraviolet and visible emitting systems are ubiquitously observed in flames,

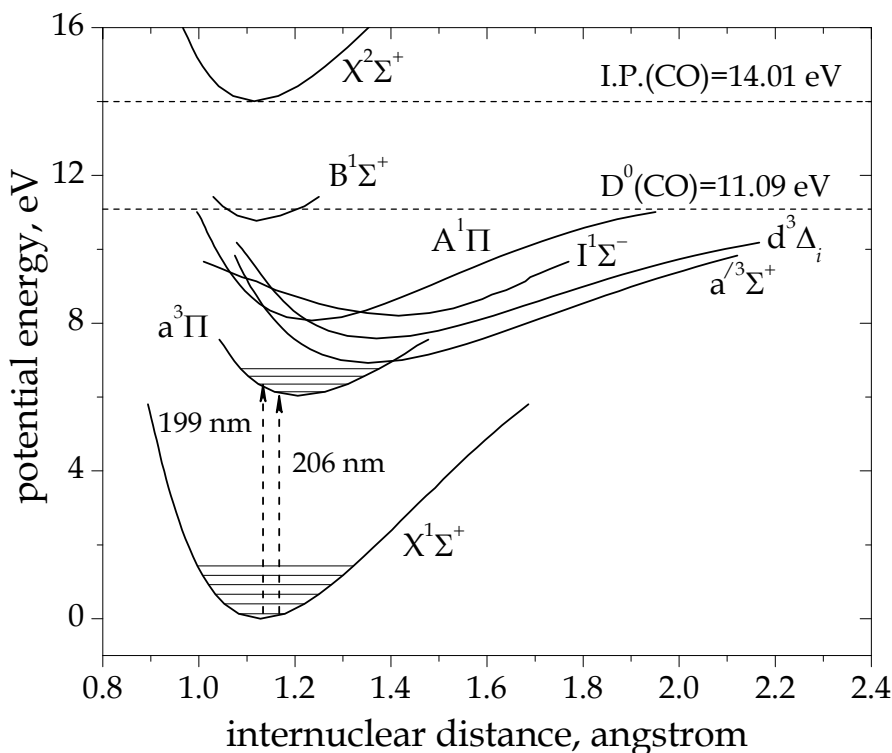


Figure 2.14: Potential energy curves of the CO molecule available from [53]. Two deep-UV absorption (0,1) and (0,0) bands, centered at 199 and 206 nm that are accessible with the setup described here, are shown as well.

combustion environments and discharges, most notable the Fourth Positive system $A^1\Pi - X^1\Sigma^+$ in the range 114–280 nm, the Third Positive system $b^3\Sigma^+ - a^3\Pi$ at 260–380 nm and the Angstrom system $B^1\Sigma^+ - A^1\Pi$ at 410–660 nm [53]. The $X^1\Sigma^+$ electronic ground state is characterized in much detail and its rotational spectrum is used for metrology purposes, resulting in very accurate molecular constants [55].

The Cameron $a^3\Pi - X^1\Sigma^+$ system that absorbs in the deep-UV is already known since 1926 and has been studied in much detail over the years [56–60]. The ground state level energies are determined with much precision by the constants given by Nolt *et al.* [55] ($B_0 = 1.92253 \text{ cm}^{-1}$, $D_0 = 6.12108 \times 10^{-6} \text{ cm}^{-1}$ and higher order centrifugal distortion constants) and by Saykally *et al.* for the $a^3\Pi$ state in CO [60].

2.3.1. CO spectra recorded by CRDS

The CRDS measurements of the 206 nm band are performed with 50 shots averaging at 4000 Pa (30 Torr) of CO in the 85 cm long cell at room temperature. The final bandwidth of the used deep-UV radiation ($\sim 0.5 \text{ cm}^{-1}$, see Section 2.2.4) is sufficient to rotationally resolve most of observed transitions. The observed linewidth is similar as in the studies by Field [58], and therefore no improvement of a rotational analysis can be achieved by the current measurements. Results of CRDS room-temperature measurements of the (0,0) absorption band of the $a^3\Pi \leftarrow X^1\Sigma^+$ system in CO around 206 nm are illustrated in Fig. 2.15. The graph is obtained when the empty cavity losses due to reflectivity of CRDS mirrors are set to zero.

The entire frequency span of 550 cm^{-1} is covered by ten individual CRDS measurements, performed in frequency intervals of about 50 cm^{-1} . The frequency scans are calibrated by comparison to the iodine reference standard [50]. The accuracy in the absolute line positions is better than 0.1 cm^{-1} .

According to the selection rule $\Delta J = 0, \pm 1$ nine rovibronic branches are expected for the $a^3\Pi - X^1\Sigma^+$ band system corresponding to *P*, *Q* and *R* – branch transitions for each component $^3\Pi_0 \leftarrow ^1\Sigma$, $^3\Pi_1 \leftarrow ^1\Sigma$ and $^3\Pi_2 \leftarrow ^1\Sigma$ [61]. The branches are designated as P_1 , Q_1 , R_1 , P_2 , Q_2 , R_2 and P_3 , Q_3 , R_3 as schematically shown in Fig. 2.16.

The intensity of the $a^3\Pi_1 \leftarrow X$ is stronger than that of the $a^3\Pi_2 \leftarrow X$ and the $a^3\Pi_0 \leftarrow X$ sub-bands, while the intensities of the latter two sub-bands are approximately equal [58]. A detailed perturbation analysis of the excited $a^3\Pi$ state, as performed in [58] shows that with the exception of $v=0-3$ and $v=6$ all vibrational levels of the $a^3\Pi$ state are perturbed at relatively low *J* states ($J < 30$) by other triplet states.

To reproduce the recorded spectrum of the CO band shown here, a simulation was performed using *PGOPHER*, a software package for simulating and fitting rovibronic, rovibrational or pure rotational spectra (<http://pgopher.chm.bris.ac.uk>). The molecular parameters were taken from [55] and [60]. The value for the band origin, $48473.201 \text{ cm}^{-1}$, is taken from [58].

A comparison between the observed and simulated spectra reveals significant deviations. At the high energy side of the (0,0) Cameron band some

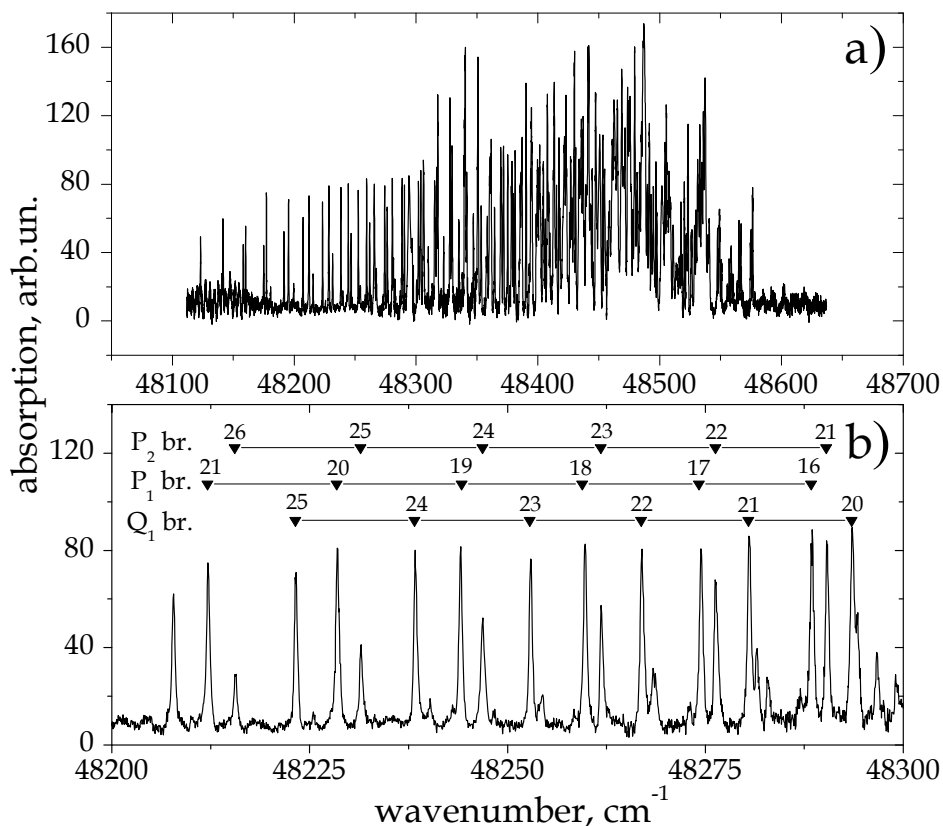


Figure 2.15: Measured CRDS spectrum of the (0,0) absorption band of the $a^3\Pi \rightarrow X^1\Sigma^+$ system of CO at 206 nm (a) and a selected detail with line assignments taken from [58] (b). For both graphs the empty cavity losses (baseline values determined by reflectivity of the CRDS mirrors) are set to zero.

additional lines are observed, as shown in Fig. 2.17. These lines (marked by asterisks) at the blue side of 48540 cm⁻¹ do not follow from the simulation, nor have been reported by Field [58]. They may originate from a contaminating gas species contained in the CO gas sample, despite the accurate cleaning procedure. Their strengths rules out an assignment as CO isotopologues in natural abundance. It appears that the extra lines are part of a molecular band system, that progresses into the range of the $a^3\Pi - X^1\Sigma^+$ (0,0) band and overlaps it in part. It is likely that the strong resonances observed at 48525 cm⁻¹ also form part of this extra spectrum.

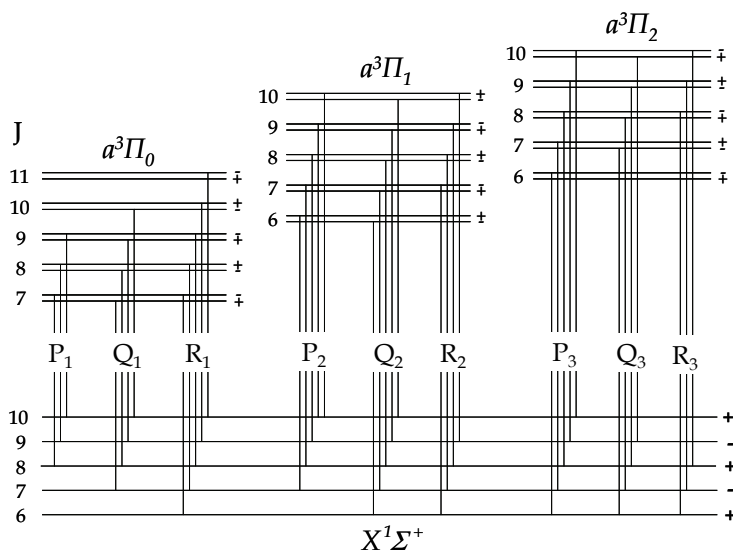


Figure 2.16: Energy level diagram for the CO Cameron band system, showing nine branches. The diagram is adopted from [61].

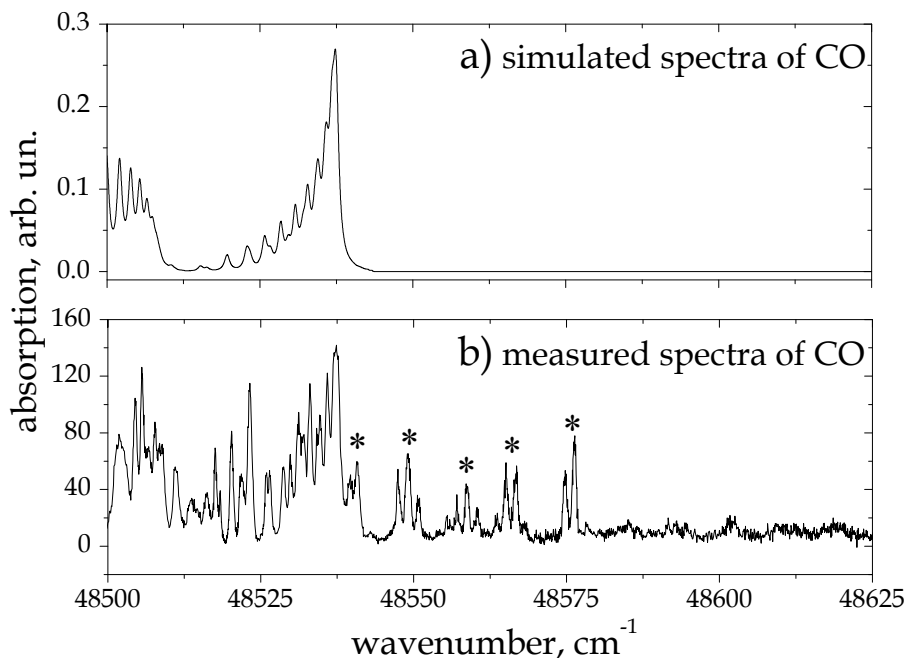


Figure 2.17: Simulated (a) and measured (b) spectra of CO, illustrating the contamination with groups of unidentified lines, marked by asterisks.

2.3.2. Pressure-ramp analysis: Rayleigh scattering and collision-induced effects

The sensitivity of cavity ring-down spectroscopy and the potential of measuring absolute cross-sections open the possibility for detecting loss processes other than linear absorption. The loss rate in CRDS experiments is proportional to:

$$\sigma^{\text{scat}}(\lambda)N + \sigma^{\text{abs}}(\lambda)N + \alpha^{\text{CIA}}(\lambda)N^2 \quad (2.22)$$

where N is the gas density, $\sigma^{\text{abs}}(\lambda)$ describes the linear (monomer) absorption on spectral resonances, $\sigma^{\text{scat}}(\lambda)$ accounts for the Rayleigh scattering cross-section of gas particles and $\alpha^{\text{CIA}}(\lambda)$ represents a collision-induced absorption cross-section, which in first order scales quadratically with the gas density [51].

As long as the mirror reflectivity, gas density, absorption and scattering behaviour remain constant, it is not possible to distinguish between different types of losses. To separate losses induced by the gas from those, caused by the finite reflectivity of the ring-down mirrors, the gas density can be varied. This experimental technique is called *pressure-ramping*. During each pressure-ramp both the pressure and the decay time of the cavity are continuously monitored, while gradually increasing the gas density in the absorption cell. This technique is used in this thesis to determine the deep-UV extinction behaviour of a number of atmospherically relevant gasses and is demonstrated here on the example of the CO measurements.

In the absence of absorption, the optical extinction is governed by Rayleigh scattering. From a series of measurements, performed at a fixed wavelength and at increasing gas density N , both the averaged mirror reflectivity $R(\lambda)$ and the absolute Rayleigh scattering cross-section $\sigma^{\text{scat}}(\lambda)$ can be obtained [52]. The latter values follow from the *slope* of each pressure-ramp measurement. The resulting value of $\sigma^{\text{scat}}(\lambda)$ is independent of the length of the cell d [51, 52].

When collision-induced effects are considered, pressure-ramp curves exhibit a *quadratic* behaviour: a collision-induced absorption increases quadratically with the gas density, reflecting the *two body* origin of the extinction process. In this case quadratic functions can be used to determine the values of the effective reflectivity $\beta_0(\lambda)$, Rayleigh scattering cross-section

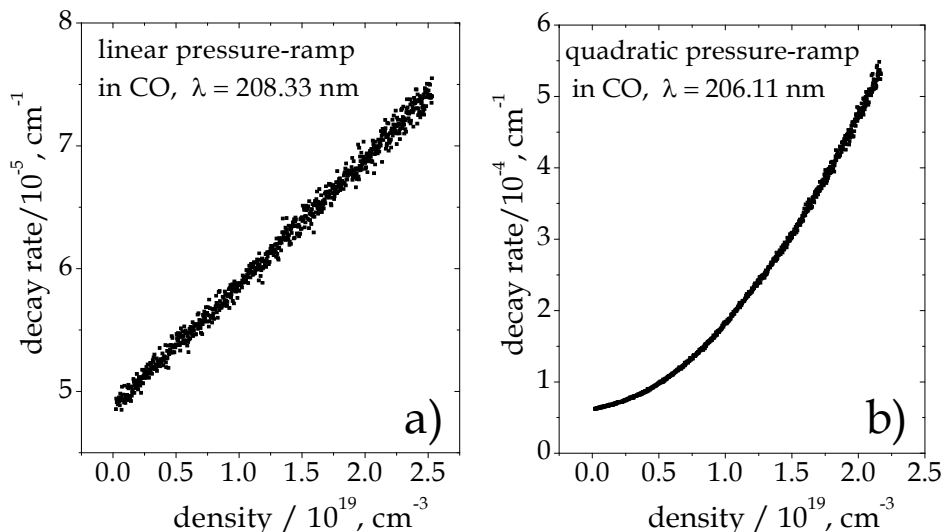


Figure 2.18: Linear (a) and quadratic (b) pressure-ramping curves in CO.

$\sigma^{\text{scat}}(\lambda)$ and the values of collision-induced absorption cross-section $\alpha^{\text{CIA}}(\lambda)$.

A series of pressure-ramps measurements in CO performed at 32 wavelength positions, covering the spectral region between 198 and 220 nm shows the presence of collision-induced resonances, observed near 199 and 206 nm. The pressure is measured using an Edwards type 600AB Baratron with an accuracy of 0.15%. The pressure-ramping curves exhibit both quadratic (at the wavelengths close to 199 and 206 nm) and linear (in 200–204 nm and 208–218 nm regions) behaviour. Typical linear and quadratic pressure-ramp curves are shown in Fig. 2.18(a) and (b), respectively.

For the CRDS optical extinction cross-section measurements linear and quadratic functions can be used for the fit. The results for 208.33 nm are shown in Fig. 2.19 and listed in Table 2.1. The values of the Rayleigh scattering cross-section are deviating about 1.5% (taken as the standard deviation over a number of repetitive measurements) from the mean value. The fit residuals demonstrate identical behaviour in both cases, as can be seen from Fig. 2.19, although the uncertainty of the Rayleigh scattering cross-section value, derived with the linear fit is significantly smaller, compared to that, determined from the quadratic fit. For an analysis of the pure quadratic pressure-ramp signals only the parabolic fit can be applied.

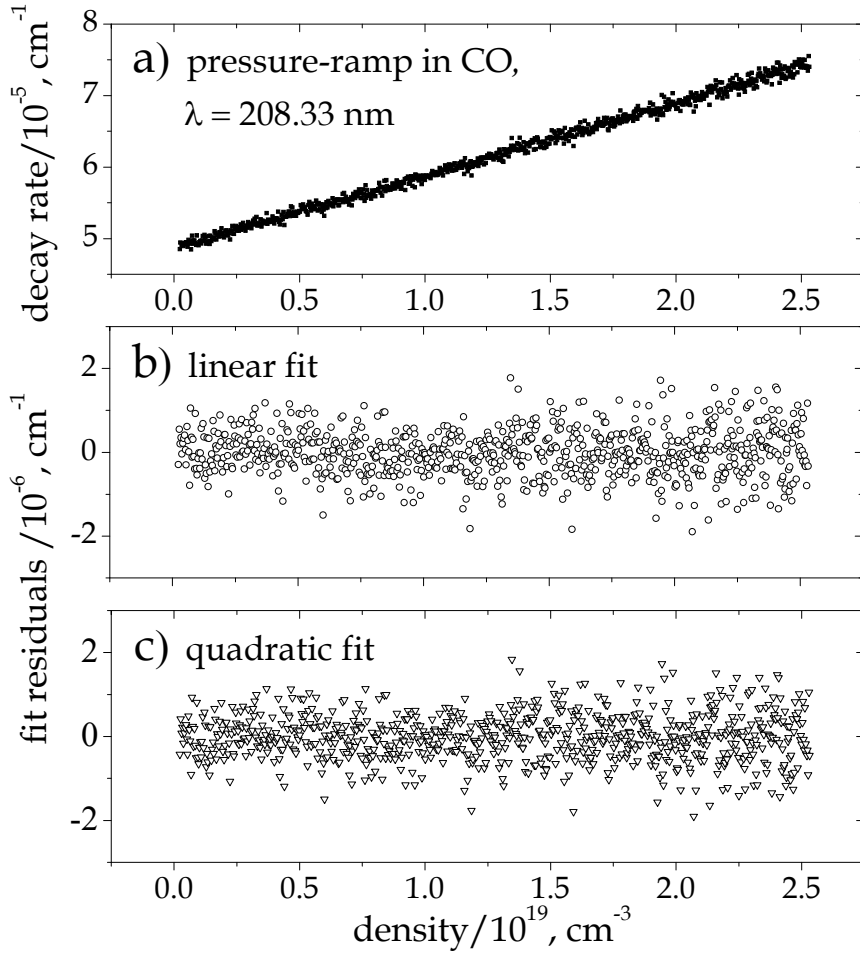


Figure 2.19: Pressure-ramp in CO, measured at 208.33 nm (a) and the residuals from the fit, performed with a linear (b) and parabolic (c) fit functions.

Table 2.1: The values of Rayleigh scattering and collision-induced absorption cross-sections, measured at 208.33 nm. The values of the losses due to mirror reflectivity are given as well.

Linear fit	Quadratic fit
$\beta_0/c = 4.863 (\pm 0.004) \times 10^{-5}$, [cm^{-1}]	$\beta_0/c = 4.871 (\pm 0.006) \times 10^{-5}$, [cm^{-1}]
$\sigma^{\text{scat}} = 1.017 (\pm 0.003) \times 10^{-24}$, [cm^2]	$\sigma^{\text{scat}} = 0.986 (\pm 0.011) \times 10^{-24}$, [cm^2]
	$\alpha^{\text{CIA}} = 1.202 (\pm 0.410) \times 10^{-45}$, [$\text{cm}^5\text{mol}^{-2}$]

2.3.3. Refractive index and King correction factor in CO

As discussed in *Chapter 1* prediction of the Rayleigh scattering cross-sections can be made, based on dispersion relationships for the refractive index and the depolarization based King correction factor, F_k . Refractive index measurements in CO in the 168–288 nm region have been performed by Smith *et al.* [62]. To derive a dispersion relation for CO the 38 experimental refractivity values measured at $T_0=273.15$ K and $P_0=101325$ Pa [62] have been fitted and can be expressed by:

$$(n-1) \times 10^6 = 240.064(\pm 0.504) + \frac{48.680(\pm 0.119) \times 10^{10}}{714.267(\pm 0.109)^2 - \nu^2} \quad (2.23)$$

with the frequency of light ν measured in cm^{-1} . The experimental data points, the fit and fit residuals are shown in Fig. 2.20(a) and (b), respectively.

Depolarization measurements in CO in the visible domain have been reported as well. Bridge *et al.* measured the depolarization ratio at 632.8 nm [17] and results of two depolarization ratio measurements, performed at 488 and 514.5 nm are available from [63]. To retrieve a dispersion relationship for the King correction factor, the three values calculated from the depolarization measurements in CO, have been fitted to the functional form:

$$F_k(\nu) = 1.01393(\pm 0.00006) + 8.7824(\pm 0.189) \times 10^{-12} \nu^2 \quad (2.24)$$

The experimental $F_k(\nu)$ values and the fit are shown in Fig. 2.20(b). The values of the refractive index of CO are reported for standard conditions $T_0=273.15$ K, $P_0=101325$ Pa, therefore n_0 values have to be recalculated for the current laboratory conditions (293 K, 101325 Pa) using the relationship [62]:

$$\frac{n_0 - 1}{n - 1} = \frac{P_0 T}{P T_0} \left\{ \frac{Z}{Z_0} \left[1 + \frac{n_0 - 1}{6} \left(1 - \frac{P T_0}{P_0 T} \right) \right] \right\} \quad (2.25)$$

where $P = 101325$ Pa, $T=293$ K, Z_i is a value of CO compressibility at (P_i, T_i) and n the refractive index at laboratory conditions (P, T) . The empirical relationship for Z , based on compressibility data from Hilsenrath *et al.* [64], is available from literature [65, 66]:

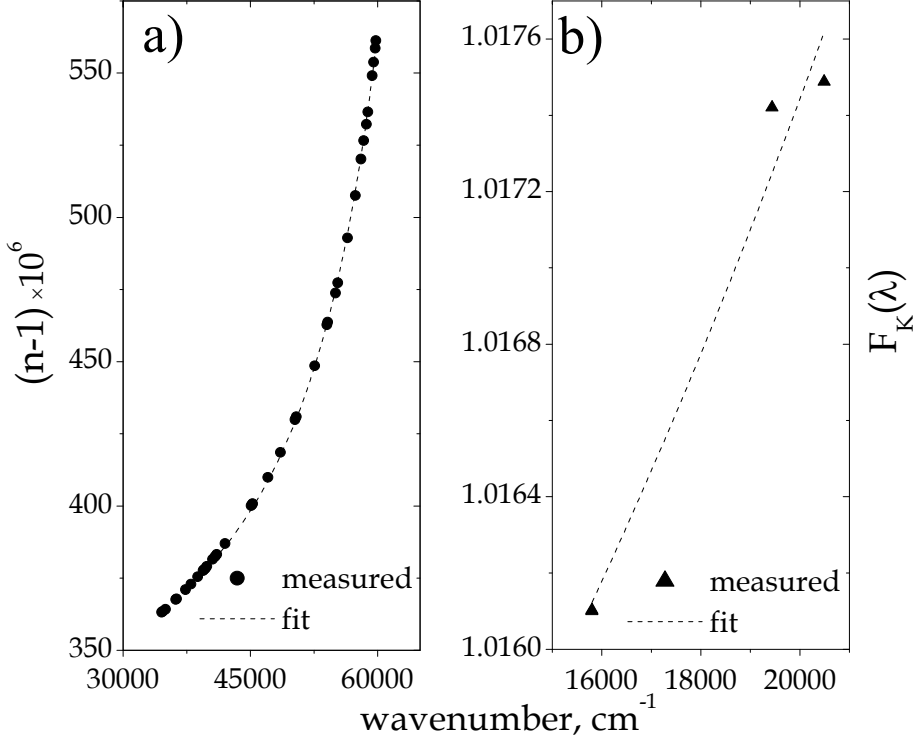


Figure 2.20: Fit values of the refractivity measurements (●) [62] in CO (a) and King correction factor, calculated from depolarization ratio measurements (▲) [17, 63] and the fit (b).

$$Z_i = 1 - \frac{P(317.6 - T_i)}{101325} \times 10^{-5} \quad (2.26)$$

The Rayleigh scattering cross-section is calculated using the formula:

$$\sigma_R = \frac{24\pi^3}{\lambda^4 N^2} \left(\frac{n^2(\lambda) - 1}{n^2(\lambda) + 2} \right)^2 F_K(\lambda) \quad (2.27)$$

where λ is the wavelength in cm, N is the density of the molecules in cm^{-3} , $n(\lambda)$ is the wavelength-dependent refractive index, and $F_K(\lambda)$ the King correction factor. Since the dispersion of the King correction factor is retrieved from the visible domain, an extrapolation of this equation towards shorter wavelengths has to be used for predictions of Rayleigh scattering cross-section values.

2.3.4. Rayleigh scattering and CIA in CO for 198–220 nm

In this paragraph systematic CRDS room-temperature measurements of Rayleigh scattering and collision-induced effects between 198 and 220 nm are described. In order to get more statistically reliable data set, a series of repetitive (typically 20) pressure-ramp scans have been made at every wavelength position. The measured pressure-ramp signals were fitted, using the second order polynomial (as discussed previously in *Section 2.3.2*) and the values of effective reflectivity of the cavity mirrors, as well as the linear and quadratic contributions to the optical extinctions have been consequently retrieved. The derived values of the linear and quadratic components of the optical extinction have been further averaged out and their mean values, as well as the values of the standard deviation, have been determined.

Rayleigh scattering:

The linear component of the optical extinction, derived from the pressure-ramp analysis is shown in Fig. 2.21 and tabulated in Table. 2.2.

On each side of the (0,1) and (0,0) absorption bands located at ~ 199 and ~ 206 nm, the extinction cross-section is expected to be equal to the Rayleigh scattering cross-section. The predicted values of the Rayleigh scattering cross-section are plotted in Fig. 2.21 as a dashed line and specified in Table. 2.2.

Collision-induced absorption:

The collision-induced absorption cross-section values determined via non-linear squares fit as described before are plotted in Fig. 2.22 and tabulated in Table 2.3.

As can be seen from the graph (represented in a logarithmic scale) strong features are observed near 206 nm and 199 nm, where the (1,0) and (0,0) absorption bands are located. The resonance centered at ~ 206 nm is resolved and five data points, measured near 199 nm show the existence of a similar resonance. In the wavelength region between 199 and 202 nm problems with the operation of the dye laser were encountered, hence the lack of data in this interval.

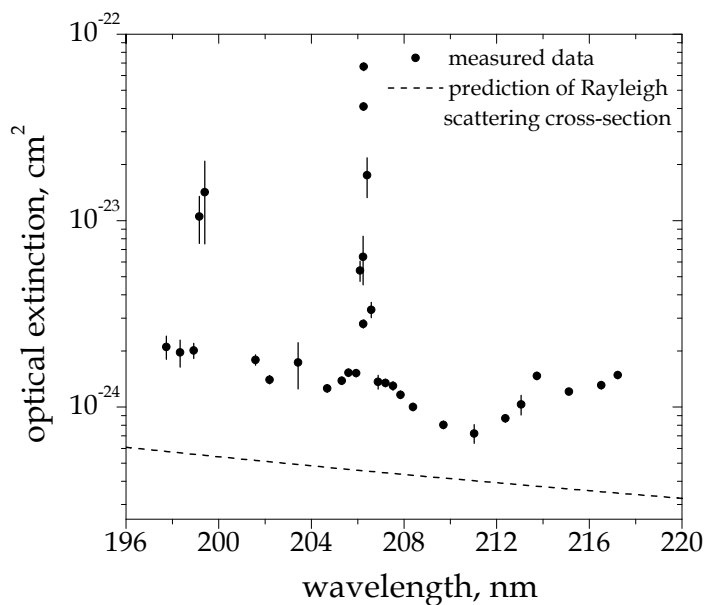


Figure 2.21: Measured values of the optical extinction cross-section (●) and the predicted Rayleigh scattering cross-section values (dashed line) in CO, plotted on a logarithmic scale.

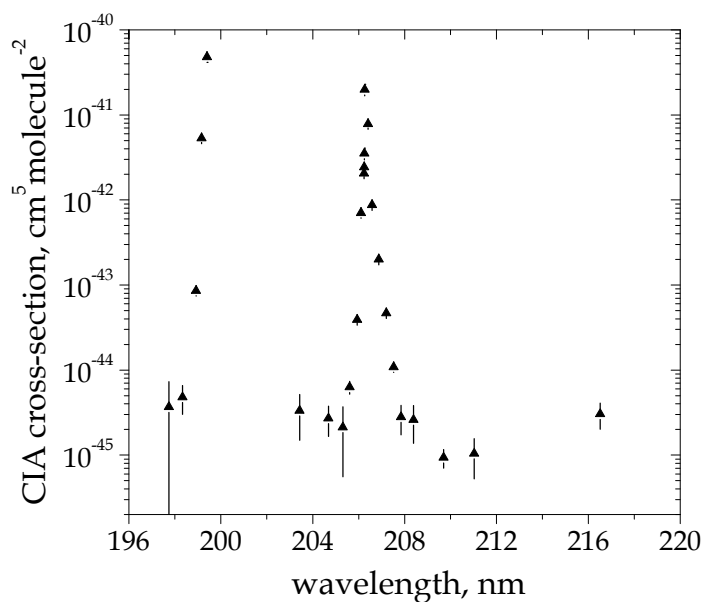


Figure 2.22: The measured collision-induced absorption cross-section values (▲) in CO, plotted on a logarithmic scale.

Table 2.2: *The measured optical extinction values, predicted Rayleigh scattering cross-section values and the discrepancy between observed and predicted data.*

λ [nm]	$\sigma^{meas} / 10^{-24}$ [cm ²]	$\sigma^{calc} / 10^{-25}$ [cm ²]	$\sigma^{meas} - \sigma^{calc} / 10^{-24}$ [cm ²]
197.74	2.10 ± 0.30	5.78	1.52
198.33	1.96 ± 0.32	5.68	1.39
198.92	2.01 ± 0.19	5.58	1.45
199.16	10.51 ± 2.98	5.54	9.96
199.40	14.18 ± 6.68	5.51	13.63
201.59	1.79 ± 0.12	5.17	1.27
202.20	1.40 ± 0.07	5.09	0.89
203.43	1.73 ± 0.48	4.92	1.24
204.68	1.26 ± 0.03	4.75	0.79
205.31	1.38 ± 0.02	4.67	0.91
205.61	1.53 ± 0.02	4.63	1.07
205.94	1.52 ± 0.03	4.59	1.06
206.11	5.39 ± 0.67	4.57	4.93
206.23	6.39 ± 1.86	4.56	5.93
206.24	2.79 ± 0.14	4.55	2.33
206.25	40.91 ± 0.69	4.55	40.45
206.26	66.93 ± 3.18	4.55	66.47
206.41	17.51 ± 4.21	4.53	17.06
206.59	3.33 ± 0.31	4.51	2.88
206.88	1.36 ± 0.12	4.48	0.91
207.20	1.35 ± 0.04	4.44	0.91
207.53	1.30 ± 0.07	4.40	0.86
207.85	1.16 ± 0.04	4.37	0.72
208.39	1.00 ± 0.04	4.30	0.57
209.71	0.80 ± 0.03	4.16	0.38
211.03	0.72 ± 0.08	4.02	0.32
212.38	0.87 ± 0.02	3.89	0.48
213.06	1.03 ± 0.12	3.82	0.65
213.74	1.47 ± 0.05	3.76	1.09
215.12	1.21 ± 0.03	3.63	0.85
216.52	1.31 ± 0.05	3.51	0.96
217.22	1.48 ± 0.03	3.45	1.13

Table 2.3: Measured collision-induced absorption cross-section values in CO.

λ [nm]	$\alpha^{CIA}(\lambda) / 10^{-44}$ [cm ⁵ mol ⁻²]	λ [nm]	$\alpha^{CIA}(\lambda) / 10^{-44}$ [cm ⁵ mol ⁻²]
197.74	0.37 ± 0.36	206.25	353 ± 56
198.33	0.48 ± 0.18	206.26	1985 ± 306
198.92	8.54 ± 1.05	206.41	785 ± 81.7
199.16	531 ± 53.1	206.59	87.17 ± 4.09
199.40	4802 ± 641	206.88	20.01 ± 0.64
203.43	0.33 ± 0.18	207.20	4.65 ± 0.05
204.68	0.27 ± 0.10	207.53	1.08 ± 0.14
205.31	0.21 ± 0.16	207.85	0.28 ± 0.11
205.61	0.63 ± 0.11	208.39	0.26 ± 0.12
205.94	3.90 ± 0.27	209.71	0.09 ± 0.02
206.11	70.35 ± 8.72	211.03	0.10 ± 0.05
206.23	205.5 ± 17.9	216.52	0.30 ± 0.10
206.24	241.8 ± 6.54		

2.3.5. Discussion

The data on the linear and quadratic extinction cross-sections require some further discussion. Firstly, the obtained extinction coefficients outside the regions of the absorption bands are higher than the expected Rayleigh scattering cross-sections as calculated from the refractive index data [62]. In order to eliminate any systematic errors in pressure-ramp measurements in CO, reference measurements of the optical extinction cross-sections in pure N₂ have been performed at some deep-UV wavelengths, scattered between 198 and 220 nm prior to the optical extinction studies in CO. The results of these control measurements were found in consistent agreement with the values of the Rayleigh scattering cross-sections, deduced from the dispersion formulas for the refractive index and King correction factor values, as described further in *Chapter 4* of the thesis.

The lack of data on the King factor in CO, presently available in literature, and the required extrapolation to the deep-UV range cannot resolve this issue; the King factor is a less than 10% effect. As shown in Fig. 2.21 the presently obtained extinction is higher by a factor of three. Secondly, enhanced linear extinction is found also outside the ranges of the strongest molecular absorption resonances of both bands (see Fig. 2.21). For this we cannot provide

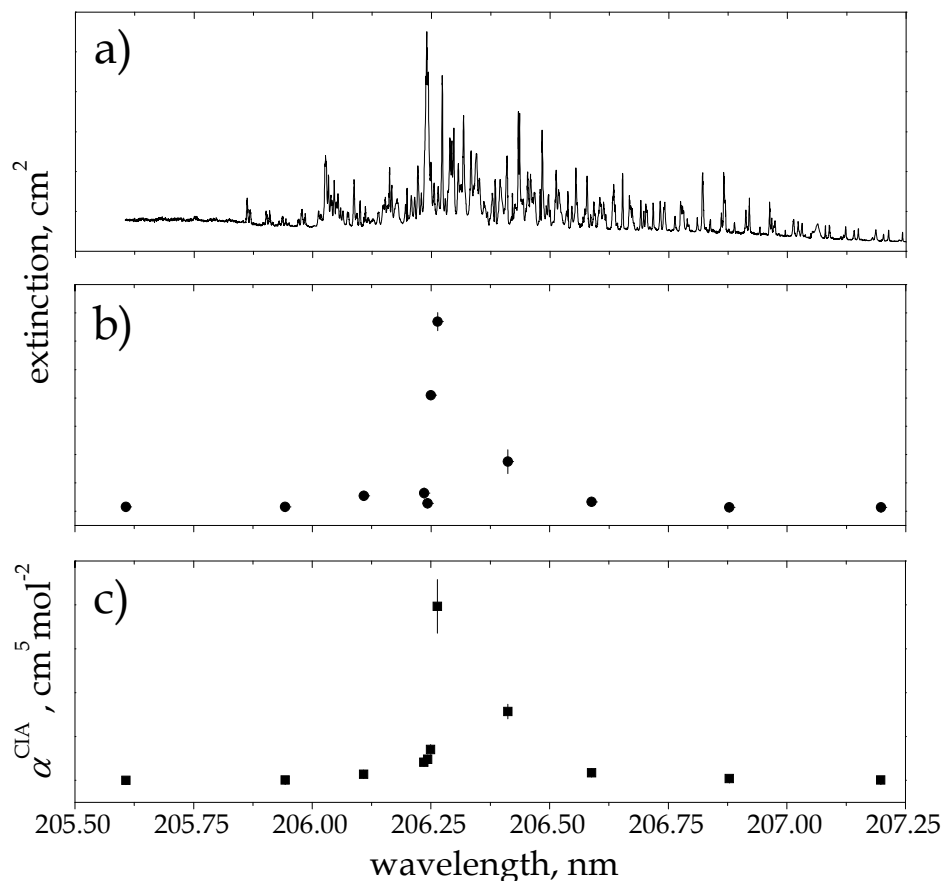


Figure 2.23: The results of optical extinction (**a**, **b**) and collision-induced absorption measurements around (0,0) absorption band in Cameron system of molecular CO. All graphs are plotted on a linear scale. The upper graph (**a**) indicates the CRDS measurements of the absorption band, as discussed in Section 2.3.1, while the graphs (**b**, **c**) represent the optical extinction values (•) and CIA cross-section values (■) derived from the CRDS pressure-ramp measurements.

an explanation other than assuming that absorbing impurities must be present in the gas samples. We note that we have encountered a similar problem in the analysis of Rayleigh scattering data for CH_4 (presented in Chapter 4 of this thesis); in that case the problem could be solved by performing verification measurements in ultra-pure samples of methane. It is a well known fact that CO gas is sometimes contaminated by Iron-pentacarbonyl, ($\text{Fe}[\text{CO}]_5$) and other

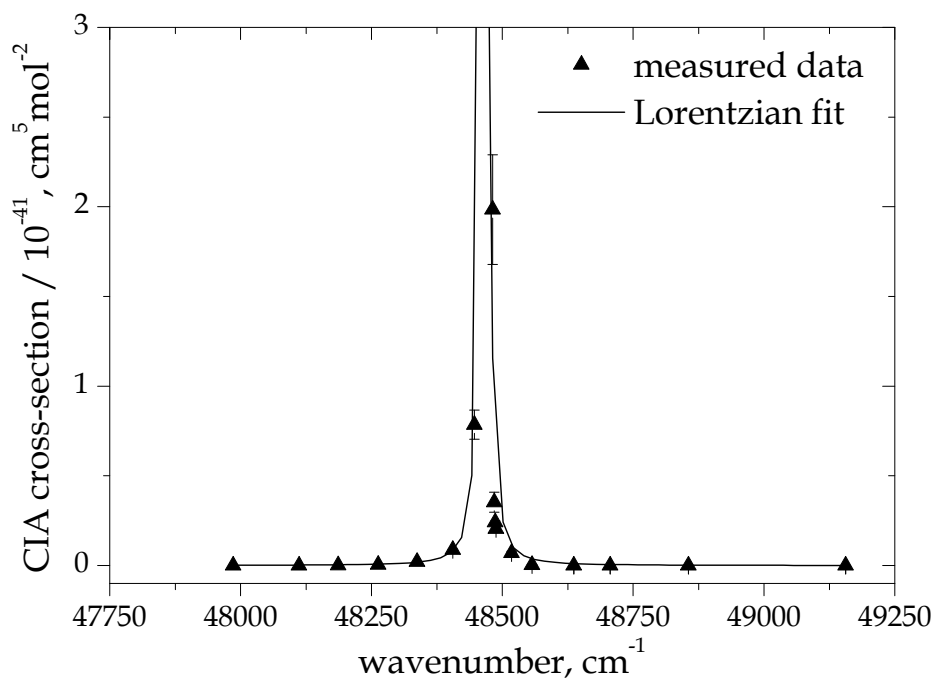


Figure 2.24: The cross-section of the observed collision-induced absorption resonance in CO around 206.19 nm following a Lorentzian fit. The solid triangles (▲) represent the actual measurements.

Table 2.4: The results of the nonlinear fit, performed to 17 measured collision-induced absorption cross-section values in CO around 206.19 nm.

Peak value	Central frequency	Width	Band integrated
α_{peak} [cm ⁵ mol ⁻²]	ν_c [cm ⁻¹]	Γ [cm ⁻¹]	$\int \alpha^{CIA}(\nu) d\nu$ [cm ⁴ mol ⁻²]
$1.15 (\pm 0.17) \times 10^{-40}$	$48466.2 (\pm 7.3)$	$10.35 (\pm 0.84)$	18.49×10^{-40}

carbonyl compounds, produced via gas-wall reactions in metal cylinders containing CO. However, we could not obtain gas samples of higher purity and mass-spectroscopic analysis of the used CO sample (with a purity of 99.997%, as specified by gas supplier). Future measurements on purified carbon monoxide may resolve this issue.

In Fig. 2.23 both the spectral recording in CO (shown on panel a) and the linear extinction components of pressure-ramp scans (shown on panel b) are plotted. The graph clearly shows that locations of enhanced extinction coincide with (or are very near to) the wavelength positions of the spectral resonances. It is not possible to tune the laser frequency during a pressure-ramp scan and since it was also not possible to verify that the laser was parked exactly in between absorption resonances, we attribute this effect of enhanced extinction as a result of wing absorption, occurring at frequencies where the wings of two adjacent absorption lines overlap or alternatively due to a *line-mixing* effect or *molecular aggregation* mechanisms, as proposed in literature [7] to explain how the spectral profiles in allowed absorption bands are changing as the density of the gas increases. The line-mixing effects lead to an increase of absorption near the band center at the expense of a decrease of the absorption in the wings, as was shown for pure vibrational spectra of water vapour at infrared wavelengths in [67]. As also discussed in literature [68–70], proper accounting for molecular aggregation (dimerization) and line-mixing effects are required to explain most of the observed density variations in infrared spectral features of pressurized CO and CO₂ in the range of densities where pair effects are expected to prevail.

In Fig. 2.23(c) the quadratic component, resulting from the pressure-ramp scans is plotted on a linear scale. Again it is found that the highest values of the quadratic component coincide with the strongest absorption lines in the (0,0) absorption band. Fig. 2.22 shows that the effect near the (1,0) is similar, although the amount of data at the shorter wavelength resonance is limited here.

The phenomenon is not fully understood, but in view of its quadratic density dependence we interpret the observation in terms of a collision-induced resonance. For a parameterization of the quadratic feature, seventeen experimental data points, measured around 206.19 nm (48500 cm⁻¹) are fit to:

$$\alpha^{CIA}(\nu) = \alpha_{peak} \frac{(\Gamma/2)^2}{(\nu - \nu_c)^2 + (\Gamma/2)^2} \quad (2.28)$$

The fit, shown in Fig. 2.24 yields a values for the width Γ , peak intensity α_{peak} , the central frequency ν_c and integrated band value, calculated between 48263.03 and 48636.43 cm^{-1} , as listed in Table 2.4.

The resonance width of $\sim 10 \text{ cm}^{-1}$ is a remarkable result, because this is much narrower than the collisional-induced absorption features, observed in other molecular systems. As discussed further in *Chapter 6* of the thesis, the widths of collision-induced resonances in $\text{O}_2\text{-O}_2$ system, measured at 477 and 577 nm at room temperature are typically about 250 and 350 cm^{-1} , respectively. It is not excluded that the quadratic extinction should be interpreted as a remnant of wing absorption. If so it is remarkable that the pronounced quadratic feature (with an observable dynamic range of 5 orders of magnitude, see Fig. 2.22) only should occur at a central frequency of 48466 cm^{-1} at a width of 10 cm^{-1} , while the absorption band spans a width of 500 cm^{-1} . Measurements of the temperature dependence of this quadratic extinction might help to reveal its origin.

Chapter 3:

Deep-UV absorption and Rayleigh scattering of carbon dioxide

Cavity ring-down spectroscopy and pressure-ramp measurements have been used to determine the extinction coefficients of CO₂ in the deep-ultraviolet wavelength region, between 198 and 270 nm. The observed optical extinction confirms that there is a clear absorption onset of CO₂ in the deep-UV wavelength region. This onset has been reported previously around 205 nm. The new set of measurements presented here shows that the onset actually starts at higher energy, around 202 nm. For longer wavelengths it is found that the optical extinction demonstrates a $1/\lambda^4$ like behavior, as typical for Rayleigh scattering.

Introduction

At deep-UV wavelengths light scattering becomes much stronger due to a $1/\lambda^4$ scaling of the Rayleigh scattering. The case of CO_2 is special as a number of studies also report an absorption onset between 200 and 205 nm [71, 72]. The exact onset of this absorption is important to model the photochemistry of planetary atmospheres that are rich of carbon dioxide, including that of the Earth and Mars. However, the exact wavelength where the CO_2 absorption onset steeply starts has been a topic of dispute, in particular due to a data set by Ogawa [73], which was suggestive of an absorption onset near 220 nm, just above the dissociation limit of CO_2 . The most recent measurements by Karaïskou *et al.* [74] providing accurate cross-sections in the wavelength range 200–206 nm at room temperature as well as at 373 K may have settled this issue, showing that the findings of [74] must be in error. They find an onset for absorption around 205 nm for carbon dioxide. Proceeding to shorter wavelengths the extinction cross-section of CO_2 increases by several orders of magnitude in the range 200–120 nm [72, 75].

In this study we present an extensive series of new data points in the 198–205 nm region where the onset is expected, combining pressure-ramp measurements and cavity ring-down spectroscopy at deep-UV wavelengths [31]. Our results confirm the Karaïskou *et al.* conclusion that the Ogawa data must be in error. At longer wavelengths in the range 215–270 nm extinction is measured and compared to Rayleigh scattering cross-sections previously obtained, either through direct cross-section measurements [52, 76] or through derivation from the index of refraction [77], where also the effect of depolarization is included [78]. Based on the combined data sets an updated functional representation of the wavelength-dependent Rayleigh scattering cross-section $\sigma_R(\lambda)$ is derived.

The present quantitative study of the CO_2 extinction in a wide wavelength region yields further insight in the absorption onset. This is important in an atmospheric context, since it is the combined effect of light scattering, photo-absorption and photo-processing that determines the impact of deep-UV light on atmospheric CO_2 . In addition, the atmospheric extinction determines the penetration of deep-UV light to lower layers in the atmosphere.

3.1. Analytical approach

Rayleigh scattering can be measured by detecting the *extinction* from a light beam (along a length z or during a time t) as given by Beer's law,

$$I = I_0 \exp(-N\sigma z) = I_0 \exp(-N\sigma c t) \quad (3.1)$$

where I_0 is the intensity at $z=0$ and $t=0$, N is the density of the molecules and σ is the value of the extinction cross-section that accounts for *both* scattering σ_R and absorption σ_{abs} contributions, and c is the speed of light. More specifically, the Rayleigh scattering cross-section is given (in units of cm^2 per molecule) by:

$$\sigma_R = \frac{24\pi^3}{\lambda^4 N^2} \left(\frac{n^2(\lambda) - 1}{n^2(\lambda) + 2} \right)^2 F_k(\lambda) \quad (3.2)$$

where λ is the wavelength in cm, N is the density of the molecules in cm^3 and $n(\lambda)$ is the wavelength-dependent refractive index. The dimensionless King correction factor $F_k(\lambda)$ accounts for the anisotropy in the scattering by non-spherical molecules. Eq. 3.2 relates the Rayleigh scattering cross-section to two directly measurable quantities, the refractive index and the gas density. Hence, a comparison between direct measurements of the Rayleigh scattering cross-section with measurements of the refractive index yields information on $F_k(\lambda)$. In addition, this factor is obtained via depolarization measurements in Raman scattering or via *ab initio* calculations of molecular properties. For CO_2 this wavelength-dependent parameter is available from literature [78] and given by Eq. 3.3:

$$F_k(\lambda) = 1.14 + \frac{25.3 \times 10^{-12}}{\lambda^2} \quad (3.3)$$

Dispersion formulas for the refractive index and the depolarization of atmospheric gases are generally available from literature and for CO_2 specifically given by Eq. 3.4 [77]. In Eqs. 3.3 and 3.4 the wavelength λ (in vacuum) is given in cm. Alternatively, a direct determination of σ_R via extinction measurements provides a test of the calculated Rayleigh scattering cross-section. Sneep and Ubachs verified in a range of visible wavelengths (near 475 nm, at 532 nm and near 560 nm) that the Rayleigh cross-section as obtained

from extinction measurements is in agreement with results from dispersion and depolarization data [76].

$$\begin{aligned} n(\lambda) - 1 = 1.1427 \times 10^6 & \left(\frac{5799.3 \cdot \lambda^2}{16.6 \cdot 10^9 \cdot \lambda^2 - 1} + \frac{120 \cdot \lambda^2}{7.96 \times 10^9 \cdot \lambda^2 - 1} + \right. \\ & \left. + \frac{5.33 \cdot \lambda^2}{5.63 \times 10^9 \cdot \lambda^2 - 1} + \frac{4.32 \cdot \lambda^2}{4.6 \times 10^9 \cdot \lambda^2 - 1} + \frac{1.22 \times 10^{-5} \cdot \lambda^2}{5.85 \times 10^6 \cdot \lambda^2 - 1} \right) \end{aligned} \quad (3.4)$$

3.2. Experimental approach

The experimental approach is based upon cavity ring-down (CRD) detection of a series of pressure-ramp measurements, a method developed by Naus and Ubachs [79]. The pressure-ramp procedure allows distinguishing the linear extinction signal, associated with molecular scattering and absorption, from a wavelength-dependent background due to variations in mirror reflectivity or due to a quadratic dependence resulting from collision-induced phenomena [51]. For this it is necessary that the laser frequency is kept constant. Details on the experimental setup, the pressure-ramp method and the extension of CRDS-techniques to deep-UV wavelengths are available from [31, 51, 52, 79].

The present measurements are performed in two distinct wavelength regions (the 215–270 nm interval and the 198–204 nm interval). The bandwidth of the deep-UV radiation in these spectral regimes is better than 0.2 cm⁻¹ and about 0.5 cm⁻¹, respectively. Wavelengths are chosen according to the availability of high-reflectivity mirrors and listed in Table 3.1. The reflectivity of the cavity ring-down mirrors is better than 99.4 % in the 215.38–270.15 nm region and ~ 98% at 210.12 nm. An effective reflectivity of 99.2% is achieved in the deep-UV region of 198–201 nm. For the 215–270 nm interval the radii of curvature of available mirrors prompted the use of a relatively short cell, at an optimal cavity length of 40 cm. In these experiments the resulting decay times amount to about 250 ns and are determined by a non-linear least-squares fitting with about 5% uncertainty. The 1 m focal distance of the mirrors for 200 nm makes it possible to use a special 82 cm long CRD cell, previously designed for pressure-ramp studies [51, 79]. It contains a large number of inlet holes for the gas to enter the scattering region, while avoiding turbulence effects.

In cases, where the laser line-width applied in the CRD scheme is negligible with respect to the molecular extinction feature, experimental decay times can be directly converted into absolute cross-sections [80]. The decay rate β obtained in a CRDS measurement, equaling the inverse of the ring-down decay time τ , scales with the gas density:

$$\beta = \frac{c|\ln R(\lambda)|}{d} + c\sigma N \quad (3.5)$$

Hence, from a series of measurements at fixed wavelength and at increasing gas density N , both the averaged reflectivity $R(\lambda)$ of the mirror set and the absolute extinction cross-section σ can be obtained. Note that the latter follows from the slope of each β vs. N measurement and that the resulting value is independent of the cell length d . In the present study CRD pressure-ramp scans are recorded in pressure ranges between 0 and 10^5 Pa, i.e. up to atmospheric pressure. All measurements have been taken at room temperature. The empirical relations given here are for 288.15 K and 101325 Pa.

The wavelength of the laser is kept fixed during a pressure-ramp measurement. Both the pressure and the decay time of the cavity are continuously monitored, while gradually increasing the gas density in the scattering region. At every momentary pressure value, five decay transients are digitized and fitted. The precise value of the pressure inside the ring-down cell is measured simultaneously with 0.15% accuracy by a pressure sensor. High purity gases are used (99.7% for CO_2) and a 0.5 micron filter cleans the injected gas from dust and aerosol particles, which may affect the scattering properties of the gas.

3.3. Results and discussion

The results of the measurements performed at 22 distinct wavelengths between 197.7 and 270.15 nm are listed in Table 3.1. The behavior of the experimentally obtained extinction cross-sections as well as a comparison with existing data is given in Fig. 3.1. The slope coefficient of each individual measurement is determined with an accuracy of a few percent. The experimental error (1 σ uncertainty) is ~15% for the measurements in the 215.38–270.15 nm interval and about 10% for observations in the wavelength region where the turbulence free

CRD cell has been used. A significant number of pressure-ramp scans had to be taken to decrease the experimental error. In none of the experiments performed signatures of quadratic density dependence were found. From this result we conclude that CO₂–CO₂ collision-induced phenomena do not play a role, for the wavelength region covered and for pressures below 1 atmosphere.

The predicted values of the Rayleigh scattering cross-sections in CO₂ are obtained from the dispersion formulas for the refractive indices [77, 78] and depolarization ratios [78]. The calculated Rayleigh-scattering cross-sections and measured extinctions, as well as their errors (1 σ uncertainties) are listed in Table 3.1.

Due to the wavelength dependence of the refractive index and the King correction factor, the Rayleigh scattering cross-section is not exactly proportional to $1/\lambda^4$ and a proper mathematical function accounting for this difference (see [52, 79]) has to be used:

$$\sigma_R = \bar{\sigma} \nu^{(4+\varepsilon)} \quad (3.6)$$

where ν is the light frequency in cm⁻¹. Hence the wavelength-dependent Rayleigh scattering σ_R is expressed in terms of two variables $\bar{\sigma}$ and ε . A two step fitting procedure has been applied in which the $\bar{\sigma}$ parameter is kept fixed to the predicted and uncorrected theoretical value (calculated from the refractive index and the King correction factor), while the value for ε is repeatedly optimized. During the second step free and fixed parameters are interchanged and statistically reliable values are found after a few iterations. A non-linear least-squares fit to Eq. 3.6 has been performed for all data points, as available from this work and from literature, apart from the older data by Ogawa [73] covering the range 202–300 nm. In the wavelength domain from 202 to 300 nm this yields values $\bar{\sigma} = 1.78(7) \times 10^{-46}$ and $\varepsilon = 0.625(3)$. Note that in this representation ε is dimensionless and the dimension of $\bar{\sigma}$ depends on the value of ε and therefore is not specified.

In Fig. 3.1 the data pertaining to this fit to the Rayleigh scattering data (fit performed in the interval 202–300 nm) is shown (full line), as well as a calculation, based on dispersion and depolarization ratios (dashed line). In the upper of the figure a deviation between both representations is given, showing that between 202 and 300 nm the agreement is within a few %, while for

Table 3.1: Extinction cross-section values in the 197.70 –270.15 nm region, obtained from CRD pressure-ramp measurements and calculated Rayleigh scattering cross-sections values σ_R^{calc} in CO₂.

λ [nm]	$\sigma_R^{calc} / 10^{-25}$ [cm ²]	$\sigma_R^{meas} / 10^{-25}$ [cm ²]
197.70	10.1	52.7 ± 2.2
197.84	10.0	51.4 ± 1.5
198.28	9.9	54.9 ± 1.9
198.38	9.9	43.2 ± 1.7
198.48	9.9	49.2 ± 2.4
198.75	9.8	32.1 ± 3.4
199.10	9.7	33.5 ± 3.5
199.55	9.6	24.0 ± 2.6
199.90	9.5	23.9 ± 0.7
200.08	9.5	30.0 ± 0.9
200.42	9.4	23.0 ± 3.0
200.76	9.3	16.9 ± 1.0
201.00	9.3	15.5 ± 1.6
201.33	9.2	12.6 ± 1.1
201.58	9.2	10.1 ± 1.3
201.78	9.1	8.0 ± 1.2
202.43	9.0	7.9 ± 0.8
203.11	8.8	7.8 ± 1.6
203.76	8.7	7.5 ± 1.5
215.38	6.7	6.6 ± 1.0
251.72	3.2	3.3 ± 0.5
270.15	2.4	2.3 ± 0.4

$\lambda > 300$ nm there is a gradually increasing discrepancy up to 20% at the longest included wavelength (532 nm). This discrepancy can be ascribed to the fact that the fit determining $\bar{\sigma}$ and ε is restricted to UV wavelengths, i.e. it is not meant to be extrapolated beyond 300 nm. Note that the Rayleigh scattering in CO₂ for the range of visible wavelengths is represented by largely differing parameters [52]. The measurements on the index of refraction in [77] represent data in the deep-UV range, covering the interval 180–254 nm (distinct atomic line emissions are used in their experiment), hence the dashed line in Fig. 3.1 is an extrapolation. Considering this the agreement between directly measured and calculated Rayleigh scattering cross-sections is rather good, within a few % in the relevant wavelength region.

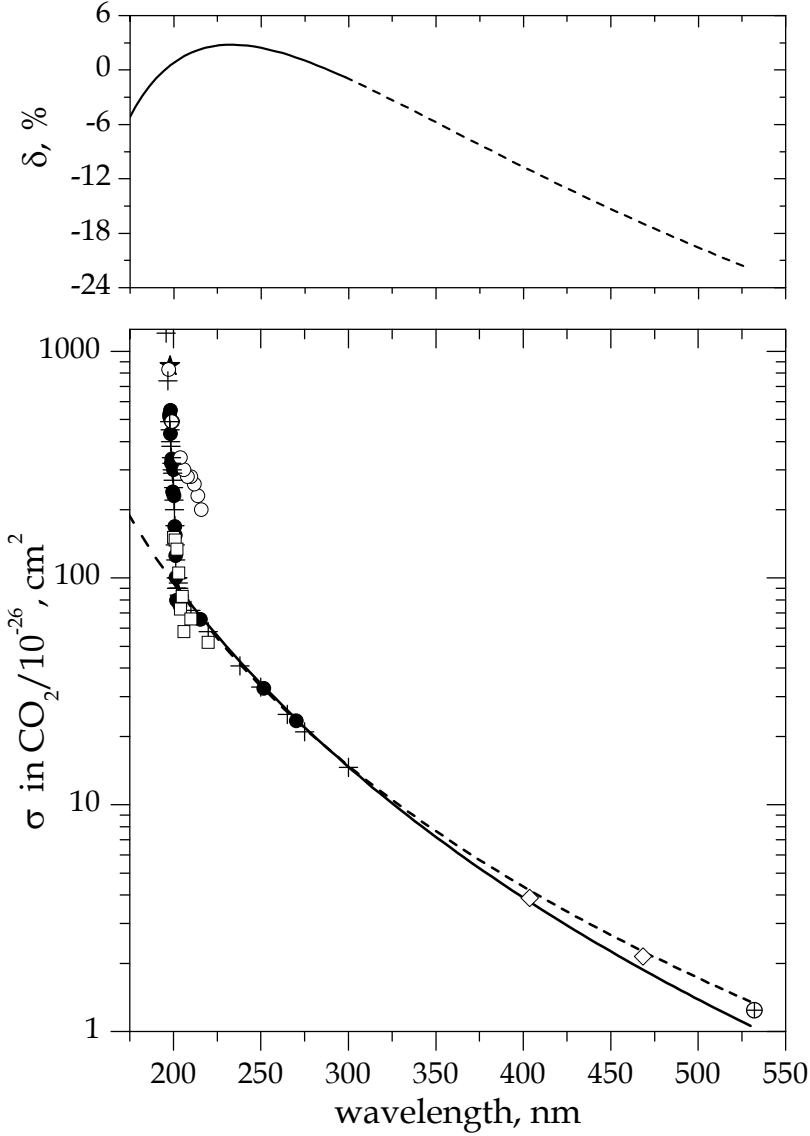


Figure 3.1: Results from extinction measurements in CO_2 . The lower trace shows the experimental data points, as presently measured in this work ($\bullet$) and those available from literature: ($\oplus$) – Snee and Ubachs [52], ($\star$) – Snee et al. [31], ($\circ$) – Ogawa [73], ($+$) – Shemansky [71], ($\square$) – Karaiskou et al. [74], ($\diamond$) – Dong and Gupta [76]. The solid black line corresponds to a fit with $\bar{\sigma} = 1.78(7) \times 10^{-46}$ and $\varepsilon = 0.625(3)$ and the dashed line corresponds to Rayleigh scattering cross-section simulation, extrapolated to the visible domain, using the dispersion formula available from [77] and depolarization from [78]. The difference between these two graphs is shown in the upper panel.

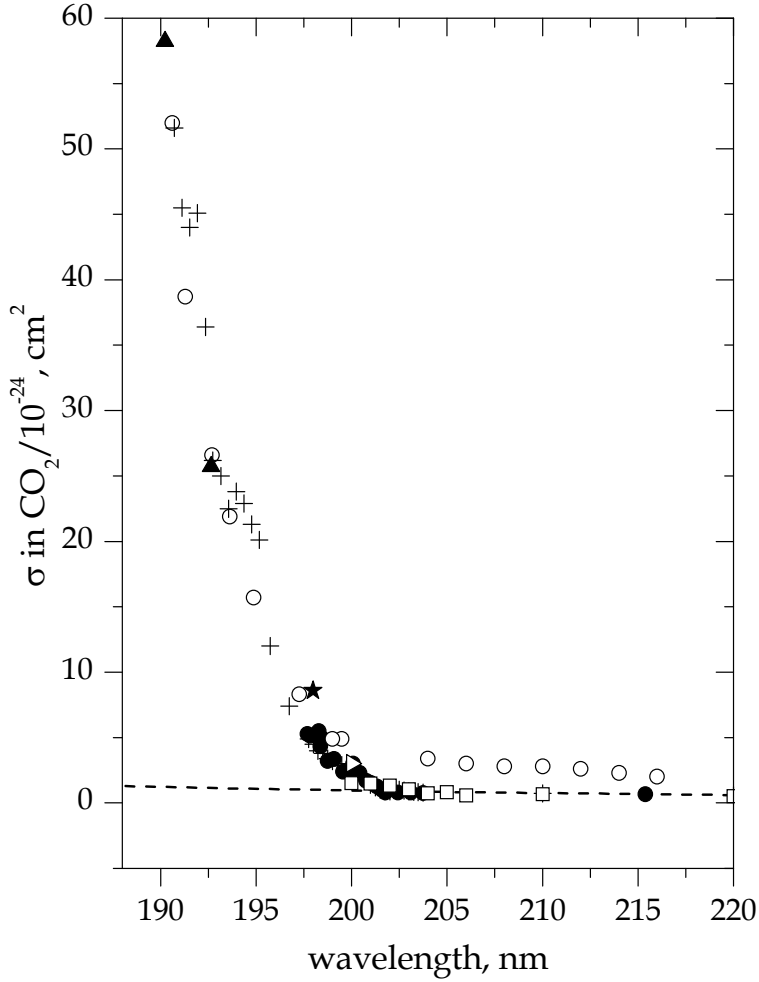


Figure 3.2: Illustration of the absorption onset in CO_2 , as derived in this study ($\bullet$) and observed in other work: (+) – Shemansky [71], ($\triangleright$) – Parkinson et al. [72], ($\circ$) – Ogawa [73], ($\square$) – Karaïskou et al. [74], ($\blacktriangle$) – Lewis and Carver [75] and ($\star$) – Sneep et al. [31]. The dashed line represents the Rayleigh scattering cross-section simulation extrapolated to the visible domain, using the dispersion and depolarization formulas available from [77, 78].

The data of Bideau-Mehu *et al.* on the index of refraction [77] imply that the Rayleigh scattering cross-section is represented down to 180 nm by Eqs. 3.2–3.4. Hence the sudden increase in Fig. 3.1 is clearly representative for the absorption onset in CO_2 . This onset is shown in more detail, and on a linear

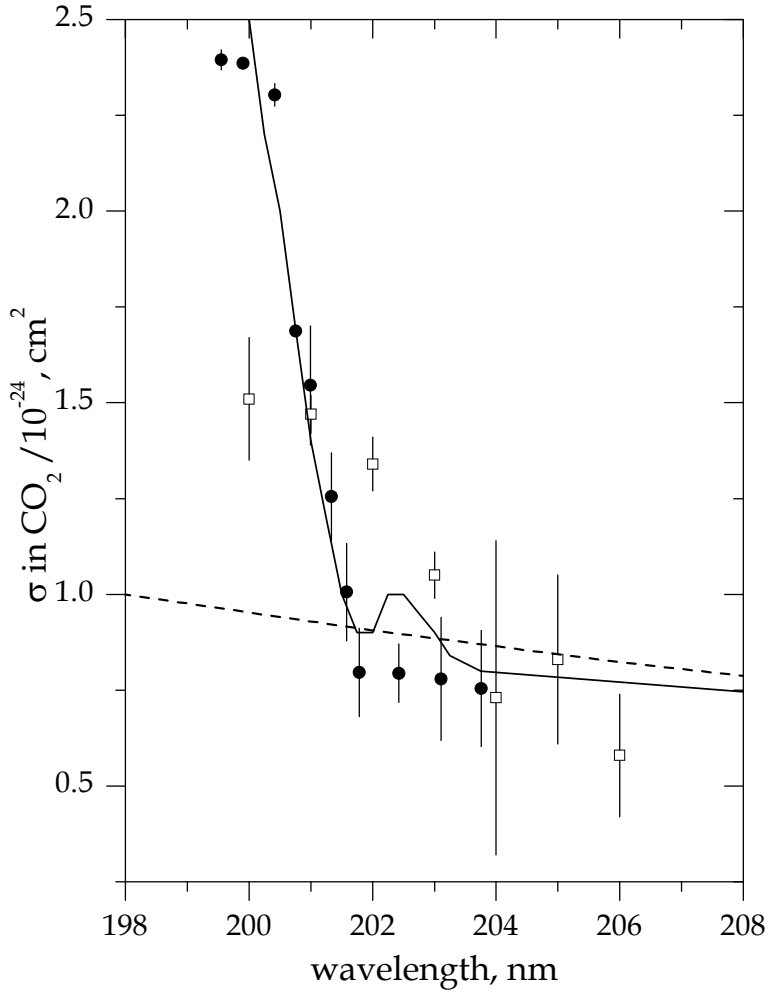


Figure 3.3: Illustration of the absorption onset in CO_2 , as derived in this study (•) and observed in other work: the solid line represents the data by Shemansky [71], (□) – are from Karaïskou et al. [74].

scale for the extinction in Fig. 3.2, where data by Shemansky [71], Ogawa [73], Sneep *et al.* [31], Karaïskou *et al.* [74], and Lewis and Carver [75] are plotted together with the present data. Overall agreement between the data sets is found, except for the data by Ogawa [73]. At the short wavelength side the data by Shemansky [71] can be matched to those of Lewis and Carver [75] and of Parkinson *et al.* [72], showing a strong increase of the absorption from the

Rayleigh scattering level below 10^{-24} cm² to a plateau in the broad absorption resonance near 130–150 nm at a cross-section level of 10^{-18} cm².

To further clarify details of the absorption onset we have magnified the scales of Fig. 3.2 around the onset point, as shown in Fig. 3.3. In previous reports the absorption onset in carbon dioxide has been put around 205 nm [74]. The large number of measurements in this region indicates that the actual onset starts at a value of about 202 nm. A comparison of the existing data sets in the 200–205 nm region shows that our data are very complementary with the Shemansky results [71], whereas the Karaïskou data yield only slightly higher values. The spread in the three data sets that now reaches agreement in the range 200–205 nm (present data, Karaïskou *et al.* [74] and Shemansky [71]) is rather large, being up to 20%. We note that this is the range where absorption is governed by vibrationally excited CO₂, making the extinction cross-section strongly dependent on temperature, as was verified in the experiments by Karaïskou *et al.* Moreover the spread demonstrates that this part of the deep-UV spectrum is a difficult region to perform experiments at high accuracy.

At wavelengths in the range 197.7–200 nm the data show signature of an oscillatory behavior, reminiscent of a vibrational structure. This structure was more clearly observed in the 180–190 nm interval by Parkinson *et al.* [72]. In principle the high resolution of the present setup would allow for unraveling these oscillations if data were collected at much smaller wavelength steps. Although this is very time consuming when applying the pressure-ramp method, it may be a topic for further study. Near 200 nm there is a slightly increased penetration of deep-UV to lower layers in the Earth's atmosphere [80] due to a gap between the strong extinctions produced by the O₂ molecule (shortward of 200 nm) and the O₃ molecule (longward of 210 nm). The onset of absorption by carbon dioxide in this wavelength interval may be of importance for a detailed modeling of the photo-physics and chemistry in the stratospheric layer of the Earth's atmosphere.

3.4. Conclusion

Through deep-UV extinction measurements and the technique of cavity ring-down spectroscopy in a wide wavelength range further clarity has been obtained on the deep-UV onset of absorption in the CO₂ molecule. The onset is

found close to 202 nm, while also a model description for the Rayleigh scattering cross-section for the entire UV range is presented.

Acknowledgements

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Chapter 4:

Deep-UV Rayleigh scattering of N₂, CH₄ and SF₆

Rayleigh scattering room-temperature cross-section values of N₂, CH₄ and SF₆ have been obtained between 198 and 270 nm by combining cavity ring-down spectroscopy (CRDS) and pressure-ramp measurements. The experimental data have been fitted to a functional representation, describing the $\sim 1/\lambda^4$ like behavior of the Rayleigh scattering cross-section over a wide wavelength range. The resulting values are compared to numerical predictions, based on refractive indices and molecular anisotropy data as available from literature. From this, values of molecular volume polarizability α_{vol} and depolarization ratios are derived. It is found that the optical extinction for all three gases is governed by Rayleigh scattering for wavelengths down to 200 nm. No absorption onsets in the specified deep-UV region have been observed.

Introduction

Detailed information of Rayleigh scattering processes is a prerequisite to quantitatively interpret e.g. atmospheric and laser diagnostic results [81-82]. This is particularly true for deep-UV wavelengths as light scattering phenomena intensify because of the $1/\lambda^4$ scaling of the Rayleigh scattering. Optical extinction studies are furthermore important to verify whether or not constituents exhibit absorption in addition to Rayleigh scattering, as demonstrated recently for CO₂ where an absorption onset was found in the atmospherically relevant window around 202 nm [71, 74, 83]. In laser diagnostics Rayleigh scattering cross-sections are needed to determine gas density and temperature distribution, e.g. in combustion or flow media [15]. In this paper the focus is on three molecular and atmospherically relevant species: N₂, CH₄ and SF₆.

Molecular nitrogen is the most abundant molecule in the Earth's atmosphere and consequently information on the absorption and scattering of UV solar radiation by N₂ is important. Nitrogen has strong dipole-allowed transitions at wavelengths shorter than 100 nm. In the wavelength region studied here only symmetry-forbidden and consequently weak transitions have been reported. More specifically, in the 200 nm region the (0,0) origin band of the Vegard-Kaplan system is located. However, the oscillator strength of this $A^3\Sigma_u^+ - X^1\Sigma_g^+$ forbidden system is small, and in addition the Franck-Condon factor of the (0,0) band is very weak. Consequently, the absorption cross-section is expected to be well below the Rayleigh scattering value, i.e. the extinction behavior should be fully Rayleigh dominated.

Information on the optical extinction behavior of the greenhouse gas CH₄ around 200 nm is largely lacking. So far only absorption studies have been reported for a series of temperatures in the 106 to 145 nm region [84, 85] and more recently theoretical results on the photodissociation of CH₄ around 124 nm has been reported [86]. Toward longer wavelengths experimental studies are lacking.

Sulphur hexafluoride is an atmospheric trace gas that is primarily of anthropogenic origin, but also occurs naturally. It is highly stable, this being the reason why it is used in a number of industrial applications. This may have

caused an atmospheric SF₆ increase of 0.24 ppt in the early 1970s to nearly 4 ppt at the end of the 20th century [87]. Deep-UV absorption spectra of SF₆ have been recorded in the 78–185 nm region [88, 89], but – again – information on the light extinction at longer wavelengths is essentially lacking.

In this paper an experimental study of the optical extinction behavior of N₂, CH₄ and SF₆ in the 198–270 nm region is presented. This is achieved by combining highly sensitive cavity ring-down spectroscopy (CRDS) and the so-called pressure-ramp technique that allows unraveling the linear extinction signal associated with molecular scattering. In the next section, first the analytical approach is described, followed by experimental details. The results are discussed within the context of existing literature values. In the conclusion the main points are summarized.

4.1. Analytical approach

Rayleigh scattering [14], being considered in terms of classical electrodynamics theory [16, 17], originates from the secondary radiation of oscillating electric dipoles, induced by an electric field from the incident light. Consequently, the Rayleigh scattering cross-section σ_R can be defined in two ways, either via molecular volume polarizability α_{vol} :

$$\sigma_R = \frac{128}{3\lambda^4} \pi^5 \alpha_{vol}^2 \quad (4.1)$$

or, more conveniently via [90, 91]:

$$\sigma_R = \frac{24\pi^3}{\lambda^4 N^2} \left(\frac{n^2(\lambda) - 1}{n^2(\lambda) + 2} \right)^2 F_k(\lambda) \quad (4.2)$$

where λ is the wavelength in cm, N is the density of the molecules in cm³ and $n(\lambda)$ is the wavelength-dependent refractive index. This convention is used throughout this work. The Rayleigh formula (Eq. 4.2) relates the scattering cross-section to two directly measurable quantities; the refractive index and the gas density. Note that the latter two are macroscopic properties of the gas related such that σ_R represents a single-particle cross-section. A comparison between measurements of the Rayleigh cross-section and the refractive index – for a known density – yields information on the dimensionless King correction

factor $F_k(\lambda)$ [16]. This factor accounts for the anisotropy in scattering by non-spherical molecules, which is important for the description of polarization and angular-dependent effects and is defined by

$$F_k(\lambda) = \frac{3 + 6\rho_p(\lambda)}{3 - 4\rho_p(\lambda)} = \frac{6 + 3\rho_n(\lambda)}{6 - 7\rho_n(\lambda)} \quad (4.3)$$

Here $\rho_p(\lambda)$ and $\rho_n(\lambda)$ stand for the depolarization ratio of either polarized or natural (unpolarized) incident light, respectively, which is specified in [17, 92–94]. The role of molecular polarization effects becomes significantly stronger in the deep-UV compared to the visible and consequently the depolarization ratio of investigated molecular species must be taken into account as well [95].

4.2. Experimental approach

The experimental setup and approach to measure Rayleigh scattering cross-sections have been described in detail previously [52, 79, 83] and are based upon direct absorption spectroscopy applying CRDS. Pulsed laser radiation is obtained by frequency doubling of the blue-green output of a Spectra Physics PDL-2 dye laser (operated on *Coumarine-152*, *Coumarin-307* and *Stilbene-3* laser dyes), pumped by a 355 nm Nd: YAG laser at 10 Hz repetition rate, yielding wavelengths at 270.15, 251.72, 215.38 and 210.12 nm. Wavelengths at 203.76, 199.27, 198.48 and 197.70 nm are generated by frequency tripling the output of a pulsed (SIRAH) dye laser, running near 600 nm on *Rhodamine-B* dye and pumped by a Nd: YAG laser at 532 nm, also at 10 Hz repetition rate. The final bandwidth of the deep-UV light is better than 0.2 cm⁻¹ (for PDL-2 dye laser experiment) and about 0.5 cm⁻¹ (for the SIRAH dye laser experiment). The absolute accuracy of the wavelength calibration, performed by an echelle-grating spectrometer, is of the order of 0.01 nm.

The laser light is focused into an optical cavity comprising of two highly reflective mirrors and the light leaking out is detected by a photomultiplier tube (Hamamatsu H9858 series) and subsequently digitized by a LeCroy 9450 (350 MHz) oscilloscope. The reflectivity of the CRD mirrors ($r_{\text{curv}} = 25$ cm) is better than 99.4 % in the 215.38 – 270.15 nm region and ~ 98% at 210.12 nm. These mirrors are mounted onto a 40 cm long cell, resulting in decay times of about 250 ns (5% uncertainty). High-quality mirrors ($r_{\text{curv}} = 100$ cm)

have been obtained (from Laser Optik) with an effective reflectivity of 99.2% in the 198-201 nm region; this constitutes a major improvement over previous deep-UV CRDS experiments [31]. The mirrors are mounted onto an 82 cm long cell previously designed for pressure-ramp CRDS studies [52] that contains a multitude of inlet holes for the gas to enter the scattering region, while avoiding turbulence effects. The pressure in both cells is measured with high precision (0.15%) using an Edwards type 600AB Baratron. Pressure-ramps are used to separate the molecular extinction signal from cavity losses and to extract absolute absorption cross-sections [79]. For this both the pressure and the decay time of the cavity are continuously monitored, while gradually increasing the gas density in the scattering region.

The decay rate β obtained in this CRDS measurement, equaling the inverse of the ring-down decay time τ , scales with the gas density:

$$\beta = \frac{c|\ln R(\lambda)|}{d} + c\sigma N \quad (4.4)$$

Hence, from a series of measurements at fixed wavelength and at increasing gas density N , both the averaged reflectivity $R(\lambda)$ of the mirror set and the absolute extinction cross-section σ can be obtained. Note that the latter follows from the slope of each β vs. N measurement and that the resulting value is independent of the cell length d . CRDS pressure-ramp scans have been recorded in pressure ranges up to atmospheric pressure. At every momentary pressure value, five decay transients are digitized and fitted. The slope coefficient of each individual pressure-ramp measurement is determined with an accuracy of a few percent. The resulting cross-section values over the entire set of measurements are spread over a relatively large range and therefore a significant number of pressure-ramp scans – typically 15 – has been taken to statistically decrease the experimental error. All measurements have been taken at 293 ± 3 K.

High purity gases are used (99.999% for N₂, 99.995% for CH₄ and 99.8% for SF₆) and a 0.5 micron filter cleans the injected gas from dust and aerosol particles, which may affect the scattering properties of the gas. It should be noted that the laser wavelength is not scanned during subsequent gas fillings, as only for fixed wavelengths frequency-dependent baseline fluctuations can be excluded. This also explains why only a limited number of optical extinction measurements is presented here, well distributed over the region of interest.

4.3. Results and discussion

The resulting extinction curves for N_2 , CH_4 and SF_6 are shown in Figs. 4.1, 4.3 and 4.5, respectively. In Table 4.1 the measured and predicted extinction cross-sections (with 1σ uncertainties) using Eq. 4.2 are listed. These predicted values are calculated to equal the Rayleigh scattering cross-section values, hence it is assumed that no absorption occurs. Formulas for the refractive indices and for the King correction factor are taken from the literature and extrapolated to the deep-UV region, if necessary.

Table 4.1: Measured and predicted light extinction cross-section values in the 197.7–270.15 nm region for N_2 , CH_4 and SF_6 , obtained from CRD pressure-ramp measurements.

λ [nm]	Extinction cross-section / 10^{-25} , [cm ²]					
	N_2		CH_4		SF_6	
	measured	predicted ^{a,b,c}	measured	predicted ^{c,e}	measured	predicted ^{d,e}
197.70	3.39 ± 0.30	3.62 ± 0.09	11.92 ± 0.64	10.82 ± 0.03	26.86 ± 2.54	23.71
198.48	3.60 ± 0.18	3.55 ± 0.08	12.59 ± 1.30	10.62 ± 0.03	19.35 ± 2.22	23.28
199.27	4.22 ± 0.80	3.48 ± 0.08	11.09 ± 2.42	10.43 ± 0.03	20.68 ± 2.14	22.86
203.76	3.38 ± 0.59	3.14 ± 0.08		9.39 ± 0.02		20.64
210.12		2.72 ± 0.06		8.13 ± 0.02	18.33 ± 4.04	17.94
215.38	2.61 ± 0.42	2.43 ± 0.06	7.79 ± 1.25	7.25 ± 0.02	16.09 ± 2.59	16.04
251.72	1.33 ± 0.10	1.21 ± 0.03	3.56 ± 0.20	3.57 ± 0.01	8.06 ± 1.35	8.00
270.15	1.17 ± 0.17	0.89 ± 0.02	2.53 ± 0.33	2.61 ± 0.01	5.98 ± 0.40	5.88

^{a)} Dispersion relationship, derived from refractive index measurements in [66].

^{b)} Dispersion formula for King correction factor, available from [18].

^{c), d)} Dispersion relationships for the refractive indices, available from [52].

^{e)} The absolute error values given here are derived from the uncertainties of the King correction factor and the refraction index dispersion relationships. For SF_6 the latter is not available, reason why in the last column no error values can be listed.

It should be noted that due to the wavelength dependence of the refractive index and the King correction factor, the Rayleigh scattering cross-section is not exactly proportional to $1/\lambda^4$ and a proper mathematical function accounting for this difference (see [96]), has to be used, as demonstrated previously [52, 79, 83]:

$$\sigma_R = \sigma \nu^{(4+\varepsilon)} \quad (4.5)$$

where ν is the light frequency in cm⁻¹. Hence the wavelength-dependent Rayleigh scattering σ_R is expressed in terms of two variables σ and ε . In this functional representation ε is a dimensionless parameter and the dimension of σ consequently depends on the value of ε . In the following this is not further specified anymore. A simultaneous fit of both variables results in large error margins because of a strong correlation. Therefore a two step fitting procedure has been applied: the σ parameter is kept fixed to the predicted and uncorrected theoretical value (calculated from the refractive index and the King correction factor), while the value for ε is repeatedly optimized. During the second step free and fixed parameters are interchanged and statistically reliable values are found after a few iterations. The experimental and predicted values for the three gases studied here are given in Table 4.2.

Table 4.2: Results of a non-linear square fit along Eq. 4.5 to the experimental data points – both from the present work and from literature – for N₂, CH₄ and SF₆ gas.

Gas	Fit representation				Wavelength interval, nm
	$\sigma / 10^{-46}$		ε		
	experimental	predicted ^a	experimental	predicted ^a	
N ₂	1.796 ± 0.056	1.796	0.534 ± 0.003	0.529	197.70 – 270.15
CH ₄	0.942 ± 0.020	0.942	0.699 ±0.002	0.689	197.70 – 270.15
SF ₆	17.897 ± 0.763	17.897	0.490 ± 0.004	0.490	197.70 – 270.15

^{a)} Values for σ and ε , derived from the fit, performed to predicted (dispersion based) values of Rayleigh scattering cross-section.

4.3.1. Molecular nitrogen

Accurate information (with an uncertainty of about 2×10⁻⁵ percent) of the N₂ refractive index behavior in the 145–270 nm region is available for 273.15 K and 101325 Pa from [18, 66]. To convert the refractive index data from [66] to the present laboratory conditions (293 K, similar pressure) the following equation is used [65, 66]:

$$\frac{n_1 - 1}{n_2 - 1} = \frac{P_1 T_2 Z_2}{P_2 T_1 Z_1} \left(1 + \frac{n_1}{6} \left(1 - \frac{P_2 T_1}{P_1 T_2} \right) \right) \quad (4.6)$$

with n_i the refractive index at pressure P_i [Pa] and temperature T_i [K] and where Z_i , the value of gas compressibility is given by [65, 66]:

$$Z_i = 1 - \frac{P_i}{101325} (317.6 - T_i) \times 10^{-5} \quad (4.7)$$

In this way 31 measured values of refractive indices $n_i(\lambda_i)$ [66] were scaled to 293 K and 101325 Pa and then fitted to a two term Sellmeier formula [97], resulting in the dispersion relationship:

$$n(\lambda) - 1 = \left(\frac{3.635\lambda^2}{43.878 \times 10^{-5} \lambda^2 - 1} + \frac{0.0261\lambda^2}{0.134 \times 10^{-5} \lambda^2 - 1} \right) \times 10^{-8} \quad (4.8)$$

The absolute uncertainty achieved during the fit is better than 0.1%. This determines the final uncertainty in the dispersion formula, since the error of the measured values of the refractive index is much smaller.

The King correction factor for the 200–632.8 nm region is available with an uncertainty better than one percent from [18] and given in Eq. 4.9.

$$F_k(\lambda) = 1.03 + \frac{3.17 \times 10^{-12}}{\lambda^2} \quad (4.9)$$

Seven data points for the wavelength-dependent Rayleigh cross-section of N_2 are indicated in Fig. 4.1(a). The points follow a dashed line that represents the prediction of the Rayleigh scattering cross-section based on dispersion relationships, given by Eqs. 4.8 and 4.9. The solid line in Fig. 4.1(a) represents the fit for the resulting $\sigma = 1.796 \times 10^{-46}$ and $\varepsilon = 0.543$ values as listed in Table 4.2. The difference between the calculated and predicted values and the corresponding uncertainty range by the present fit representation is plotted on the lower panel (b) in Fig. 4.1.

Since N_2 is a non-spherical molecule significant depolarization effects are expected in the deep-UV domain. To estimate how strong these effects are, a

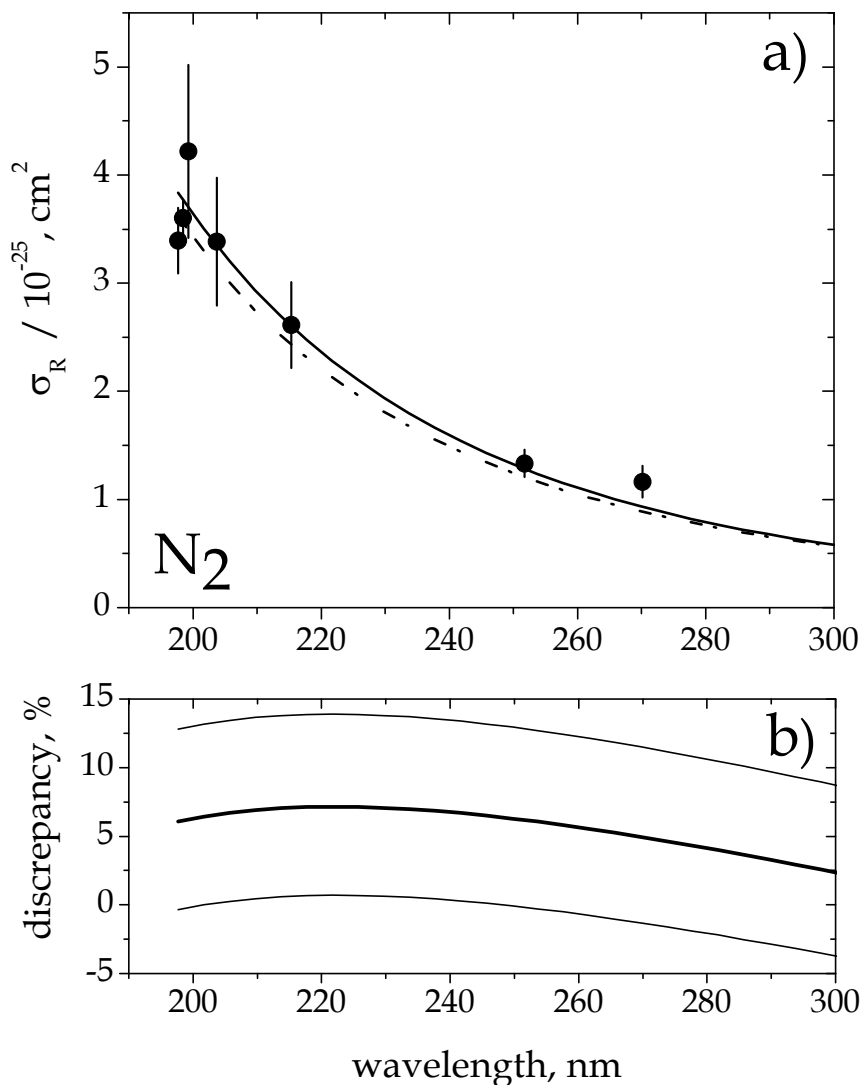


Figure 4.1:

(a): The Rayleigh scattering cross-section behavior of N₂ derived from a combined cavity ring-down pressure-ramp experiment (•). The dashed line represents the Rayleigh scattering cross-section values, calculated from dispersion data for refractive indices taken from [66] and for a King correction derived in [18]. The solid line shows the fit representation for $\sigma = 1.796(56) \times 10^{-46}$ and $\epsilon = 0.534(3)$.

(b): The difference between calculated (from the dispersion) and fitted (from CRDS measurements) values, plotted as a solid line. The dashed lines indicate the confidence interval, based on the uncertainties of σ and ϵ (Table 4.2).

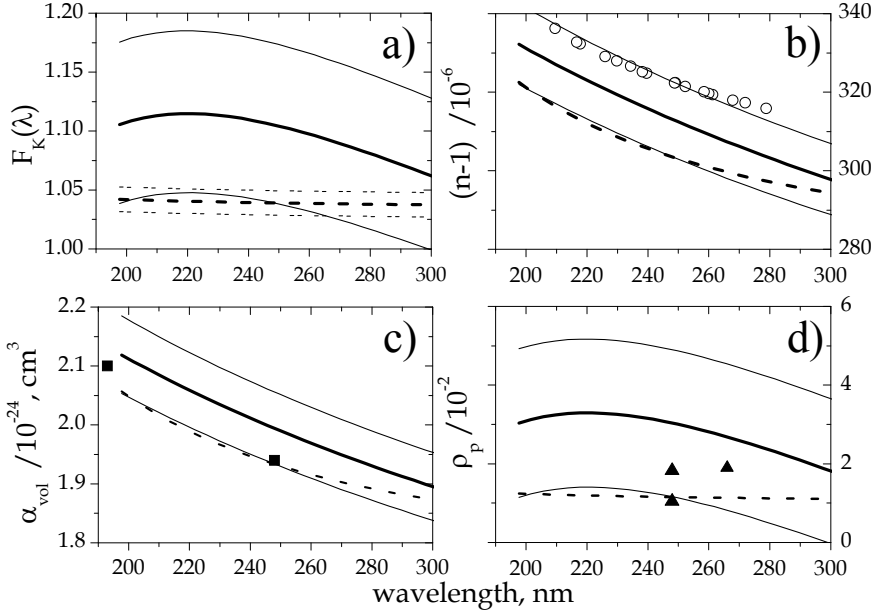


Figure 4.2: Different comparisons between the present experimental results and previous dispersion data:

(a): Calculated behavior of the N_2 King correction factor: the black dashed line follows Eq. 4.9 [18] and the thin dashed lines indicate the corresponding error margins. The solid black line is calculated from the present Rayleigh scattering cross-section measurements and the refractive index values, given by Eq. 4.8. Error margins are again plotted as thin solid lines.

(b): Calculated behavior of the N_2 refractive index: the black dashed line corresponds to the dispersion relationship, given by Eq. 4.8, ($\circ$) – indicate the refractive index measurements from [66] at 273.15 K. The black solid line corresponds to refractive index values as calculated from the present Rayleigh scattering cross-section measurements and the King correction factor, given by Eq. 4.9. The error margins are indicated by thin solid lines.

(c): N_2 molecular volume polarizability values (black solid line), calculated from the fit representation of the present Rayleigh scattering cross-section measurements. The error margins are indicated by thin solid lines. The dashed line represents values, calculated from the dispersion formulas (Eqs. 4.8, 4.9) for the refractive index and King correction factor. The reported results on $\alpha(\lambda)$ in [15] are indicated by ($\blacksquare$).

(d): Calculated values of the N_2 depolarization ratio, derived from Eq. 4.8 for the King correction factor [18] are shown by a black dashed line. The black solid line corresponds to the calculated values, derived from the present Rayleigh scattering cross-section measurements. Error margins are shown as thin solid lines. The ($\blacktriangle$) – correspond to direct depolarization measurements as reported in [94].

further quantitative analysis of the experimental data set has been performed and refractive index and King correction factor values have been derived using the current fit representation, as defined in Eq. 4.5. The King correction factor values are derived using Eq. 4.2, assuming that the dispersion of the refractive index is equal to Eq. 4.8. A similar approach has been used to calculate the refractive index values for N₂, using Eq. 4.9. The molecular volume polarizability values have been calculated directly from Eq. 4.1, assuming that the Rayleigh scattering cross-sections are equal to those, predicted by the fit representation, as given by Eq. 4.5. The values of the depolarization ratio for polarized light have been calculated using Eq. 4.3. The resulting values for $F_k^{exp}(\lambda)$, $n^{exp}(\lambda)$, $\alpha_{vol}^{exp}(\lambda)$ and $\rho_p^{exp}(\lambda)$ are plotted in Figs. 4.2(a) through (d), respectively (see figure caption for detailed information). In all cases the confidence intervals, based on the experimental uncertainties are plotted as well. This shows that the values calculated from the fit representation using the measured Rayleigh scattering cross-sections are in good quantitative agreement (within the specified uncertainty) with data available from literature [15, 18, 66]. The deviation between the calculated values of the King correction factor, refractive index, molecular volume polarizability and the depolarization ratio becomes smaller towards 300 nm. It should be noted that the difference between values of the King correction factor, derived from the present Rayleigh scattering cross-sections determinations and the values, available from [18] is larger than that of the refractive index data. This is also reflected in the discrepancy between calculated and theoretical values of the molecular volume polarizability and the depolarization ratio. The reason for this is a general lack of depolarization measurements in the deep-UV domain (shorter than 300 nm).

The outcome confirms that the light extinction in the deep-UV for N₂ is fully determined by Rayleigh scattering and there is no evidence for a (detectable) absorption onset in the studied wavelength region.

4.3.2. Methane

Six data points for the wavelength-dependent Rayleigh cross-section of CH₄ were measured and are plotted in Fig. 4.3.

Methane refractive index data have been reported only in the interval between 325.13 and 632.99 nm, based on the polarizability measurements given

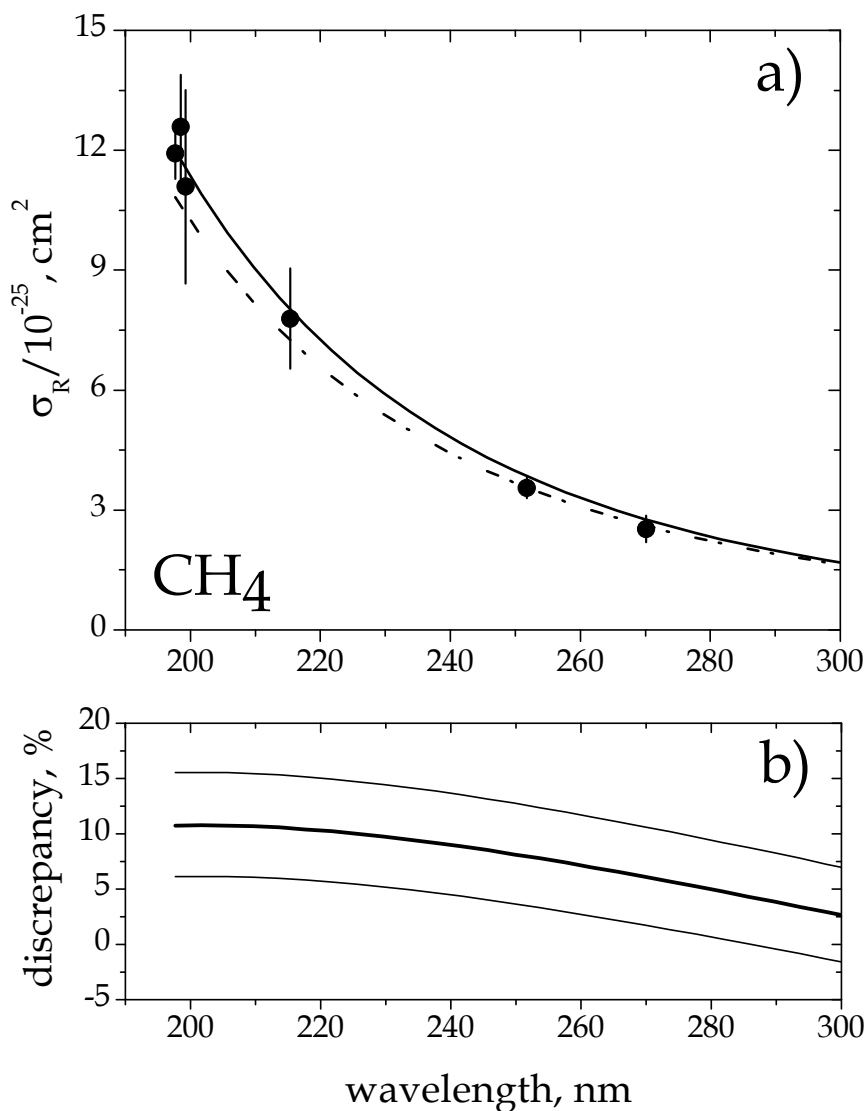
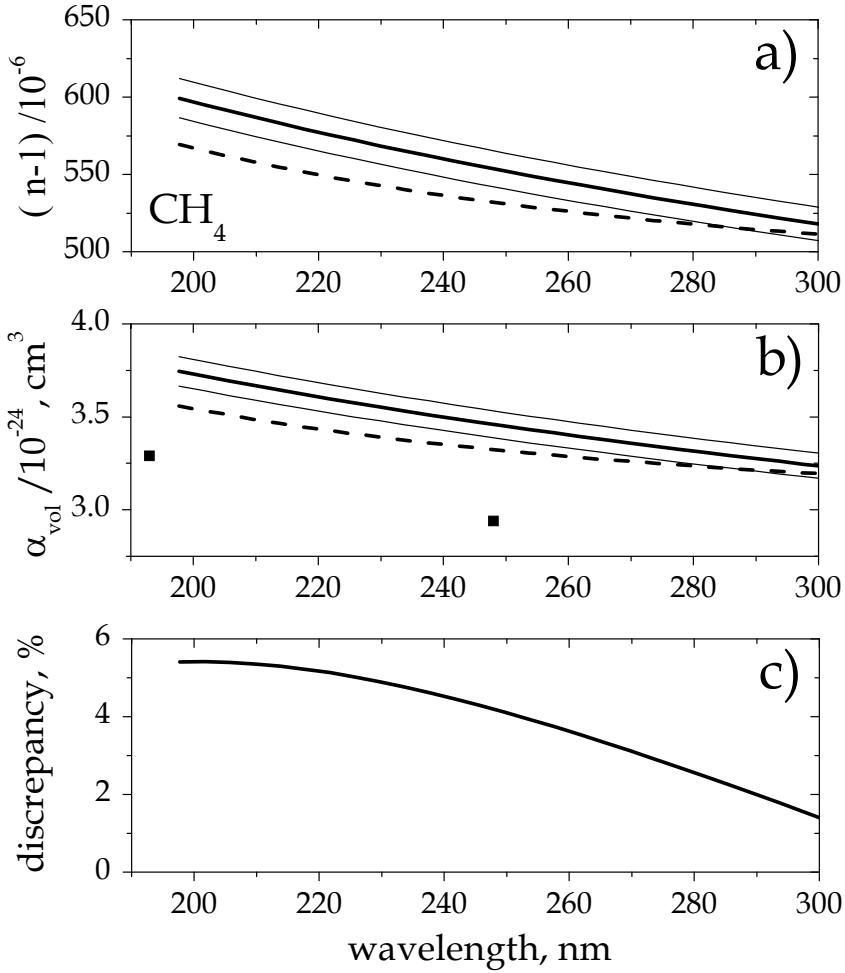


Figure 4.3:

(a): Rayleigh scattering cross-section behavior of CH_4 derived from a combined CRDS – pressure-ramp measurement (•) and the fit representation (solid line) for $\sigma = 0.94(2) \times 10^{-46}$ and $\epsilon = 0.699(2)$. The dashed line represents the Rayleigh scattering cross-sections values, calculated from dispersion relationships [52].

(b): Difference between calculated and fitted values is shown as a black solid line. Solid thin lines indicate the error margins.

**Figure 4.4:**

(a): CH₄ refractive index values, calculated from the Rayleigh scattering cross-section measurements (black solid line). The error margins are indicated by thin solid lines. The black dashed line corresponds to the dispersion formula for the refractive index, given by Eq. 4.10.

(b): Values of the CH₄ molecular volume polarizability, calculated from the present study (black solid line). The error margins are plotted as solid grey lines. The dashed line represents the calculated values, calculated from the dispersion formula for the refractive index [52]. The (■) correspond to data, calculated in [99] from results obtained in [101].

(c): Discrepancy between the refractive index values derived from the present Rayleigh scattering cross-section measurements and predicted refractive index values, using the dispersion formula as given by Eq. 4.10.

in [98]. Other information, particularly depolarization measurements, is largely lacking. A comparison with the depolarization effects for the symmetrically comparable CCl_4 at 632.8 nm suggests that these are small [17] and it seems reasonable to set $F_k(\lambda)=1$ for methane. The dispersion formula for the refractive index, as extracted in [52] from the experimental data in [98], is used to calculate the Rayleigh scattering cross-sections:

$$n(\lambda) - 1 = \left(46662 + \frac{4.02 \times 10^{-6}}{\lambda^2} \right) \times 10^{-8} \quad (4.10)$$

In view of the very limited number of refractive index measurements the accuracy of this equation is assumed to be on the level of 4% [52]. Extrapolation to the deep-UV, as necessary here, most likely gives rise to additional uncertainty.

The values that result from the extinction measurements are plotted in Fig. 4.3(a). For a quantitative estimate of the difference between the measured and predicted $\sim 1/\lambda^4$ Rayleigh scattering behavior in CH_4 (based on dispersion), a non-linear least square fit along Eq. 4.5 has been made that is included in Fig. 4.3 as well. The resulting values for σ and ε are listed in Table 4.2. The discrepancy between the dispersion related and CRDS derived cross-sections is below 10%, as can be seen from Fig. 4.3(b).

As for molecular nitrogen, values of the refractive index and the molecular volume polarizability have been also derived for methane. For this depolarization effects are neglected and $F_k(\lambda)=1$ is taken for all wavelengths. The resulting curves for the refractive index and molecular volume polarizability are plotted in Figs. 4.4(a-b). The estimated discrepancy between the calculated and predicted values of the refractive index values is less than 6% (Fig. 4.4 (c)), originating from inaccuracies in the CRDS measurements and from the extrapolation of the dispersion formula for the refractive index in CH_4 . This is comparable with the absolute uncertainty of the dispersion formula of $\sim 4\%$ in the 325–632 nm region [52, 98]. Also here, the outcome confirms that the deep-UV light extinction is fully governed by Rayleigh scattering and the refractive index in CH_4 in the deep-UV domain can be described by the dispersion relationship in form of Eq. 4.10 within a few percents uncertainty. The molecular volume polarizability values, calculated from the present CRDS

measurements are found to be in a good agreement with the data available from [99].

It is important to note that the purity of the CH₄ gas used is critical. In a first set of measurements with purity less than 99.5% and most likely hydrocarbon like pollutions an absorption onset was found around ~ 210 nm that definitely cannot be attributed to methane.

4.3.3. Sulphur hexafluoride

In Fig. 4.5 the data point set for the wavelength-dependent Rayleigh cross-section of SF₆ is shown.

In the literature a limited data set of SF₆ refractive indices and extinction coefficient measurements have been reported [88, 89, 52]. Sulphur hexafluoride is a highly symmetrical molecule, so $F_k(\lambda) = 1$ is used. The derived empirical formula for dispersion of the refractive index, based on measurements at 633 and 1300 nm [100] has been used in the UV-VIS [31, 52, 79]:

$$n(\lambda) - 1 = \left(71517 + \frac{5 \times 10^{-6}}{\lambda^2} \right) \times 10^{-8} \quad (4.11)$$

The data points follow a dashed line that represents predictions of Rayleigh scattering cross-section values based on available dispersion data, as can be seen in Fig. 4.5. This line coincides with a solid line that is the fit representation for $\sigma = 17.897 \times 10^{-46}$ and $\varepsilon = 0.490(4)$ as summarized in Table 4.2. The measured and predicted Rayleigh scattering cross-sections agree within 2% for the deep-UV domain, and the overall picture indicates that light extinction in SF₆ gas is governed by Rayleigh scattering in the entire studied wavelength interval.

Additional information is available from Fig. 4.6 that shows the refractive index (solid black line in Fig. 4.6(a)) and the molecular volume polarizability (solid line in Fig. 4.6(b)) values, derived from the fit representation of the measured Rayleigh scattering cross-section values. The dashed lines in Fig. 4.6 show the predicted values derived from the Rayleigh scattering cross-section, based on dispersion data available from literature [52]. The comparison made for calculated molecular volume polarizability values shows that SF₆ has the largest polarizability among all investigated gas species. The error margins

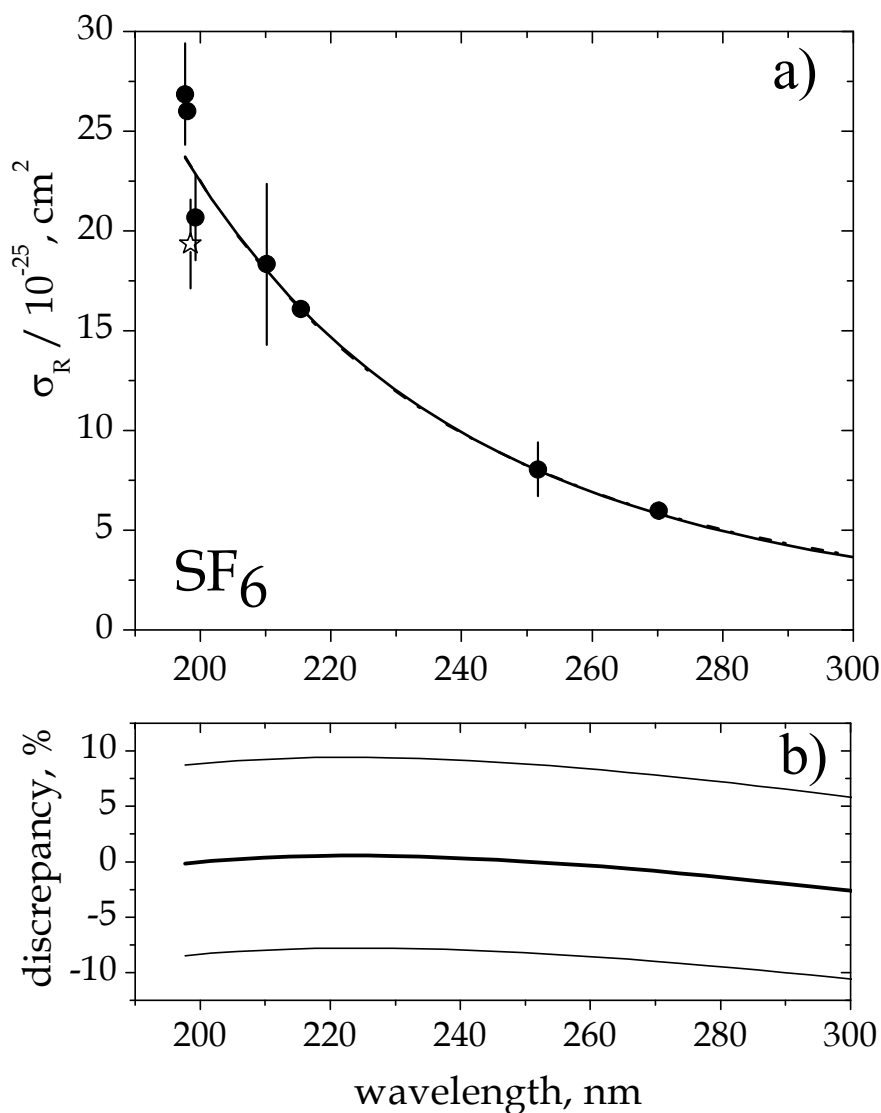


Figure 4.5:

(a): The SF₆ Rayleigh scattering cross-section behavior derived from a combined CRDS and pressure-ramp approach (●) and data available from [31] - (☆). The dashed line represents the calculated Rayleigh scattering cross-sections values and the solid line corresponds to the fit representation for $\sigma = 17.90(76) \times 10^{-46}$ and $\epsilon = 0.490(4)$.

(b): Difference between calculated and fitted values is shown as a solid black line. Solid thin lines indicate the error margins.

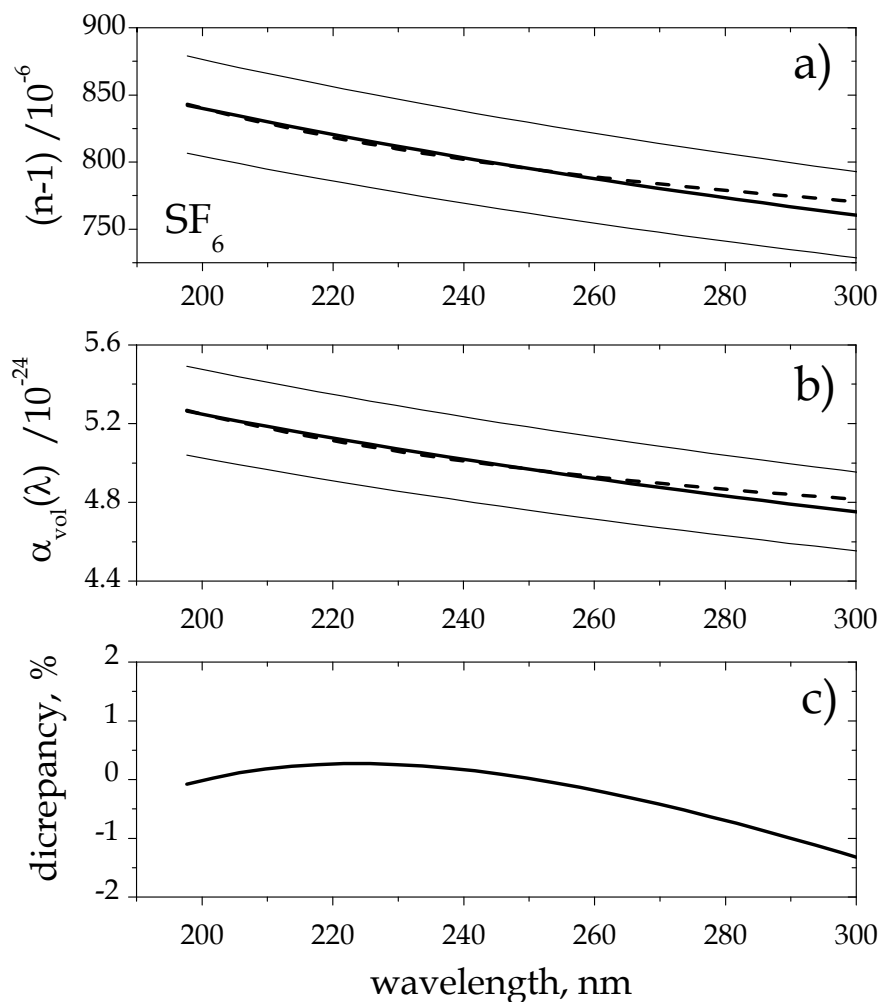


Figure 4.6:

(a): SF₆ refractive index values, calculated from the Rayleigh scattering cross-section measurements (black solid line). The error margins are given by grey solid lines. The black dashed line corresponds to the dispersion formula for the refractive index taken from [100] and given by Eq. 4.11 [52].

(b): The molecular volume polarizability behavior, calculated from the present CRDS measurements (black solid line). The error margins are plotted as solid grey lines. The dashed line represents the calculated values, calculated from the dispersion formula for the refractive index [52].

(c): Discrepancy between the refractive index values, derived from the present Rayleigh scattering cross-section measurements and the predicted values using the dispersion formula, as given by Eq. 4.11.

that originate from the absolute uncertainty of the σ and ε values are shown as grey solid lines in Fig. 4.6 as well. The literature values [52, 100] are indicated for comparison. From the numerical analysis it can be concluded that despite the lack of laboratory data, the refractive index of SF₆ follows the dispersion formula, given by Eq. 4.11, within a few percent uncertainty, even when extrapolated to the deep-UV region.

4.4. Conclusion

Extinction coefficients have been measured for gaseous N₂, CH₄ and SF₆ at room temperature between 197.7 and 270.15 nm applying cavity ring-down spectroscopy to pressure-ramp measurements. A non-linear squares fit of a $\sim 1/\lambda^4$ like function shows the actual behavior of the Rayleigh scattering and gives an estimate of the discrepancy between measured and predicted values, based on dispersion formulas as available from literature. The light extinction in the deep-UV is for all three molecular systems dominated by Rayleigh scattering. Due to the present lack of experimental data for light extinction cross-sections and refractive indices between the deep-UV and visible domain, it is not yet possible to construct a universal empirical relation that accurately predicts the $1/\lambda^4$ Rayleigh scattering behavior for the entire UV–VIS region.

Acknowledgements

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Chapter 5:

Rotational analysis of the $A^2\Sigma^+_{(v=1,2)}-X^2\Pi_{(v=0)}$ electronic bands of $^{15}\text{N}^{18}\text{O}$

Deep-UV spectra of $^{15}\text{N}^{18}\text{O}$ have been recorded using cavity ring-down spectroscopy in the 205–216 nm region. The rotationally resolved spectra have been assigned for a first time as originating from the $v''=0$ $X^2\Pi_r$ states toward $v'=1$ and 2 vibrationally excited levels in the upper $A^2\Sigma^+$ state. Nearly 400 individual line positions have been identified and included in a fit using an effective Hamiltonian method. Accurate ground state values as available from literature were used to derive rovibronic parameters for the $A^2\Sigma^+_{v=1}$ and $A^2\Sigma^+_{v=2}$ levels. This results in the following values: $T_1 = 46427.21(2)$ cm^{-1} , $B_1 = 1.79635(7)$ cm^{-1} , $D_1 = 4.14(6) \times 10^{-6}$ cm^{-1} and $T_2 = 48636.04(2)$ cm^{-1} , $B_2 = 1.78055(18)$ cm^{-1} , $D_2 = 5.8(3) \times 10^{-6}$ cm^{-1} .

Introduction

NO is definitely one of the best studied diatomics in the deep-UV. This has several reasons. The strong NO absorption features that correspond to an excitation of the electronic γ -system ($A^2\Sigma^+ - X^2\Pi_r$) are of atmospheric interest and are used to derive NO column densities in the mesosphere. In addition, NO plays an important role in the atmospheric ozone budget; as a direct reaction product of N₂O oxidation NO contributes both to the tropospheric destruction of ozone and its photochemical formation through smog. Furthermore, NO is one of the major polluting products in combustion and the γ -system is suited for diagnostic tools [102]. Nitric oxide is also interesting from a pure fundamental point of view. Spectroscopic data of NO have been reported over the years by many groups providing a rather complete set of vibronic, rovibrational and pure rotational molecular parameters, for both the main isotopologue $^{14}\text{N}^{16}\text{O}$ [103–115] and several nitric oxide isotopologues $^x\text{N}^y\text{O}$, with $x = 14, 15$ and $y = 16, 17, 18$ [104, 107–108, 112–113, 115–121].

The present work has to be set within the latter context; it focuses on the analysis of so far unreported rovibronic transitions of the heaviest chemically stable NO isotopologue – $^{15}\text{N}^{18}\text{O}$ – in its γ -system. The analysis of the data benefits strongly from previous work for this isotopologue. Accurate $^{15}\text{N}^{18}\text{O}$ ground state values are available from a series of high resolution studies in the submillimeter and infrared [117, 120] and rotationally resolved electronic spectra have been reported in the anode glow of a two-column hollow-cathode discharge tube, yielding rovibronic parameters for the $A^2\Sigma_{(v=0)}^+ - X^2\Pi_{r(v=0,1,2,3)}$ bands [113]. In the present work this set of spectroscopic parameters is extended towards wavelengths deeper in the UV-range for excited levels in the upper electronic state: $A^2\Sigma_{(v=1,2)}^+ - X^2\Pi_{r(v=0)}$.

5.1. Experimental approach

The natural abundance of ^{15}N is about 0.37 % and of ^{18}O about 0.20 %, i.e. the natural abundance of the $^{15}\text{N}^{18}\text{O}$ is well below 10 ppm. Therefore, the experimental detection of $^{15}\text{N}^{18}\text{O}$ absorptions is based upon a sensitive cavity ring-down detection scheme of an isotopically enriched sample (99 % ^{15}N , 95 % ^{18}O) that is kept at a stationary pressure of 2 mbar in a 48 cm long cell. Special

mirror holders are mounted on opposite sites of the cell for precision alignment of plano-concave mirror sets ($r_{\text{curve}}=25$ cm) with a typical reflectivity of $R = 99.5\%$ and covering the 200–220 nm regime. Tunable laser deep-UV radiation, generated by frequency tripling the output of a 10 Hz Nd: YAG pumped dye laser, running near 600 nm (*Rhodamine-B*), is focused into the cell after spatial filtering. The light leaking out of the cavity is recorded by a photo-multiplier tube and subsequently digitized by a 350 MHz oscilloscope. Typical decay times amount to 300 ns and for each frequency value 50 decay events are averaged before a data point is stored. The final bandwidth of the UV light is about 0.5 cm^{-1} , sufficient to record many of the transitions resolved. However, as the spectrum is rather dense - as will be shown later - this does not prohibit spectral overlaps or blending. An absolute frequency calibration is achieved through a simultaneous I_2 -calibration. The accuracy in the absolute line position is estimated to be better than 0.1 cm^{-1} . All measurements have been performed at room temperature. Further experimental details are available from [83, 122, 123].

5.2. Results and discussion

The 46250 to 48800 cm^{-1} region has been scanned for transitions of the $(v',v'') = (1,0)$ and $(2,0)$ bands and these are found in the 46280 – 46800 and 48488 – 48760 cm^{-1} range, respectively. Referring to [103] and more specifically to [113] where a detailed description of the energy level scheme for the γ -system of NO is given, we expect to observe two sets of rovibronic transitions. These start from the $^2\Pi_{1/2}$ component - $R_{21\text{ff}}$, $R_{11\text{ee}}/Q_{21\text{fe}}$, $Q_{11\text{ef}}/P_{21\text{ff}}$ and $P_{11\text{ee}}$ - and the $^2\Pi_{3/2}$ component - $R_{22\text{ff}}$, $Q_{22\text{fe}}/R_{12\text{ee}}$, $Q_{12\text{ef}}/P_{22\text{ff}}$, $P_{12\text{ee}}$. Here we use the identification of branches as shown in Fig. 2 of [113]. As the experiment is performed at room temperature both components are populated and the overall spectrum consists of eight resolvable branches. The resolution in the present experiment does not permit to resolve the p -doublet components associated with the spin-rotation interaction in the excited state, as was done in Doppler-free excitation studies for the $A^2\Sigma^+_{(v=0)}$ state [124] and the $A^2\Sigma^+_{(v=1)}$ state [124] of the main isotopologue. Fig. 5.1 shows a scan in the band head region of the $P_{12\text{ee}}$ branch for the $A^2\Sigma^+_{(v=2)} - X^2\Pi_{r(v=0)}$ band. This is a relatively clean region of the spectrum where

transitions due to other isotopic species are very weak. From the figure it also becomes clear that higher rotational transitions are blended by lower J -values.

The vacuum wavenumbers for all sub-bands are summarized in Tables 5.1 and 5.2 for the $A^2\Sigma^+_{(v=1)} - X^2\Pi_{r(v=0)}$ and $A^2\Sigma^+_{(v=2)} - X^2\Pi_{r(v=0)}$, respectively. The assignment for transitions starting from $\Omega = 1/2$ and $3/2$ is indicated separately in the Tables. In total nearly 400 transitions (from both bands) have been included in a least squares analysis of $^2\Sigma - ^2\Pi$ transition. For the $^2\Pi$ ground state we have adopted the effective Hamiltonian as described in the analysis of the infrared spectrum by Amiot *et al.* [108, 117]. In the fit we have fixed the molecular constants for the $X^2\Pi$ ground state of $^{15}\text{N}^{18}\text{O}$ ground state constants to accurate values as available from literature. In three papers [113, 117, 120] consistent and nearly coinciding sets of constants have been published. We have adopted the values derived from the infrared spectrum [117], which are considered to give the most accurate representation of the $X^2\Pi_{(v=0)}$ ground state up to high J -levels as probed in the present work. The values used are: $B''_0 = 1.5482463 \text{ cm}^{-1}$, $D''_0 = 4.55190 \times 10^{-6} \text{ cm}^{-1}$, $A''_0 = 123.13895 \text{ cm}^{-1}$, and $A''_{D,0} = 1.5118 \times 10^{-4} \text{ cm}^{-1}$. Although only marginally relevant in the present study we also included Λ -doubling parameters for the ground state representation: $p''_0 = 1.06 \times 10^{-2} \text{ cm}^{-1}$ and $q''_0 = 7.93 \times 10^{-3} \text{ cm}^{-1}$.

For the $A^2\Sigma^+$ excited state the levels are represented by [125]:

$$E = T_v + B_v[x(x \mp 1)] - D_v[x^2(x \mp 1)^2] - \gamma_v(1 \mp x) \quad (5.1)$$

with $x = J + 1/2$. We have, in our fitting procedures, used a representation including the last term representing the ρ -doubling, which is inverted in the $A^2\Sigma^+$ state of NO (hence a negative value for γ). We have adopted a value $\gamma'' = -2.64 \times 10^{-3} \text{ cm}^{-1}$, based on results for other isotopologues [114, 115, 125], but we have verified that adopting $\gamma = 0$ does not influence the outcome on the other molecular constants in our fit. This means that effectively the representation:

$$E = T_2 + BN(N+1) - DN^2(N+1)^2 \quad (5.2)$$

may be used for both the lower ρ -doublet level (F_1 level, or e-level), with $J = N + 1/2$, and the upper ρ -doublet level (F_2 level, or f-level), with $J = N - 1/2$.

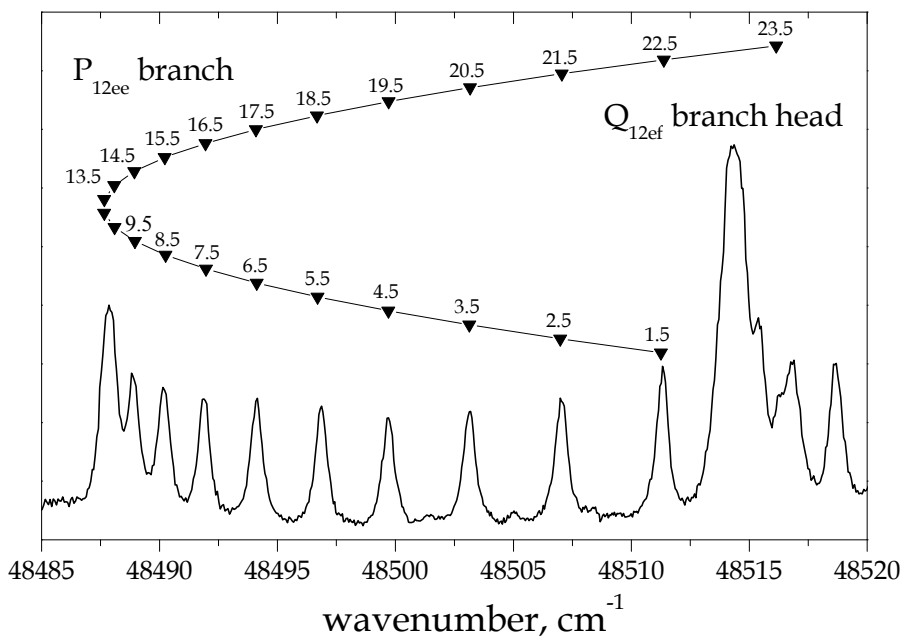


Figure 5.1: The P_{12ee} band head region of the $A^2\Sigma^+_{(v=2)} - X^2\Pi_{r(v=0)}$ band.

The calibrated line positions, as listed in Tables 5.1 and 5.2 for the observed (2,0) and (1,0) bands, were used in the input deck of a weighted least-squares minimization routine, where most of the unblended lines with good signal-to-noise ratio in the (1,0) band were given an estimated uncertainty of 0.1 cm^{-1} . For the lines in the (2,0) recorded at somewhat lower signal strength (due to lower CRD mirror reflectivity) a nominal uncertainty of 0.15 cm^{-1} was adopted, although for the best lines also 0.1 cm^{-1} was taken. Blended lines were assigned with larger uncertainties (depending on the amount of blending) and therewith given a lower weight in the fitting routine. The spectral region of the (2,0) band is covered with additional spectral lines, most likely originating from the (2,0) band of $^{15}\text{N}^{17}\text{O}$ spectrum; due to this overlap a number of lines are missing in Table 5.2. In the final round of fitting a total χ^2 of 257 is found for a data set with 380 degrees of freedom (386 lines and 6 parameters). The resulting values for the molecular constants are listed in Table 5.3. For comparison the molecular constants pertaining to the $A^2\Sigma^+_{(v=0)}$ level in $^{15}\text{N}^{18}\text{O}$ are also listed [113]. Also included in Table 5.3 are the estimated B -values for the excited state using the

Table 5.1a: List with rovibronic transitions in the $A^2\Sigma_{(v=1)}^+ - X^2\Pi_{r(v=0)}$ band for $\Omega = 1/2$. All values are in $[\text{cm}^{-1}]$. An index *b* indicates that the transition is blended; *bh* refers to overlapping lines in a band head.

J	P _{11ee}		Q _{11ef} / P _{21ff}		R _{11ee} / Q _{21fe}		R _{21ff}	
	Observed	o-c	observed	o-c	observed	o-c	observed	o-c
0.5			46427.37 ^b	0.17	46430.95	0.15		
1.5	46422.57	-0.06	46426.13 ^{bh}	-0.07	46433.44	0.04	46444.17 ^b	0.00
2.5			46426.13 ^{bh}	0.40	46436.62	0.08	46450.77 ^b	-0.12
3.5	46415.05 ^b	-0.03	46426.13 ^{bh}	0.32	46440.48	0.26	46458.04	-0.11
4.5	46411.89 ^b	-0.21	46426.13 ^{bh}	-0.29	46444.17 ^b	-0.26	46465.91	-0.04
5.5	46409.85 ^b	0.18	46427.37 ^b	-0.20	46449.20	0.02	46474.28 ^b	0.00
6.5	46407.60 ^b	-0.17	46429.19	-0.06	46454.46	0.00	46483.09 ^b	-0.05
7.5	46406.36 ^b	-0.05	46431.71 ^b	0.25	46460.33 ^b	0.05	46492.55	0.01
8.5	46405.55 ^{bh}	-0.03	46434.40	0.19	46466.71	0.08	46502.22	-0.25
9.5	46405.55 ^{bh}	0.27	46437.54	0.04			46512.85	-0.09
10.5	46405.55 ^{bh}	0.03	46441.62	0.30	46480.97	0.04	46524.15 ^b	0.22
11.5	46406.36 ^b	0.06	46445.75	0.08	46488.95	0.08	46535.57	0.11
12.5	46407.60 ^b	0.00	46450.77	0.22	46497.27	-0.08	46547.44	-0.07
13.5	46409.32	-0.12	46455.91	-0.06	46506.55	0.19	46560.01	-0.09
14.5	46411.89 ^b	0.08	46461.98	0.06	46516.02	0.12	46573.21	0.00
15.5	46415.05 ^b	0.33	46468.46	0.07	46526.16	0.20	46586.99	0.14
16.5	46418.16	0.01	46475.40	0.00	46536.56	0.00	46601.04 ^b	0.03
17.5	46422.13	0.02	46483.09	0.16			46615.69	-0.01
18.5			46491.07	0.07	46559.33	0.01		
19.5	46431.71	0.08	46499.45	-0.14	46571.48	-0.02	46646.60	-0.06
20.5			46508.79	0.09	46584.16	-0.03	46662.92	0.00
21.5	46443.31	0.05	46518.52	0.17	46597.60	0.19	46679.74	0.04
22.5	46449.85	-0.01	46528.35	-0.17	46611.19	0.04	46696.74	-0.27
23.5	46457.04 ^b	0.05			46625.25	-0.17	46714.75	-0.08
24.5	46464.65	0.00	46550.35	-0.08			46733.05	-0.12
25.5	46472.63	-0.21					46751.89	-0.14
26.5	46481.40	-0.14	46574.31 ^b	-0.12			46771.25	-0.16
27.5	46490.63	-0.15	46587.67	0.45			46791.54	0.23
28.5								
29.5	46510.98 ^b	0.17	46614.18 ^b	-0.17				
30.5	46521.45	-0.17	46628.48	-0.22				
31.5			46643.58	0.01				

Table 5.1b: List with rovibronic transitions in the $A^2\Sigma_{(v=1)}^+ - X^2\Pi_{r(v=0)}$ band for $\Omega = 3/2$. All values are in $[\text{cm}^{-1}]$. An index *b* indicates that the transition is blended; *bh* refers to overlapping lines in a band head.

J	P _{12ee}		Q _{12ef} / P _{22ff}		R _{12ee} / Q _{22fe}		R _{22ff}	
	observed	o-c	observed	o-c	observed	o-c	observed	o-c
0.5								
1.5	46302.37	-0.08	46306.33 ^{bh}	0.29	46313.61 ^b	0.38	46324.02 ^b	0.01
2.5	46298.18	-0.02	46305.54 ^{bh}	0.15	46316.15 ^b	-0.02	46330.54	0.00
3.5	46294.40	-0.01	46305.20 ^b	0.01	46319.55	-0.01	46337.61 ^b	0.08
4.5	46291.05	-0.02	46305.54 ^{bh}	0.09	46323.38	-0.03		
5.5	46288.06	-0.13	46306.33 ^{bh}	0.16	46327.66	-0.06	46352.86	-0.01
6.5	46285.72	-0.06	46307.30	-0.04	46332.37	-0.12	46361.27	0.05
7.5	46283.81	-0.01	46308.94	-0.04	46337.61	-0.10	46370.04 ^b	0.00
8.5	46282.30	-0.02	46310.99	-0.08	46343.39	-0.01	46379.45	0.15
9.5	46280.97 ^{bh}	-0.31	46313.67 ^b	0.05	46349.51	-0.03	46388.89 ^b	-0.14
10.5	46280.60 ^{bh}	-0.10	46316.31 ^b	-0.33			46399.17	-0.05
11.5	46280.60 ^{bh}	0.01	46320.11	0.00	46363.25	0.05	46409.85	-0.02
12.5	46280.97 ^{bh}	0.03	46324.02	-0.03	46370.67	-0.06	46421.05	0.07
13.5	46281.78	0.03	46328.40	-0.06	46378.72	0.00	46432.52	-0.03
14.5	46283.07	0.04	46333.21	-0.11	46387.17 ^b	0.00		
15.5	46284.82	0.04	46338.63	-0.03	46396.1	0.01	46457.04	-0.03
16.5	46286.92	-0.08	46344.70	0.24	46405.55	0.08	46470.07	0.04
17.5	46289.64	-0.05	46350.78 ^b	0.05	46415.05	-0.27	46483.50	0.05
18.5	46292.86	0.01	46357.46	-0.01	46425.41	-0.23	46497.52 ^b	0.18
19.5	46296.58	0.10	46364.61	-0.07	46436.62 ^b	0.19	46511.69	0.00
20.5	46300.65	0.07	46372.34	-0.02	46447.58	-0.10	46526.49	-0.03
21.5	46305.20 ^b	0.04	46380.42	-0.09	46459.37	-0.04	46541.78	-0.03
22.5	46310.17	-0.05	46388.89 ^b	-0.25	46471.61	0.00	46557.52	-0.05
23.5	46315.90	0.15			46484.30	0.02	46573.68	-0.12
24.5	46321.82	0.05	46407.60 ^b	-0.23	46497.52	0.09	46590.44	-0.07
25.5	46328.40 ^b	0.14	46418.00	0.12	46510.98	-0.08		
26.5	46335.25	0.02			46525.03	-0.13	46625.25	-0.08
27.5	46342.65	-0.04	46439.34	-0.10	46539.73	-0.01	46643.58	0.12
28.5	46350.78 ^b	0.15			46554.57	-0.23		
29.5	46359.13	0.07						
30.5	46368.07	0.10	46475.4	0.01	46586.27 ^b	-0.08		
31.5	46377.39	0.01			46602.78	-0.07		
32.5	46387.17 ^b	-0.10	46501.99	0.21				
33.5	46397.98 ^b	0.33	46515.89	0.19				
34.5	46408.48	-0.04	46529.81	-0.30				
35.5	46420.00	0.11	46545.11	0.10				
36.5	46431.71 ^b	-0.04	46560.77	0.36				
37.5	46444.17 ^b	0.07	46576.03	-0.26				
38.5	46457.04	0.09	46592.52	-0.15				
39.5	46470.31	0.01						
40.5								
41.5	46498.33	-0.17						

Table 5.2a: List with rovibronic transitions in the $A^2\Sigma_{(v=2)}^+ - X^2\Pi_{r(v=0)}$ band for $\Omega = 1/2$. All values are in $[\text{cm}^{-1}]$. An index b indicates that the transition is blended.

J	P _{11ee}		P _{21ff} / Q _{11ef}		Q _{21fe} / R _{11ee}		R _{21ff}	
	Observed	o-c	observed	o-c	observed	o-c	observed	o-c
0.5			48635.72 ^b	-0.31	48639.95 ^b	0.35		
1.5	48631.33	-0.13	48634.81 ^{bh}	-0.19	48642.51 ^b	0.37		
2.5	48627.44	0.06	48634.81 ^{bh}	0.34	48645.21 ^b	0.02	48659.44	0.03
3.5	48623.98	0.17	48634.81 ^{bh}	0.36	48648.48 ^b	-0.26	48666.79 ^b	0.28
4.5	48620.71	-0.04	48634.81 ^{bh}	-0.13	48652.64 ^b	-0.15		
5.5			48635.72 ^b	-0.20			48682.26	0.04
6.5	48615.85 ^b	-0.28	48637.65 ^b	0.24			48691.30 ^b	0.47
7.5	48614.91 ^b	0.34	48639.95 ^b	0.54	48668.03	0.06	48700.05 ^b	0.11
8.5	48613.33 ^{bh}	-0.19	48642.54 ^b	0.64	48673.91	-0.12	48709.54 ^b	-0.01
9.5	48613.33 ^{bh}	0.36	48645.21 ^b	0.31	48680.62	0.03	48719.30 ^b	-0.35
10.5	48613.33 ^{bh}	0.41	48648.48 ^b	0.09	48687.64 ^b	-0.01	48730.14 ^b	-0.12
11.5	48613.33 ^{bh}	-0.04	48652.49 ^b	0.10	48695.26	0.06	48741.52 ^b	0.16
12.5	48614.91 ^b	0.59	48656.94 ^b	0.06	48703.25	-0.01	48752.94	-0.01
13.5	48615.85 ^b	0.08	48661.68 ^b	-0.19	48711.68	-0.12		
14.5			48667.37 ^b	0.01	48720.48 ^b	-0.37		
15.5	48620.71 ^b	0.55	48673.48 ^b	0.14				
16.5	48622.81 ^b	-0.29	48679.77	-0.04	48740.60 ^b	0.20		
17.5	48626.64	0.11	48686.84	0.06	48750.83	-0.09		
18.5	48630.51	0.06	48694.17	-0.06	48761.99	0.07		
19.5			48701.87 ^b	-0.31				
20.5			48710.57	-0.04				
21.5			48719.30 ^b	-0.23				
22.5	48651.07	0.02	48728.88 ^b	-0.06				
23.5			48738.71 ^b	-0.11				
24.5			48749.16	-0.03				

Table 5.2b: List with rovibronic transitions in the $A^2\Sigma^+_{(v=2)} - X^2\Pi_{r(v=0)}$ band for $\Omega = 3/2$. All values are in $[\text{cm}^{-1}]$. An index *b* indicates that the transition is blended.

J	$P_{12\text{ee}}$		$Q_{12\text{ef}} / P_{22\text{ff}}$		$R_{12\text{ee}} / Q_{22\text{fe}}$		$R_{22\text{ff}}$	
	observed	o-c	observed	o-c	observed	o-c	observed	o-c
0.5								
1.5	48511.32 ^b	0.04			48521.76 ^b	-0.21	48532.70	0.05
2.5	48507.04 ^b	0.04	48514.42 ^{bh}	0.29	48524.68	-0.13	48538.79 ^b	-0.27
3.5	48503.13 ^b	-0.01	48514.42 ^{bh}	0.59	48528.11 ^b	0.03	48545.53 ^b	-0.35
4.5	48499.71	0.00	48514.42 ^{bh}	0.45	48531.68	-0.09	48553.08	-0.05
5.5	48496.86 ^b	0.15	48514.42 ^{bh}	-0.11			48560.74	-0.07
6.5	48494.11 ^b	-0.02	48515.53	0.02	48540.28	-0.15	48568.93	0.02
7.5	48491.90 ^b	-0.08	48516.68	-0.24	48545.53 ^b	0.13	48577.35	-0.08
8.5	48490.17 ^b	-0.09	48518.69	-0.07	48550.80	0.01	48586.38	0.00
9.5	48488.90 ^b	-0.06	48520.98	-0.04	48556.69	0.08	48595.93	0.18
10.5			48523.68	-0.03	48562.80 ^b	-0.06	48605.57 ^b	0.02
11.5			48526.97 ^b	0.14	48569.44 ^b	-0.09	48615.85 ^b	0.08
12.5	48487.85 ^{bh}	0.19	48530.42	0.04	48576.54 ^b	-0.09	48626.64 ^b	0.22
13.5	48487.85 ^{bh}	-0.23			48584.19	0.03	48637.65 ^b	0.16
14.5	48488.90 ^b	-0.04	48538.79 ^b	0.02	48592.10	-0.02		
15.5	48490.17 ^b	-0.06	48543.62	0.02	48600.49	-0.01		
16.5	48491.90 ^b	-0.05	48548.77	-0.10	48609.25	-0.07	48673.48 ^b	0.22
17.5	48494.11 ^b	0.01	48554.67	0.10	48618.78 ^b	0.22	48685.95	-0.09
18.5	48496.86 ^b	0.17	48560.74	0.04	48628.29 ^b	0.06	48699.30	0.05
19.5	48499.71 ^b	-0.01	48567.33	0.06			48712.73 ^b	-0.15
20.5	48503.13 ^b	-0.05	48574.41 ^b	0.15			48726.96	0.02
21.5	48507.04 ^b	-0.03	48581.56	-0.14				
22.5	48511.32	-0.08	48589.42 ^b	-0.14	48671.57 ^b	0.35	48756.71 ^b	0.38
23.5	48516.20	0.03	48597.87	0.01	48683.10	0.05		
24.5	48521.32 ^b	-0.06	48606.73	0.14	48695.26 ^b	-0.05		
25.5	48526.97 ^b	-0.05	48615.85 ^b	0.09	48707.69	-0.30		
26.5			48625.54 ^b	0.18	48721.32	0.21		
27.5								
28.5					48748.49	-0.16		

Table 5.3: Molecular parameters for $v=0,1$ and 2 in the $A^2\Sigma^+$ state of $^{15}\text{N}^{18}\text{O}$.

$A^2\Sigma^+$	$v = 0^a$	$v = 1^b$	$v = 2^b$
T	44130.244 (2)	46427.21 (2)	48636.04 (2)
B (observed)	1.812980 (7)	1.79635 (7)	1.78055 (18)
B (estimated)	1.813000	1.796685	1.780370
D (10 ^e)	4.694 (6)	4.14 (6)	5.8(3)

^a Taken from [113].

^b Present work

standard relation $B_v = B_e - \alpha_e(v + 1/2)$, where the $^{14}\text{N}^{16}\text{O}$ equilibrium values as available from [113] are used to derive $B_e(^{15}\text{N}^{18}\text{O}) = 1.821157 \text{ cm}^{-1}$ and $\alpha_e(^{15}\text{N}^{18}\text{O}) = 1.631 \times 10^{-2} \text{ cm}^{-1}$. From the table it becomes clear that the values derived here are close to the estimated values.

We note that the findings on the centrifugal distortion constants D for the various vibrational levels are close to each other, but still lacking some consistency. This small deviation may be due to a perturbation in the excited state, which is not accounted for in our fit, and consequently at this stage the D -constants should be regarded primarily as effective parameters.

In conclusion we have performed a rotational analysis of two bands in the γ -system of the $^{15}\text{N}^{18}\text{O}$ isotopologue yielding for a first time accurate molecular constants for the $A^2\Sigma^+_{(v=1)}$ and $A^2\Sigma^+_{(v=2)}$ vibrational levels.

Acknowledgments

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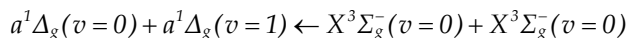
Chapter 6:

Temperature-dependent cross-sections of O₂-O₂ collision-induced absorption resonances at 477 and 577 nm

Two collision-induced absorption features of oxygen have been investigated by means of the laser based cavity ring-down technique at pressures between 0 and 1000 hPa and at temperatures in the range 184–294 K. Peak cross-sections, resonance widths and integrated cross-sections, as well as spectral profiles, have been determined for the broad O₂-O₂ resonances centered at 477 and 577 nm. Results are compared with previous measurements to establish updated temperature dependence for the cross-sections of both resonances, yielding integrated cross-sections, that exhibit a minimum near 200 K and that increase in a near-linear fashion in the atmospherically relevant range of 200–300 K. A significant increase in the widths of the resonance profiles upon temperature increase is firmly established. Parameters and temperature-dependent trends for the shape and strengths of the resonances are produced, that can be implemented in cloud retrieval in atmospheric Earth observation.

Introduction

The oxygen molecule has a series of collision-induced absorption (CIA) resonances, involving molecular pairs that jointly absorb a single photon, whereby both molecules undergo a transition to an electronically excited state. These resonances were discovered in the study of liquid oxygen in 1933 by Ellis and Kneser [126], and even that early-just a few years after the advent of molecular quantum mechanics-were understood as bi-molecular absorptions and could correctly be assigned in terms of quantum numbers. The resonance at 477 nm is assigned as an excitation of two oxygen ground-state molecules, one into the $a^1\Delta_g(v=0)$ state and one into the $b^1\Sigma_g^+(v=0)$ state. The resonance near 577 nm can be assigned to the transition:



The absorption strength of the collision-induced features is rather high, when compared to monomer absorption, because these phenomena are associated with symmetry breaking. Whereas, the O₂ molecule is homonuclear and exhibits no dipole moment, all three lowest electronic states connected in the visible spectrum of oxygen have *gerade* symmetry, and hence transitions between these states are highly forbidden. Binary collisions give rise to distortions of the electronic wave functions and to a breaking of the inversion symmetry, which then permits optical transitions. It is noted further that the two collision-induced features at 477 and 577 nm are not associated with monomer absorption at the same wavelengths; that would contradict the distribution of excitation energy over the two collision partners. The fact that the 577 nm resonance overlaps the $b^1\Sigma_g^+ - X^3\Sigma_g^-(3,0)$ monomer band is a happenstance coincidence. As was discussed by Naus and Ubachs [127], the interference of both phenomena can be avoided experimentally.

Atmospheric observations of the features related to O₂ - CIA date back to the 19th century [6]. Since then a large number of laboratory investigations have been pursued to quantitatively assess the cross-sections related to the collisional absorption features. Accurate results in the high pressure regime were obtained by Dianov-Klokov [128] and Greenblatt *et al.* [129], while focus on low temperature effects prevailed in the studies by Ewing and coworkers [130, 131]. Perner and Platt [132] performed measurements on atmospheric

absorptions at long path length, Pfeilsticker *et al.* [133] determined altitude profile spectral features of (O₂)₂ absorption bands from balloon observations, and Wagner *et al.* [134] detected the oxygen collisional features in the Earth's atmosphere against the moonlight. In [133] a value for the enthalpy of formation of the O₄ complex was derived, in good agreement with findings from molecular scattering experiments [135, 136].

Besides these investigations on the *electronic* CIA features observable in the visible wavelength range, oxygen collisional features were also studied at longer wavelengths, and there exists an extensive literature on this subject. For the 6 μ m vibrational excitation we cite the laboratory investigations by Orlando *et al.* [137] and Baranov *et al.* [138]. The same vibrational CIA band was investigated under stratospheric conditions with use of a balloon-borne FT-interferometer by Rinsland *et al.* [139]. In the far-infrared domain oxygen exhibits translation-rotation spectrum with collisional features, which was investigated experimentally by Bosomworth and Gush [140] and theoretically by Boisssoles *et al.* (see [141] and references cited therein). At the other end of the spectrum, in the deep-ultraviolet, absorption features were observed, that were in part ascribed to O₂-O₂ resonances [142].

Theoretical treatment of oxygen and its dimer dates back to 1924 when Lewis proposed the existence of a weak chemical bond establishing an O₄ molecule that would not be paramagnetic [143]. While Lewis focused on the spin aspects, Pauling singled out the O₄ molecule for its exceptionally strong Van der Waals forces that might give rise to a chemical bond [144]. Thus, *ab initio* calculations on the oxygen dimer are complicated by the fact that both the Van der Waals interaction and the spin interactions between two paramagnetic molecules play a role. The O₂ triplet ground state gives rise to singlet, triplet and quintet states in the dimer, therewith giving rise to a system with fine structure splitting [145]. Further complications arise from tunneling through internal barriers [146]. Calculations of full potential energy surfaces of the O₂-O₂ Van der Waals complex yield minimum energy structures for the singlet and triplet states in a parallel planar *D*_{2h} geometry at an equilibrium inter-molecular separation of (6.1–6.2)*a*₀ at binding energies of 154 and 140 cm⁻¹ [147]. Later, also *ab initio* potentials involving electronically excited O₂ were calculated [148]. Such calculations provide a basis for an assignment of the rotational

structure in the bound dimer systems [149].

Whether the two O_2 molecules form a bound Van der Waals complex, or are essentially unbound and absorb the photon during a collisional fly-by, has been a matter of discussion in the literature. Low-temperature measurements show some ripple structure-indicating that bound $(\text{O}_2)_2$ states play a role in the absorption resonance [131]. Measurements by Biennier *et al.* [149] and Campargue [150] in a slit-jet expansion have indeed shown many narrow resonances in the oxygen dimer. The latter studies prove that at low temperatures bound states exist, since the resonances are unequivocally associated with bound rotational states of the oxygen dimer. However, these measurements were carried out at the characteristically low final temperatures in molecular expansions, strongly deviating from atmospheric conditions, where the bound states are presumed to play no role. Vigasin and coworker [151–153] have analyzed the contribution of bound and free-free dimers to the absorption in collision-induced spectra, thereby dividing phase space into three compartments, including that of metastably bound dimers in which molecules are slightly bound by a centrifugal barrier. From their thermodynamic model it follows that even at temperatures as low as 150 K bound complexes do not contribute significantly to the collisional spectral features [154].

Obviously, the oxygen CIA resonances are of importance for atmospheric physics. The oxygen collisional complex is held responsible for a non-negligible fraction (1–2%) of the absorption of solar radiation [155, 156]. The cross-sections of the O_4 features depend quadratically on pressure, and they are particularly useful to determine cloud top heights in the lower atmospheric layers. Acarreta *et al.* [157] have introduced a cloud detection algorithm, which also yields the effective cloud fraction within a ground pixel, using the O_2 – O_2 resonance at 477 nm. This resonance falls within the spectral window (270–500 nm) sampled by the Ozone Monitoring Instrument (OMI) aboard the EOS-Aura satellite, which was launched in summer 2004 with the aim to detect global ozone columns. Using [158] it is estimated that a 10% error in the peak absorption of the 477 nm O_2 – O_2 resonance leads to errors of about 1 km in the retrieved cloud altitude. This, in turn, leads to an error of about 1% in the total column density of ozone. As the target accuracy of the total ozone column is about 1%, which is needed to detect trends in ozone and to detect

tropospheric pollution; errors in the peak absorption of O₂-O₂ should not be larger than 5%. Since the scatter in the literature values on the band integrated CIA cross-section amounts to 15%, the uncertainty in the retrieved ozone column densities from OMI for cloudy measurements is dominated by the uncertainty in the O₂-O₂ resonance; the cloud-free uncertainty is 1.2% and is mostly due to instrument noise.

The above-mentioned relation to ozone retrieval warrants detailed and accurate laboratory measurements to provide the integrated cross-section and shape function of the O₂-O₂ resonances. In the distant past Tabisz *et al.* [159], McKellar *et al.* [160] and Ewing and coworkers [130, 131] determined absorption cross-sections for both the 477 and 577 nm resonances at a number of temperatures. Recently, studies were performed by Newnham and Ballard [161] and Hermans *et al.* [162] applying Fourier-transform spectroscopy, and Morville *et al.* [163] as well as Tiedje *et al.* [164], who performed cavity ring-down measurements. As a continuation of previous studies in our laboratory on O₂-O₂ cross-sections at room temperature [127, 165] we have built a special cell to carry out cavity ring-down experiments at controlled low temperatures in the range 184–294 K. In view of the relevance for ozone column density retrieval, as discussed above, the focus has been on the 477 nm O₂-O₂ feature, but also new data were collected for the 577 nm resonance.

6.1. Description of the setup and the experimental procedure

6.1.1. CRD-setup and the pressure-ramp method

The present laser based cavity ring-down measurements at low temperatures are an extension of previous investigations on O₂-O₂ at room temperature [127, 165]. The ring-down cell, especially constructed for the purpose of controlled low-temperature measurements (see Fig. 6.1), is built from two highly reflective mirrors (Research Electro Optics) with a diameter of 25.4 mm, radius of curvature of 100 cm and a reflectivity of $R \approx 99.99\%$ (one set coated for 470 nm and one for 580 nm), leading to typical decay times of $\sim 30 \mu\text{s}$ in the cavity with length $d = 80$ cm. A special methodological feature in our studies is the application of the pressure-ramp method that was first applied to quantitatively

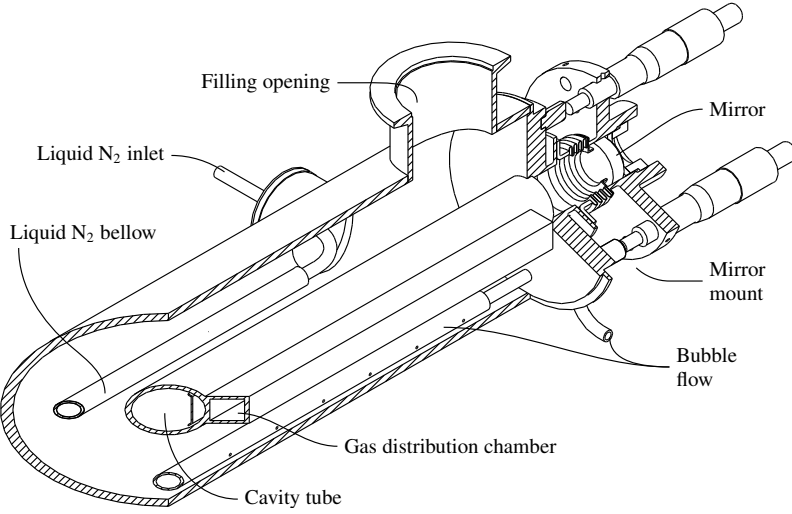


Figure 6.1: Three-dimensional drawing of the cell used for the present low-temperature CRD measurements. The coolant liquid (ethanol, acetone or anti-freeze) is poured into the outer volume and then cooled by liquid nitrogen flowing through the bellow. Oxygen, freed from aerosols and pre-cooled by letting it pass through two sintered steel filters, first enters a gas distribution chamber alongside the ring-down inner cavity. To ensure a homogeneous distribution and a monotonic increase of gas density at the laser beam path, the oxygen enters the inner cell via a number of holes connecting the gas distribution chamber and the inner cell. The micrometer screws and bellows between the mirrors and the rest of the cell allow for careful alignment. Dry nitrogen is blown against the outside of the mirrors to keep them free from ice.

assess the cross-sections for Rayleigh scattering by Naus and Ubachs [79]. This method implies that the cell is first evacuated and then slowly filled with oxygen, while the loss rate in the cavity and the pressure in the cell are continuously monitored. In Fig. 6.2 typical examples of such pressure-ramp curves are displayed at various frequency positions on the 477 nm resonance, displaying different quadratic contributions to the loss rate.

The frequency and pressure-dependent loss in the cavity contains three terms: an offset representing the frequency-dependent reflectivity of the mirrors (or background), a linear contribution associated with Rayleigh scattering and a quadratic contribution representing the bimolecular or CIA:

$$\beta_v(N)/c = \beta_v^0/c + \sigma_v^R N + \alpha_v^{CIA} N^2 \quad (6.1)$$

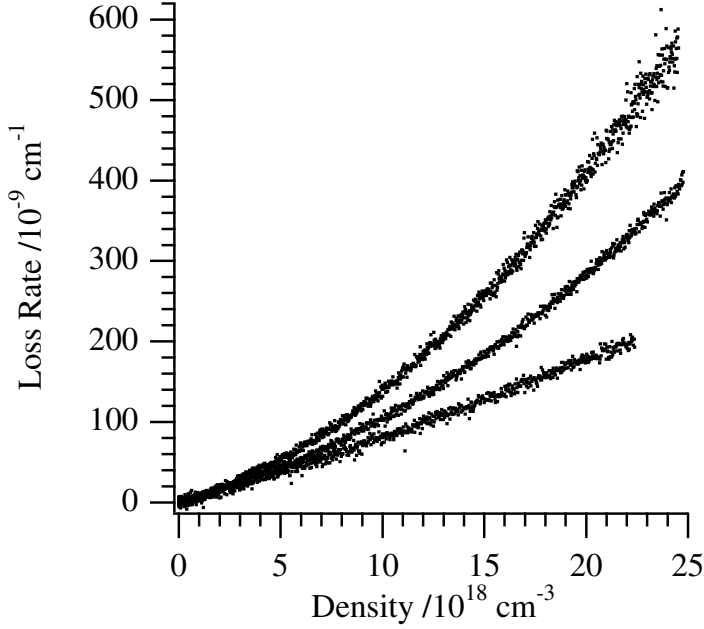


Figure 6.2: Three typical pressure-ramps, recorded for different frequencies at room temperature on the 477 nm resonance. From top to bottom the positions of the traces were 20 951 cm⁻¹ (near the top of the resonance), 20 137 cm⁻¹ (in the red-wing) and 21 392 cm⁻¹.

with c the speed of light, σ_v^R the Rayleigh scattering cross-section, N the number density and α_v^{CIA} the CIA cross-section. The decisive advantage of this pressure-ramp method, whereby pressure-dependent measurements are performed at each fixed-frequency position, is that the background, the Rayleigh scattering and the true collisional contribution can be disentangled. In addition to the terms in Eq. 6.1 higher-order terms may play a role in principle, e.g. as a result of tertiary collisions. Based on the findings of Tabisz *et al.* [159] and others (see below) such features are insignificant at sub-atmospheric pressures, as used in the present investigation.

A Nd: YAG pumped pulsed dye laser system (Quanta-Ray PDL-3) is used for the ring-down measurements. For the blue region (477 nm resonance) 355 nm pumping of *Coumarine-480* dye is routinely employed, while for the yellow range *Rhodamine-B* is pumped by the 532 nm output of the Nd: YAG laser. As discussed in literature (see, e.g. [44]) the determination of cross-

sections in CRD experiments is hampered by the linewidth problem, giving rise to multi-exponential decays on narrow resonances. But here the opposite is the case: the resonances are almost as wide as the gain profiles of the dyes. The principle of CRD detection makes the measurements independent of laser pulse intensity; hence the linewidth problem poses no specific problems in the present experiments. Only when the laser wavelength is tuned to the wings of the dye gain curve appreciable amounts of amplified spontaneous emission (ASE) can be produced in the dye laser, which may result in systematic offsets in the measured cross-sections. In our experiments this was the case on the short-wavelength edge of the 477 nm resonance. At these wavelengths additional measurements were performed with *Coumarine-460* dye, thus producing a reliable set of ring-down transients at these wavelengths.

6.1.2. Reaching and maintaining low temperatures

The lowest temperatures are obtained by submerging the CRD cell (see Fig. 6.1) in a low temperature bath, consisting of a solid-liquid mixture of acetone, which has a freezing point of $-94.8\text{ }^{\circ}\text{C}$ or 178.4 K . Since liquids undergo a first-order phase transition at the freezing point, the cell can be reasonably well stabilized at that temperature. Usually, an equilibrium temperature is established slightly above the freezing point; for that reason the 477 nm resonance was investigated at 184 K and the 577 nm resonance at 190 K , when using acetone as a coolant. The measurements at 268 K (only for the 577 nm $\text{O}_2\text{-O}_2$ feature) were performed with a different cooling technique; here, a chiller filled with anti-freeze (1, 2 ethane-diol/ethylene-glycol mixture) was used to bring down the temperature. The filler opening and the bubble-flow pipes were used as the connection points for the hoses and the chilled liquid was pumped around by the chiller. The lowest temperature reached with the chiller was 268 K ($-5\text{ }^{\circ}\text{C}$). A separate series of measurements was performed (only for the 477 nm $\text{O}_2\text{-O}_2$ feature) at a temperature of about 230 K ($-45\text{ }^{\circ}\text{C}$) using the anti-freeze mixture as coolant. Similar to the experiments using acetone, the anti-freeze mixture was frozen by flushing liquid nitrogen through the bellow. Due to the lack of a latent heat step at the freezing-point phase transition, difficulties were encountered in keeping the temperature at a constant value, but eventually

controlled measurements at a temperature of 230 ± 5 K could be performed. For the 477 nm resonance again a large set of data was taken at room temperature, therewith verifying previous results by our team [165] taken in a different cell. The results were analyzed and are included in this paper. For the 577 nm resonance no additional room-temperature measurements are added.

After the cell is aligned and evacuated, the outer volume is filled with the coolant to a level well above the ring-down cell. Liquid nitrogen is then flowed through a bellow, cooling down the coolant substance, in which the actual ring-down cavity is immersed. For the coolants used, frozen parts will sink to the bottom of the outer volume. To ensure a homogeneous temperature throughout the cell, and to bring the coldest coolant into contact with the ring-down cavity, nitrogen gas is blown through a tube with a series of holes located at the bottom of the outer volume. To reduce the heat load of this gas-flow, the nitrogen gas is cooled down by leading it through another container with liquid nitrogen. The bubbles will mix the liquid and bring the temperature of the entire cell down to the freezing point of the coolant. Reaching the freezing point of acetone takes between 4 and 5 hours, and after this time the temperature can be maintained by keeping a steady flow of liquid nitrogen through the bellow. A specific advantage of the present cell is that the low temperature is maintained homogeneously over almost the entire length of the cavity; even the mirror mounts are in contact with the coolant.

6.1.3. Measurements

As with the measurements at room temperature [127, 165], the CIA cross-section is determined with the pressure-ramp method. To fill the cell with oxygen at a predetermined low temperature, the gas is purged through a sintered stainless steel filter with 7 μm pores, located inside the outer tube and submerged in the coolant. This filter provides a large contact surface area, and after purging, the temperature of the gas is assumed to be the same as that of the fluid. Because this thermalization filter is inaccessible from the outside, a second filter with 0.5 μm pores is used outside the cell to filter aerosols from the oxygen and prevent contamination of the thermalization filter. Apart from this filter, oxygen with a specified purity of 99.999% is used without further

treatment. The rate of flow is controlled by a needle valve and set for the pressure-ramps to last about 15 min. The temperature of the coolant is measured by a thermocouple - type K (Ni+10%Cr) against (Ni+2%Al+2%Mn+1%Si) - with the tip placed close to the oxygen thermalization filter. A pressure sensor is placed in the top part inside the cell, in an effort to reduce the heat load on the system. The capacitance baratron for the range 0–1333 hPa has an uncertainty of 2 hPa. The oxygen gas density is calculated from the measured temperature and pressure using the Van der Waals equation of state. During the pressure-ramps the ring-down times (or loss rates β_v) are constantly monitored at a 10 Hz repetition rate, by methods described by Naus *et al.* [44], while also the pressure and temperature measurements are continuously stored in the data-handling computer.

The measurements are performed after the ring-down cell is aligned to yield single exponential decays. As discussed in [44] only under such conditions can the characteristic retrieved ring-down times be interpreted in terms of cross-sections. In the first step of the measurement and data analysis an exponential decay function is fitted to the ring-down transients. This results in typical density-ramp traces as shown in Fig. 6.2 for some measurements on the 477 nm resonance.

As in the previous measurements [127, 165], the wavelength of the laser was measured after each CRD pressure-ramp at a fixed wavelength position, with an echelle-grating spectrometer yielding an absolute accuracy of 0.2 cm⁻¹.

6.1.4. Data analysis

The density-ramps are fitted with a second-order polynomial, as given by Eq. 6.1. In a first run the data were subjected to a three parameter fit, from which a fitted value of the linear term is derived. Results for this linear term are displayed in Fig. 6.3 for several data sets.

As the linear terms should coincide with the values for the Rayleigh scattering cross-section σ_v^R , calculated from the refractive index and King correction factor [18], they are a consistency check of the experimental approach. As shown in Fig. 6.3, the variation of the linear terms from the three parameter fits exhibits a statistically random distribution around the curve

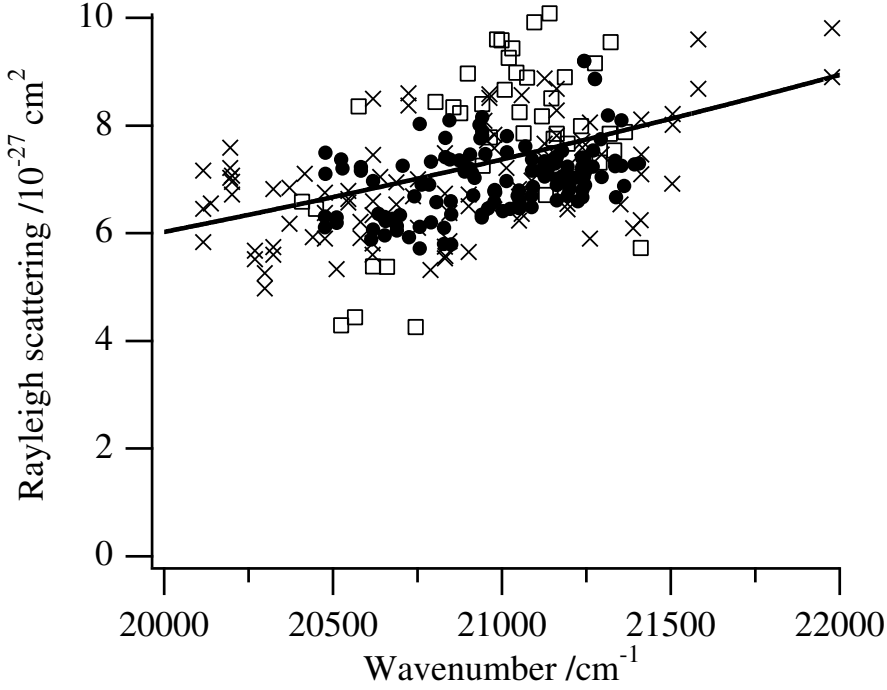


Figure 6.3: Fitted values for the linear scattering terms as obtained from three parameters fits for the data sets pertaining to the 477 nm resonance at room temperature ($\bullet$), at 230 K ($\times$), and at 184 K ($\square$). The full line corresponds to the value of the calculated Rayleigh scattering cross-section, σ_v^R for the specific wavelength.

representing the calculated value, where the actual variations, in fact, give some insight in the accuracy of the fits. The statistical deviations on the data recorded at the other temperatures were taken as a selection criterion; those pressure-ramps, where the fitted linear term was off by more than 20% from the calculated σ_v^R (for room-temperature data) or 40% (for the other data) were discarded.

In a second round of fitting (two parameter fits) the linear term is kept fixed at the calculated σ_v^R , which is calculated from the refractive index and King correction factor [18]. Values to be taken for σ_v^R were discussed in a previous paper focusing on direct Rayleigh scattering measurements [51]. This second round of fitting yields an improved accuracy for the determination of the quadratic term, corresponding to the CIA cross-section α_v^{CIA} . In Figs. 6.4

and 6.5, the final results of the measurements on the 477 and the 577 nm resonances of O₂-O₂ CIAs are shown. The measurements at 294 K on the 577 nm resonance are taken from Naus and Ubachs [127]. The room-temperature measurements on the 477 nm resonance stem from new series of measurements in combination with similar data, obtained in a previous investigation [165].

6.1.5. Further reduction of the data

In Figs. 6.4 and 6.5 resulting data for the quadratic components a_v^{CIA} are plotted as a function of frequency. In the same figures fits to the measured data are shown using a model function. The solid lines are the least-square best-fit results. The dashed lines in these figures indicate the confidence interval for the fit-result at the 2 σ (95.4%) level. This means that if the experiments were repeated, 95.4% of the sets would yield a fit that falls within the indicated interval. The dotted lines indicate the confidence interval for the prediction at the same level, indicating that 95.4% of the measured points should fall within the indicated band.

Currently there exists no good theoretical description of the O₂-O₂ CIA profile, and empirical model functions are used to describe the shape function of the resonance feature. In principle, the resonance profile could be calculated based on multi-dimensional *ab initio* potential energy surfaces and dipole moments, with integration over kinetic energy and angular distributions of the vectorial properties (velocities and angular momenta) of the collision partners, but such elaborate procedures have not yet been attempted. The purpose of representing the shape of the resonance in terms of an analytical representation is twofold: the shape function is used to derive an integrated CIA cross-section $-\int_{Band} \alpha_v^{CIA} dv$ – and the shape function can be used in retrieval procedures for the determination of column densities and profiles of species in the Earth's atmosphere. The shape function we use to describe the 477 nm resonance was first suggested by Watanabe and Welsh [166], and has been used by several authors [130, 159, 160]. In this empirical model, the high and low frequency wings of the transition show a Boltzmann related ratio:

$$\frac{A(v_c - \Delta v)}{A(v_c + \Delta v)} = \exp\left(-\frac{hc\Delta v}{k_B T_{eff}}\right) \quad (6.2)$$

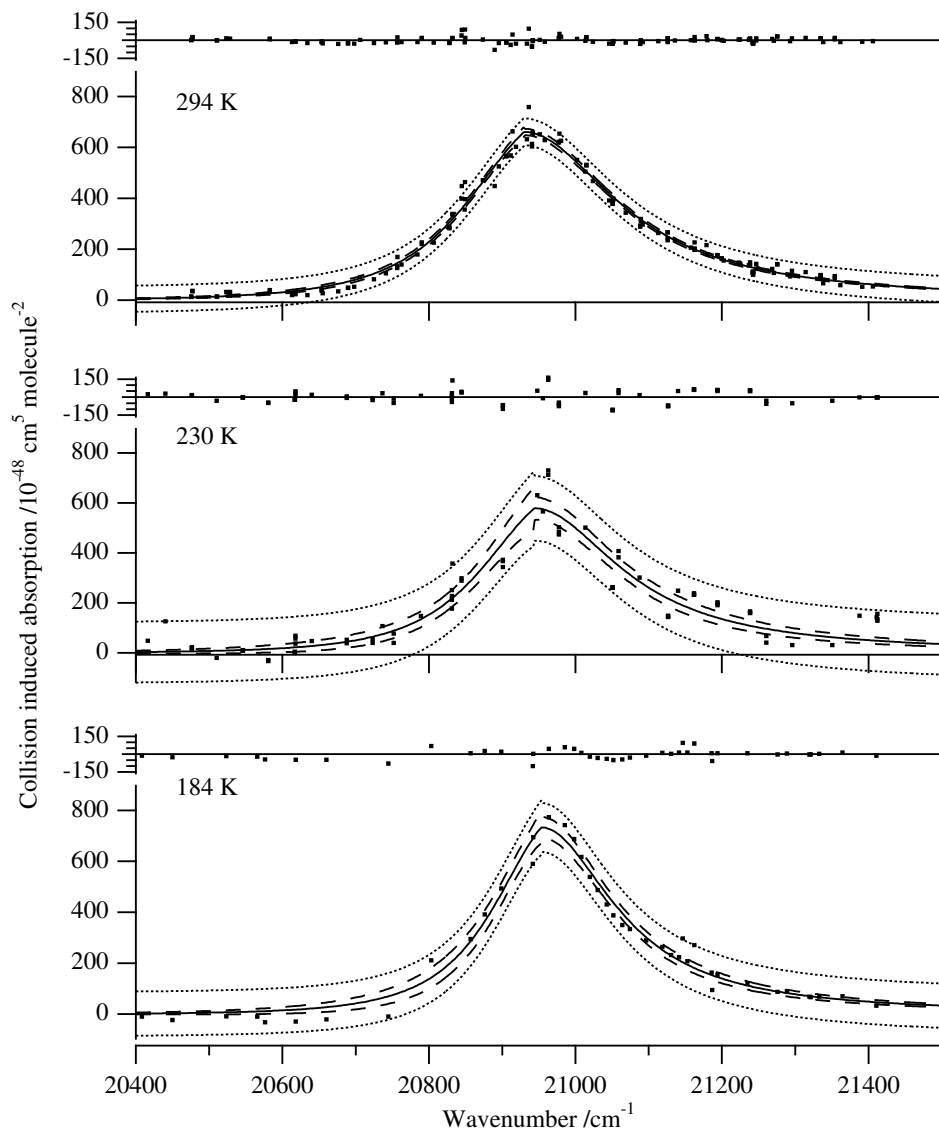


Figure 6.4: The absorption profiles of the O₂-O₂ feature near 477 nm at 294 K, 230 K and 184 K. Residuals from a comparison to a model function are shown as well. Further details are given in Section 6.2.5.

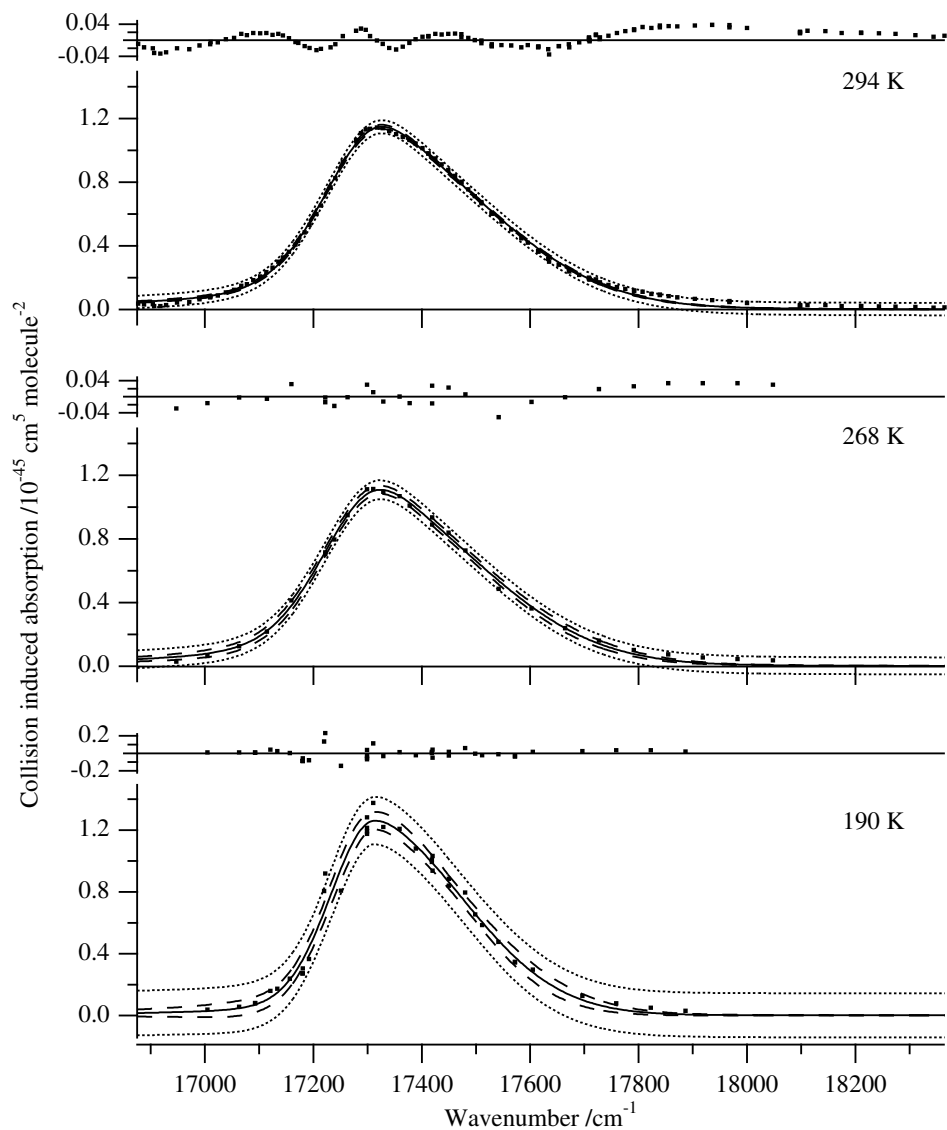


Figure 6.5: The absorption profiles of the $\text{O}_2\text{-O}_2$ feature near 577 nm at 294 K taken from [127], 268 and 190 K. Residuals from a fit to a model function as discussed in Section 6.2.5 are shown as well.

with A the intensity of the absorption, ν_c the central position of the absorption resonance, $\Delta\nu = \nu - \nu_c$, T_{eff} the effective temperature of the gas and h , c and k_B are Planck's constant, the speed of light and Boltzmann's constant, respectively.

Eq. 6.2 does not specify the shape of the profile, it only determines the high and low frequency ratios. For the overall shape of the underlying line a Lorentz profile is assumed, leading to:

$$A(\nu) = \frac{a(\Gamma/2)^2}{(\Delta\nu)^2 + (\Gamma/2)^2}, \quad \text{if } \Delta\nu > 0$$

$$A(\nu) = \frac{a(\Gamma/2)^2}{(\Delta\nu)^2 + (\Gamma/2)^2} \exp\left(\frac{hc\Delta\nu}{k_B T_{eff}}\right), \quad \text{if } \Delta\nu \leq 0 \quad (6.3)$$

where a and Γ represent parameters for the amplitude and the width of the absorption feature. In [165], the temperature in Eq. 6.3 was taken to be the temperature at which the measurements were performed. Especially at lower temperatures, this leads to unsatisfactory fit results. The effective temperature T_{eff} is now a fit-parameter and it is adjusted to give the best fit to the data. During the analysis of the data, it became apparent that the model given by Eq. 6.3 works well for the description of the 477 nm resonance, but when it is applied to the 577 nm resonance, large residuals and a very poor fit are found.

Following the analysis of Naus and Ubachs [127], a skewed Voigt profile was used to describe the shape of the 577 nm resonance. The skewed Voigt profile is approximated by a linear combination of a Gauss and a Lorentz profile, where the left and right hand sides have a different linear scale:

$$V(\nu) = (1-b) \frac{a}{1 + [2\Delta\nu / \Gamma\zeta]^2} + ab \exp\left[-4 \ln\left(\frac{\Delta\nu}{\Gamma\zeta}\right)^2\right] \quad (6.4)$$

with

$$\zeta = 1 + 2 \arctan(x) / \pi, \quad \text{if } \Delta\nu > 0$$

$$\zeta = 1 - 2 \arctan(x) / \pi, \quad \text{if } \Delta\nu \leq 0$$

where a and b amplitudes and x is the skew factor.

Table 6.1: Parameters describing the absorption profile of the O₂–O₂ feature near 477 nm at three different temperatures. The parameters were found using Eq. 6.3 as the model function and a least-square fit. The indicated errors are 1 σ values. A graphical representation of the data and the fit results are shown in Fig. 6.4.

Temperature, [K]	294	230	184
Coolant	None	Anti-freeze	Acetone
ν_c , [cm ⁻¹]	20929.9 $\pm$ 2.8	20943 $\pm$ 11	20953 $\pm$ 6
λ_c , [nm]	477.79 $\pm$ 0.06	477.47 $\pm$ 0.26	477.25 $\pm$ 0.14
FWHM, [cm ⁻¹]	247.1 $\pm$ 6.8	228 $\pm$ 26	197 $\pm$ 14
FWHM, [nm]	5.64 $\pm$ 0.16	5.2 $\pm$ 0.6	4.5 $\pm$ 0.3
Γ , [cm ⁻¹]	306.4 $\pm$ 6.8	283 $\pm$ 26	239 $\pm$ 14
$a / 10^{-48}$, [cm ⁵ molecule ⁻²]	660 $\pm$ 6	578 $\pm$ 23	733 $\pm$ 20
T_{eff} , [K]	361 $\pm$ 37	331 $\pm$ 138	316 $\pm$ 102
$\int A(\nu)d\nu / 10^{-42}$, [cm ⁴ molecule ⁻²]	0.470 $\pm$ 0.006	0.447 $\pm$ 0.013	0.406 $\pm$ 0.024

Table 6.2: Parameters describing the absorption profile of the O₂–O₂ feature near 577 nm at three different temperatures. The parameters were found using Eq. 6.4 as the model function and least-squares fit. The indicated errors are 1 σ values. A graphical representation of the data and the fit-result are shown in Fig. 6.5. ^aMeasurements taken from Naus and Ubachs [127].

Temperature, [K]	294 ^a	268	190
Coolant	None	Chiller	Acetone
ν_c , [cm ⁻¹]	17325.8 $\pm$ 1.7	17322.8 $\pm$ 3.5	17313 $\pm$ 7
λ_c , [nm]	577.17 $\pm$ 0.06	577.3 $\pm$ 0.1	577.6 $\pm$ 0.2
FWHM, [cm ⁻¹]	346.5 $\pm$ 3.0	342.3 $\pm$ 7.1	290 $\pm$ 10
FWHM, [nm]	11.5 $\pm$ 0.1	11.3 $\pm$ 0.2	9.6 $\pm$ 0.3
Γ , [cm ⁻¹]	318 $\pm$ 3	317 $\pm$ 7	257 $\pm$ 10
$a / 10^{-45}$, [cm ⁵ molecule ⁻²]	1.15 $\pm$ 0.01	1.11 $\pm$ 0.03	1.26 $\pm$ 0.05
skew factor	-0.64 $\pm$ 0.02	-0.60 $\pm$ 0.05	-0.65 $\pm$ 0.11
b	0.782 $\pm$ 0.012	0.784 $\pm$ 0.034	0.91 $\pm$ 0.06
$\int V(\nu)d\nu / 10^{-42}$, [cm ⁴ molecule ⁻²]	0.470 $\pm$ 0.006	0.447 $\pm$ 0.013	0.406 $\pm$ 0.024

The parameters found in the fitting procedure are shown in Tables 6.1 and 6.2. The two sets use different model functions and therefore have different parameters in their respective tables. The resulting effective temperatures found in the fitting routines using Eq. 6.3 are systematically and significantly higher than the real measured temperatures of the oxygen gas. Once again we note that T_{eff} should by no means be regarded as a temperature, rather than as a fitting parameter in a model.

The uncertainties indicated are found from the fitting procedure. An attempt was made to propagate the error estimates found from the fit of the ring-down transients, but the resulting errors were unrealistically small. The currently indicated errors assume that the errors in all measured points are equal and that the model function is accurate. In that case χ^2 scaling is possible and the uncertainties resulting from this procedure are reported. The indicated accuracy on the band integrated absorption cross-section is found by applying a Gaussian variation with the indicated standard deviation to the parameters describing the model function and taking the standard deviation of the resulting distribution of integrated cross-sections.

6.2. Discussion and comparison with other measurements

In order to give a complete picture of the measurements of temperature dependence of the collisional (O₂)₂ resonances at 477 and 577 nm all available information in literature was collected in conjunction with the presently obtained data. For this purpose, scaling to the appropriate units is required and in some cases digitization of information contained in plotted figures was employed to extract information on three relevant parameters: the peak cross-sections, the widths (FWHM) and the integrated cross-sections. Final values are included in Figs. 6.6 and 6.7. Note here, that notwithstanding the fact that the resonance features are clearly asymmetric, widths (FWHM) were determined. The restriction is imposed to collect data obtained from laboratory experiments (in Section 6.3.1), because these are considered to originate from well-controlled experiments. From these data, displayed in Fig. 6.6 (for the 477 nm resonance) and in Fig. 6.7 (for the 577 nm resonance) temperature-dependent trends are deduced, which are discussed in Section 6.3.2. Subsequently, a comparison with

data and trends obtained from atmospheric measurements is made in *Section 6.2.3*.

6.2.1. Data collection of laboratory measurements

For both the 477 and 577nm resonances, Tabisz *et al.* [159] list the band integrated cross-sections at 297 K, but not the widths nor the peak cross-sections; those were extracted by digitization procedures. From the work of McKellar *et al.* [160] all three parameters were deduced from the digitized plots. Blickensderfer and Ewing [130] give the integrated absorption cross-sections, the half-widths at 300 and 87 K and the peak heights at 300 and 290 K (at different pressures). The difference between the latter two values is taken as a measure for the error on the peak height. The peak height values at 87 K are taken from a digital readout of the graphs. Greenblatt *et al.* [129] give some parameters for both resonances; in addition, digitized data of the room-temperature measurements in [129] were obtained via the authors of [157] from which the band integrated cross-section was calculated. Morville *et al.* [163] give the width and peak height for the 577 nm band at three temperatures. The band integrated values were extracted via the digitized plot, using direct numerical integration. From the noise on the plot, and the baseline seen in the graph, the uncertainty on the integral is estimated to be around 10%. Tiedje *et al.* [164] give all three values for the 577 nm band in their paper. Newnham and Ballard give the peak absorption cross-section and the integrated absorption cross-section plus the error estimate for both resonances at two temperatures in Tables 6 and 7 of their paper; a value for the FWHM value was deduced by us from their raw data [161]. Finally, Hermans *et al.* [162] performed Fourier-Transform measurements at pressures in the range 0.3–1 bar, applying multi-passing in a 50 m cell at room temperature. Values for the peak cross-sections and the widths are obtained from Table 3 in [162], while a value for the integrated cross-section is obtained from the raw data. These raw data, in combination with the margins indicated in [162], were also used to derive an estimate for the uncertainty.

The data near room temperature are too congested to obtain a clear picture of the asymptotic values. For this reason, the room-temperature region

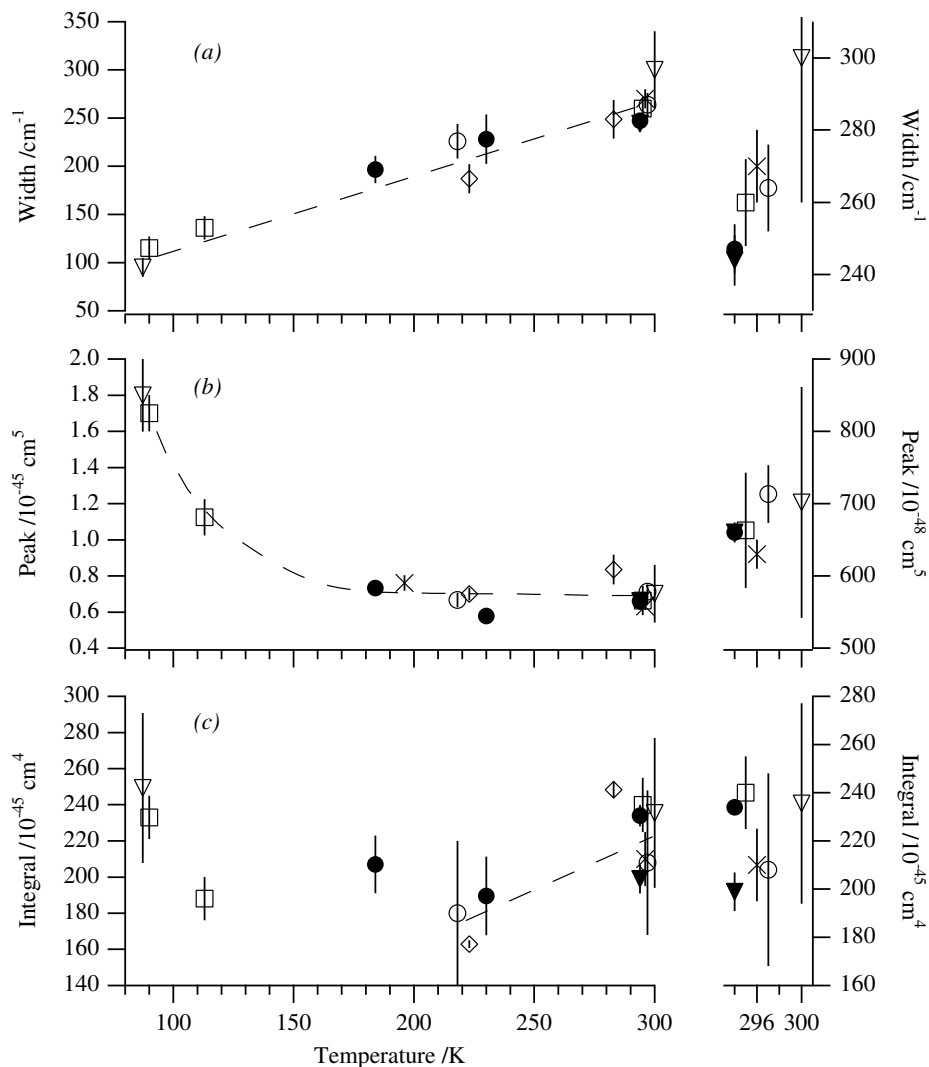


Figure 6.6: Temperature dependence for parameters of the 477 nm O_2 - O_2 resonance. The width is shown in (a), the height in (b) and the band integrated intensity in (c). The vertical bars indicate the 1σ confidence level on each point. Sources: (∇) – Ewing et al. [130]; ($\times$) – Greenblatt et al. [129]; ($\diamond$) – Newnham and Ballard [161]; ($\circ$) – Tabisz et al. [159]; ($\square$) – McKellar et al. [160]; ($\blacktriangledown$) – Hermans et al. [162]; ($\bullet$) – this work. The sections at the right-hand sides duplicate the data already contained in the main section of the graphs at enlarged scales. The dashed lines are drawn to guide the eye, and to indicate temperature dependences.

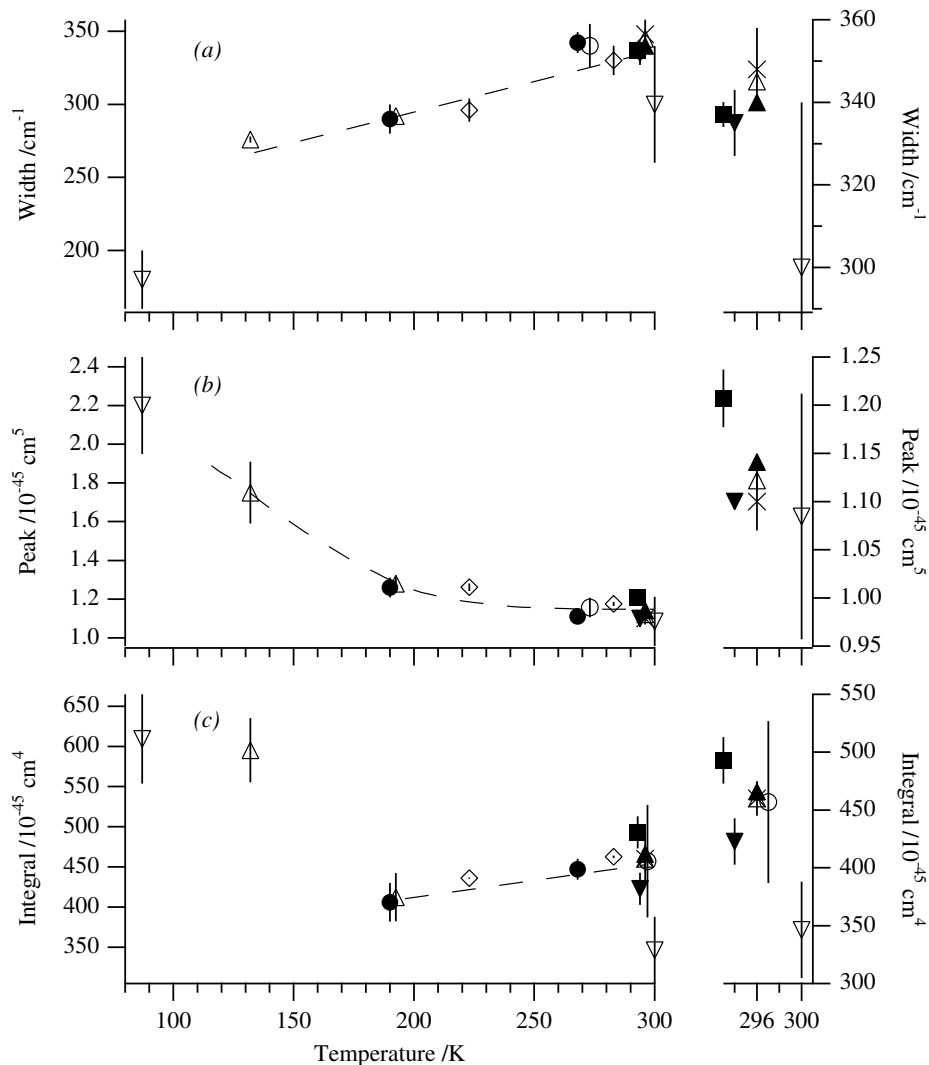


Figure 6.7: Temperature dependence for parameters of the 577 nm O_2-O_2 resonance. The width is shown in (a) the height in (b) and the band integrated intensity in (c). The vertical bars indicate the 1 σ confidence level on each point. Sources: (Δ) – Morville et al. [163]; ($\diamond$) – Newnham and Ballard [161]; ($\blacktriangle$) – Naus and Ubachs [127]; (∇) – Ewing et al. [130]; ($\blacksquare$) – Tiedje et al. [164]; ($\square$) – McKellar et al. [160]; ($\circ$) – Tabisz et al. [159]; ($\times$) – Greenblatt et al. [129]; ($\blacktriangledown$) – Hermans et al. [162]; ($\bullet$) – this work. The sections at the right-hand sides duplicate the data already contained in the main section of the graphs at enlarged scales. The dashed lines are drawn to guide the eye, and to indicate temperature dependences.

for this feature is enlarged in the right hand side of Fig. 6.6. Hence, this part duplicates the data between 292 and 300 K already contained in the main section of the graphs, while also the vertical scale is appropriately enlarged. The same is done for the data on the 577 nm resonance in Fig. 6.7.

The focus in the present study is on the collision-induced cross-section, which scales, according to Eq. 6.1, with the density squared N^2 , and it should not depend on the range of pressures or densities at which the measurements are performed. The quadratic dependence on pressure was verified for a number of O₂–O₂ CIA features, including the 477 and 577 nm resonances, in early work by Tabisz *et al.* [159], and by Dianov–Klokov [128] for pressures upto 35 bar, while Greenblatt *et al.* followed the quadratic pressure dependence of the 577 nm resonance up to 55 bar [129]. In the data collection from previous measurements a number of sets are used, that are recorded at elevated pressures. In the following, all data sets are compared without further reference to the actual pressures at which the data were recorded. It is noted again that the present results on the CIA cross-sections, obtained with the pressure-ramp method, relate to pressures throughout the range 0–1 bar.

6.2.2. Temperature-dependent trends

A comparison of results on the CIA features should be based on the entire band profiles including the particular shapes of the resonances. Since detailed information on the actual shapes in previous investigations is sparse and difficult to extract, we have chosen to represent the profiles in terms of three parameters: the peak and integrated cross-sections and the widths (FWHM), even though the profiles are definitely asymmetric. As discussed, there exists no closed theory for the band shapes of the CIA O₂–O₂ features and the two different functions given by Eqs. 6.3 and 6.4 are just phenomenological parameterizations of the shapes observed.

In Fig. 6.6, all available information on the collision-induced 477 nm resonance is contained and some unequivocal conclusions can be drawn from it. The width (FWHM) of the resonance exhibits a monotonic increase in the entire temperature range 87–300 K from 100 cm⁻¹ at the lowest temperature to 245 cm⁻¹ at room temperature. All data points fall close to the dashed lines, serving as an

indicator for the temperature dependence. For the room-temperature value of the width we have taken the average value of the present investigation and that of Hermans *et al.* [162] (yielding $244 \pm 7 \text{ cm}^{-1}$). These data were recorded at lower pressures, while the other data at room-temperature conditions correspond to high-pressure measurements. As discussed by Blickensderfer *et al.* [130] elevated pressures may give rise to additional broadening.

The peak cross-section of the 477 nm feature sharply drops when departing from the lowest temperature, then leveling off asymptotically to the room-temperature value of $(660 \pm 6) \times 10^{-48} \text{ cm}^5 \text{ molecule}^{-2}$. The latter value is obtained from a weighted fit on the set of data available on (near) room-temperature measurements, comprising the present value and literature values. Again the trend is indicated by a dashed line drawn in section (b) of Fig. 6.6. Based upon the entire set of available data no definite statement can be made on the temperature trend in the atmospherically relevant domain of 200–300 K. However, for a subclass of investigations, where measurements were performed at varying temperatures under otherwise similar measurement conditions, such a statement can be made. In the present series of measurements, using CRDS, a peak cross-section is measured at 230 and at 294 K yielding a clear indication of an *increase* of $14 \pm 5\%$ over this temperature interval. Similarly, Newnham and Ballard find an increase, even more pronounced, from their recent FT-spectroscopic measurements [161]. Notwithstanding the fact that the two most accurate and most recent data sets indicate an increase in the peak cross-section at atmospheric temperatures the dashed line in section (b) of Fig. 6.6 shows a constant temperature behavior in this range, thus reflecting the entire manifold of data sets available.

The combination of these trends in the widths and peak cross-sections results in a minimum for the integrated cross-section lying somewhat near 225 K. As a further consequence, the integrated cross-section exhibits an increase in the 200–300 K range; this trend is again indicated by the dashed line in section (c) of Fig. 6.6. In view of the spread in the data it is difficult to extract a value for the room-temperature integrated cross-section with a reliable error estimate; an unweighted fit on the entire data set yields $(2.1 \pm 0.17) \times 10^{-43} \text{ cm}^4 \text{ molecule}^{-2}$.

Without going into the details of the temperature dependences of the essential features of the 577 nm resonance as extensively, the dashed lines

inserted in Fig. 6.7 indicate the same trends: an increase of the width toward higher temperatures and a clear indication of an increase of the integrated cross-section, at least in the atmospherically relevant range 200–300 K. Also here the integrated cross-section exhibits a dip near 200 K, even clearer than in the case of the 477 nm resonance. For the peak height again a clear overall decrease is found from the lowest temperatures toward room temperature. In the atmospherically relevant range, between 200 and 300 K, this trend appears to be sustained (i.e. shows a slight decrease) in contradiction to the case of the 477 nm feature. Averaging over all available information yields the following values for the 577 nm resonance at room temperature (294 K): width 340 ± 6 cm⁻¹, peak cross-section $(1.14 \pm 0.15) \times 10^{-45}$ cm⁵ molecule⁻² and integrated cross-section $(4.66 \pm 0.15) \times 10^{-43}$ cm⁴ molecule⁻².

6.2.3. Trends derived from atmospheric measurements

Absorption peak cross-sections for various O₄ bands including the 477 and 577 nm bands have also been derived using atmospheric measurements. Both ground-based [134] and balloon-based [133] measurements have been performed, the latter also providing temperature-dependent peak cross-sections. Although these atmospheric measurements are obtained under less-controlled conditions compared to laboratory measurements, the derived peak cross-sections are comparable to the ones presented here. However, some notable differences are observed as well. The temperature-dependent data from Pfeilsticker *et al.* [133] yield two major conclusions: (a) the band shapes do not change with temperature, nor with pressure; (b) the peak intensities exhibit a decrease of 11% in the atmospherically relevant temperature domain of 200–250 K. In comparison, the full set of laboratory measurements presented in Fig. 6.6 (a) shows a marked monotonic increase in the width of the resonance over the entire temperature range. The fact that Pfeilsticker *et al.* observe no change in absorption band shapes for any of the O₄ absorption bands may result from the coarser spectral resolution in the balloon-borne measurements. The situation for the peak intensity on the 477 nm resonance is less unambiguous. When all laboratory values are included, the average in the 200–300 K range indeed yields a constant value, represented by the dashed line in Fig. 6.6(b). In view of

the large spread, an 11% decrease in the 200–250 K range may be accommodated. However, the two most recent data sets (the present one and the one of [161]) suggest an increase in the peak intensity over that range. It is not excluded that the peak cross-section exhibits an even more fine-tuned structure with a decrease in the range 200–250 K (in agreement with the findings of [133]), a minimum somewhere in the range 250–270 K (in agreement with the behavior of the pair distribution function, see below) and again an increase toward room temperature (in agreement with the present findings and those of [161]).

6.2.4. On a model for the observed temperature trend

The observation of a minimum in the temperature dependence of the integrated absorption cross-sections of $\text{O}_2\text{--O}_2$ collision-induced resonances at a certain intermediate temperature is similar to recent findings by Baranov *et al.* [138], who investigated the CIA spectrum of the O_2 fundamental (vibrational) band near 6 mm. In that specific case, the minimum occurs near $T = 270$ K, while minima in the temperature dependences of the CIA features associated with electronic excitation are found near 225 K (for 477 nm) and 200 K (for 577 nm). Vigasin [154] has discussed this behavior in a simple semi-quantitative model, arguing that the integrated cross-section of CIA features in the region of dipole-forbidden transitions is built from two distinctive contributions. On the one hand, in the lower temperature regime, the main contribution stems from molecular pairs in the vicinity of the minimum $R = R_e$ of the intermolecular potential. On the other hand, in the regime of high temperatures, in which all vibrational states in the intermolecular potential are populated, absorption occurs at intermolecular separations near the repulsive branch of the potential. Invoking parameters associated with a simple Lennard-Jones potential, parabolic temperature dependence is derived exhibiting a minimum near 270 K for the CIA fundamental. Qualitatively these arguments may be transferred to the case of electronic excitation of collision partners as well, explaining the parabolic behavior in the integrated cross-section. The behavior of the integrated absorption coefficient with its minimum at intermediate temperatures may thus be associated with the temperature dependence of the

pair distribution function. A differing location of the minimum can then be ascribed to the fact that the intermolecular potential for the electronically excited final state is different.

More detailed and quantitative calculations, based on true and multi-dimensional potentials, may reveal whether such an explanation is correct. Full *ab initio* calculations may also provide insight into the cross-sections of the various CIA oxygen features. An outstanding issue is the question why the 577 nm resonance is so strong. This CIA resonance excites one of the molecules into a $v=1$ state, and from the perspective of monomer absorption this excitation is associated with a small Franck-Condon factor. Hence, the symmetry-breaking effect must be large in case of the 577 nm resonance.

6.3. Conclusion

Cavity ring-down experiments have been performed on the O₂-O₂ CIA features at 477 and 577 nm at various temperatures in the range 184–294 K, employing the pressure-ramp method, whereby the linear Rayleigh scattering contribution to the extinction can be separated from the quadratic CIA contribution. The presently obtained data for the temperature-dependent cross-sections are included in a compilation of relevant previously obtained data. From the entire set of laboratory data trends are derived in the parameters (widths, peak and integrated cross sections) for both CIA resonances that bear relevance for the use of the data for future satellite monitoring in the Earth's atmosphere.

Of particular importance is the finding that both resonances appear to exhibit a minimum in the integrated cross-section, associated with a slow increase in the atmospherically relevant temperature domain 200–300 K. Furthermore, both resonances exhibit a linear increase in their width, a marked and strong effect that is quantified. As for the peak intensity on the cross-section a clear decrease is found in the low-temperature region (100–200 K), but the effect is less pronounced in the atmospherically relevant region. In the case of the 477 nm resonance, neither a significant decrease nor increase of the peak cross-section is found, when all laboratory data are included in a trend analysis. However, the present study reveals a clear indication of an increase in the peak cross-section from measurements at atmospherically relevant pressures (0–1 bar) and at varying temperatures recorded by the same instrument. Herewith,

we validate the independent finding by Newnham and Ballard from FT-spectroscopic measurements [161]. The combined set of results provides a better constraint on the parameters (width, peak and integrated cross-section) and temperature trends for the $\text{O}_2\text{--O}_2$ features and should help improve Earth observation studies.

The present study marks progress in the laboratory investigation of CIA resonances in oxygen, but the goal of producing a set of parameters describing the cross-sections at the 1–5 % accuracy level has not yet been achieved. Therefore it remains an important issue to perform extended laboratory measurements, using both independent techniques of CRD-spectroscopy and FT spectroscopy, at a larger set of temperatures leading to an undisputed set of temperature-dependent CIA parameters. Also, above room-temperature measurements may be useful to establish unequivocal temperature dependencies. Validation of the temperature dependencies by *ab initio* quantum chemical methods to support the experimental findings on profiles and cross-sections may be useful as well.

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List of publications

This thesis is based on the following papers:

Chapter 3

Deep-UV absorption and Rayleigh scattering of carbon dioxide.

D. Ityaksov, H. Linnartz, W. Ubachs.

Chem. Phys. Lett., 462, 31-34, (2008).

Chapter 4

Deep-UV Rayleigh scattering of N_2 , CH_4 and SF_6 .

D. Ityaksov, H. Linnartz, W. Ubachs.

Mol. Phys., 106, 2471-2479, (2008).

Chapter 5

Rotational analysis of the $A^2\Sigma_{(v=1,2)}^+ - X^2\Pi_{(v=0)}$ electronic bands of $^{15}N^{18}O$.

D. Ityaksov, S. Stolte, H. Linnartz, W. Ubachs.

J. Mol. Spectr., 255, 139-143, (2009).

Chapter 6

Temperature-dependent cross-sections of O_2-O_2 collision-induced absorption resonances at 477 and 577 nm.

M. Snee, D. Ityaksov, I. Aben, H. Linnartz, W. Ubachs.

J. Quant. Spectr. Rad. Transfer, 98, 405-424, (2006).

Furthermore the author contributed to:

- *A compact CH_4 -stabilized laser with a telescopic cavity.*

A.K. Dmitriyev, S. N. Bagayev, D.V. Ityaksov, A.A. Lugovoy.

Conf. Digest, 218, Conf. on Precision Electromagnetic Measurements, Ottawa, Ontario, Canada (2002).

- *Laser frequency standards with telescopic cavities.*

S.N. Bagayev, A. K. Dmitriyev, D.V. Ityaksov, A.A. Lugovoy, V.M. Semibalamut.

Frequency Standards and Metrology: Proc. of the 6 Symp., St. Andrews, Scotland, 45-50, (2001).

Summary

The amount of solar radiation reaching the surface of the Earth is determined by scattering and absorption of light by particles, present in the Earth's atmosphere. Both processes are frequency-dependent and are responsible for the attenuation - optical extinction - of the light crossing our atmosphere.

We are daily confronted with the influence of both absorption and scattering phenomena. The atmosphere is opaque for quite some wavelengths, protecting life for strong UV radiation and prohibiting ground-based astronomical observations at submillimeter wavelengths. A blue sky and a red sunset, both are a direct consequence of the fact that light with shorter wavelengths (blue) is scattered more than light with longer wavelengths (red). These observations have been known for a long time, but it took up to 1899 before Lord Rayleigh was able to quantitatively describe them as electromagnetic waves being scattered by small particles in the air. The simplicity of Rayleigh scattering theory and the prediction of the strong wavelength dependence ($\sim\lambda^{-4}$) of the molecular scattering immediately gained interest of the scientific community.

Light scattering by small molecular species has been extensively studied theoretically, but only in the last years laboratory techniques have become sensitive enough to directly determine the optical extinction due to Rayleigh scattering, addressing the scattering cross-section of single species (previously the Rayleigh scattering cross-section was indirectly assessed via the index of refraction). The majority of these studies have been focusing on frequency domains that are accessible by laser based experiments, particularly the visible part of the electromagnetic spectrum, but progress in sensitive laser detection schemes at shorter wavelengths, the ultraviolet and vacuum UV, allow detailed scattering studies at wavelengths as low as 200 nm. This is the main topic of this thesis.

Harmonic frequency generation of tunable laser radiation is used to cover the UV/VIS with high spectral purity, with a focus on the deep-UV between 198 and 270 nm. A sensitive detection scheme, based upon cavity ring-down spectroscopy applied to pressure-ramp measurements, is used to perform systematic laboratory studies of the optical extinction of a series of atmospheric

molecules (N_2 , O_2 , CO , CO_2 , CH_4 , NO and SF_6). The findings directly relate to the extinction of the deep-UV electromagnetic radiation in atmospheric gases, either via Rayleigh scattering or absorption phenomena. The results are of interest for both molecular physics and atmospheric sciences. The quantitative results, reported in this thesis are needed as input in radiative transfer models, for the evaluation of the altitude-dependent concentrations of atmospheric molecular constituents via column density measurements, and the study of photochemical and ozone depletion processes.

The thesis is organized in the following way.

Chapter 1 is a general introduction and puts the work described in the following chapters in an atmospheric context, also focusing on the fundamental molecular physics behind the processes. The Earth's atmosphere, altitude-dependent variation of physical properties and the amount of short wavelength solar radiation within the atmosphere are described, as well as the light scattering (by molecules and somewhat larger particles), linear and collisionally induced absorption phenomena.

Chapter 2 deals with the experimental approach used for the deep-UV optical extinction measurements and details of the tunable pulsed cavity ring-down setup and pressure-ramp method are given. Room-temperature optical extinction measurements in molecular CO between 198 and 220 nm are presented to illustrate the performance of the setup.

Chapter 3 is devoted to room-temperature extinction measurements of CO_2 between 198 and 270 nm. It is shown that the Rayleigh scattering is a dominant phenomenon that determines the optical extinction between 202 and 270 nm, whereas a clear absorption onset is found at shorter wavelengths.

Chapter 4 describes measurements to determine the absolute values of the Rayleigh scattering cross-sections of N_2 , CH_4 and SF_6 . Molecular scattering is found to govern the attenuation of radiation at short wavelengths. A significant part of the work described here, is devoted to a quantitative comparison of the present observations with numerical predictions that are based on dispersion of the optical properties of the gases. From the deep-UV measurements presented here, values for the refractive index and molecular polarizability are derived and compared to literature values.

Chapter 5 is a pure spectroscopic study and describes a cavity ring-down study of the heaviest NO isotopologue - $^{15}\text{N}^{18}\text{O}$ - in its γ -system between 205 and 216 nm. Laboratory room-temperature measurements of nearly 400 individual rotational transitions, corresponding to the electronic ($A^2\Sigma^+ - X^2\Pi_r$) band system are fitted using a rovibronic analysis yielding for a first time accurate molecular constants for the $A^2\Sigma^+_{(v=1)}$ and $A^2\Sigma^+_{(v=2)}$ vibrational levels.

The final chapter, *Chapter 6*, describes cavity ring-down measurements of collision-induced absorption resonances in O_2 - O_2 performed at 477 and 577 nm at different atmospheric temperatures. The observed absorption features are quantitatively analyzed for temperatures between 184 and 294 K and the temperature-dependent variation of the main parameters of the resonances are qualitatively determined and compared with data, as available from the literature.

Samenvatting

De hoeveelheid zonlicht dat het aardoppervlak bereikt is afhankelijk van de mate waarin het door deeltjes in onze atmosfeer wordt verstrooid of geabsorbeerd. Beide processen, verstrooiing en absorptie, zijn frequentie- of golflengtegevoelig, en de totale lichtverzwakking – optische extinctie – is dus voor verschillende kleuren anders.

We ervaren dagelijks de invloed van atmosferische absorptie en verstrooiing op ons leven. De atmosfeer is ondoorzichtig voor een aantal golflengtes: het leven op de Aarde ervaart geen hinder van de harde ultraviolette straling zoals die in de ruimte voorkomt en astronomen moeten voor waarnemingen in het submillimeter gebied gebruik maken van satellieten die zich buiten de dampkring bevinden. Ook de blauwe kleur van de hemel en de rode kleur van de zon tijdens zonsop- of zonsondergang zijn een direct gevolg van de interactie van licht met atmosferische deeltjes: licht met kortere golflengtes (blauw licht) wordt meer verstrooid dan licht met langere golflengtes (rood licht). Dit verschijnsel is al lang bekend, maar werd pas in 1899 verklaard door Lord Rayleigh, die aantoonde dat electromagnetische golven door kleine stofdeeltjes in de lucht worden verstrooid en daarbij een sterke golflengte afhankelijkheid ($\sim \lambda^{-4}$) vertonen.

De verstrooiing van licht aan kleine stofdeeltjes is theoretisch goed onderzocht, maar het is pas sinds kort mogelijk ook experimenteel de optische extinctie a.g.v. Rayleigh verstrooiing te meten. Met gevoelige lasertechnieken kan de frequentieafhankelijke werkzame doorsnede van de lichtverstrooiing voor een specifiek gas daadwerkelijk worden gemeten en het is niet meer nodig om deze waarde af te schatten uit de brekingsindex. Het merendeel van deze experimenten houdt zich bezig met kleuren die met lasers goed toegankelijk zijn, vooral het zichtbare deel van het electromagnetische spectrum. Dit proefschrift richt zich echter ook op het ultraviolette en vacuum ultraviolette bereik, waar extinctie effecten bij gebrek aan geschikte lasersystemen lange tijd niet in detail zijn onderzocht.

Daartoe wordt het licht van een verstembare kleurstoflaser m.b.v. kristallen gemanipuleerd en de resulterende hogere harmonische frequenties dekken met een hoge spectrale zuiverheid het gebied tussen 198 en 270 nm af.

Cavity ring-down spectroscopie wordt gebruikt als een gevoelige detectietechniek om de optische extinctie te meten van atmosferische gasen, zoals stikstof (N_2), zuurstof (O_2), koolstofmonoxide (CO), stikstofmonoxide (NO), de broeikasgasen koolstofdioxide (CO_2) en methaan (CH_4), en het zeer stabiele zwavelhexafluoride (SF_6), dat vooral door menselijke factoren in steeds grotere hoeveelheden in de atmosfeer wordt aangetroffen. Een speciale methode, gebaseerd op een continue toenemende druk in een afgesloten cel, de *pressure-ramp* methode, laat zien welk deel van de optische extinctie een gevolg is van absorptie en verstrooiing. De resultaten zijn van belang voor zowel de moleculaire fysica als de atmosferische chemie. De kwantitatieve resultaten, die in dit proefschrift worden gepresenteerd, dienen als uitgangspunt voor stralingsmodellen, die bv. de hoogte afhankelijke concentratie van atmosferische bestanddelen voorspellen. De conclusies zijn verder van belang om fotochemische processen of processen die verantwoordelijk zijn voor de afname van atmosferisch ozon kwantitatief te beschrijven.

Dit proefschrift is als volgt opgebouwd.

Hoofdstuk 1 is een algemene inleiding en beschrijft de atmosferische relevantie van het onderzoek, evenals de moleculaire fysica die eraan ten grondslag ligt. Het hoofdstuk behandelt de opbouw van onze atmosfeer, de hoogte-afhankelijke variatie van de fysische omstandigheden, de hoeveelheid kortgolvlige zonnestraling waaraan onze atmosfeer wordt blootgesteld en het principe van lichtverstrooiing (door moleculen en grotere deeltjes), evenals lineaire en botsingsgeïnduceerde absorpties.

Hoofdstuk 2 beschrijft de laseropstelling waarmee verstembare straling in het diepe UV wordt gegenereerd en de gecombineerde *cavity ring-down* en *pressure-ramp* methode waarmee het merendeel van de resultaten is verkregen. De werking van de opstelling wordt besproken aan de hand van optische extinctie metingen van CO tussen 198 en 220 nm bij kamertemperatuur.

Hoofdstuk 3 behandelt extinctie metingen van CO_2 bij kamertemperatuur en golflengtes tussen 198 en 270 nm. Het onderzoek laat zien dat tussen 202 en 270 nm de extinctie vooral door Rayleigh verstrooiing wordt bepaald, en dat voor kortere golflengtes ook moleculaire absorpties een rol gaan spelen.

Hoofdstuk 4 bouwt hierop voort en laat vergelijkbare metingen zien voor N_2 , CH_4 en SF_6 waaruit de absolute waarde van de werkzame doorsnede van de Rayleigh verstrooiing wordt bepaald. Ook hier blijkt moleculaire verstrooiing bij korte golflengtes een belangrijke rol te spelen. Uit de metingen worden waarden afgeleid voor de brekingsindex en de moleculaire polariseerbaarheid en deze worden vergeleken met beschikbare gegevens uit de literatuur.

Hoofdstuk 5 is een spectroscopische studie en beschrijft *cavity ring-down* metingen aan de elektronische γ overgang ($A^2\Sigma^+ - X^2\Pi_r$) van het zwaarste NO-isotoop, $^{15}N^{18}O$. De rovibronische analyse van bijna 400 individuele overgangen resulteert in nauwkeurige moleculaire constanten voor de ($v=1$) en ($v=2$) vibraties in de elektronisch geëxciteerde $A^2\Sigma^+$ toestand.

Het laatste hoofdstuk, *Hoofdstuk 6*, beschrijft voor verschillende drukken *cavity ring-down* metingen aan botsingsgeïnduceerde overgangen rond 477 en 577 nm in O_2-O_2 . De waargenomen absorpties zijn onderzocht als functie van de temperatuur tussen 184 en 294 K. De temperatuur afhankelijkheid van de belangrijkste parameters worden kwalitatief beschreven en vergeleken met in de literatuur voorhanden zijnde data.

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As I sit here, on this summer afternoon in July 2009, I have in front of me the pages of my complete manuscript, marking the end of a winding research way that started yet in 2004. It was a way full of outbursts of constructive inspiration, scientific ardour and sweet victories, however, sometimes darkened by sad disenchantments, and accomplished during long hours, days, weeks and years of hard work. It summarizes scientific results obtained in a laboratory illuminated by glimpses of a “physicist-made laser show under laboratory controlled conditions” and flavoured by monotonous roars of running pumps of the nearby standing “blue monster” setup. The climate in the Netherlands is quite mild and change of seasons is said to be very smooth and barely perceptible. On the contrary to many inhabitants of Amsterdam, I could easily identify the approach of summer and winter when it was suddenly getting colder or warmer in the lab due to a malfunction of the air-conditioning system. Both situations are well comfortable for a guy like me, who was born and had been living in Central Asia for 17 years, before I relocated to Siberia. Here, in Amsterdam I became a real expert in replacing laser dyes and nearly 100 one by one records in the public dye-consumption diary in the dye room speak for themselves, as does the amount of consumed methanol and 10 cent coffee mugs.

Today, looking back to the period of my work in the Laser Centre Vrije Universiteit in Amsterdam (in fact I was a member of both the teams of Atomic, Molecular and Laser Physics, as well as Physical Chemistry) I recall that time with warmth and smiles. Dear friends! My work and my thesis would have been never completed without your support and participation.

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