# Spontaneous Rayleigh-Brillouin Scattering on Atmospheric Gases

Ziyu Gu

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#### VRIJE UNIVERSITEIT

### Spontaneous Rayleigh-Brillouin Scattering on Atmospheric Gases

#### ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad Doctor aan de Vrije Universiteit Amsterdam, op gezag van de rector magnificus prof. dr. F.A. van der Duyn Schouten, in het openbaar te verdedigen ten overstaan van de promotiecommissie van de Faculteit der Exacte Wetenschappen op maandag 23 maart 2015 om 13.45 uur in de aula van de universiteit, De Boelelaan 1105

 $\operatorname{door}$ 

#### Ziyu Gu

geboren te Nanjing, China

promotor: prof. dr. W. M. G. Ubachs copromotor: prof. dr. ir. W. van de Water

to my mother and my wife

## 天问 Heavenly Questions

曰燧古之初,谁传道之? In the beginning of the universe, who narrated the truth? 上下未形,何由考之? When the sky and the earth were not formed yet, who was there to verify it?

圜则九重,孰营度之? It says the sky has nine layers, who managed to measure? 惟兹何功,孰初作之? How big the work to construct it, and who was the constructor?

天何所沓? 十二焉分? What does the sky tread upon? How is it partitioned into twelve? 日月安属?列星安陈? How the sun and moon are coupled, and how the stars are arranged?

自明及晦,所行几里? From light until dark, how many miles travels the sun? 夜光何德,死则又育? What virtue the moon has, to flourish after death? This thesis is reviewed by the members of the reviewing committee:

prof. dr. J. F. de Boer (VU University Amsterdam)prof. dr. D. Lohse (University of Twente)dr. A. G. Straume-Lindner (European Space Agency)dr. B. Witschas (German Aerospace Center)prof. dr. W. J. van der Zande (ASML)





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### Chapter 1

## Introduction

Lidar (Light detection and ranging), utilizing continuous laser beams or laser pulses for active remote sensing, has been used in atmospheric physics for more than 40 years, starting shortly after the invention of the laser. The backscatter lidar, based on a 180° geometry, is the least complicated hence the most frequently used configuration. Lidar systems can be classified into different types such as polarization lidars, Raman lidars, differential absorption lidars, and Doppler lidars, aiming for exploring different properties of the atmosphere. A polarization lidar, consisting of two channels - one with a polarization filter oriented parallel to the polarization of the emitted laser light and the other oriented perpendicular to the polarization of the emitted laser light, is used to characterize the structure of particles (especially the structure of aerosols) in the atmosphere, based on the concept from electrodynamics that non-spherical particles depolarize light. A Raman lidar, taking advantage of the inelastic Raman scattering of photons by molecules, is commonly used to measure the temperature of the atmosphere. Since the population of the molecules in thermal equilibrium should follow a Boltzmann distribution, the intensity pattern of the Raman scattering signal can be related to the temperature of the local area. One of the most important disadvantages of Raman lidar techniques is that due to the low Raman scattering cross section, Raman lidars are less accurate in daytime, when the broadband background resulting from the scattered sun light is strong. The differential absorption lidar techniques, which utilize two wavelengths with one exactly set to the absorption peak of the targeted molecules and the other set to the absorption minima, are typically used to trace the concentration of specific molecules, such as water vapor, carbon dioxide or methane in the atmosphere. It is based on the extinction difference between the two wavelengths. Therefore, it is important that the two wavelengths have almost the same averaged extinction cross section for the rest of the particles in the atmosphere, so the two wavelengths have to be close to each other.

The Doppler lidar techniques, based on the frequency shift of the scattered

light by the moving particles (Doppler shift) in the atmosphere, are typically used to measure the wind velocity, which is equal to the mean velocity of the total amount of particles in the local area. Depending on the objects, two different approaches, the coherent Doppler lidar approach and the direct-detection approach, are regularly used. Light scattering by aerosols at sizes similar to or larger than the wavelength of the laser is known as Mie scattering, and the backscattered light maintains a bandwidth exactly equal to the bandwidth of the incident light. Therefore, the frequency shift of the received light can be obtained from the optical interference of the back-scattered signal with the original lidar light. This approach can only be applied under conditions where sufficient amounts of aerosols are present. In contrast, the direct-detection method, which inspired the work of this thesis, focuses on the Doppler shift of the broadband Rayleigh-Brillouin scattering profile of air  $(N_2+O_2)$  molecules, with their sizes much smaller than the wavelength of the incident light. Utilizing the much broader bandwidth of the scattered light (typically  $\sim 3$  GHz), two identical bandpass filters can be symmetrically placed (in the frequency domain) on both sides of the emitted laser frequency with  $\sim 1$  GHz frequency shift. When there exists a velocity of the molecular ensemble (i.e. wind), the entire symmetric Rayleigh-Brillouin scattering profile will experience a frequency shift, resulting in a difference in the amount of transmitted photons through the two filters. Therefore, measuring the difference of the transmitted signals, the frequency shift of the Rayleigh-Brillouin scattering profile, hence the line-of-sight speed of the gas, can be determined. Since this technique is based on the measurement of the Rayleigh-Brillouin spectra scattering profile, accurate determination of wind (gas) velocities requires accurate knowledge of RB reference profiles, preferably in terms of model functions. Using a simple Gaussian assumption of the scattering profile of air, which is the special case for very low pressures, will result in unacceptable errors in the velocity determination.

#### 1.1 Motivation for this thesis

The present study on laboratory Rayleigh-Brillouin scattering is intimately linked to future space-based Doppler lidar missions of the European Space Agency (ESA) [1–3]. The immediate connection is to the ADM-Aeolus mission aiming to measure wind profiles in the Earth atmosphere on a global scale [4]. This is pursued by active remote sensing, i.e. by measuring the spectral profile of the back-scattered light from an ultraviolet laser on board of a satellite. In the recent past it was noted that the deviations from gaussianity of molecular scattering functions will influence the Doppler measurements and impact the wind profile analysis. In particular acoustic phenomena known to produce the characteristic Brillouin side-wings on the Doppler profile have a strong effect. This was identified as a major problem in previous studies and it was estimated that neglecting the Brillouin effect will result in errors in the radial wind measurement of up to 10% [5; 6]. These estimations were made on the basis of kinetic models in the 1970s, known as S7 [7] and S6 [8] models. These models, which succeeded in relating scattering profiles to the macroscopic gas transport coefficients, namely the heat conductivity, the shear viscosity, and the bulk viscosity, as well as the internal specific heat capacity per molecule, had only been tested for a few measurement configurations and for a very small subspace of gases, pressures and mixtures; especially these models had never been verified for air before the present study. Moreover, the elusive input parameter for the kinetic models, the bulk viscosity, which is related to the energy exchange between the translational and internal motions of gas molecules, is effectively an unknown parameter for light scattering experiment for two reasons: 1, few measurements had been performed to determine its values for gases; 2, most of values were obtained by using sound-absorption measurements at mega-hertz frequencies, which cannot be directly applied to light scattering experiments, where hypersound effects at giga-hertz frequencies prevail. A typical example is that the light-scattering values of  $CO_2$  gas deviate from the sound absorption values by 4 orders of magnitude [9]. Hence the goal of the ESA-funded project was defined as: measuring the spontaneous Rayleigh-Brillouin (RB) scattering profiles and comparing them to the kinetic models in conditions relevant for upcoming ESA lidar missions. More specifically, RB scattering profiles of air, and its major components N<sub>2</sub> and O<sub>2</sub> at pressures of  $0.3 \sim 3$  bar and temperatures of  $250 \sim 340$  K were to be measured to the highest accuracy and to be compared with the kinetic models. Values of the bulk viscosity for the three gases at different conditions were to be determined by comparing the measurements to the models. In addition, the experiments were extended to atomic and polyatomic gases such as He, Ar, Kr, CO<sub>2</sub>. Mixtures of the abovementioned gases were also investigated since air is actually a mixture of  $N_2$ ,  $O_2$ , Ar and other minority species.

#### **1.2** The origin of light scattering

Scattering occurs as the result of fluctuations in a medium; light in a fully homogeneous medium only exhibits forward scattering. The fluctuations of the optical properties of a medium can be described by the elements of the dielectric tensor [10]:

$$\epsilon_{ik} = \epsilon_0 \delta_{ik} + \Delta \epsilon_{ik}, \tag{1.1}$$

where  $\epsilon_0$  is the mean dielectric constant and  $\Delta \epsilon_{ik}$  represents the fluctuations in the dielectric tensor. These fluctuations can be further separated:

$$\Delta \epsilon_{ik} = \Delta \epsilon \delta_{ik} + \Delta \epsilon_{ik}^{(t)} = \Delta \epsilon \delta_{ik} + \Delta \epsilon_{ik}^{(s)} + \Delta \epsilon_{ik}^{(a)}.$$
(1.2)

Here  $\Delta \epsilon$  is a scalar contribution of the dielectric tensor, arising from fluctuations in thermodynamic quantities such as the pressure, entropy, density, or temperature. It results in scalar light scattering, including Rayleigh scattering and Brillouin scattering.  $\Delta \epsilon_{ik}^{(t)}$  represents a traceless tensor contribution of the dielectric tensor, which can be separated into  $\Delta \epsilon_{ik}^{(s)}$  and  $\Delta \epsilon_{ik}^{(a)}$ , the symmetric part and the anti-symmetric part, respectively, with the former giving rise to Rayleigh-wing scattering and the latter (rotational and vibrational) Raman scattering. It is worth noting that due to the traceless nature of  $\Delta \epsilon_{ik}^{(t)}$ , Rayleigh-wing scattering and Raman scattering are depolarizing processes.

For Rayleigh-Brillouin scattering, we only need to focus on the scalar contribution of the fluctuations,  $\Delta \epsilon$ , arising from fluctuations in thermodynamic quantities. Because the density  $\rho$  and temperature T are independent thermodynamic variables, we can separate the scalar fluctuations into two terms: the density fluctuations at constant temperature and the temperature fluctuations at constant density, namely

$$\Delta \epsilon = \left(\frac{\partial \epsilon}{\partial \rho}\right)_T \Delta \rho + \left(\frac{\partial \epsilon}{\partial T}\right)_\rho \Delta T \tag{1.3}$$

According to [11], the second part of Eq. (1.3) contributes only for  $\sim 2\%$  to the light scattering in gases, hence it is usually ignored. Furthermore, we can choose the entropy s and pressure p to be the independent thermodynamic variables to represent the density fluctuations:

$$\Delta \rho = \left(\frac{\partial \rho}{\partial p}\right)_s \Delta p + \left(\frac{\partial \rho}{\partial s}\right)_p \Delta s. \tag{1.4}$$

Here the first term describes pressure fluctuations (acoustic waves) leading to Brillouin scattering, and the second term describes entropy fluctuations (isobaric density fluctuations) leading to Rayleigh-center scattering [10]. As a result, in order to calculate the RB-scattering profile, one must calculate the density fluctuations of the medium. Actually, it has been demonstrated that RB scattering profile of a gas corresponds to the density-density correlation function  $G(\mathbf{r}, t)$ , more specifically its space-time Fourier-transform  $S(\mathbf{k}, \omega)$  [12]. For compressed gases in the hydrodynamic regime, where many-body collisions frequently happen,  $G(\mathbf{r}, t)$  is represented as an ensemble average of density correlations [13]. For diluted gases in the kinetic regime, where mainly two-body collisions occur,  $G(\mathbf{r}, t)$  can be expressed in the phase-space distribution function  $f(\mathbf{r}, \mathbf{v}, t)$  obtained via the linearized Boltzmann equation [14]. For the pressure conditions below 4 bar investigated in this thesis, hence corresponding to the kinetic regime where two-body collisions dominate, the linearized Boltzmann equation is the approach of choice.

#### 1.3 From the Boltzmann equation to the Tenti S6 model

The Boltzmann equation for the microscopic phase space distribution  $f(\vec{r}, \vec{v}, t)$ , with  $\vec{r}$  the position and  $\vec{v}$  the velocity of the particle at time t, reads

$$\frac{\partial f(\vec{r}, \vec{v}, t)}{\partial t} + \vec{v} \cdot \nabla f + \vec{a} \cdot \nabla_v f = -\left(\frac{\partial f}{\partial t}\right)_{coll},\tag{1.5}$$

where  $\nabla_v = \hat{x}\partial/\partial v_x + \hat{y}\partial/\partial v_y + \hat{z}\partial/\partial v_z$  and  $\vec{a}$  is the acceleration experienced by the gas molecules. For coherent Rayleigh-Brillouin scattering [15; 16], which uses a standing-wave optical field to drive the fluctuations,  $\vec{a}$  is equal to the optical dipole force generated by the laser pulses, whilst for spontaneous Rayleigh-Brillouin scattering  $\vec{a}$  is negligible. The right hand side of Eq. (1.5) is the collision term, which reads:

$$-\left(\frac{\partial f}{\partial t}\right)_{coll} = \int |\vec{v} - \vec{v}_1| \sigma(f_1'f' - f_1f) d\Omega d^3 v_1, \qquad (1.6)$$

where  $\vec{v}$  and  $\vec{v}_1$  are the velocities of two different particles,  $\sigma$  the collision cross section,  $d\Omega$  the solid angle element,  $f_1 = f(\vec{r}, \vec{v}_1, t)$ , and f and  $f_1$  are the phase space distribution functions of the two particles before the collision, while f'and  $f'_1$  are those after the collision. It is clear that, according to Eq. (1.6), the Boltzmann equation only deals with two-body collisions, corresponding to gases in the kinetic regime. It is worth mentioning that for gases in the hydrodynamic regime, where many-body collisions frequently exist, the Navier-Stokes equations should be used instead.

For atomic gases, we only need to consider translational energy. For molecular gases, however, rotational and vibrational energy of molecules may also be changed via collisions. Therefore, we need to use a modified version of the Boltzmann equation, which takes rotational and vibrational degrees of freedom into account. One of the modified equations was proposed by Wang-Chang and Uhlenbeck [17] (referred as WCU equation in the following part), which is written as [17]:

$$\frac{\partial f_i}{\partial t} + \vec{v} \cdot \nabla f_i + \vec{a} \cdot \nabla_v f_i = \sum_{jkl} \int (f'_k f'_l - f_i f_j) |\vec{v} - \vec{v}_1| \sigma^{kl}_{ij} d\Omega d^3 v_1, \qquad (1.7)$$

where i, j, k, and l label the internal states of molecules.

We assume that there are only small deviations h for f from the the equilibrium form, the Maxwell distribution. After substitution of  $f_i(\vec{v}, \vec{r}, t) = n_0 x_i \phi(v) [1 + h_i(\vec{v}, \vec{r}, t)]$ , where  $n_0$  is the average number density,  $\phi(v)$  the Maxwell distribution function,  $x_i$  the averaged fraction of molecules in the internal state, the linearized WCU equation is:

$$\left(\frac{\partial}{\partial t} + \vec{v} \cdot \nabla\right) h_i = n_0 \sum_{jkl} x_j \int \int d^3 v_1 d\Omega \phi(v_1) |\vec{v} - \vec{v_1}| \sigma_{ij}^{kl} [h_k(\vec{v'}) - h_l(\vec{v_1}) - h_i(\vec{v}) - h_j(\vec{v_1})]$$

$$\tag{1.8}$$

Note that because we only deal with spontaneous Rayleigh-Brillouin scattering, where the gas molecules do not experience any external force, we set  $\vec{a} = 0$ .

Let us list the appropriate hydrodynamic quantities expressed in terms of  $h_i(\vec{v}, \vec{r}, t)$ . The deviation of the total number density can be written as:

$$n_0\nu(\vec{r},t) = n_0 \sum_i x_i \int \phi(v) h_i(\vec{v},\vec{r},t) d^3v.$$
(1.9)

The macroscopic flow velocity is

$$v_0 \vec{u}(\vec{r}, t) = \sum_i x_i \int \vec{v} \phi h_i d^3 v.$$
 (1.10)

The deviation of the translational temperature is

$$T_0 \tau_{tr}(\vec{r}, t) = \frac{1}{k_B c_{tr}} \sum_i x_i \int \left(\frac{1}{2}mv^2 - \frac{3}{2}k_B T_0\right) \phi h_i d^3 v, \qquad (1.11)$$

with  $c_{tr} = 3/2$  being the translational specific heat capacity per molecule. The deviation of the internal temperature reads

$$T_0 \tau_{int}(\vec{r}, t) = \frac{1}{k_B c_{int}} \sum_i x_i \int \left( E_i - \langle E \rangle \right) \phi h_i d^3 v, \qquad (1.12)$$

where  $\langle E \rangle = \sum_{i} x_i E_i$  stands for the mean energy of all internal states, and  $c_{int}$  is the internal specific heat capacity per molecule. The translational and internal heat flux are given respectively by:

$$n_0 k_B T_0 v_0 \vec{q}_{tr} = n_0 \sum_i x_i \int \left(\frac{1}{2}mv^2 - \frac{5}{2}k_B T_0\right) \vec{v} \phi h_i d^3 v, \qquad (1.13)$$

$$n_0 k_B T_0 v_0 \vec{q}_{int} = n_0 \sum_i x_i \int \left( E_i - \langle E \rangle \right) \vec{v} \phi h_i d^3 v, \qquad (1.14)$$

and the deviation of the traceless pressure tensor from equilibrium is

$$n_0 k_B T_0 \pi_{\alpha\beta} = n_0 m \sum_i x_i \int \left( v_\alpha v_\beta - \frac{1}{3} \delta_{\alpha\beta} v^2 \right) \phi h_i d^3 v.$$
(1.15)

For convenience, Eq. (1.8) can be simplified as

$$\left(\frac{\partial}{\partial t} + \vec{v} \cdot \nabla\right) h_i = n_0 \boldsymbol{J} h_i, \qquad (1.16)$$

where J is the collision operator, which can be separated by the elastic one J' with k = i and l = j and the inelastic one J'' with  $k \neq i$  and  $l \neq j$ . The eigenvectors and eigenvalues for the elastic collision operator J' and for the inelastic collision operator have been studied by Wang-Chang and Uhlenbeck [17] and Hanson and Morse [18], respectively. Following the method of Gross and Jackson [19], which suggests that all of the eigenvalues except for a particular set are set equal to a common constant (degenerated), Boley et al. [7] selected 7 non-degenerate eigenvectors for the collision operator (see Appendix for more details). These 7 eigenvectors are related to 7 physical concepts: the fraction of particles in different internal states, the momentum, the translational energy, the translational heat flux, the internal energy, the internal heat flux, and the traceless pressure tensor. Since the 7 eigenvalues, with a Chapman-Enskog analysis [18], can be expressed in terms of three transport coefficients (i.e. the shear viscosity  $\eta$ , the bulk viscosity  $\eta_b$ , and the thermal conductivity  $\kappa$ ), the atomic mass m of the particles, and the internal specific heat capacity per molecule  $c_{int}$ , Eq. (A.1) can be solved, and the RB scattering profile, which is proportional to  $S(\vec{k}, \omega)$ , the time-space Fourier-transform of the density-density correlation function  $G(\vec{r}, t)$ , can be written as:

$$I(\vec{k},\omega) \propto S(\vec{k},\omega) = n_0 \nu(\vec{k},\omega), \qquad (1.17)$$

where  $\nu(\vec{k},\omega)$  is the Fourier transform of  $\nu(\vec{r},t)$  in Eq. (1.9). It is worth mentioning that, since the measured RB-scattering profiles included in this thesis are always normalized to area unity, the proportionality relation in Eq. (1.17) suffices. Because this model keeps 7 non-degenerated eigenvectors for the collision operator, it is commonly referred to as the S7 model. The very important conclusion to be made for the S7 model is: all of the collision physics is represented by the macroscopic transport coefficients for the gaseous substance, which can be measured by independent techniques.

Aiming to reduce the discrepancies between the S7 model and the measurements in hydrogen and its isotope gases [20], two years later, Tenti *et al.* refined the S7 model by neglecting one of the eigenvectors related to the traceless pressure tensor  $\pi_{\alpha\beta}$  (see Appendix). Since it uses 6 eigenvalues to solve the linearized WCU equation, this model is regarded as the S6 model or Tenti S6 model, after the major contributor. Similarly as in the S7 model, all of the collision physics can again be represented by the macroscopic transport coefficients. It has been proved that, without taking the traceless pressure tensor into account, the S6 model generally gives a better representation than the S7 model. So for most of the time, experimental data will only be compared with the S6 model in this thesis.

#### 1.4 Bulk viscosity

Most of the input parameters used in the Tenti S6 model to calculate the RB scattering profiles are known to high accuracy. However, the bulk viscosity, which was introduced by Stokes in 1845, is an elusive transport coefficient. In the general presentation of the Navier-Stokes equation, the bulk viscosity enters the friction that a compressible fluid experiences,  $(\eta_b + \frac{4}{3}\eta) \cdot \nabla(\nabla \cdot v)$ , where v stands for the velocity of the fluids. For incompressible liquids,  $\nabla \cdot v = 0$ , the bulk viscosity does not play a role in the equation. Assumed by Stokes, which is known as Stokes' hypothesis, it is safe to set the value to be 0 for some gases.

It is understood that the bulk viscosity is related to the energy exchange between the translational and internal motions of molecules. Therefore, Stokes' hypothesis is true for atomic gases, where no internal (i.e. rotational and vibrational) motions exist. For molecular gases, on the other hand, the bulk viscosity is not negligible. The translational motions of molecules respond to pressure fluctuations immediately, while the internal motions normally respond within a certain period through inelastic collisions, which is known as the relaxation time  $\tau$  of the internal modes [21]. Therefore, the bulk viscosity arises in pressure (sound) waves or in an expansion/contraction of a fluid. (The latter is the reason why the bulk viscosity is also named as the volume viscosity in some studies.) Similar to the shear viscosity, which is related to the energy exchange between translational motions, the bulk viscosity also reduces the energy of acoustic waves travelling through the medium, thus can be measured by sound absorption methods. To date, only a few sound absorption measurements, corresponding to mega-hertz acoustic frequencies, have been performed to measure the bulk viscosity in gases. Prangsma et al. measured the bulk viscosity of  $N_2$ , CO, CH<sub>4</sub> and CD<sub>4</sub> between 77 and 300 K [22]. Based on Kneser's measurements [23], Tisza in [24] analyzed the ratio of the bulk viscosity to the shear viscosity to be  $\sim 2000$  for both CO<sub>2</sub> and NO<sub>2</sub>, while for air the ratio is on the order of 1. Truesdell gives  $\eta_b/\eta \approx 1000$  for CO<sub>2</sub> at 293 K [25]. According to Meijer et al. [26], the value of the bulk viscosity can be quantified by the product of  $\omega \tau_j$ , where  $\omega$  is the angular frequency of sound waves and  $\tau_j$  is the relaxation time of the internal mode j. When  $\omega \tau_j \to \infty$ , the sound waves are so fast that there is no energy transfer between the sound-driven translational motions and the motion of internal mode i within a period, so mode j is frozen and gives no contribution to the bulk viscosity. In contrast, if  $\omega \tau_i \ll 1$ , there are sufficient collisions within one wave period to maintain local thermodynamic equilibrium, and the contribution of mode j to the bulk viscosity is frequency-independent. In the general case, however, the bulk viscosity is a frequency-dependent parameter. Since the sound frequency in light-scattering experiment is  $|\mathbf{k}_s - \mathbf{k}_i| v \sim 1$  GHz (with  $\mathbf{k}_i$  and  $\mathbf{k}_s$  being the wave vector of the incident and scattered light), it is questionable whether the values measured at mega-hertz frequencies can be directly used in light scattering. Indeed, Pan et al. [9] found  $\eta_b/\eta$  should be 0.25 for their coherent RBS experiments, more than 3 orders of magnitude smaller than the values found by Tisza and by Truesdell. This large discrepancy between  $\eta_b$  values at ultrasound (MHz) and hypersonic (GHz) frequencies is attributed to the relatively slow relaxation time for vibrational motions of CO<sub>2</sub>, which is  $\tau_v = 6 \times 10^{-6}$  s at atmospheric pressures. For light scattering experiments, probing the hypersound domain,  $\omega \tau_v \approx 1000$ , so the vibrational modes are frozen and the bulk viscosity is much smaller than the values obtained from sound absorption measurements with  $\omega \tau_v \approx 1$ . Proposed by Pan *et al.* [9], values of the bulk viscosity at hypersonic frequencies can be measured by RB-scattering experiments through comparison between the measured and calculated scattering profiles, for the reason that the bulk viscosity is the only uncertain parameter in the Tenti S6 model. In this thesis, a comprehensive study of the bulk viscosity for different gases using RB scattering experiments will be reported.

#### **1.5** Rayleigh-Brillouin scattering experiments in history

Experiments of Rayleigh-Brillouin scattering started in the 1960s, firstly in liquids and solids [27; 28], then in gases [29]. In the early 1970s, the scattering spectrum of the three isotopic variants of molecular hydrogen (i.e. H<sub>2</sub>, HD and  $D_2$ ) at 90° scattering angle was investigated with a HeNe laser and a pressurescanned Fabry-Perot interferometer [20], directly resulting in the famous S7 and S6 models. In 1976, Sandoval and Armstrong [30] reported their study of Rayleigh-Brillouin scattering in  $N_2$  at a range of pressures (1-661 Torr) for a scattering angle of 15°, and compared their work with the model developed by Sugawara and Yip [31], which has three input parameters: the internal specific heat and the elastic and inelastic collision frequencies. Simultaneously, Lao et al. [32; 33] investigated Rayleigh-Brillouin scattering in a number of gases (CO<sub>2</sub>,  $N_2$ ,  $C_2F_6$ , and  $C_2H_6$ ) and He-Kr and Ar-Kr gas mixtures, with a 500 mW Arion laser (514.5 nm). Although most of the measurements contain significant amounts of stray light, which results in an additional sharp peak at the laser frequency, good agreement between the measurements and three models [34; 8; 35] (used for different conditions) were found at Brillouin frequencies. It was firstly noted by them (then by Pan et al. [9] 30 years later) that the vibrational modes of  $CO_2$  have no contribution to the bulk viscosity. Rayleigh-Brillouin scattering experiments in noble gases were reported by Ghaem-Maghami and May in 1983 [36; 37]. Instead of using p, T conditions, they directly connected their measured profiles to the reduced frequency  $x = \omega/(\sqrt{2kv_0})$  and the ratio of scattering wavelength to the molecular mean free path  $y = nk_BT/(\sqrt{2kv_0\eta})$ , and found good agreement (up to 3% level) with calculations. It is worth mentioning that their methods to parameterize the RB scattering profiles in terms of x and y parameters should only work well for atomic gases. For molecular gases, however, accurate knowledge of the internal relaxation number  $z = 3\eta_b/(2\gamma_{int}\eta)$ , with  $\gamma_{int} = c_{int}/(\frac{3}{2} + c_{int})$ , and the Eucken factor  $f = m\kappa/[\eta k_B(\frac{3}{2} + c_{int})]$  are also required [7]. Experiments on binary gas mixtures of noble gases and mixtures of He with hydrogen isotopes at various scattering angles from  $30^{\circ}$  to  $150^{\circ}$  were done by Letamendia *et al.* [38; 39]. At both hydrodynamic and kinetic conditions, their measurements in H<sub>2</sub>-He and D<sub>2</sub>-He mixtures agree much better with theory than the measurements in the Xe-He mixture, where the masses for the two components are significantly different. As suggested by Letamendia *et al.*, for the Xe-He mixture, theories need to be substantially modified.

The research of RB scattering stood still until this century, when a new research technique known as coherent Rayleigh-Brillouin scattering (CRBS) was developed [40; 15]. As mentioned in Sec. 1.3, the only theoretical difference between the coherent and the traditional (now termed as spontaneous)

Rayleigh-Brillouin scattering is that the acceleration term a in the Boltzmann equation is not 0, but related to the optical dipole force induced by the coherent laser pulses. As the fluctuations are driven by the laser pulses, the coherent scattering signal can be much stronger than the spontaneous one, which makes a single shot measurement of the CRBS spectra possible [41]. On the other hand, because of the stability and narrow bandwidth of the continuous laser, the spontaneous RB scattering, which is the topic of this thesis, has a signifiant advantage in measurement accuracy and signal-to-noise ratio, although a measuring period normally takes several hours.

#### **1.6** Heuristic models for the line shape

Although S7 and S6 model models, which are based on a physical approximation of the kinetic equations, can be computed extremely fast and efficiently, they are mathematically complex. Therefore, it is sometimes handy to work with a heuristic model for the line shape. Recently, two heuristic models have been tried, one consisting of three Gaussian function (named as G3 model) [42], the other consisting of three pseudo-Voigt functions (regarded as V3 model) [43].

The G3 model is written as:

$$G(\nu) = \frac{1}{\sqrt{2\pi}\Gamma_R} A \cdot \exp\left[-\frac{1}{2}\left(\frac{\nu}{\Gamma_R}\right)^2\right] + \frac{1-A}{2\sqrt{2\pi}\Gamma_B} \cdot \exp\left[-\frac{1}{2}\left(\frac{\nu+\nu_B}{\Gamma_B}\right)^2\right] + \frac{1-A}{2\sqrt{2\pi}\Gamma_B} \cdot \exp\left[-\frac{1}{2}\left(\frac{\nu-\nu_B}{\Gamma_B}\right)^2\right],$$
(1.18)

where  $\nu$  is the frequency of the incident light source (note this  $\nu$  is different from the  $\nu$  defined in the previous section), A is a parameter representing the spectral intensity,  $\nu_B$  is the Brillouin shift, and  $\Gamma_R$  and  $\Gamma_B$  are the linewidths of the Rayleigh peaks and Brillouin peaks, respectively. In this model both the Rayleigh and Brillouin peaks are treated as Gaussians, so the modeled spectrum is actually a combination of three Gaussian profiles.

Alternatively, the V3 model contains three pseudo-Voigt functions. A pseudo-Voigt function  $V(\nu)$ , which is a linear combination of Gaussian and Lorentzian functions, has the form of:

$$V(\nu) = \rho \cdot L(\nu; \Gamma_L, \nu_L) + (1 - \rho) \cdot G(\nu; \Gamma_L, \nu_L), \qquad (1.19)$$

where  $0 < \rho < 1$  is a parameter representing the proportion of the Lorentzian profile in the pseudo-Voigt profile,  $L(\nu; \Gamma_L, \nu_L)$  representing a Lorentzian and  $G(\nu; \Gamma_L, \nu_L)$  a Gaussian profile, which can be written as:

$$G(\nu; \Gamma_G, \nu_G) = \frac{2\sqrt{\ln 2}}{\sqrt{\pi} \cdot \Gamma_G} \cdot \exp\left\{\frac{-4\ln 2(\nu - \nu_G)^2}{\Gamma_G^2}\right\},\tag{1.20}$$

and

$$L(\nu; \Gamma_L, \nu_L) = \frac{2}{\pi} \cdot \frac{\Gamma_L}{4(\nu - \nu_L)^2 + \Gamma_L^2}.$$
 (1.21)

Here  $\Gamma_G$  and  $\nu_G$  are the width and center frequency of the Gaussian profile, and  $\Gamma_L$  and  $\nu_L$  are the width and center frequency of the Lorentzian profile.

Therefore, the V3 model is written as:

$$V_{RB} = \begin{bmatrix} A \\ B \\ B \end{bmatrix}^{T} \cdot \left\{ \begin{bmatrix} \rho_{R} & 0 & 0 \\ 0 & \rho_{B} & 0 \\ 0 & 0 & \rho_{B} \end{bmatrix} \cdot \begin{bmatrix} G_{R} \\ G_{B}^{+} \\ G_{B}^{-} \end{bmatrix} + \begin{bmatrix} 1 - \rho_{R} & 0 & 0 \\ 0 & 1 - \rho_{B} & 0 \\ 0 & 0 & 1 - \rho_{B} \end{bmatrix} \cdot \begin{bmatrix} L_{R} \\ L_{B}^{+} \\ L_{B}^{-} \end{bmatrix} \right\},$$
(1.22)

where A and B stand for the the spectral intensity of the Rayleigh and Brillouin portion,

$$\begin{bmatrix} G_R \ G_B^+ \ G_B^- \end{bmatrix}^T = \begin{bmatrix} G(\nu; \Gamma_{GR}, 0) \ G(\nu; \Gamma_{GB}, +\nu_B) \ G(\nu; \Gamma_{GB}, -\nu_B) \end{bmatrix}^T \quad (1.23)$$

the Gaussian component in the three (Rayleigh and Brillouin) peaks, and

$$\begin{bmatrix} L_R \ L_B^+ \ L_B^- \end{bmatrix}^T = \begin{bmatrix} L(\nu; \Gamma_{LR}, 0) \ L(\nu; \Gamma_{LB}, +\nu_B) \ L(\nu; \Gamma_{LB}, -\nu_B) \end{bmatrix}^T$$
(1.24)

the Lorentzian component in the three peaks.

Ma *et al.* have compared the G3 and V3 models with the S6 model in [43] and with the experimental RB scattering profiles that included in this thesis in [44], concluding that the V3 model agrees with both the S6 model and the measurements better than the G3 model. This may due to the fact that Brillouin peaks, resulting from the collisions of the gas molecules, maintain Lorentzian forms, which are included as components in the V3 model, but are dismissed in the G3 model. Although the V3 and G3 models may fit measured scattering profiles, they are not based on physical principles. There is no a priori prediction for the dependence of their fitting parameters on temperature, pressure or the other parameters.

### Chapter 2

# A Rayleigh-Brillouin scattering spectrometer for ultraviolet wavelengths

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A spectrometer for the measurement of spontaneous Rayleigh-Brillouin scattering line profiles at ultraviolet wavelengths from gas phase molecules has been developed, employing a high-power frequency-stabilized UV-laser with narrow bandwidth (2 MHz). The UV light from a frequency-doubled titanium:sapphire laser is further amplified in an enhancement cavity, delivering a 5 Watt UV-beam propagating through the interaction region inside a scattering cell. The design of the RB-scattering cell allows for measurements at gas pressures in the range 0 - 4 bar and at stably controlled temperatures from  $-30^{\circ}$ C to  $70^{\circ}$ C. A scannable Fabry-Perot analyzer with instrument resolution of 232 MHz probes the Rayleigh-Brillouin profiles. Measurements on N<sub>2</sub> and SF<sub>6</sub> gases demonstrate the high signal-to-noise ratio achievable with the instrument, at the 1% level at the peak amplitude of the scattering profile.

#### 2.1 Introduction

Rayleigh-Brillouin (RB) light scattering is a powerful method to investigate intrinsic thermodynamic material properties, such as thermal diffusivity, speed of sound, heat capacity ratios, and relaxation times of various dynamical processes occurring in media. Immediately after the invention of the laser as a source of narrow bandwidth radiation in the 1960s, techniques were developed to measure the characteristic scattering profiles, resolving the Brillouin doublet peaks shifted from a central elastic Rayleigh peak, first in the liquid and solid phase[27; 28] and subsequently in the gas phase[29]. During the 1970s detailed studies on RB-scattering in gas phase media were performed, in particular on molecular hydrogen [20], on molecular nitrogen[30], on various polyatomic gases exhibiting internal relaxation [32], and on deriving scaling laws for the noble gases [36]. Over the years various formalisms were derived to describe the spectral scattering profiles based on density fluctuations in the hydrodynamic regime [13] and in the kinetic regime [7; 8]. The latter models, that have become known as the Tenti-models, have been most succesfull in describing RB-scattering over a wide range of conditions, including the transition from the kinetic to the hydrodynamic regime. In particular, in recent studies the 6-component version of the Tenti-model<sup>[8]</sup> (Tenti S6) was found to accurately describe the RB-scattering profile in various atomic and molecular gases [45] and in air [46].

The Rayleigh-Brillouin scattering profile can be measured by different means. The direct method analyzes the scattered light via a Fabry-Perot interferometer, as was pursued in the early studies [29; 32; 38]. Later various forms of optical beating were pursued [47; 48], including superheterodyne techniques making use of frequency tunable lasers [49]. While most studies have been directed towards measuring the spectral profiles in spontaneous RB-scattering, in the last decade also methods were developed for the investigation of coherent RB-scattering [15; 16; 26].

In this paper, we describe an apparatus to accurately measure spectral profiles of Rayleigh-Brillouin scattering in molecular gases at ultraviolet wavelengths. The apparatus employs a high-intensity continuous-wave narrowband laser source in the ultraviolet range, extended with an enhancement cavity yielding 5 W of scattering power to record the RB-profiles at 1% peak-intensity fluctuations even at sub-atmospheric pressures. Such accurate assessment of the scattering profiles of air at atmospheric and sub-atmospheric pressures is required for implementation in modern Doppler-wind remote sensing applications as envisioned for the ADM-Aeolus satellite mission of the European Space Agency (ESA) [4].



**Figure 2.1** – Schematic of the experimental apparatus. The Ti:Sa laser, pumped by a 10 W Millennia Xs pump laser, yields after frequency doubling (in an LBO crystal) in an external enhancement cavity a cw power of 500 mW at a UV-wavelength of 366.8 nm. The UV laser beam is then directed into a second enhancement cavity for amplification by a factor of 10. The RB-scattering cell is placed in the intracavity focus of the UV beam to ensure a maximum scattering intensity. Scattered light is collected at 90° with respect to the beam direction. The geometrically filtered scattered light is directed to the Fabry-Perot Interferometer (FPI), which has a  $232\pm4$ MHz instrumental linewidth. The photons transmitted by the FPI are detected by a photo-multiplier tube (PMT). Note that a small fraction of the UV-light transmitted through mirror M<sub>5</sub> is used as a reference beam for aligning beam paths and for characterizing the detecting system. Mirrors, lenses and diaphragms are indicated with M<sub>i</sub>, L<sub>i</sub> and D<sub>i</sub>.

#### 2.2 Experimental Apparatus

The experimental apparatus for measuring Rayleigh-Brillouin scattering is sketched in Fig. 2.1. It consists of a narrowband tunable laser source with an external frequency-doubling cavity for the production of UV-light, an RB-scattering cell mounted inside an enhancement cavity for increasing the effective scattering power, and a Fabry-Perot Interferometer (FPI) for analyzing the spectral profile of the scattered light. The choice was made to detect at a 90° scattering angle. The apparatus and the comprising units are further described in the following subsections.

#### 2.2.1 Characteristics of the laser source

The laser system is based on a continuous-wave (cw) Titanium:Sapphire (Ti:Sa) ring laser (Coherent 899-21), pumped by a frequency-doubled Nd:YVO<sub>4</sub> pump laser (Spectra-Physics Millennia Xs) with 10 W power at 532 nm. The wavelength of the Ti:Sa laser is tunable in the range 690 to 1100 nm, with a maximum output power more than 2 W near 800 nm. While at its second harmonic (corresponding to 400 nm) in excess of 1 W could be produced, the actual wavelength for RB-scattering was chosen deeper into the UV, compromising between a high scattering cross section and high achievable UV-powers; though in many remote sensing LIDAR applications 355 nm is the wavelength of choice, most of the experiments were carried out at 366.8 nm, where the UV yield of the laser system is much higher. For this setting the Ti:Sa laser produces 1.5 W at 733.6 nm at 1 MHz bandwidth.

An external frequency-doubling cavity, with a brewster-cut lithium-triborate  $(LiB_3O_5; LBO)$  nonlinear crystal mounted in the focus was employed for efficient production of UV light. Methods of impedance matching, phase matching, mode matching and locking the cavity by a Hänsch-Couillaud scheme were detailed in a previous report from our laboratory [50]. This unit delivers an output power of more than 500 mW at 366.8 nm, with a bandwidth estimated at 2 MHz. This narrow bandwidth is the reason for choosing a CW laser source. While pulsed lasers might have some advantages in noise rejection and detection, a bandwidth of 2 MHz cannot be achieved with pulsed lasers suffering from Fourier limitations.

Locking the Ti:Sa laser to a reference cavity ensures a frequency drift limited to 18 MHz per hour, as measured by a wave meter (ATOS Lambdameter), which itself exhibits a drift limited to 10 MHz/hour. Therefore, the actual drift of the frequency is expected to be less than 36 MHz/hour at UV wavelengths.

#### 2.2.2 Scattering Cell and Enhancement Cavity

To achieve a high scattering signal, amplification of the UV laser beam is accomplished by a second enhancement cavity, similarly built as the frequencydoubling cavity: a flat input coupler M<sub>8</sub>, a small flat mirror M<sub>9</sub> attached to a piezo tube for Hänsch-Couillaud locking, and two curved mirrors M<sub>6</sub> and M<sub>7</sub> with -75 mm radius-of-curvature. The center of the RB scattering cell is placed at the mid-point of M<sub>8</sub> and M<sub>9</sub>, where the UV laser beam is focused to  $\sim 200 \ \mu \text{m}$  by the lens L<sub>EC</sub> for mode matching of the in-coupling beam to the cavity. This enhancement cavity yields a power enhancement of 10 times at 366.8 nm, thus delivering a UV-light intensity of 5 W in the scattering volume.

Fig. 2.2 displays a side view of the RB-scattering cell mounted inside the enhancement cavity. The trapezoidal shape of the cell, with a 34° leg-to-base angle, maintains the windows tilted at Brewster's angles for 366.8 nm to reduce reflection losses and to introduce a polarization-dependent element required for Hänsch-Couillaud locking. The RB scattering signal is collected from the center



**Figure 2.2** – Side view of the RB-scattering cell. The UV beam enters the enhancement cavity through mirror  $M_8$ .  $P_1$  and  $P_2$  are pinholes for blocking photons scattered from the mirrors and the windows. Pt100 elements are temperature sensors.

of the cell, with a direction perpendicular to the incident beam. Two additional windows, with anti-reflection coatings on both sides, are mounted at the front and rear surfaces of the cell, in order to transmit the alignment laser beam and the Rayleigh-Brillouin scattered light in the direction of the detector.

The gas is let in and pumped out through the valve mounted on the top of the RB-scattering cell. The windows, sealed with viton O-rings, allow for a pressure variation from 0 bar to 4 bar. Four Peltier elements (indicated in red), disciplined by a temperature controlled water cooling system, can be used both as coolers and heaters and allow for a temperature variation of the gas sample from  $-30^{\circ}$ C to  $70^{\circ}$ C. The temperature of the cell and the gas contained inside is measured by two Pt-100 elements stuck to the top right and bottom left corners of the cell. At two extreme conditions, namely  $-30^{\circ}$ C and  $70^{\circ}$ C, these two elements display less than  $0.5^{\circ}$ C reading difference, indicating that the temperature distribution is homogeneous. The cell itself, machined from solid aluminum, is capable of maintaining the temperature of the sample gas constant over a measuring period of typically 3 hours.

Several measures are taken to reduce stray light reaching the detector to a minimum level. Two pairs of pinholes,  $P_1$  with 1 mm in diameter and  $P_2$ with 1.5 mm in diameter, are placed along the beam path to filter out the UV light scattered from the cavity mirrors  $M_8$  and  $M_9$  as well as from the surfaces of the Brewster-cut entrance and exit windows for the UV-laser beam (see Fig. 2.2). The remaining reflections from the two sides of the exit window are captured and absorbed by two light traps, drilled inside the bottom of the cell and painted black inside. By aligning the incident and the reflected beams to pass exactly through the center of each pinhole, it is ensured that only the light scattered by the gaseous molecules will be detected.

#### 2.2.3 Light collection and alignment

Scattered light is collected from the scattering volume inside the cell by a sequence of optical elements, which have the function to select a narrow opening angle for the scattered light, therewith defining the scattering geometry, to convert the scattered light into a collimated beam that can be accepted by the FPI analyzer, and to reduce the amount of stray light reaching the detector.

A low power auxiliary UV laser beam, leaking through mirror  $M_5$  (in Fig. 2.1) is used to adjust the beam cleaning optics and to align and characterize the FPI. This reference laser beam is aligned to exactly cross the RB-scattering interaction volume and is subsequently used to fine-adjust the lenses  $L_4$  to  $L_6$  and to center the diaphragms  $D_1$  and  $D_3$ . The light emerging from the interaction volume is mode-cleaned by a spatial filter  $S_2$  (diameter 50  $\mu$ m) in combination with two confocal lenses  $L_5$  and  $L_6$  (both f = 50 mm). The collimated output of the light cleaning section is further narrowed by diaphragm  $D_3$  (2.5 mm diameter) and is coupled by lens  $L_{\rm FP}$  to the FPI. This sequence of optics serves to match the acceptance mode profile of the FPI, while the narrow acceptance toward the FPI effectively reduces stray light originating from other locations than the scattering center.

The opening angle of the RB-scattering geometry is controlled by the diaphragm D<sub>1</sub>. Its diameter is kept at  $0.8 \pm 0.2$  mm, while D<sub>1</sub> is placed  $31 \pm 1$  mm away from the scattering center, thus yielding an opening angle of  $0.7 \pm 0.2^{\circ}$ . To assess the effect of angular alignment of the scattering geometry RB-scattering profiles are simulated by the Tenti-S6 model. RB profiles have been calculated for N<sub>2</sub> at 1 bar and 24°C, assuming the scattering to 89°, 90° and 91°, respectively. The scattering profiles are normalized and compared in Fig. 2.3 (a). Deviations between these spectra, as plotted in Fig. 2.3 (b), indicate that for near-perpendicular scattering geometries amplitude deviations of up to 1 percent may occur as a result of a wrong estimation of the scattering angle by 1°.

#### 2.2.4 Fabry-Perot Interferometer

To measure the RB scattering profile, a Fabry-Perot Interferometer, consisting of a flat in-coupling mirror and a concave out-coupling mirror, has been constructed. The rear sides of both mirrors (M<sub>10</sub> and M<sub>11</sub>) are anti-reflection coated for 366.8 nm to minimize losses. The 30' wedge on the in-coupler (M<sub>10</sub>) serves to suppress mode structure arising from the reflections between its surfaces. Compromised by the coupling efficiency and the finesse, the reflectivity of the out-coupling mirror (M<sub>11</sub>) is chosen to be  $R = 99.0 \pm 0.2\%$  for 366.8 nm. For impedance matching the reflectivity of the in-coupling mirror (M<sub>10</sub>) is chosen to be  $R = 98.0 \pm 0.2\%$ . With these choices and settings the in-coupling efficiency is around 75% when the FPI is on resonance.

This plano-concave interferometer is in fact a folded spherical FPI sharing the advantages of a high light gathering power, proportional to the resolving



**Figure 2.3** – (a) Rayleigh-Brillouin scattering profiles for 1 bar N<sub>2</sub> at 24°C simulated with the Tenti S6 model for scattering angles of 89° (black), 90° (red) and 91° (blue). All the spectra are normalized to area unity for comparison. (b) Calculated deviations of RB-scattering profiles measured at 89° and 91° from that measured at 90°. The deviation are shown in percentages of the peak amplitude at 90°.

power, and its insensitivity to small variations of incident angle [51]. In Fig. 2.4 the folded plano-concave FPI of length  $L_1$  (in panel (a)) is compared with the fully confocal FPI of length  $L_2 = 2L_1$ . By carefully setting the mirror spacing to 5 mm, the focal point of  $M_{11}$ , which has a radius of curvature r of -10 mm, is pointing on the left surface of  $M_{10}$ . The in-coupling lens  $L_{FP}$ , with a focal length of f = 50 mm, is positioned such that its focal point coincides with that of  $M_{11}$ . Hence, the collimated light beam incident from the light collection section, is mode matched to couple into the FPI. The out-coupling mirror  $M_{11}$  is mounted on a piezo tube which serves as the scanning element to retrieve the RB-scattering spectra.

#### 2.2.4.1 Free Spectral Range

For a FPI with two plane mirrors, the free spectral range (FSR) is c/2nL, resulting from the self interference of light beams between round trips (2nL), where n is the refractive index of the material in between mirrors, L the distance between the mirrors, and c the speed of light in vacuum. The FPI is operated



**Figure 2.4** – (a) The design of the Fabry-Perot Interferometer. The in-coupling mirror  $M_{10}$  is flat and wedged by 30'. The out-coupling mirror  $M_{11}$  is a concave mirror, with radius of curvature being -10 mm. The distance between these two mirrors is adjusted to be 5 mm. Thus the focal point O of  $M_{11}$  is on the left surface of  $M_{10}$ . The out-coupler is mounted on a piezo for scanning. (b) A confocal Fabry-Perot Interferometer consisting of two concave mirrors both with the same radius of curvature as  $M_{11}$ . This FPI is shown to explain the fourfold mode pattern in the plano-concave interferometer.

under ambient conditions. For a confocal FPI with mirror separation L equal to the common radius of curvature r of both mirrors, it can be shown in a ray-tracing analysis that optical rays retrace their paths after four successive reflections [51]. This results in a FSR of c/4nL for the confocal geometry as displayed in Fig. 2.4(b). Therefore, the effective FSR of our plano-concave FPI of length  $L_1$ , mimicked by a spherical FPI of length  $L_2$  is

$$\frac{c}{4nL_2} = \frac{c}{8nL_1} \approx 7.5 \text{ GHz}$$

$$(2.1)$$

As discussed in Ref. [51], however, if the incident beam is spatially coherent, additional interferences between different light rays in the confocal FPI can occur. For instance, after two reflections, the ray indicated in blue arrow in Fig. 2.5(b) will follow the same path as the ray indicated in purple arrow, and interference can occur. This phenomenon effectively enlarges the FSR by a factor of 2. However, this does not occur for incoherent light as produced in RB-scattering. In addition, if the incident beam is extremely paraxial, the plano-concave FPI almost works as a plane FPI, yielding an effective FSR of  $c/2nL_1$ , corresponding to ~ 30 GHz.

These phenomena are experimentally demonstrated by recordings of FPI transmission fringes by (i) making use of the spatially coherent reference laser beam leaking through mirror  $M_5$  and aligned paraxially through the scattering cell, and (ii) by monitoring the transmission fringes of RB incoherently scattered light. Results are shown in Fig. 2.5. The FPI transmission fringes for the reference laser are monitored by continuously scanning its frequency, while keeping the FPI-mirrors at fixed distance; here the frequency separations are calibrated with an ATOS-wavelength meter, having a relative accuracy better than 50 MHz. The FPI transmission pattern shows the major fringes with separations of  $\sim 30$  GHz corresponding to the paraxial alignment of the reference beam (FSR= $c/2nL_1$ ). The center fringe at 0 GHz in Fig. 2.5 results from the wave-vector mismatch of the additional interferences in the plano-concave FPI. The two smaller peaks are due to the incomplete coherence of the reference beam [51]. The measurements of transmission fringes for RB-scattered light were performed by keeping the laser frequency fixed and by scanning the piezo-voltage on the FPI, and performing the calibration by interpolation (see below in section 2.3.1). These spectra show all four modes, spaced by  $\sim 7.5$ GHz, as expected for incoherent light.

#### 2.2.4.2 Instrument Function

The instrument function of the FPI is characterized in the same way as the FSR in a continuous scan of the UV-laser. Fig. 2.6 shows a typical measurement of the FPI transmission function. The experimental data (black dots) are fitted to a Lorentzian profile function (indicated in red curve), delivering a line width of  $228.8 \pm 1.4$  MHz for this specific measurement. Reproducibility tests yield a mean value of  $232 \pm 4$  MHz for the fringe width, which then determines the resolution  $\Delta_{\rm I}$  of the FPI Rayleigh-Brillouin spectrum analyzer. The laser bandwidth (2 MHz) is so small that it does not effectively contribute to the instrument linewidth of the FPI.

#### 2.3 Experimental Methods & Results

#### 2.3.1 Data Processing Procedure

Rayleigh-Brillouin scattering profiles are measured by scanning the length of the FPI, while keeping the laser frequency fixed. An amplified computercontrolled voltage is applied to the piezo tube attached to the FPI out-coupling mirror  $M_{11}$ . Typical scans cover a voltage increasing from 0 V to 500 V at step sizes of 0.05 V. The piezo retracts over a maximal distance of 4.5  $\mu$ m, resulting in frequency scans of tens of effective FSR's. Data acquisition proceeds by detecting the transmitted light by a photo-multiplier tube (PMT) at typical exposure times of 1 s per step.

Fig. 2.7 illustrates the measurement and calibration procedures for determining the RB scattering profiles. Part (a) shows an example measurement



**Figure 2.5** – The FPI transmission curve probing the output of the coherent UVlaser is indicated by the (black) dots. The full (blue) curves represent the FPItransmission of the Rayleigh-Brillouin scattered light. Since the scattered light is not spatially coherent nor fully paraxial, the amplitude of all modes connected to the four-transit path interference appear equally strong.

of an RB scattering time trace for  $N_2$  at 3 bar, recorded at 23.6°C for 1.8 hours (6500 seconds). Along the vertical axis the absolute number of photon counts detected per second is plotted. The horizontal (red) bars in Fig 2.7(a) connecting the main transmission fringes separated by 30 GHz, show a nonlinearity along the time axis. There are several causes for this phenomenon: (i) the nonlinear conversion of piezo voltage into distance in the FPI; (ii) a temperature-induced drift of the FPI; (iii) frequency drift of the laser. The first effect gives the dominant contribution. The measuring time traces are linearized and converted to a frequency scale by fitting the transmission peaks to a series of Lorentzians, and subsequently linearizing the horizontal scale by matching the peak separations to the measured FSR. This results in the series of RB profiles along a frequency axis as displayed in Fig. 2.7(b). This series of RB-profiles are cut at the midpoints between the transmission peaks into individual RB-profiles. The individual spectra are finally added and normalized to area unity to yield a final RB-scattering profile as shown in Fig 2.7(c).


**Figure 2.6** – The transmission intensity of the FPI with respect to the frequency change of the reference laser. The Lorentzian linewidth of the transmission curve indicates the width of the instrument function, being  $228.8 \pm 1.4$  MHz in this specific measurement.

The experimental profile may be compared to a theoretical description in terms of the Tenti S6 model [45; 46]. The calculated S6 curves are convolved with the measured instrument function of width 232 MHz; the fact that the series of overlapping RB-profiles measured by the FPI never reaches the zero level is accounted for (see also Ref. [45]). A result of the convolved S6 model is shown as the full (red) line in Fig 2.7(c).

In the final panel (Fig. 2.7(d)) the residuals between the Tenti S6 model and experiment are shown on a percentage scale (of the full amplitude). This final result indicates that the difference between measured RB-profile and the Tenti S6-theory are at the 1% level of the maximum amplitude, with some outliers to the 2% level. The result of Fig. 2.7(d) also demonstrates that the rms measurement noise in the neighborhood of the RB-peak amplitude is at the 1% level.

#### 2.3.2 Temperature-dependent Rayleigh-Brillouin scattering

To demonstrate the capabilities of the instrument to record RB-scattering profiles as a function of the gas temperature, measurements were performed for



Figure 2.7 – (a) The recorded RB scattering intensity from  $N_2$  at 3 bar and 23.6°C for 90° scattering angle. The exposure duration of the photon multiplier tube is 1 s for each data point. (b) The RB scattering intensity on the horizontal scale converted to a frequency axis. (c) The final RB scattering profile (indicated in black dots), averaged from the spectra in (b) and normalized in unit area. The red curve is the calculated theoretical Tenti S6 model for comparison. Fig. (d) shows the difference between the measurement and the Tenti S6 model, in percentage of the maximum amplitude.



**Figure 2.8** – (a) The normalized Rayleigh-Brillouin scattering profiles of N<sub>2</sub> measured at three different temperatures:  $-18.4^{\circ}$ C (black),  $23.6^{\circ}$ C (red) and  $63.5^{\circ}$ C (blue). The number density N of the molecules inside the RB scattering cell is kept the same for all three measurements; it corresponds to a pressure of 3 bar at  $23.6^{\circ}$ C. (b) The deviations (in percentage of maximum amplitude of the scattering profile) of the scattering profiles at the other two temperatures from that at  $23.6^{\circ}$ C.

molecular nitrogen gas at three temperatures:  $-18.4^{\circ}$ C,  $23.6^{\circ}$ C and  $63.5^{\circ}$ C. The measurements pertain to pressures of approximately 3 bar; the molecular number density was kept constant by following a procedure of filling the cell



**Figure 2.9** – Normalized scattering profiles of  $SF_6$  at 200 mbar (indicated in black) and 3000 mbar (indicated in red).

at 3 bar at room temperature, and subsequently lowering or increasing the temperature while keeping the cell sealed; the pressures are then, 2560, 3000 and 3400 mbar respectively, calculated from the ideal gas law.

To avoid ice condensation on the windows of the light scattering cell at temperatures below the freezing point, significantly reducing the enhancement of the cavity and resulting in large amounts of stray light, the cell is placed inside an isolated box with a flush of dry  $N_2$ . The resulting RB-profiles are normalized to area unity and compared in Fig. 2.8, indicating a shift of the Brillouin side peaks from the center as temperature increases. The central Rayleigh peak is broadened due to temperature-dependent Doppler Broadening.

Figure 2.8(b) displays the differential temperature effects, whereby the experimental RB-profiles recorded at elevated temperature  $(63.5^{\circ}C)$  and lower temperature  $(-18.4^{\circ}C)$  are plotted, after subtraction of the profile measured at room temperature. It is demonstrated that the temperature effects in this range result in deviations of about 10% of the peak amplitudes.

#### **2.3.3** SF<sub>6</sub> measurements at different pressures

As another application RB scattering profiles were measured in sulphur-hexafluoride  $(SF_6)$  gas, the molecular species with the largest scattering cross section [52]. Figure 2.9 shows the measured scattering profiles of SF<sub>6</sub> at 200 mbar (indicated in black) and 3000 mbar (indicated in red). For 200 mbar, the normalized scattering profile closely resembles a Gaussian shape, resulting from Doppler Broadening. In the normalized spectrum at 3000 mbar the Brillouin side peaks, Stokes and anti-Stokes shifted from the center have become more pronounced than the central Rayleigh peak. The maximal measured intensity for 200 mbar are 1900 counts/s, while for 3000 mbar 27,500 counts/s are recorded. At these large amounts of photon counts the scattering profiles are smoothly resolved; even at low pressures the noise level at the peak amplitude is within the 1% level.

#### 2.4 Conclusion

In this paper, we describe a new instrument for the sensitive spectral measurement of Rayleigh-Brillouin scattering profiles in gases at atmospheric pressures in the UV wavelength range; such profiles, in particular for air and at UV wavelengths, are of importance for modern spaceborne lidar projects such as the ADM-Aeolus project[4]. By application of frequency doubling of a titanium:sapphire laser in connection with an enhancement cavity, 5 Watt of UV-light is available in the scattering volume. The scattering measurements on N<sub>2</sub> and SF<sub>6</sub> demonstrate that rms measurement noise levels of 1% can be achieved, even when the scattering opening angle for scattered RB light is as small as  $0.7^{\circ}$ . The setup is designed to allow for measuring RB profiles as a function of temperature in the range  $-30^{\circ}$ C -  $70^{\circ}$ C.

### Chapter 3

# Temperature-dependent bulk viscosity of nitrogen gas determined from spontaneous Rayleigh-Brillouin scattering

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Values for the bulk viscosity  $\eta_b$  of molecular nitrogen gas (N<sub>2</sub>) were derived from spontaneous Rayleigh-Brillouin (RB) scattering at ultraviolet wavelengths ( $\lambda = 366.8 \text{ nm}$ ) and at a 90° scattering angle. Analysis of the scattering profiles yield values showing a linear increasing trend, ranging from  $\eta_b = 0.7 \times 10^{-5}$  to  $2.0 \times 10^{-5} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$  in the temperature interval from 255 K to 340 K. The present values, pertaining to hypersound acoustics at frequencies in the GHz domain, are found to be in agreement with results from acoustic attenuation experiments in N<sub>2</sub> performed at MHz frequencies.

The concept of bulk viscosity,  $\eta_b$ , also referred to as volume viscosity is part of a thermodynamic description of gases as a transport coefficient in addition to the shear viscosity  $\eta_s$  [53; 54]. The bulk viscosity results from the collisional energy exchange between the translational and internal (rotational and vibrational) degrees of freedom in fluids. The value of  $\eta_b$  of gases can be measured via sound absorption but only a limited number of studies have been reported [23; 22]. Furthermore, such measurements yield values for  $\eta_b$  related to acoustic frequencies in the MHz range, while bulk viscosity is regarded as a frequency-dependent parameter [55], resulting from the competition between the internal relaxation time of molecules and the period of acoustic waves. Therefore, the values measured at MHz frequencies should not be directly applicable to much higher frequencies, such as in light scattering experiments, where the (hypersound) acoustic waves are in the GHz domain. For example, Pan et al. found that bulk viscosity for CO<sub>2</sub> in their coherent Rayleigh-Brillouin scattering (CRBS) experiment, is 1000 times smaller than the sound absorption value [9]. They suggested that values of bulk viscosity at high frequencies could be derived by comparing the light scattering profiles of gases to accurate models developed by Boley *et al.* [7] and Tenti *et al.* [8], given that in these models the only unknown parameter is  $\eta_b$ .

In this Letter, we present measurements of spontaneous Rayleigh-Brillouin scattering (SRBS) profiles of  $N_2$  in a temperature range of 255 K to 340 K and a pressure range of 850 mbar to 3400 mbar. The measured scattering profiles are compared to the so-called Tenti S6 model [8], which is generally considered as the most accurate model to describe the RB-scattering profile [56]. Implicit in the model is that the Brillouin side peaks to the central Rayleigh peak in the scattering profile are shifted by [10]:

$$\Omega_B = \pm 2n\omega \frac{v}{c} \sin \frac{\theta}{2} \tag{3.1}$$

with n and v the index of refraction and the sound velocity in the gas, and  $\omega$ and  $\theta$  the angular frequency of the light and the scattering angle. The Brillouin side peaks exhibit a profile, associated with the damping of acoustic waves, and dependent of the thermodynamic properties of the gaseous medium as well as the light scattering parameters, yielding a Lorentzian profile of full width half maximum:

$$\Gamma_B = \frac{1}{\rho v^2} \left[ \frac{4}{3} \eta_s + \eta_b + \frac{\kappa}{C_p} (\gamma - 1) \right] \Omega_B^2$$
(3.2)

with  $\rho$  the density,  $\kappa$  the thermal conductivity, and  $\gamma = C_p/C_v$ . The code implementing the Tenti model (version S6) was based on that of Pan *et al.* [16], and was used for previous studies on spontaneous and coherent RB scattering in gases [45; 46]. This method via the Tenti model must be followed for extracting  $\eta_b$  in gases where the central Rayleigh peak overlays the Brillouin side peak, unlike for liquids where the Brillouin features are fully isolated and  $\eta_b$  can be determined directly by measuring the width  $\Gamma_B$  [57].



**Figure 3.1** – Rayleigh-Brillouin scattering profiles (black dots) as measured for various (p, T) pressure-temperature combinations as specified. A comparison is made with calculations via the Tenti S6 model (red lines), convolved for the instrument width of 232 MHz and for values of the bulk viscosity  $\eta_b$ , deduced from the profiles recorded at 3 bar. Residuals between the measurements and the calculations are given underneath.

Details of the experimental setup and methods for measuring high signalto-noise RB scattering profiles have been reported in [58]. The profiles are recorded for scattering at  $\theta = 90^{\circ}$  induced by an effective intra-cavity circulating power of 5 Watt at  $\lambda = 366.8$  nm, via a plano-concave Fabry-Perot interferometer (FPI) with an instrument linewidth of 232 MHz. For each measurement, the scattering cell is initially charged to one of the designated pressures, namely 1 bar or 3 bar, at room temperature, followed by sealing the cell and then setting the temperature to one of the designated values: 255 K, 275 K, 297 K or 336 K. The actual pressure of each measurement thus differs from the initial pressure, while the number density of the gas molecules remains the same. The actual pressure is derived via the ideal gas law.

Scattering profiles of N<sub>2</sub> at eight different (p, T) pressure-temperature combinations are shown as black dots in Fig 3.1. Since the effect of  $\eta_b$  is most significant at the highest pressures, where the Brillouin side peaks become pronounced (see Fig. 3.1), the data recorded with an initial pressure of 3 bar are used for determining  $\eta_b$ .

Fig. 3.2 elucidates the method for extracting a value for  $\eta_b$  in the comparison of the Tenti S6 model with the RB-profiles for the specific recording of an RB-profile in N<sub>2</sub> under conditions T = 336.6 K and p = 3.40 bar. Panel (a) shows the measurement (black dots) and the modeled scattering profiles, for three different values of bulk viscosity, and for values of the N<sub>2</sub> transport coefficients as obtained from literature (listed in Table 3.1). For the dimensionless internal specific heat capacity of internal degrees of freedom  $c_{int}$  a value of 1 is used throughout. Residuals between the measurement and the three



Figure 3.2 – (a) Experimental Rayleigh-Brillouin scattering profile in N<sub>2</sub> for 3.40 bar and 336.6 K (black dots), and convolved Tenti S6 calculations for bulk viscosity being  $1.0 \times 10^{-5}$  (green line),  $2.0 \times 10^{-5}$  (red line) and  $3.0 \times 10^{-5}$  (yellow line) kgm<sup>-1</sup>s<sup>-1</sup>, respectively. (b) Residuals between measured and calculated scattering profiles for these three values of the bulk viscosity. (c) A plot of the  $\chi^2$  as a function of bulk viscosity. The optimized value of bulk viscosity is found at the minimum of  $\chi^2$ , with the gray area indicating the estimated statistical error, calculated according to procedures discussed in [26; 45].

modeled scattering profiles are shown in (b). Panel (c) shows a  $\chi^2$ -calculation as a function of bulk viscosity employed in the Tenti S6 model.

This procedure of optimizing  $\eta_b$  was applied to the RB-scattering measure-

T $\kappa$  $\eta_s$  $\eta_b$  $W \cdot K^{-1} \cdot m^{-1}$  $kg \cdot m^{-1} \cdot s^{-1}$  $kg \cdot m^{-1} \cdot s^{-1}$ Κ 254.7 $1.57 \times 10^{-5}$  $2.28 \times 10^{-2}$  $0.7 \times 10^{-5}$  $1.67 \times 10^{-5}$  $2.44 \times 10^{-2}$  $1.1 \times 10^{-5}$ 275.2 $1.76 \times 10^{-5}$  $2.52 \times 10^{-2}$  $1.4 \times 10^{-5}$ 296.7 $2.88 \times 10^{-2}$  $1.95 \times 10^{-5}$  $2.0 \times 10^{-5}$ 336.6 Present data 3.0x10 Vieitez et al Bulk Viscosity (kg m<sup>-1</sup> s<sup>-1</sup>) Meiier et al Pan et al. 2.5x10 Prangsma et al. (acoustic) 2.0x10<sup>-6</sup> 1.5x10 1.0x10<sup>-6</sup> 5.0x10<sup>-6</sup> 0.0 150 200 250 300 350 T (K)

**Table 3.1** – Transport coefficients used for modeling the RB-profiles of N<sub>2</sub>. Values for  $\eta_s$  and  $\kappa$  are calculated according to the Sutherland formula in [59], and  $\eta_b$  from the present experiment.

**Figure 3.3** – Comparison of bulk viscosity measured from different experiments. Note that the result of Pan *et al.* [16] overlays a data point by Prangsma *et al.* [22]. Data of Vieitez *et al.* [45] and Meijer *et al.* [26] also included.

ments for initial pressure of 3 bar N<sub>2</sub>. The resulting values for  $\eta_b$  and their uncertainties are plotted in Fig. 3.3, combined with values from literature. Prangsma *et al.* [22] determined bulk viscosities for  $N_2$  using sound absorption measurements in the temperature range  $T = 70 \sim 300$  K. The experiment investigated a wide range of acoustic frequency to pressure ratios, but all in the MHz domain. Pan *et al.* [16] used the value from Prangsma *et al.* [22] and found good agreement between their CRBS profile and a calculation using the Tenti model (the S7 variant) [7], suggesting that the value of bulk viscosity for N<sub>2</sub> obtained at MHz frequencies is also valid for the GHz range. Cornella et al. [60] successfully modeled CRBS profiles in N<sub>2</sub> assuming a  $\eta_b/\eta_s$  ratio of 0.73 from [22], valid at room temperature, and extrapolated this to 500 K. Values previously obtained by Vietez *et al.* [45] using SRBS at 3 bar  $N_2$  slightly deviate; however, no uncertainty was specified and if a similar uncertainty is assumed as in the present study agreement within combined  $1\sigma$  follows. Meijer et al. [26] using CRBS (at 532 nm) at 5 bar  $N_2$  deduce an even larger value, but still agreement within  $2\sigma$  results.

The present experimental results for  $\eta_b$  in the temperature interval 254-337 K, shown as black dots in Fig. 3.3 show a linear dependence with temperature, roughly similar as in [22]. While the data of [22] extend to temperatures as low as 180 K, and the present data extend to 337 K, for the overlapping range 250 - 300 K good agreement is found. It is assumed that for dilute gases the bulk viscosity is independent of pressure, similar to shear viscosity and thermal conductivity [59]. The RB-profiles recorded for 1 bar N<sub>2</sub> gas, shown in the upper panels of Fig. 3.1, are modeled with the  $\eta_b(T)$  values obtained for 3 bar, also yielding good agreement. While the shear viscosity  $\eta_s$  is known to exhibit a linear temperature dependence in the window 254 - 337 K [59], the ratio  $\eta_b/\eta_s$  grows from 0.46 to 1.01 for the present data. This behaviour may be related to the freezing out of internal degrees of freedom at lower temperatures.

A general conclusion is drawn that for pure nitrogen  $(N_2)$  gas the bulk viscosity at acoustic frequencies in the MHz regime is the same as for hypersound frequencies in the GHz regime. This result is surprising in view of the results in carbon dioxide  $(CO_2)$  gas where differences by orders of magnitude were found [9].

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## Chapter 4

# Rayleigh-Brillouin scattering profiles of air at different temperatures and pressures

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Rayleigh-Brillouin (RB) scattering profiles for air have been recorded for the temperature range from 255 K to 340 K and the pressure range from 640 mbar to 3300 mbar, covering the conditions relevant for the Earth's atmosphere and for planned atmospheric LIDAR missions. The measurements performed at a wavelength of  $\lambda = 366.8$  nm detect spontaneous RB-scattering at a 90° scattering angle from a sensitive intra-cavity setup, delivering scattering profiles at a 1% rms noise level or better. The experimental results have been compared to a kinetic line-shape model, the acclaimed Tenti S6 model, considered to be most appropriate for such conditions, under the assumption that air can be treated as an effective single-component gas with temperature-scaled values for the relevant macroscopic transport coefficients. The elusive transport coefficient, the bulk viscosity  $\eta_b$ , is effectively derived by a comparing the measurements to the model, yielding an increased trend from 1.0 to  $2.5 \times 10^{-5}$  $kg \cdot m^{-1} \cdot s^{-1}$  for the temperature interval. The calculated (Tenti S6) line shapes are consistent with experimental data at the level of 2%, meeting the requirements for the future RB-scattering LIDAR missions in the Earth's atmosphere. However, the systematic 2% deviation may imply that the model has a limit to describe the finest details of RB scattering in air. Finally, it is demonstrated that the RB scattering data in combination with the Tenti S6 model can be used to retrieve the actual gas temperatures.

#### 4.1 Introduction

Light scattering in gases can be described in terms of a wavelength-dependent cross section and a scattering profile. After Rayleigh's celebrated derivation from electromagnetism the cross section, exhibiting its characteristic  $\lambda^{-4}$  behavior, was understood in terms of the index of refraction of the gas [61]. In recent years, laser techniques have made it possible to directly measure the total cross section, also accommodating small deviations from Rayleigh's formula associated with depolarization effects [62]. The scattering profile function is, in the Knudsen approximation of non-colliding particles, governed by the Doppler effect adopting a purely Gaussian shape. However, this approximation only holds for the lowest pressures, while under realistic atmospheric pressures collisions and acoustic modes cannot be neglected [46]. In more general terms, the RB-scattering profile is dependent on a dimensionless parameter y, which is the ratio of scattering wavelength  $2\pi/k$  to the mean free path of the molecules between collisions, hence

$$y = \frac{p}{kv_0\eta} = \frac{Nk_BT}{kv_0\eta},\tag{4.1}$$

where p is the pressure, k the absolute value of the scattering wave vector  $\mathbf{k} = \mathbf{k}_s - \mathbf{k}_i$  with  $\mathbf{k}_i$  and  $\mathbf{k}_s$  the wave vector of the incident and scattered light beam, N the number density,  $k_B$  the Boltzmann constant, T the temperature,  $v_0 = (2k_BT/M)^{1/2}$  the thermal velocity with M being molecular mass, and  $\eta$  the shear viscosity.

While in the Knudsen regime  $y \ll 1$  holds, in the opposite hydrodynamic regime with  $y \gg 1$  the scattering profile can be represented by three distinct features with two Brillouin side-peaks accompanying the central Rayleigh peak. These Brillouin side peaks are shifted toward lower (Stokes component) or higher frequencies (anti-Stokes component) by an acoustic wave vector  $|\mathbf{k}_a| = |\mathbf{k}| = 2|\mathbf{k}_i| \sin(\theta/2), \theta$  representing the scattering angle. This implies that the shift of the Brillouin side-peaks in the frequency domain  $f_b$ , given by

$$f_b = 2nf \frac{v}{c} \sin(\frac{\theta}{2}), \tag{4.2}$$

with n the index of refraction, c the velocity of light in vacuum, v the velocity of sound, and f the frequency of the incident light, depends on the scattering geometry. In the intermediate regime, 0.3 < y < 3, of relevance for practical atmospheric conditions, the mean free path between collisions is comparable to the scattering wavelength and the continuum approach breaks down. In this regime several successful kinetic models have been designed to describe the scattering profile, based on approximate solutions of the linearized the Boltzmann equation [7; 8]. In the well-known Tenti S6 model, the collision integrals are expanded in 6 basis functions, with coefficients determined by the values of the transport coefficients: shear viscosity  $\eta$ , bulk viscosity  $\eta_b$ , thermal conductivity  $\kappa$ , and internal specific heat capacity  $c_{int}$ . This model appears to be the most accurate model to describe the RB-scattering profile [56]. Not only does it describe spontaneous RB scattering, but it also covers the recently discovered coherent RB scattering phenomenon [15; 16].

With the advent of Doppler wind LIDAR (light detection and ranging) techniques to obtain the global wind profile of the Earth's atmosphere, such as the ADM-Aeolus mission of the European Space Agency (ESA) [4], a renewed interest has surfaced in experimentally measuring the RB scattering profile functions of molecular gases, particularly of air, at the highest possible accuracies [46; 45]. In addition, a horizontal LIDAR experiment was reported to prove the Brillouin scattering effect in the atmosphere [63]. Since the RB-profiles cannot be measured under all possible conditions (combinations of wavelengths, scattering angles, pressure, temperature, gas composition) it is of importance to convert the experimental content into theoretical line profiles to be used in satellite retrieval algorithms. Such line profiles should be tested for an as wide as possible part of the parameter space of experimental conditions.

To date, no experiments have been conducted to verify the Tenti S6 model in air for different temperatures. Here, we expand on previous work [46; 45] recording spontaneous RB-scattering profiles of air at an ultraviolet wavelength of 366 nm in a temperature range from 250 K to 340 K for various pressures. For the scattering angle a choice was made for 90°, compromising between reasonably pronounced RB side bands and a not too small free-spectral range of the Fabry-Perot analyzing instrument. The measured scattering profiles are compared with Tenti S6 model calculations, based on a code produced by Pan [64], and adapted for comparison to our experiments [45]. In these calculations the bulk viscosity, quantifying the relaxation of internal molecular modes of motion due to collisions, is a parameter. Because of the absence of internal degrees of freedom it is zero for atomic gases. It is an essential frequency-dependent quantity, but most information about its numerical value comes from experiments at ultrasound frequencies [22], hence in the MHz regime. Recently, studies have been carried out with the intention to derive a value for the bulk viscosity from light scattering [57], in particular from coherent RB-scattering [16]. Meijer et al. [26] compared values for  $\eta_b$  for various gases as obtained from coherent RB scattering, acoustic measurements and molecular structure calculations, showing that there are still many unknowns in the understanding of the bulk viscosity. In the present work we follow the path of deriving optimized Tenti S6 model functions by adapting the numerical values of the bulk viscosity,  $\eta_b$ .

#### 4.2 Scattering profile modeling in the kinetic regime

Rayleigh-Brillouin scattering in gases results from density perturbations  $\Delta \rho$ , which can be written as a sum of distinctive contributions [10]. The entropy perturbations of the medium at constant pressure,

$$\Delta \rho = \left(\frac{\partial \rho}{\partial s}\right)_p \cdot \Delta s,\tag{4.3}$$

result in the central Rayleigh scattering peak, while the pressure perturbations at constant entropy,

$$\Delta \rho = \left(\frac{\partial \rho}{\partial p}\right)_s \cdot \Delta p,\tag{4.4}$$

can be regarded as acoustic waves traveling through the medium (gases in our case), resulting in Brillouin scattering with the Stokes and anti-Stokes scattering peaks shifted by the frequency of the acoustic waves. Contrary to the hydrodynamic regime, where the gas density perturbations can be sufficiently described by Navier-Stokes equations, in the intermediate regime (kinetic regime) the perturbations should be solved from the Boltzmann equation. Since the collision integral of Boltzmann equation is difficult to compute, the Tenti S6 model is based the Wang-Chang-Uhlenbeck equation [17], which is used to construct the collision integral from the transport coefficients.

To compute the scattering profiles of air at different temperatures and pressures, the Tenti S6 model requires values for three transport coefficients, shear viscosity, thermal conductivity and bulk viscosity at the specific conditions as inputs. The assumption is made that air may be treated as a single-component gas with an effective particle mass 29.0 u [65], and effective transport coefficients as obtained from experiment. Shear viscosity and thermal conductivity are known to be nearly independent of pressure. For instance, an increase of pressure p from 1 bar to 50 bar will only result in 10% change of the shear viscosity [66]. Because in the present study, the pressure remains below 3.5 bar, pressure effects on the transport coefficients are treated as negligible. On the other hand, temperature has a significant influence on the transport coefficients. Values of shear viscosity  $\eta$  and thermal conductivity  $\kappa$  for air at certain temperatures can be calculated by [65]:

$$\eta = \eta_0 \cdot \left(\frac{T}{T_0}\right)^{3/2} \cdot \frac{T_0 + T_\eta}{T + T_\eta},\tag{4.5}$$

and

$$\kappa = \kappa_0 \cdot \left(\frac{T}{T_0}\right)^{3/2} \cdot \frac{T_0 + T_A \cdot e^{-T_B/T_0}}{T + T_A \cdot e^{-T_B/T}},\tag{4.6}$$

where  $\eta_0 = 1.864 \times 10^{-5} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$  is the reference shear viscosity and  $\kappa_0 = 2.624 \times 10^{-2} \text{ W} \cdot \text{K}^{-1} \cdot \text{m}^{-1}$  is the reference thermal conductivity, at reference temperature  $T_0 = 300 \text{ K}$ ;  $T_\eta = 110.4 \text{ K}$ ,  $T_A = 245.4 \text{ K}$  and  $T_B = 27.6 \text{ K}$  are characteristic constants for air.

The bulk viscosity,  $\eta_b$ , expressing the resistance of a gas to rapid compression, is a parameter which is not well-understood. This parameter is effectively a second macroscopic viscosity parameter depending on the internal degrees of freedom in the molecular constituents, and therefore does not play a role  $(\eta_b = 0)$  in the thermodynamics of mono-atomic gases [24; 55]. Here, for the measurements on air it must be considered what degrees of freedom effectively contribute to the bulk viscosity. For light-scattering experiments hypersound acoustic frequencies in the GHz range are of relevance; the acoustic frequency  $f_b$  corresponds to GHz frequencies. Under room temperature conditions the vibrational degree of freedom for most gases is frozen due to its long relaxation time, and can therefore be safely neglected. The dependence on the accessible degrees of freedom causes  $\eta_b$  to be temperature dependent. The value of  $\eta_b$  can in principle be measured via sound absorption and a number of studies have been performed [22] in a variety of gases. However, such measurements yield values for  $\eta_b$  in the MHz frequency domain, and they are most likely not directly applicable to the GHz regime of hypersound as is assessed via Rayleigh-Brillouin scattering. Pan *et al.* [16; 9] have proposed to measure the bulk viscosity through RB-scattering experiments, in particular for the case of its coherent form.

The RB-profile depends on the macroscopic transport coefficients, the shear viscosity  $\eta$ , the heat conductivity  $\kappa$ , the internal specific heat capacity  $c_{int}$ , and the bulk viscosity  $\eta_b$ , as well as the temperature T, pressure p of the gas, the mass of the particle constituents, and the wavelength  $\lambda$  or the frequency f of the incident light beam, and the scattering angle  $\theta$ . While the laser and scattering parameters can be measured,  $c_{int}$  and particle mass readily caculated, the transport coefficients  $\eta$  and  $\kappa$  are known from literature to high accuracy. Hence the final, more elusive transport coefficient  $\eta_b$  can be derived from RB-scattering if a model is established that links the scattering profile to the transport coefficients. By this means Pan *et al.* found large discrepancies, up to orders of magnitude, between values for  $\eta_b$  as measured by light scattering compared to previous measurements via sound absorption [16; 9] for the specific example of  $CO_2$ . In this work, we determine the effective bulk viscosity as the value which provides the best fit between the measured line profiles (at high pressures) and the one computed from the Tenti S6 model. It remains a question whether this approach is adequate. As a test, the temperature dependence of the bulk viscosity will be determined, and the obtained values will be further verified with low pressure data, assuming the pressure dependence of  $\eta_b$  is negligible (similar to the shear viscosity).

#### 4.3 Experimental Setup

Details of the experimental setup and methods for measuring RB scattering profiles have been reported in [58]. A narrow bandwidth frequency-doubled titanium:sapphire laser delivers a collimated beam of 500 mW of continuous wave ultraviolet light at 366.8 nm. This intensity is further amplified by an order of magnitude in an enhancement cavity. In a beam focus inside the enhancement cavity, a gas scattering cell is mounted, designed to permit a controlled and stable temperature setting between 250 K and 340 K and a pressure setting between 0 bar and 4 bar. Rayleigh-Brillouin scattered photons are collected at a scattering angle of 90° and subsequently analyzed spectrally by a home-built plano-concave Fabry-Perot interferometer (FPI) with an instrument linewidth of 232 MHz, and an effective free spectral range (FSR) of 7440 MHz. A high gain photo-multiplier tube (PMT) is used for detection and to record the scattered light passing through the FPI. A typical recording period is around 3 hours, during which a typical frequency span of 400 GHz (corresponding to some 50 FSR) is covered. Procedures are followed that correct for drift of the laser frequency and the FPI during data recording, and then all data collected in a 3 hour scan are averaged and normalized to area unity. The scattering profiles are finally compared with the numerical calculations, performed for the exact measurement conditions, and convolved with the instrument function of the FPI (referred to as convolved Tenti S6 model afterwards).

Although the dark counts of the PMT, and the background of the Airy function corresponding to the overlap of consecutive FSRs, have already been taken into account in the calculations, the background of the measurements is always higher than the background of the calculations. This phenomenon had been addressed previously [45] to broadband fluorescence of the cell windows. However, fluorescence is unlikely to play a role here, because non-coated windows are used for the laser beam to pass through the cell and bare fused silica exhibits a fluorescence spectrum longward of 400 nm [67], while this part of the spectrum is filtered before detection. Raman scattering, amounting to  $\sim 2.5\%$  of the total cross section, is another possible source of background. The rotational Raman scattered light, with a large number of individual components of width  $\sim 3$  GHz distributed over several nm, is effectively spread over many modes of the FPI, resulting in a broad structureless background. This additional background, which amounts to  $\sim 2\%$  of the central Rayleigh peak intensity, is corrected by using the same method as in [45]. In addition stray light from the cell and optics might play a role. But this would result in a narrow frequency window at the central frequency (see below).

The sample gas, air, is cooled to  $-40^{\circ}$ C to freeze out the water content to 128 ppm, and then reheated before using. While charging the cell, particles larger than 500 nm were removed by an aerosol filter in the gas inlet line. For each measurement, the gas scattering cell is charged to a designated pressure first and sealed at room temperature. The uncertainty of the pressure meter is calibrated to be 0.5% of the reading. The temperature of the cell together with the gas inside is varied and kept constant by four Peltier elements and a temperature-controlled water cooling system, and simultaneously measured by two Pt-100 elements, leading to 0.5 K uncertainty. The actual pressure of each measurement is thus different from the initial pressure and calculated according to the ideal gas law, while the number density of the gas molecules in the scattering volume is the same. Therefore, the measurements are separated into 3 measurement sets by the number density in Tab. 4.1, with the actual *p*-*T* conditions listed.

The value of the scattering angle was previously determined via assessment of the geometrical layout of the experimental setup, with an uncertainty of  $0.9^{\circ}$  [45]. This value can be further verified from the actual scattering data, as the RB-scattering profile is rather sensitive to the scattering angle [58]. A complicating factor is that for data Set III both the bulk viscosity  $\eta_b$  and

**Table 4.1** – Conditions and values of transport coefficients for the Rayleigh-Brillouin scattering measurements. Values of  $\eta$  and  $\kappa$  are calculated by Eq. (6.3) and Eq. (6.4), from Ref. [65]. Values of  $\eta_b$  for data Set III are obtained directly from a least squares fit, while those for data Set I and II are calculated by Eq. (4.9). The y parameter for each measurement is indicated in the last column.

	р	Т	$\eta$	$\eta_b$	$\kappa$	y
	(mbar)	(K)	$(\mathrm{kg}\cdot\mathrm{m}^{-1}\cdot\mathrm{s}^{-1})$	$(\mathrm{kg}\cdot\mathrm{m}^{-1}\cdot\mathrm{s}^{-1})$	$(W \cdot K^{-1} \cdot m^{-1})$	
Set I	643	254.8	$1.624 \times 10^{-5}$	$0.97 \times 10^{-5}$	$2.265 \times 10^{-2}$	0.427
	704	276.7	$1.734 \times 10^{-5}$	$1.34 \times 10^{-5}$	$2.441 \times 10^{-2}$	0.418
	726	297.1	$1.832 \times 10^{-5}$	$1.68 \times 10^{-5}$	$2.601 \times 10^{-2}$	0.396
	777	317.8	$1.929 \times 10^{-5}$	$2.03 \times 10^{-5}$	$2.761 \times 10^{-2}$	0.390
	827	337.3	$2.017{ imes}10^{-5}$	$2.36 \times 10^{-5}$	$2.908{ imes}10^{-2}$	0.382
Set II	858	254.8	$1.624 \times 10^{-5}$	$0.97 \times 10^{-5}$	$2.265{ imes}10^{-2}$	0.574
	947	276.7	$1.734{ imes}10^{-5}$	$1.34 \times 10^{-5}$	$2.441 \times 10^{-2}$	0.564
	1013	297.3	$1.832 \times 10^{-5}$	$1.68 \times 10^{-5}$	$2.603 \times 10^{-2}$	0.550
	1013	318.3	$1.931 \times 10^{-5}$	$2.04 \times 10^{-5}$	$2.765{ imes}10^{-2}$	0.505
	1017	337.8	$2.020 \times 10^{-5}$	$2.36 \times 10^{-5}$	$2.912 \times 10^{-2}$	0.470
Set III	2576	255.0	$1.625 \times 10^{-5}$	$0.96 \times 10^{-5}$	$2.267 \times 10^{-2}$	1.718
	2813	278.0	$1.740 \times 10^{-5}$	$1.34 \times 10^{-5}$	$2.451 \times 10^{-2}$	1.681
	2910	297.6	$1.835 \times 10^{-5}$	$1.92 \times 10^{-5}$	$2.605 \times 10^{-2}$	1.589
	3128	319.3	$1.936 \times 10^{-5}$	$1.87 \times 10^{-5}$	$2.773 \times 10^{-2}$	1.562
	3304	337.7	$2.019 \times 10^{-5}$	$2.36{ imes}10^{-5}$	$2.911 \times 10^{-2}$	1.537

the scattering angle  $\theta$  influence the RB-profile, with  $\eta_b$  value having a larger impact. Moreover the scattering angle  $\theta$  mainly affects the total width of the RB-scattering profile, where the bulk viscosity  $\eta_b$  determines the pronounced occurrence of Brillouin side features; hence the two parameters are not strongly correlated. For this reason, a procedure is adopted to determine an initial value for the bulk viscosity  $\eta_b$ , and then subsequently perform a fit to the scattering angle, minimizing the residual between model and experiment. The  $\chi^2$  residual is defined as [26]:

$$\chi^{2} = \frac{1}{N} \sum_{i=1}^{N} \frac{[I_{e}(f_{i}) - I_{m}(f_{i})]^{2}}{\sigma^{2}(f_{i})}, \qquad (4.7)$$

where  $I_e(f_i)$  and  $I_m(f_i)$  are the experimental and modeled amplitude of the spectrum at frequency  $f_i$ , and  $\sigma(f_i)$  the statistical (Poisson) error. An example of such a least-squares minimization to angle  $\theta$ , for an experimental RB scattering profile of air at 337.7 K and 3.30 bar is presented in Fig. 4.1. Panel (a) shows the residuals between the measurement (black dots) and the modeled scattering profile (red line), when three different scattering angles, 89.2°, 89.8° and 90.4°, are used for modeling. The  $\chi^2$ -values calculated from the residuals are 2.55, 1.68, and 2.44 for these three angles. In Fig. 4.1 (b), values of  $\chi^2$  are plotted as a function of scattering angles  $\theta$  employed in the S6 model. The  $\chi^2$ -fit, represented by the full (green) line yields an optimized scattering of  $\theta = 89.8^{\circ}$  with a  $1\sigma$  standard deviation less than  $0.1^{\circ}$ . This agrees well, with the direct geometrical assessment of the angle  $90 \pm 0.9^{\circ}$ . The determined scattering angles for all the 5 temperatures in data Set III are plotted in Fig. 4.1 (c), indicating that the scattering angles for the same temperature settings (hence number densities) are the same. It is noted that the two left most points in (c) pertain to data recorded with time intervals of several months; after such downtime, a full alignment of the optical system had to be performed, explaining the  $0.4^{\circ}$  scattering angle deviation.

This approach of optimizing scattering angles is further applied to the other two data sets, yielding an averaged  $\theta$  to be 90.2° for the data Set I, 90.4° for the data Set II, and 89.7° for the data Set III. Therefore, all the derived values of  $\theta$  were found in the range 90  $\pm$  0.9°. The slight deviations are attributed to realignment of the laser beam-path through the scattering cell. The number density variation inside the cell causes the index of refraction to change and therewith the angle of the laser beam with respect to the Brewster windows; note that outside the cell atmospheric pressure is maintained [58]. In order to keep the enhancement cavity at optimized circulating intensity angular variations of a few 0.1° have to be imposed consequently.

#### 4.4 Measurements and Analysis

In the present study, the relevant pressure and temperature parameter space for Rayleigh-Brillouin scattering in air is mapped. A choice was made for three different initial charging pressures (725 mbar, 1000 mbar, and 3000 mbar), combined with five different temperature settings at 255 K, 277 K, 297 K, 318 K and 337 K, at intervals of ~20 K. While the super-atmospheric pressure of 3 bar is not relevant in an Earth atmospheric context, its data are important for a stringent test of the Tenti S6 model, in view of the higher signal-tonoise ratio obtained and the more pronounced Brillouin side peaks occurring at higher pressures. The experimental data, plotted in black dots in Figs. 4.2, 4.3, and 4.4, present the central scientific content of this study. Note that the temperature settings are not exactly reproduced for different data sets; actual values of p and T are given in the figures and in Table 4.1. The RB-data were analyzed adopting values for the scattering angle  $\theta$  as discussed in the experimental section.

The present data on spontaneous RB scattering were used to assess the effect of the bulk viscosity in air. The bulk viscosity is related to the damping of sound, thus, the Brillouin side peaks, which become more pronounced at large pressures. Therefore the data recorded at 3 bar (data set III) are used to determine  $\eta_b$  in a least-square procedure. Fig. 4.5 shows an example of a least-squares fit for the measurement at 337.7 K and 3.30 bar. Beside the measurement (black dots), three typical model calculations are plotted in



Figure 4.1 – Graphical representation of the procedure for verifying the scattering angle  $\theta$ ; (a) Residuals between the experimental RB-scattering profile, measured for 337.7 K and 3.30 bar, and the Tenti S6 calculations, for three selected scattering angles:  $89.2^{\circ}$ ,  $89.8^{\circ}$  and  $90.4^{\circ}$ ; note that a value of  $\eta_b = 2.36 \times 10^{-5} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ , a result of the present study, was adopted to produce the theoretical curve. (b) The values of  $\chi^2$ , calculated according to the residuals, as a function of scattering angle used for Tenti S6 modeling. The green line is the parabolic fit to the  $\chi^2$  values, giving a minimum at  $89.8^{\circ}$ . The estimated error  $(1\sigma)$  for this angle determination is less than  $0.1^{\circ}$ . (c) Optimized scattering angles together with their standard errors for all the measurements in data Set III).

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Figure 4.2 – Data set I; Normalized Rayleigh-Brillouin scattering profiles of air recorded at  $\lambda = 366.8$  nm, for pressures ~ 725 mbar and temperatures as indicated. The scattering angle for this data set was determined as  $\theta = 90.2^{\circ}$  in the previous section. Experimental data (black dots) are compared with the convolved Tenti S6 model calculations (red line), with the input parameters listed in Table 4.1. Values of  $\eta_b$  at different temperatures are calculated from Eq. (4.9).



**Figure 4.3** – Data set II; Normalized Rayleigh-Brillouin scattering profiles of air recorded for pressures ~ 1000 mbar and temperatures as indicated. The scattering angle for this data set was determined as  $\theta = 90.4^{\circ}$  in the previous section. Values of  $\eta_b$  at different temperatures are calculated from Eq. (4.9).

Fig. 4.5 (a), for  $\eta_b$  at  $1.3 \times 10^5$  kg·m<sup>-1</sup>·s<sup>-1</sup> (green),  $2.4 \times 10^5$  kg·m<sup>-1</sup>·s<sup>-1</sup> (red), and  $3.5 \times 10^5$  kg·m<sup>-1</sup>·s<sup>-1</sup> (yellow). Fig. 4.5 (b) indicates the residuals between the measurement and the three calculations. Fig. 4.5 (c) shows the  $\chi^2$ -plot versus the bulk viscosity, and provides insight into the significance of the optimized value for  $\eta_b$ . The statistical error of this determination is calculated according to [26; 45]:

$$\sigma_{\eta_b} = \left(\frac{N'}{2} \frac{d^2 \chi^2}{d\eta_b^2} \Big|_{\tilde{\eta}_b}\right)^{-1/2},\tag{4.8}$$

with N' the number of the independent samples in the spectrum, and  $\tilde{\eta}_b$  the location of the minimum of  $\chi^2$ . Accordingly, the statistical error in this case is  $0.6 \times 10^{-6} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ . The uncertainty of measured temperature (~ 0.5 K) and of measured pressure (0.5% of the reading), propagate as errors in the bulk viscosity determination, because both temperature and pressure are input parameters for the Tenti S6 model calculation. By allowing the pressure and temperature to vary at their uncertainty ranges, the derived bulk viscosity changes by  $1.1 \times 10^{-6} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ . Therefore, the total estimated error is  $1.7 \times 10^{-6} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ .



**Figure 4.4** – Measurement set III; Normalized Rayleigh-Brillouin scattering profiles of air recorded for pressures ~ 3000 mbar. The scattering angle for this data set was determined as  $\theta = 89.7^{\circ}$  in the previous section. Values of  $\eta_b$  at different temperatures are directly obtained from the least squares fit.

This fitting procedure for  $\eta_b$  was applied to the other measurements in data set III. The resulting values obtained for  $\eta_b$  are plotted in (black) rectangular dots in Fig. 4.6. In view of the observed monotonic increase a first order phenomenological model is adopted in terms of a linear dependence to which the results are fitted:

$$\eta_b = a + b \cdot T,\tag{4.9}$$

This functional form represents the temperature effect on the bulk viscosity (black dashed line). This approach yields an intercept  $a = (-3.33\pm0.60)\times10^{-5}$ , and a slope  $b = (1.69\pm0.21)\times10^{-7}$ , with  $\eta_b$  expressed in kg·m<sup>-1</sup>·s<sup>-1</sup>, T in K, and the proportionality constants a and b in the corresponding units.

Finally, the convolved Tenti S6 model is calculated for all the experimental conditions pertaining to the data sets I, II, and III. A parametrization of the Tenti S6 model, as presented in [45] is used. Values for the scattering wavelength  $\lambda = 366.8$  nm, scattering angle  $\theta$  as discussed above, instrument function with linewidth  $\Delta \nu = 232$  MHz, particle mass 29.0 u, and values for the macroscopic transport coefficients are invoked in the model. Values for the shear viscosity and thermal conductivity are calculated according to Eqs. (6.3) and (6.4). While values for the bulk viscosity for the RB-data of data set III are



**Figure 4.5** – (a) Experimental Rayleigh-Brillouin scattering profile in air for 3.30 bar and 337.7 K (black dots), and convolved Tenti S6 calculations for bulk viscosity being  $1.3 \times 10^5$  (green line),  $2.4 \times 10^5$  (red line), and  $3.5 \times 10^5$  (yellow line) kg·m<sup>-1</sup>·s<sup>-1</sup> respectively. (b) Residuals between measured and theoretical scattering profiles for three values of the bulk viscosity. The vertical dotted lines indicate the frequency where the Brillouin side peaks occur. (c) A plot of the  $\chi^2$  as a function of bulk viscosity. The statistical error for this fit is  $0.6 \times 10^{-6} \text{ kg·m}^{-1} \cdot \text{s}^{-1}$ .



**Figure 4.6** – Bulk viscosities  $\eta_b$  for air plotted as a function of temperature (black rectangular symbols) as determined from RB-scattering measurements around 3 bar air pressure and at  $\lambda = 366.8$  nm. The black straight line represents a linear fit to the experimental  $\eta_b$  values (see text). A comparison is made with values for the shear viscosity  $\eta$  (blue upper triangles) calculated by Eq. (6.3) in [65]. The blue dashed line is a linear fit to the  $\eta$  values. The (red) circular dots represent the values of derived bulk viscosity when stray light is taken into account. Note that the red dots are offset to the right by 2 K to circumvent overlap of data points.

directly obtained from a least squares fit to the experimental spectra, the data of sets I and II do not permit such a direct determination of bulk viscosity since at low pressures the Brillouin side peaks are less pronounced. Assuming that  $\eta_b$  is independent of pressure, values for  $\eta_b$  for data sets I and II are derived through the temperature dependency found in Eq. (4.9).

All information on the measurement conditions and values of the transport coefficients are listed in Table 4.1. In the last column, the values of the y parameter are also indicated. The convolved Tenti S6 model calculations (red line) are compared with the measurement at each condition in Fig. 4.2, Fig. 4.3 and Fig. 4.4, with the residuals in percentage of the peak amplitude of each measurement shown below. Two conclusions can be derived from the residuals: firstly, the rms noise, which is the standard deviation of the noise distribution, are at or below the 1% level; secondly, the deviation between each measurement and the modeling calculation seems systematic but within 2%.

Due to the small scattering cross section of the gas molecules, any RB

detection setup is sensitive to stray light from cell walls, cell windows, and from the beam-steering optics. Stray light typically exhibits the same bandwidth as the incident laser beam (2 MHz), and should not be frequency shifted. Therefore, stray light will appear as a Lorentzian line located exactly in the center of the RB scattering profile with 232 MHz bandwidth, corresponding to the FWHM of the Fabry-Perot interferometer. It is noted that Mie scattering induced by aerosol particles in the scattering cell would result in a similar frequency profile; precautions were taken to avoid aerosol scattering. Because there is a systematic structure of the residuals for nearly all measurements (see Fig. 4.2 to Fig. 4.4), with the measured central Rayleigh peak slightly higher than the calculation and the Brillouin peaks lower, this may be interpreted as evidence for stray light contributing to the scattering profile in the present measurements. The fact that the deviations are most apparent at the low pressure measurements, supports this hypothesis: the relative contribution of stray light should be largest at low pressures. However, it is worth noting that the additional residuals at the central Rayleigh peak always have a FWHM much larger than 232 MHz. This may imply that the increased intensity is not just attributable to stray light.

In order to test the stray light hypothesis, we added a spectral contribution  $S\delta(f_i)$  for stray light to the modeled amplitude function  $I_m(f_i)$ , thus yielding a total amplitude of  $I'_m(f_i) = I_m(f_i) + S\delta(f_i)$ . After replacing the amplitude function  $I_m(f_i)$  by  $I'_m(f_i)$  in the analysis, the entire modeling procedure was repeated using the least-squares procedure of Eq. (6.6). Via this means, in most cases, an improved fit to the scattering profile was obtained, for stray light intensities of S = 0 - 0.4 %. Fig. 4.7 shows four residuals of profiles with and without stray light being included. Some cases, Fig. 4.7 (a) and (c), were selected, where indeed deviations were obviously present, and better fits are obtained if a stray light contribution is added. The  $\chi^2$  are reduced from 2.15 to 1.93 when S = 0.33% for Fig. 4.7 (a), and the  $\chi^2$  decreases from 5.67 to 4.00 when S = 0.44% for Fig. 4.7 (c). However, in several exceptional cases such as Fig. 4.7 (b), although the  $\chi^2$  is reduced from 2.65 to 1.80, this stray light subtraction procedure may lead to overfitting, resulting in a conspicuous dip for the residuals  $I_e(f_i) - I'_m(f_i)$  at  $f_i = 0$ , with a systematic deviation around  $\pm$  1 GHz remaining, at the positions of the Brillouin peaks. For a few cases, Fig. 4.7 (d) for example, the stray light does not play a role: a minimum of  $\chi^2$ is found when S = 0%.

Although the fitted stray light contribution (S) is always small (less than 0.5%), it is questionable whether this contribution may significantly influence the values of bulk viscosity. Therefore, the values of bulk viscosity are derived again with a stray light contribution included. The newly derived values are plotted as red circular dots in Fig. 4.6. Indeed the  $\eta_b$  values are changed, but by less than  $0.05 \times 10^{-5} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$  for all the temperatures, much smaller than the error margins.



**Figure 4.7** – A comparison of residuals for four selected sample measurements of Rayleigh-Brillouin scattering profiles in air for (p, T) conditions without and with stray light included.

#### 4.5 Discussion

The method of extracting  $\eta_b$  values from RB-scattering profiles was applied by Vietez *et al.* [45] both for coherent RBS and for spontaneous RBS. Meijer *et al.* [26] have further detailed the CRBS studies, and at the same time performed model calculations for  $\eta_b$  in various gases, while they also reviewed the literature on available quantitative information on bulk viscosity in gases.

At room temperature, Prangsma *et al.* [22] had made measurements on sound absorption in N<sub>2</sub>, yielding  $\eta_b = 1.28 \times 10^{-5} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ ; in their study they reviewed a survey of 14 independent sound absorption data for near-roomtemperature N<sub>2</sub> finding all values in the range  $(0.75 - 1.5) \times 10^{-5} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ . In comparison light scattering yields  $\eta_b = (2.6 \pm 0.5) \times 10^{-5} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$  for CRBS [26] and  $\eta_b = 2.2 \times 10^{-5} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$  for SRBS [45]. Pan *et al.* [16] and Cornella *et al.* [60] used a value of  $\eta_b = 1.28 \times 10^{-5} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$  for N<sub>2</sub> at room temperature in their modeling of RB-profiles. So for N<sub>2</sub> at room temperature differing values for  $\eta_b$  are found for low and high frequencies, but the difference is only a factor 2 - 3, much less than in the case of CO<sub>2</sub>, where orders of magnitude discrepancies were obtained [9].

In the study by Prangsma *et al.* [22] temperature effects on the bulk viscosity were also investigated, for N<sub>2</sub> and other singular molecule gases. Values for  $\eta_b(N_2)$  were obtained from 77 K to 300 K, yielding linearly increasing values  $\eta_b = (0.2-1.3) \times 10^{-5} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$  [22]. Recently, a similar linear *T*-dependence of bulk viscosity for N<sub>2</sub>, with the values from  $0.7 \times 10^{-5} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$  at 255 K to  $2.0 \times 10^{-5} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$  at 337 K, has been reported by our group [68]. To the authors' knowledge, no *T*-dependence of the bulk viscosity has been investigated for air, which is a mixture of gases.

In the present study  $\eta_b$  is derived from SRBS in air for various temperatures, results of which are displayed in Fig. 4.6. At 297.2 K the result is  $\eta_b = (1.9 \pm 0.2) \times 10^{-5} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ . This is in reasonable agreement with the values established for the atmospheric constituents:  $\eta_b(N_2) = (2.6 \pm 0.5) \times 10^{-5}$ kg·m<sup>-1</sup>·s<sup>-1</sup> and  $\eta_b(O_2) = (2.3\pm0.3)\times10^{-5}$  kg·m<sup>-1</sup>·s<sup>-1</sup> [26]. In the analysis the assumption was made to treat air in a Tenti S6 model as a single-component gas with transport coefficients as measured for air. The present outcome shows a quantitative outcome in correspondence with findings for  $N_2$  and  $O_2$ . While the uncertainties are rather large the data nevertheless demonstrate a clear example of a bulk viscosity increasing with temperature. Assuming that all rotational degrees of freedom are accessible, the temperature dependence of  $\eta_b$ owes to the collisional velocity dependence of the rotational relaxation time. For hard–sphere collisions, this would imply  $\eta_b \propto T^{1/2}$ , which is not observed. A similar temperature dependence  $\eta \propto T^{1/2}$  would be expected for the shear viscosity [69]. That the assumption of hard-sphere collisions is too simple is already implicit in Eq. (6.3) for the shear viscosity.

It has been argued that there should exist a fixed ratio between shear viscosity and bulk viscosity, independent of temperature and pressure [70]. This assumption, however, was questioned, because the bulk viscosity should exhibit a frequency-dependence due to the competition between the internal relaxation time of molecules and the period of sound waves [55]. Moreover, the velocity dependence of momentum exchange collisions can be different from those for the relaxation of rotational modes. The present results on the temperaturedependent bulk viscosities in air, in comparison with literature data on the shear viscosity (see Fig. 4.6), show that the increase in  $\eta_b$  is more rapid than for  $\eta$ . This was also the case for previous studies[22; 68].

#### 4.6 Temperature retrieval from SRBS profiles

Besides determining wind velocities, retrieval of temperatures of the atmosphere with Rayleigh-Brillouin LIDAR methods is another interesting target for aero-scientists [70]. However, due to the low RB-scattering cross section and complicated scattering profile calculations for air, the accuracy is limited [56]. Therefore, Brillouin LIDAR techniques have only been applied to measure the temperature of water [71; 72]. Here we demonstrate that with the Rayleigh-Brillouin scattering method, in comparison with the Tenti S6 model, it is possible to measure the temperature of air under atmospheric pressures.

Fig. 4.8 shows the comparisons between the measured temperatures (with the PT-100 temperature sensors in the experimental setup) and derived temperatures for data Set I and data Set II. The derived values are obtained by fitting T to a minimal  $\chi^2$ , when the other parameters are fixed to the values used in the Tenti S6 calculations. Note that under these pressure conditions the bulk viscosity, for which we used the simple linear temperature dependence shown in Fig. 4.6, does not play a significant role. The solid black lines represent the condition where the derived and measured temperatures are equal. It is obvious that the derived temperatures agree well with the real (measured) temperatures for all the conditions: the maximal difference is 0.4 K.

An accuracy of less than 0.5 K can be obtained, provided that all the other conditions  $(p, \theta)$  and the transport coefficients  $(\eta, \eta_b, \text{ and } \kappa)$  are known to a high accuracy.

#### 4.7 Conclusion

In conclusion, Rayleigh-Brillouin scattering profiles of air at 15 different pressuretemperature combinations have been recorded. From a quantitative analysis of the data at higher pressures, values for the bulk viscosity of air are determined. Values obtained for  $\eta_b$  at different temperatures provide evidence for the temperature-dependent effect of this gas transport coefficient in air:  $\eta_b$  tends to increase toward higher temperatures. With these newly derived values, all experimental Rayleigh-Brillouin scattering profiles in the parameter space p = 0.6 - 3.3 bar and T = 255 - 340 K can be reproduced by the Tenti S6 model within 2% deviation. The persistence of the systematic deviations between measured spectra and the model, even after allowing for the instru-



Figure 4.8 - Temperature retrieval form RB-scattering profiles in air. The derived temperatures for (a) data Set I and (b) data Set II, as function of measured temperatures. The dashed lines indicate where derived and measured values are equivalent.

mental effects (scattering angle and elastic scattering), may suggest that either the Tenti model does not adequately describe our experiment, or our method to treat air as a single component gas with effective values for its molecular mass and transport coefficients leads to deviations. Also, the additionally detected background, which may be due to rotational Raman scattering, is still not fully understood. Nevertheless, the 2% deviation with the Tenti S6 model for a wide parameter space bears prospect of using the model for future LIDAR missions employing RB-scattering in the Earth's atmosphere. The results of temperature retrieval suggest that the Tenti S6 model could accurately predict the temperature of air within 0.5 K if all the other experimental conditions and the transport coefficients are known.

## Chapter 5

# Rayleigh-Brillouin scattering of carbon dioxide

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The spectral lineshape of spontaneous Rayleigh–Brillouin scattering in CO<sub>2</sub> is studied in a range of pressures. The spectrum is influenced by the bulk viscosity  $\eta_b$ , which is a relaxation phenomenon involving the internal degrees of freedom of the molecule. The associated relaxation rates can be compared to the frequency shift of the scattered light, which demands precise measurements of the spectral lineshape. We find  $\eta_b = (5.7 \pm 0.6) \times 10^{-6} \text{ kg} \text{ m}^{-1} \text{s}^{-1}$  for the range of pressures p = 2 - 4 bar and for room temperature conditions.

We present a study on the precise spectral shape of light which is quasielastically scattered off a gas of CO<sub>2</sub> molecules. The spectrum depends on the internal degrees of freedom of the molecule. For CO<sub>2</sub> the rotational relaxation rate, the rate of energy exchange between the translational and rotational degrees of freedom through collisions, is comparable to the frequency shift of the scattered light, while the vibrational relaxation rates are comparable to the MHz frequencies of conventional ultrasound experiments. This makes an interesting case to test models of the spectral lineshape using precise experiments. The relaxation of internal degrees of freedom determines the bulk viscosity  $\eta_b$ , which is a parameter in models of the line shape.

This study was inspired by a recent debate in the literature about the precise value of  $\eta_b$  of CO<sub>2</sub> [9]. It was made possible by the construction of a new experimental setup which provides spectra with unprecedented statistical accuracy [58]. Accurate information about the spectral line shape of Rayleigh-Brillouin backscattered light is of relevance for remote sensing applications in the Earth atmosphere [73] as well as for oceanographic applications [74]. In particular detailed information is needed for ESA's future ADM-Aeolus mission which will provide global observations of wind profiles from space utilizing an active satelite-based remote sensing instrument in the form of a Doppler Wind Lidar [4]. Information on scattering from CO<sub>2</sub> is of relevance for investigations of the atmospheres of Venus and Mars where carbon dioxide is the main constituent.

Rayleigh-Brillouin scattering is caused by spontaneous density fluctuations: The spectral lineshape of the scattered light is influenced by the sound. damping of sound through the molecular viscosity of the gas. If the gas consists of molecules with internal degrees of freedom, such as rotation or vibration, the viscosity is also influenced by the relaxation of these freedoms. For  $CO_2$  at atmospheric pressures, the relaxation time for rotational motion  $\tau_r$  is  $\tau_r = 3.8 \times 10^{-10}$  s, while for vibrational motion it is  $\tau_v = 6 \times 10^{-6}$  s [75]. The relaxation of internal modes of motion determines the bulk viscosity  $\eta_b$ . At low sound frequencies f in the range of MHz, both rotational and vibrational modes couple with translation, and  $\eta_b$  is large,  $\eta_b = 1.46 \times 10^{-2} \text{ kg} \text{ m}^{-1} \text{s}^{-1}$ , however, in light scattering experiments, the typical period of sound is  $\sim (10^{-9} \text{ s})$ , which is much shorter than  $\tau_v$ , so that the vibrational modes are frozen, and the bulk viscosity is reduced dramatically. This was noticed by Lao et al. [32], and again by Pan et al. [9] in the context of coherent Rayleigh-Brillouin scattering. Lao et al. find  $\eta_b = 4.6 \times 10^{-6}$  kg m<sup>-1</sup>s<sup>-1</sup>, while Pan et al. find  $\eta_b = 3.7 \times 10^{-6}$  kg m<sup>-1</sup>s<sup>-1</sup>. In coherent Rayleigh–Brillouin scattering, density variations are induced by dipole forces by crossing laser beams. Spontaneous Rayleigh–Brillouin scattering and coherent Rayleigh–Brillouin scattering share the same statistical description of the scattered light spectrum, and both can be used to determine the bulk viscosity at hypersound frequencies. However, coherent scattering results in a large increase of the scattered light intensity [16; 26]. Note also that the scattering spectral lines shapes in the coherent and spontaneous forms of Rayleigh-Brillouin scattering are markedly different,

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therewith providing independent means to determine the bulk viscosity of a gas.

Our spontaneous Rayleigh-Brillouin scattering experiments are in the kinetic regime, where the inverse scattering wavevector can be compared to the mean free path between collisions. This regime is characterized by a non-uniformity parameter,  $y \approx 1$ , where y is defined as  $y = p/(k v_0 \eta) =$  $nk_{\rm B} T/(k v_0 \eta)$ , with k the scattering wave vector, n the number density,  $k_{\rm B}$ the Boltzmann constant, T the temperature, p the pressure,  $v_0$  the thermal velocity,  $v_0 = (2 k_{\rm B} T/M)^{1/2}$ , with M the mass of the molecular scatterers, and  $\eta$  the (shear) viscosity. Accordingly, the Boltzmann equation must be used to describe the scattered light spectrum. In the Tenti model the collision integral of the linearized Boltzmann equation is approximated with the Wang Chang and Uhlenbeck approach, using six (S6) or seven (S7) moments [7; 8].

We revisit the bulk viscosity of CO<sub>2</sub> and present scattered light spectra of CO<sub>2</sub> for pressures p = 1-4 bar. In order to extract the bulk viscosity from the spectrum, the measured Rayleigh–Brillouin scattering spectra are compared to spectra predicted using the Tenti models, with  $\eta_b$  used as a fit parameter. Since the bulk viscosity is a relaxation parameter, and since the mean free time between collisions is inversely proportional to pressure, we expect a (slight) dependence of  $\eta_b$  on pressure.

From a straightforward extension of the arguments in [21], the frequency– dependent bulk viscosity can be related to the relaxation time of the internal degrees of freedom,

$$\eta_{\rm b} = 2nk_{\rm B}T \left| \frac{\sum_{j} N_{j}\tau_{j}(1+i\omega\tau_{j})^{-1}}{N\left(3 + \sum_{j} N_{j}(1+i\omega\tau_{j})^{-1}\right)} \right|$$
(5.1)

where  $N_j$  is the number of internal degrees of freedom with relaxation time  $\tau_j$ ,  $N = 3 + \sum_j N_j$  is the total number of degrees of freedom, n the molecular number density, and where it is assumed that the internal degrees of freedom do not interact with other ones having a different relaxation time, and the density is small. When the frequency of sound waves  $\omega = 2\pi f$  is much larger than  $1/\tau_j$ , the mode j remains frozen and does not contribute to the bulk viscosity. On the other hand, when  $\omega$  is much smaller than all relaxation rates, Eq. (5.1) reduces to the relation [21]

$$\eta_{\rm b} = 2nk_{\rm B}T \sum_j N_j \tau_j / N^2.$$
(5.2)

Since an increase of the pressure results in an increase of the collision rates thus a decrease of the relaxation time of internal modes of motion, and since the sound frequency and the relaxation time appear in the combination  $\omega \tau_j$ , we expect that the bulk viscosity *increases* with increasing pressure.

The interpretation of  $\eta_b$  as a relaxation parameter is not without controversy [76]. Here we use  $\eta_b$  as a parameter in a kinetic model for the scattered



Figure 5.1 – Schematic diagram of the experimental setup for spontaneous Rayleigh–Brillouin scattering (not to scale). The UV laser beam (full black line) is reflected several times in the enhancement cavity to increase the scattering intensity. A reference beam (gray line), split off the main beam, is used for detector alignment. Scattered light is detected at  $90^{\circ}$  using a pinhole, a Fabry-Perot interferometer and a photo-multiplier (PMT).

light line shape. In the context of a continuum description, Meador *et al.* [76] also arrive at an equation expressing  $\eta_b$  in terms of a relaxation time, which they deem incomplete. Similarly, also Eq. (5.1) cannot be complete as it still contains the multiplicity  $N_j$  of frozen modes for which  $\omega \tau_j = \infty$ .

A schematic view of the used setup used for spontaneous Rayleigh–Brillouin scattering is shown in Fig. 8.1, with a detailed description provided in [58]. Briefly, the light from a narrowband continuous–wave laser is scattered off the CO<sub>2</sub> gas contained in a temperature-controlled gas cell. The laser is a frequency-doubled Ti:Sa laser delivering light at 366.8 nm, 2 MHz bandwidth and 500 mW of output power. The long-term frequency drift was measured with a wavelength meter to be smaller than 10 MHz per hour. The scattered light is collected at an angle of 90° from an auxiliary focus inside an enhancement cavity, in which a scattering-cell is mounted. The cell is sealed with Brewster windows. The circulation of the light inside the enhancement cavity amplifies the power by a factor of 10. A hemispherical scanning Fabry-Perot interferometer (FPI) is used to resolve the frequency spectrum of the scattered light. The drift of the laser frequency is much smaller than the drift of the FPI, with both drifts being corrected for by a frequency linearization procedure. All experiments were performed in CO<sub>2</sub> gas at  $T = 296.5 \pm 0.5$ K.

The spectral response S(f) of the FPI was measured in a separate experiment, and could be parametrized very well by the formula

$$S(f) = \left\{ 1 + \left[ (2f_{\rm FSR}/\pi f_{\rm w}) \sin(\pi f/f_{\rm FSR}) \right]^2 \right\}^{-1}, \tag{5.3}$$

where  $f_{\rm FSR}$  is the free spectral range of the FPI,  $f_{\rm FSR} = 7440$  MHz, and


Figure 5.2 – (a-d) CO<sub>2</sub> Rayleigh–Brillouin scattering spectra at pressures p = 1, 2, 3and 4 bars and for conditions of  $296.5 \pm 0.5$  K. The spectra are shown together with the Tenti S7 model; the lower line indicates the difference between the model and experiment. The model calculations include a convolution with the instrument function of the FP-analyzer. The used bulk viscosities are indicated by the open symbols in frame (f). (e) Lines are  $\chi^2$  differences between the experimental spectra and the Tenti S7 model as a function of  $\eta_b$ , the open balls indicate the minimum  $\chi^2$ . (f) Symbols indicate the bulk viscosity obtained by fitting the Tenti model to the experimental spectra. Dots are for the Tenti S6 model, open balls are for the Tenti S7 model. Full line: prediction using Eq. (5.1) with two rotational degrees of freedom and relaxation time  $\tau_r = 3.8 \times 10^{-10}$  s. The dashed line represents the prediction of Eq. 28 in [76]. The points at p = 1.5 bar (indicated with filled squares for an analysis with Tenti S6 and open squares for Tenti S7) were measured using 403.0 nm laser light, and an FP-analyzer with  $f_{\rm FSR} = 7553$  MHz, and  $f_w = 139$  MHz. To avoid congestion, only the error bars for the S6 model are shown, those of the S7 model are roughly the same.

 $f_{\rm w} = 232$  MHz is the Airy-width of the transmission peak. All computed model spectra were convolved with S(f), and since the free spectral range is relatively small, it is important to allow for the periodic nature of S(f). The light that passes through the FPI is detected using a photo-multiplier tube (PMT) which is operated in the photon-counting mode and read out by a computer.

The experimental and computed spectra were normalized such that  $\int_{-f_b}^{f_b} I(f) df$ = 1, where the integral extends over one free spectral range (FSR),  $f_b = f_{\text{FSR}}/2$ . In addition, the background of the model spectra was fitted to the experimental data. An estimate of the  $\chi^2$  error was obtained assuming Poissonian statistics of the photon counts.

The results are shown in Fig. 5.2. We fit the bulk viscosity  $\eta_b$  in both Tenti S6 and S7 models and find the values for  $\eta_b$  which minimize the  $\chi^2$  difference between model and experiment. As Fig. 5.2(e) indicates, the minimum of  $\chi^2$  is well defined at high pressures where the Brillouin side peaks are pronounced. and not very well defined at p = 1 bar. We find significant systematic differences between the model and the experiment, corresponding to large values of  $\chi^2$ . These differences are also shown in Fig. 5.2(a–d). The model-Brillouin peaks appear shifted towards larger (absolute) frequencies compared to those of the experiment. The position of the Brillouin peaks represents the velocity of sound, which is determined by the internal degrees of motion of the molecule. It is tempting to vary the heat capacity of internal motion in order to obtain a better fit. At these frequencies only rotations should partake in the relaxation of the internal energy, with the heat capacity of internal motion  $c_{\rm int} = 1$ . A slightly better fit of the peak locations could be obtained by setting  $c_{\text{int}} = 1.16$ , but now discrepancies at other frequencies become more obvious. Therefore, we kept  $c_{\text{int}} = 1$ , whilst we used  $\eta = 1.46 \times 10^{-5} \text{ kg} \text{ m}^{-1} \text{s}^{-1}$  for the shear viscosity and  $\kappa = 1.31 \times 10^{-2} \text{ W K}^{-1} \text{m}^{-1}$  for the thermal conductivity [9].

The measured bulk viscosities are shown in Fig. 5.2(f), which collects the results of two experimental runs recorded at  $\lambda = 366.8$  nm, taken a few months apart and an additional measurement recorded at  $\lambda = 403.0$  nm and p =1.5 bar. The uncertainties in the derived values for  $\eta_b$  is composed of three contributions. The typical contribution of the statistical uncertainty, as a result of the fitting procedure shown in Fig. 5.2(e), is  $5 \times 10^{-8}$  kg m<sup>-1</sup> s<sup>-1</sup>. The  $0.9^{\circ}$  uncertainty in the determination of the scattering angle translates into a systematic uncertainty of typically  $5 \times 10^{-7}$  kgm<sup>-1</sup>s<sup>-1</sup>, while the 1% uncertainty in the pressure reading corresponds to a contribution of  $2 \times 10^{-7}$  kg m<sup>-1</sup> s<sup>-1</sup>. Here it is noted that for the lower pressures  $(p \leq 2 \text{ bar})$ , where the information content of the spectrum is lower, all three contributions to the uncertainty are larger. At the highest pressure (p = 4 bar), where the effect of the bulk viscosity is most decisive, the total uncertainty is less than  $5 \times 10^{-7} \,\mathrm{kg \, m^{-1} \, s^{-1}}$ . Further it should be noted that the systematic uncertainty of the determination of the scattering angle yields the largest contribution to the uncertainty budget, and that all measurements were performed in the same scattering geometry. Hence the relative uncertainties are lower than the error bars indicated in Fig. 5.2(f). For large pressures in the range p = 2 - 4 bar we obtain  $\eta_b = (6.0 \pm 0.3) \times 10^{-6}$  kg m<sup>-1</sup>s<sup>-1</sup> using the Tenti S7 model and  $\eta_b = (4.5 \pm 0.6) \times 10^{-6}$  kg m<sup>-1</sup>s<sup>-1</sup>. The measured  $\eta_b$  appear to *decrease* with increasing pressures, which does not agree with the simple idea that at finite frequencies  $\omega$ ,  $\eta_b$  should *increase* with increasing pressures, an idea which is embodied by Eq. (5.1). We compare the measured pressure dependence of  $\eta_b$  to the predictions of Eq. (5.1) and to Eq. 28 of [76] using a rotational relaxation time  $\tau_r = 3.8 \times 10^{-10}$  s. These predictions disagree significantly with the experiments.

An averaged value of  $\eta_b = (5.7 \pm 0.6) \times 10^{-6}$  kg m<sup>-1</sup>s<sup>-1</sup> for the bulk viscosity as obtained via the Tenti S6 and S7 models in the pressure range p = 2 - 4 bar can be compared to  $\eta_b = 4.6 \times 10^{-6}$  kg m<sup>-1</sup>s<sup>-1</sup> by Lao *et al.* [32], and  $\eta_b = (5.8 \pm 1) \times 10^{-6}$  kg m<sup>-1</sup>s<sup>-1</sup> by Meijer *et al.* using coherent Rayleigh–Brillouin scattering [26], but which is somewhat larger than the value  $\eta_b = 3.7 \times 10^{-6}$  kg m<sup>-1</sup>s<sup>-1</sup> found by Pan *et al.* [9]. It is very different for light scattering experiments compared to acoustical experiments performed at MHz frequencies. A problem is the significant difference between experiment and the Tenti models that were used to determine  $\eta_b$ . For our experiments on nitrogen gas at comparable pressures the Tenti S6 model fits the data much better [45; 68].

The core part of the code that computes the Tenti models has been kindly provided to us by X. Pan. Also, the authors would like to thank A. G. Straume and O. Le Rille (European Space Agency), and B. Witschas (DLR Oberpfaffenhofen, Germany) for helpful discussions. This work was funded by the European Space Agency, contract no. 21396.

# Chapter 6

# A systematic study of Rayleigh-Brillouin scattering in air, $N_2$ and $O_2$ at 403 nm measurements

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Spontaneous Rayleigh-Brillouin scattering experiments in air, N<sub>2</sub> and O<sub>2</sub> have been performed for a wide range of temperatures and pressures at a wavelength of 403 nm and at a 90 degrees scattering angle. Measurements of the Rayleigh-Brillouin spectral scattering profile were conducted at high signal-tonoise ratio for all three species, yielding high-quality spectra unambiguously showing the small differences between scattering in air, and its constituents  $N_2$ and  $O_2$ . Comparison of the experimental spectra with calculations using the Tenti S6 model, developed in 1970s based on linearized kinetic equations for molecular gases, demonstrates that this model is valid to high accuracy for N<sub>2</sub> and  $O_2$ , as well as for air. After previous measurements performed at 366 nm, the Tenti S6 model is here verified for a second wavelength of 403 nm, and for the pressure-temperature parameter space covered in the present study (250 -340 K and 0.6 - 3 bar). In the application of the Tenti S6 model, based on the transport coefficients of the gases, such as thermal conductivity  $\kappa$ , internal specific heat capacity  $c_{int}$  and shear viscosity  $\eta$  as well as their temperature dependencies taken as inputs, values for the more elusive bulk viscosity  $\eta_b$  for the gases are derived by optimizing the model to the measurements. It is verified that the bulk viscosity parameters obtained from previous experiments at 366 nm, are valid for wavelengths of 403 nm. Also for air, which is treated as a single-component gas with effective gas transport coefficients, the Tenti S6 treatment is validated for 403 nm as for the previously used wavelength of 366 nm, yielding an accurate model description of the scattering profiles for a range

of temperatures and pressures, including those of relevance for atmospheric studies. It is concluded that the Tenti S6 model, further verified in the present study, is applicable to LIDAR applications for exploring the wind velocity and the temperature profile distributions of the Earth's atmosphere. Based on the present findings at 90° scattering and the determination of  $\eta_b$  values predictions can be made on the spectral profiles for a typical LIDAR backscatter geometry. These Tenti S6 predictions for Rayleigh-Brillouin scattering deviate by some 7% from purely Gaussian profiles at realistic sub-atmospheric pressures occurring at 3-5 km altitude in the Earth's atmosphere.

# 6.1 Introduction

Knowledge of light scattering in gases dates back to the 19th century, when Lord Rayleigh (John William Strutt) explained that the blue sky was due to the scattering of sun light by gas molecules with diameters much less than the wavelength of the light [61]. Using Maxwell's formalism of electromagnetism, Rayleigh successfully derived the scattering cross section as a function of the index of refraction of the gas and exhibiting the characteristic  $\lambda^{-4}$  behavior. Under the assumption of no collisions, molecular velocities follow a Maxwellian distribution and the spectral scattering profile exhibits a Gaussian line shape, produced from Doppler shifts associated with the molecular velocity distribution. In denser gases collisions occur between molecules, and Brillouin doublet peaks, Stokes and anti-Stokes shifted by the frequency of the acoustic waves, are formed and mix with the pure Rayleigh peak producing a complex Rayleigh-Brillouin (RB) scattering profile. According to Yip and Nelkin's work [12], this spectral profile corresponds to the space-time Fourier-transform of the density-density correlation function  $G(\mathbf{r}, t)$ . For compressed gases in the hydrodynamic regime, where many-body collisions frequently happen,  $G(\mathbf{r},t)$ is represented as an ensemble average of density correlations [13]. For diluted gases in the kinetic regime, where mainly two-body collisions occur,  $G(\mathbf{r},t)$  is connected to the phase-space distribution function  $f(\mathbf{r}, \mathbf{v}, t)$  in the Boltzmann equation [14]. Therefore, the calculation of the spectral scattering profile of gases in the kinetic regime requires solving the Boltzmann equation. In view of the mathematical difficulty in computing the collision integrals in the Boltzmann equation, kinetic models were developed to linearize it by assuming that only small deviations from equilibrium in the gaseous medium pertain [7; 8]. The Tenti S6 model [8], describing the collision integrals in 6 basis functions with their coefficients represented by the values of the macroscopic transport coefficients, such as thermal conductivity  $\kappa$ , shear viscosity  $\eta$ , bulk viscosity  $\eta_b$ , as well as the internal specific heat capacity per molecule  $c_{int}$ , has proven to be the most accurate model to represent the RB-scattering profile in the kinetic regime [77; 36]. Furthermore, although this model is developed for gases in the kinetic regime, it is proven to be accurate in the hydrodynamic regime as well [78]. Since the Tenti S6 model is mathematically involved, simpler analytical models consisting of 3 Gaussian [42] or 3 pseudo-Voigt functions [44] have been proposed, aiming to provide fast and simple representations of RB scattering spectra for remote sensing applications of the atmosphere. In any case the models must be validated against experiment, which is the purpose of the present study.

Experiments on RB spectral scattering profiles started in the 1960s, immediately after the invention of the laser as a source of narrow bandwidth radiation. Brillouin doublet peaks, frequency-shifted from the central elastic Rayleigh peak, were detected both in liquids and solids [27; 28], as well as in gases [29]. Subsequently, a number of studies were performed in molecular hydrogen [20], molecular nitrogen [30], various polyatomic gases [32], and in noble gases [36], and compared with numerical models for the hydrodynamic regime [13] and for the kinetic regime [7; 8]. The latter studies led to the conclusion that the Tenti S6 model is the most successful approach in describing RB-scattering over a wide range of conditions [56]. Later, the research on RB scattering attracted less interest, until this century, when a new research technique known as coherent Rayleigh-Brillouin scattering (CRBS) was developed [40; 15]. Unlike the classical or spontaneous RB-approach, where the gas density fluctuations are spontaneously generated due to random thermal motion, this coherent method uses two laser pulses to drive the fluctuations. After adding a term in the Boltzmann equation for the induced optical dipole force, kinetic models such as the S6 model can be used for describing the coherent RB scattering profiles [15; 16]. The CRBS techniques were recently extended for measuring the temperature of a flame [79] and for monitoring  $\sim 1$  nm nano-particles in bulk gases or weakly ionized plasmas [80].

Renewed research on spontaneous RB scattering is driven by the possible applications of LIDAR (light detection and ranging) techniques to obtain the wind speed distributions in the Earth's atmosphere, such as will be pursued by the ADM-Aeolus mission of the European Space Agency (ESA) [1–3], for the temperature LIDAR experiments currently performed by German Aerospace Center (DLR) [73], as well as for aerosol LIDAR [81]. Experimental measurements on RB scattering profiles of molecular gases, particularly of air as a gas mixture, are required to the highest possible signal-to-noise ratio to test the accuracy of the S6 model, which is proposed to be used in retrieval algorithms of LIDAR applications. Previous studies have proven that the Tenti S6 model is accurate to the 2% level for a number of molecules, temperatures and pressures, at a wavelength of 366 nm, and for values of the bulk viscosity  $\eta_b$  to be used in the S6 model as derived from RB-scattering experiments [45; 68; 82].

The bulk viscosity is in principle a frequency or wavelength-dependent parameter, as has become evident from strongly varying values obtained from acoustic and optical measurements [9; 83]. While the main purpose of the present study is to collect RB-scattering data for  $N_2$ ,  $O_2$  and air for atmospheric pressure and temperature conditions, values for the bulk viscosity will be derived for the additional wavelength 403 nm, where 366 nm was used in a previous study measuring RB-scattering in air |82| and in N<sub>2</sub> |68|. This is the reason why measurements are performed at elevated pressures up to 3 bar, under which conditions the Brillouin side peaks become more pronounced in the spectral profiles and a reasonably accurate determination of the bulk viscosity parameter  $\eta_b$  is feasible. These values are of crucial importance for future modeling of RB-profiles under conditions of atmospheric LIDARS. The present accurate measurements of RB-scattering in  $N_2$ ,  $O_2$  and air allow for a detailed comparison of the spectral profiles addressing the question whether air may be treated as a mono-molecular species as is usually the case in atmospheric study.

### 6.2 Theoretical models

Light scattering is a result of fluctuations in a medium through which it propagates: in a completely homogeneous medium only forward scattering exists. The RB scattering phenomenon can be described by the elements of the dielectric tensor, representing fluctuations in thermodynamic quantities [10]:

$$\Delta \epsilon = \left(\frac{\partial \epsilon}{\partial \rho}\right)_T \Delta \rho + \left(\frac{\partial \epsilon}{\partial T}\right)_\rho \Delta T, \tag{6.1}$$

with the first term being the density fluctuations at constant temperature T and second term the temperature fluctuations at constant density  $\rho$ .

Since scattering due to the temperature fluctuations of gases, corresponding to the second term in Eq. (6.1), contributes only for ~ 2% [11], this term is usually ignored. Furthermore, the entropy s and pressure p may be chosen to be independent thermodynamic variables representing the density fluctuations, thus yielding:

$$\Delta \rho = \left(\frac{\partial \rho}{\partial p}\right)_s \Delta p + \left(\frac{\partial \rho}{\partial s}\right)_p \Delta s. \tag{6.2}$$

The first term of Eq. (6.2), describing pressure fluctuations also known as acoustic waves, results in Brillouin scattering, while the second term describing entropy fluctuations, causes the Rayleigh scattering [10]. For gases in the kinetic regime, where two-body collisions dominate, the Boltzmann equation is adequate to describe the density fluctuations. Since the collision integral of the Boltzmann equation is difficult to compute, models of RB scattering in molecular gases based on the linearized Wang-Chang-Uhlenbeck equation [17], a modified version of the Boltzmann equation for molecular gases, have been developed. In these models the Boltzmann equation is cast into seven [7] or six [8] matrix elements (now regarded as the S7 or S6 model, respectively), which are directly related to the macroscopic transport coefficients, namely the shear viscosity  $\eta$ , the thermal conductivity  $\kappa$ , the bulk viscosity  $\eta_b$ , as well as the internal specific heat capacity per molecule  $c_{int}$ . Therefore, based on experimental knowledge of these coefficients at specific temperatures and pressures, and inserting the molecular mass of the gas constituents, RB scattering profiles can be calculated by the S6 or S7 models.

In this framework air has been successfully treated as a single-component gas with an effective particle mass 29.0 u and with effective transport coefficients obtained from independent measurements [65]. For diatomic gases, such as N<sub>2</sub>, O<sub>2</sub>, or air with its major components being N<sub>2</sub> and O<sub>2</sub>,  $c_{int}$  is always equal to 1. The shear viscosity  $\eta$  and thermal conductivity  $\kappa$  are known to be independent of pressure [66] (especially for the pressure ranges employed in the present study). However, these transport coefficients are dependent on temperature, following the Sutherland formulas [59]:

$$\frac{\eta}{\eta_0} = \left(\frac{T}{T_0}\right)^{3/2} \frac{T_0 + S_\eta}{T + S_\eta},\tag{6.3}$$

**Table 6.1** – Coefficients for the calculation of the shear viscosity  $\eta$  and the thermal conductivity  $\kappa$  of air, N<sub>2</sub> and O<sub>2</sub> via the Sutherland formulas Eqs. (6.3) and (6.4).

	$T_0$	$\eta_0$	$\kappa_0$	$S_{\eta}$	$S_{\kappa}$
	(K)	$({\rm kgm^{-1}s^{-1}})$	$(WK^{-1}m^{-1})$	$(\mathbf{K})$	(K)
Air	273	$1.716 \times 10^{-5}$	0.0241	111	194
$N_2$	273	$1.663  imes 10^{-5}$	0.0242	107	150
$O_2$	273	$1.919\times10^{-5}$	0.0244	139	240

and

$$\frac{\kappa}{\kappa_0} = \left(\frac{T}{T_0}\right)^{3/2} \frac{T_0 + S_\kappa}{T + S_\kappa},\tag{6.4}$$

where  $\eta_0$  is the reference shear viscosity and  $\kappa_0$  the reference thermal conductivity, at reference temperature  $T_0$  (normally 273 K) and  $S_\eta$  and  $S_\kappa$  are called Sutherland parameters. Values for  $\eta_0$ ,  $\kappa_0$ ,  $T_0$ ,  $S_\eta$  and  $S_\kappa$  are adopted from [59] for N<sub>2</sub>, O<sub>2</sub>, and air, and listed in Table 6.1. All Tenti S6 calculations in the present study are based on the transport coefficients derived from these constants, as well as on a value  $c_{int} = 1$  for the internal specific heat capacity.

Another transport coefficient required for the S6 modeling, the bulk viscosity  $\eta_b$ , is related to the energy exchanges between the translational and internal (rotational and vibrational) degrees of freedom of molecules through collisions. For mono-atomic gases, it is straightforward to set  $\eta_b = 0$ , since there are no internal degrees of freedom [24]. For molecular gases, on the other hand, it must be considered how many internal degrees of freedom effectively contribute to the bulk viscosity. As pointed out by Meijer et al. [26], the bulk viscosity is determined by the product of  $\omega \tau_i$ , where  $\omega$  is the angular frequency of sound waves and  $\tau_j$  is the relaxation time of the internal mode j. In the extreme case of  $\omega \tau_j \to \infty$ , the fluctuations resulting in sound waves are so fast that there is no energy transfer between the sound-driven translational motion and the motion of internal mode j, so mode j is frozen and there is a zero contribution to the bulk viscosity. In contrast, if  $\omega \tau_j \ll 1$ , there are sufficient collisions within one wave period to maintain local thermodynamic equilibrium, and the contribution of mode j to the bulk viscosity is frequency-independent. In general cases, however, the bulk viscosity is known as a frequency-dependent parameter. Of course,  $\eta_b$  is a temperature-dependent parameter, since at higher temperatures more degrees of freedom will participate in the internal motion of the molecules and the relaxation time for the internal motion are shorter as collisions more frequently happen [84].

Most information about the numerical values of the bulk viscosity  $\eta_b$  for diluted gases comes from ultrasound experiments at MHz frequencies [22]. Since the sound frequency in light-scattering experiment is  $|\mathbf{k_s} - \mathbf{k_i}| v \sim 1$  GHz (with  $\mathbf{k_i}$  and  $\mathbf{k_s}$  being the wave vector of the incident and scattered light, and v the speed of sound in the gases), it is questionable whether the values measured at

low frequencies can be directly used in the S6 model. Indeed, Pan et al. [16; 9] found a 3 orders of magnitude discrepancy for  $\eta_b$  values derived from acoustic (ultrasound) and optical (coherent RBS) experiments for the case of  $CO_2$ . For these studies Pan *et al.* had proposed that values of the bulk viscosity at hypersonic frequencies can be measured by RB-scattering experiments through comparison between the measured and calculated scattering profiles, for the reason that the bulk viscosity is the only uncertain parameter in the Tenti S6 model. Measurements on spontaneous RB-scattering, also in comparison with the Tenti S6 model, validated the hypersonic  $\eta_b$  value for CO<sub>2</sub> [83]. This large discrepancy between  $\eta_b$  values at ultrasound (MHz) and hypersonic (GHz) frequencies is attributed to the relatively slow relaxation time for vibrational motion of CO<sub>2</sub> at atmospheric pressures, which is  $\tau_v = 6 \times 10^{-6}$  s. For light scattering experiments, probing the hypersound domain,  $\omega \tau_v \approx 1000$ , so the vibrational modes are frozen and the bulk viscosity is much smaller than the values obtained from sound absorption measurements with  $\omega \tau_v \approx 1$ . Meijer *et* al. [26] recorded values of  $\eta_b$  for various gases at room temperatures using coherent RB scattering at 532 nm, and compared them with the values from acoustic measurements and molecular structure calculations, indicating that for polyatomic gases the values at hypersonic frequencies are generally smaller than at ultrasonic frequencies. Gu et al. extended the study to a range of temperatures [82; 68] using spontaneous RB scattering at 366 nm, demonstrating that the bulk viscosity increases with the temperature, but is insensitive to a change of pressure, at least in the regime up to 3 bar. In the present work values for the bulk viscosity for air, N<sub>2</sub>, and O<sub>2</sub> are derived from spontaneous RB-scattering experiments at 403 nm for a range of temperatures.

# 6.3 Experimental

Fig. 6.1 displays a sketch of the experimental setup used for this study, exhibiting the same geometry as the one reported in [58] for RB scattering experiments at 366 nm. Some relevant details on the experimental parameters are specified in the caption. Due to the significant change of the wavelength (from 366 nm to 403 nm), all optical components are replaced, and the alignment is readjusted.

RB-scattering measurements are performed for various pressures and temperatures in a p-T parameter space following the experimental procedure outlined here. Before each measurement, the scattering cell is charged with one of the sample gases (air, N<sub>2</sub> or O<sub>2</sub>) to one of the three approximate initial charging pressures, 1000 mbar, 2000 mbar, and 3000 mbar, at room temperature. After sealing the cell, the temperature is set to a designated value, with 0.5 K uncertainty. Hence the pressure of the gas inside the scattering cell is changed and its value is calculated from the ideal gas law. The cell allows for pressure settings of the sample gas between 0 – 4 bar with 0.5% uncertainty. The temperature of the sample gas inside the scattering cell can be controlled and stabilized within the range 250 K – 350 K. The actual p - T settings for



**Figure 6.1** – Layout of the experimental apparatus. The Ti:Sa laser beam, pumped by a 10 W 532 nm Millennia Xs laser, is intracavity frequency-doubled in a Lithium-Borate (LiB<sub>3</sub>O<sub>5</sub> or LBO) crystal, yielding a cw power of 600 mW at 403 nm. The blue laser beam is then directed into a second enhancement cavity for amplification by a factor of 10, in which the RB-scattering cell is placed to ensure a maximum scattering intensity. The polarizing beam splitters (PBS), quarter wave plates (QW), piezo tubes (PZT) and servo loops (SL) are required elements to lock these two cavities. Scattered light is collected at 90° with respect to the beam direction. The geometrically filtered scattered light is directed onto a Fabry-Perot Interferometer (FPI), where transmitted photons are detected by a photo-multiplier tube (PMT). A small fraction of the 403 nm light is used as a reference beam for aligning beam paths and for characterizing the detecting system (dashed lines). This reference beam is blocked when measurements are performed.



**Figure 6.2** – Left: Measurement series of frequencies of transmission fringes of the Fabry-Perot interferometer while scanning the laser and calibration by a wavelength meter; from the span of 20 modes the FSR is determined. Right: Recording of a single transmission fringe of the FPI for a measurement of the instrument profile; while this single measurement yields  $139 \pm 1.9$  MHz, an average over multiple measurements delivers the instrument width of  $140 \pm 4$  MHz to be used in the analyses.

the measurements are listed in Table 6.2. Throughout the paper the wavelength will be referred to as 403 nm, while the exact wavelength is always set in the window  $\lambda = 402.99 - 403.00$  nm, as measured with a wavelength meter (ATOS).

While Rayleigh-Brillouin scattering measurements were intended for a right angles geometry, the actual scattering angles depended on the final adjustment of the alignment of laser-beam and the beam-path of the scattered light. All the initial measurements for 1 bar (in air, N<sub>2</sub>, and O<sub>2</sub>) were performed for a scattering angle of  $91.5^{\circ} \pm 0.9^{\circ}$ , while for the later measurements at other pressures the scattering was re-adjusted to  $90^{\circ} \pm 0.9^{\circ}$ .

The scattered photons are spectrally resolved by a home-built plano-concave Fabry-Perot interferometer (FPI) that was characterized by scanning the laser over an extended range covering a number of free-spectra-ranges (FSR), while monitoring the wavelength on the wavelength meter (ATOS). This procedure, further detailed in [58], delivers an accurate effective value for the FSR of 7553 MHz, when covering a span of 20 modes (see Fig. 6.2). The FSR-scale was used to calibrate the laser scan in a recording of the profile of the spectral profile of an individual transmission fringe, yielding an instrument linewidth of  $140 \pm 4$  MHz, when averaging over multiple calibrations. A high gain photomultiplier tube (PMT) is used to detect the photons passing through the FPI. The RB-spectral profiles are recorded by keeping the laser frequency fixed, while scanning the FPI with a piezo for a typical period of 3 hours. During such observation a frequency span of 7500 GHz (corresponding to  $\sim 100$  FSRs) is covered. Measures for correcting the drift of the laser frequency and the FPI are applied, followed by linearizing, averaging and normalizing the  $\sim 100$ resolved scattering line shapes to area unity [58].

**Table 6.2** – Conditions and values of transport coefficients for the Rayleigh-Brillouin scattering measurements for air, N<sub>2</sub> and O<sub>2</sub> at pressures p and temperatures T as indicated. Values for  $\eta$  and  $\kappa$  are calculated by Eq. (6.3) and Eq. (6.4), using the constants given in Table 6.1. Values for the bulk viscosity  $\eta_b$  are obtained from the data at ~ 3 bar by fitting to the Tenti S6 model, while for other pressure-temperature conditions values are derived by the interpolation procedure discussed in section 6.5. Also specified is the angle  $\theta$  at which the data are recorded. All data measured at  $\lambda$  in the range 402.99 - 403.00 nm.

	p	Т	$\eta$	$\eta_b$	κ	$\theta$
	(mbar)	(K)	$(\mathrm{kgm}^{-1}\mathrm{s}^{-1})$	$(\mathrm{kgm}^{-1}\mathrm{s}^{-1})$	$\left(\mathrm{WK^{-1}m^{-1}}\right)$	degrees
	880	256.6	$1.633 \times 10^{-5}$	$0.909 \times 10^{-5}$	$2.279 \times 10^{-2}$	91
Air	953	278.3	$1.741 \times 10^{-5}$	$1.252 \times 10^{-5}$	$2.453 \times 10^{-2}$	91
$\sim 1~{\rm bar}$	1012	295.8	$1.826 \times 10^{-5}$	$1.527 \times 10^{-5}$	$2.591 \times 10^{-2}$	91.5
	1095	320.1	$1.940 \times 10^{-5}$	$1.913 \times 10^{-5}$	$2.779 \times 10^{-2}$	91.5
	1165	339.9	$2.029 \times 10^{-5}$	$2.226 \times 10^{-5}$	$2.928 \times 10^{-2}$	91.5
	1898	280.8	$1.754 \times 10^{-5}$	$1.291 \times 10^{-5}$	$2.474 \times 10^{-2}$	90.5
Air	2000	295.5	$1.825 \times 10^{-5}$	$1.524 \times 10^{-5}$	$2.589{ imes}10^{-2}$	90.5
$\sim 2~{\rm bar}$	2131	314.9	$1.916 \times 10^{-5}$	$1.831 \times 10^{-5}$	$2.739{ imes}10^{-2}$	90.5
	2300	339.9	$2.029 \times 10^{-5}$	$2.226 \times 10^{-5}$	$2.928 \times 10^{-2}$	90.5
	2604	254.5	$1.622 \times 10^{-5}$	$0.905 \times 10^{-5}$	$2.263 \times 10^{-2}$	89.5
Air	2831	279.6	$1.748 \times 10^{-5}$	$1.220 \times 10^{-5}$	$2.464 \times 10^{-2}$	90.5
$\sim 3~{\rm bar}$	3000	296.8	$1.831 \times 10^{-5}$	$1.580 \times 10^{-5}$	$2.599 \times 10^{-2}$	90.5
	3196	315.7	$1.919 \times 10^{-5}$	$1.805 \times 10^{-5}$	$2.745 \times 10^{-2}$	90.5
	3444	340.2	$2.030 \times 10^{-5}$	$2.255 \times 10^{-5}$	$2.930 \times 10^{-2}$	90.5
	863	253.8	$1.570 \times 10^{-5}$	$0.751 \times 10^{-5}$	$2.272 \times 10^{-2}$	91
$N_2$	945	277.0	$1.682 \times 10^{-5}$	$1.121 \times 10^{-5}$	$2.441 \times 10^{-2}$	91
$\sim 1~{\rm bar}$	948	296.3	$1.772 \times 10^{-5}$	$1.428 \times 10^{-5}$	$2.593 \times 10^{-2}$	91.5
	1010	315.7	$1.859 \times 10^{-5}$	$1.738 \times 10^{-5}$	$2.733 \times 10^{-2}$	91.5
	1093	341.2	$1.970 \times 10^{-5}$	$2.144 \times 10^{-5}$	$2.912{ imes}10^{-2}$	91.5
	1898	280.8	$1.700 \times 10^{-5}$	$1.181 \times 10^{-5}$	$2.479 \times 10^{-2}$	90.5
$N_2$	2000	295.8	$1.774 \times 10^{-5}$	$1.420 \times 10^{-5}$	$2.597{ imes}10^{-2}$	90.5
$\sim 2~{\rm bar}$	2133	315.7	$1.859 \times 10^{-5}$	$1.738 \times 10^{-5}$	$2.733{ imes}10^{-2}$	90.5
	2275	336.5	$1.950 \times 10^{-5}$	$2.069 \times 10^{-5}$	$2.880 \times 10^{-2}$	90.5
	2589	254.8	$1.575 \times 10^{-5}$	$0.793 \times 10^{-5}$	$2.279 \times 10^{-2}$	90
$N_2$	2828	279.8	$1.695 \times 10^{-5}$	$1.130 \times 10^{-5}$	$2.471 \times 10^{-2}$	90
$\sim 3~{\rm bar}$	3000	297.3	$1.776 \times 10^{-5}$	$1.400 \times 10^{-5}$	$2.601 \times 10^{-2}$	90
	3194	315.4	$1.858 \times 10^{-5}$	$1.805 \times 10^{-5}$	$2.732 \times 10^{-2}$	90
	3417	338.1	$1.957 \times 10^{-5}$	$2.075 \times 10^{-5}$	$2.890 \times 10^{-2}$	90.5
	1000	295.5	$2.033 \times 10^{-5}$	$1.291 \times 10^{-5}$	$2.591 \times 10^{-2}$	91.5
	1150	339.7	$2.180 \times 10^{-5}$	$2.633 \times 10^{-5}$	$2.778 \times 10^{-2}$	91.5
$O_2$	2000	295.8	$2.034 \times 10^{-5}$	$1.300 \times 10^{-5}$	$2.593 \times 10^{-2}$	90
	2270	335.7	$2.167 \times 10^{-5}$	$2.512 \times 10^{-5}$	$2.762 \times 10^{-2}$	90
	3000	297.6	$2.040 \times 10^{-5}$	$1.355 \times 10^{-5}$	$2.600 \times 10^{-2}$	90
	3419	339.1	$2.178{ imes}10^{-5}$	$2.615 \times 10^{-5}$	$2.776{ imes}10^{-2}$	90

Finally, the normalized scattering profiles are compared with the numerical S6 calculations, performed for the exact measurement conditions, and convolved with the instrument function of the FPI, which is written as:

$$A = I_0 \cdot \frac{1}{1 + \left(\frac{2 \cdot FSR}{\pi \cdot FWHM}\right)^2 \cdot \sin^2\left(\frac{\pi}{FSR} \cdot f\right)},\tag{6.5}$$

where f is the frequency, and values of FSR = 7553 MHz and FWHM = 140 MHz are included.

It is worth mentioning that previous measurements reported in [45; 68; 82] suffered from background problems, in that the side wings of the measured scattering profiles were found to be higher than the side wings of the Tenti S6 calculations, even though the dark counts of the PMT and the overlap of the scattering profiles between two FSRs were accounted for. This background was firstly ascribed to broadband fluorescence of the cell windows in [45], and was later understood as an influence of Raman scattering [82]. In order to investigate the influence of Raman scattering, most of which maintains a large frequency shift from the incident light, a high transmission (90%) narrowband ( $\Delta \lambda = 1$  nm) bandwidth filter with its central wavelength at 403 nm is implemented in front the PMT in this study to block most of the Raman scattering. Indeed, it is found that the measurements reported in the present study no longer suffer from Raman-associated background problems.

To illustrate the sensitivity of the Rayleigh-Brillouin spectrometer in Fig. 6.3 typical recordings of the RB-profile for the three gases, N<sub>2</sub>, O<sub>2</sub> and air are shown for conditions of 1 bar, room temperature,  $\lambda = 403.00$  nm and a scattering angle of  $\theta = 91.5^{\circ}$ . While these spectra, all three normalized to unity, correspond to top-lowered Gaussian-like profiles, the shapes are mainly determined by the masses of the constituent molecules through the Doppler effect. Where N<sub>2</sub> has a mass of 28 u, O<sub>2</sub> has 32 u, and air may be treated as a species of effective mass 29 u. Indeed the profile for O<sub>2</sub> is narrower and hence exhibits an increased intensity near the line centre, while the profile of N<sub>2</sub> is only slightly broader (and lower in the centre) than that of air. But the differences are still measurable, thus demonstrating the sensitivity of the RB-spectrometer.

### 6.4 Measurements and Analysis

Comprehensive data sets on measurements of spontaneous Rayleigh-Brillouin scattering in air, N<sub>2</sub>, and O<sub>2</sub> at different temperatures and pressures are reported. A choice was made to record spectra for three different initial charging pressures, 1000 mbar, 2000 mbar and 3000 mbar, combined with five different temperature settings at 255 K, 277 K, 297 K, 318 K and 337 K, at intervals of  $\sim$ 20 K. The conditions under which the data were recorded are listed in Table 6.2. The raw data, after linearization and calibration on a frequency scale, and subsequent averaging, are made available in Supplementary Material to this paper.



**Figure 6.3** – Measurement of the Rayleigh-Brillouin scattering spectral profiles for N<sub>2</sub>, O<sub>2</sub> and air at 1 bar pressure, room temperature,  $\lambda = 403.00$  nm and  $\theta = 91.5^{\circ}$ . In the bottom part differences between N<sub>2</sub>-air (red) and O<sub>2</sub>-air (blue) are plotted.



Figure 6.4 – Normalized Rayleigh-Brillouin scattering profiles of air recorded at  $\lambda = 403.0$  nm (black dots), for pressures ~ 1000 mbar and temperatures as indicated. The scattering angle for this data was  $\theta = 91.7^{\circ}$ . Experimental data (black dots) are compared with the convolved Tenti S6 model calculations (red line), with values of  $\eta$ ,  $\kappa$ , and  $\eta_b$  as input parameters listed in Table 6.2.



**Figure 6.5** – Normalized Rayleigh-Brillouin scattering profiles of air (black dots) recorded for pressures ~ 2000 mbar and temperatures as indicated. The scattering angle for this data set was  $\theta = 90.0^{\circ} \pm 0.9^{\circ}$ .



**Figure 6.6** – Normalized Rayleigh-Brillouin scattering profiles of air (black dots) recorded for pressures ~ 3000 mbar. The scattering angle for all the measurements in this figure is  $\theta = 90.0^{\circ} \pm 0.9^{\circ}$ . Values of  $\eta$ ,  $\kappa$  are listed in Table 6.2, while values of  $\eta_b$  at different temperatures are directly obtained from the least-squared fit to the S6 model (red curves).



**Figure 6.7** – Normalized Rayleigh-Brillouin scattering profiles of N<sub>2</sub> recorded at  $\lambda = 403.0$  nm, for pressures ~ 1000 mbar and temperatures as indicated. The scattering angle for this data was  $\theta = 91.7^{\circ}$ . Experimental data (black dots) are compared with the convolved Tenti S6 model calculations (red line), with the input parameters,  $\eta$ ,  $\kappa$ , and  $\eta_b$ , listed in Table 6.2.



**Figure 6.8** – Normalized Rayleigh-Brillouin scattering profiles of N<sub>2</sub> (black dots) recorded for pressures ~ 2000 mbar and temperatures as indicated. The scattering angle for this data set was  $\theta = 90.0^{\circ} \pm 0.9^{\circ}$ .



**Figure 6.9** – Normalized Rayleigh-Brillouin scattering profiles of N<sub>2</sub> (black dots) recorded for pressures ~ 3000 mbar. The scattering angle for all the measurements in this figure was  $\theta = 90.0^{\circ} \pm 0.9^{\circ}$ . Values of  $\eta$ ,  $\kappa$  are listed in Table 6.2, while values of  $\eta_b$  at different temperatures are directly obtained from the least-squared fit of the S6 model (red curves) to the measurements.



**Figure 6.10** – Normalized Rayleigh-Brillouin scattering profiles of O<sub>2</sub> recorded for pressures and temperatures as indicated. For the two measurements on the first row, corresponding to pressures ~ 1 bar, the scattering angle is  $\theta = 91.7^{\circ}$ , while for the measurements in the lower two rows, the scattering angle is  $90.0^{\circ} \pm 0.9^{\circ}$ .

Spectral recordings for Rayleigh-Brillouin scattering under different p - T conditions and for the three gases is shown in a series of figures, from Fig. 6.4 to Fig. 6.10, with results from calculations using the S6 model overlaid, and residuals (in percentage of the peak of the scattering profiles) plotted underneath each measurement. Values of the gas transport coefficients implemented in the S6 model, according to Eq. (6.3) and Eq. (6.4), are listed in Table 6.2. The bulk viscosity  $\eta_b$  at hypersonic frequencies is treated as a unknown parameter, and is derived from a least squares fitting procedure to the S6 model, using [26]:

$$\chi^2 = \frac{1}{N} \sum_{i=1}^{N} \frac{[I_e(f_i) - I_m(f_i)]^2}{\sigma^2(f_i)},$$
(6.6)

where  $I_e(f_i)$  and  $I_m(f_i)$  are the experimental and modeled amplitude of the spectrum at frequency  $f_i$ , and  $\sigma(f_i)$  the statistical (Poisson) error [82]. Since it follows from previous studies, that the bulk viscosity exhibits a linearly increasing trend with the temperature [82; 68], as it is expected from theoretical considerations [84], values of the bulk viscosity are derived for the different temperature settings for the experiments, for the three different gases. The thus obtained values for the derived bulk viscosities for air, N<sub>2</sub> and O<sub>2</sub> as a function of temperature (for further discussion see below) are employed to interpolate the values for the other settings in p-T parameter space as listed in Table 6.2. Here it is assumed that the bulk viscosities are pressure-independent, and that for S6 calculations at lower pressures (1 bar and 2 bar) the values for  $\eta_b$  derived from measurements at 3 bar can be used.

For all the measurements shown in Fig. 6.4 to Fig. 6.10, the measurement noise is ~ 1% of their peak intensity, while the difference between the measurements and the calculations is ~ 2%, at approximately the same difference as reported in [82; 68]. In previous analyses of RB-scattering at 366 nm the elastic scattering from dust particles (Mie scattering) or scattering from the inner walls of the cell had been identified as sources of deviations at the center of the RB-spectrum [82]. Such effects should appear at widths of 140 MHz, corresponding to the instrument bandwidth, but in fact appear as much broader features in the present spectra. This reduces the possibility of elastic scattering contributing in the present measurements, where indeed special care was taken to avoid dust entering the cell.

Rotational Raman scattering, contributing to ~ 2.5% of the total cross section, is not considered in the Tenti S6 model, hence could be another possible source for the deviation. However, since a 1 nm bandwidth filter is used for all the measurements presented here, most of the rotational Raman scattering should be filtered out, and indeed the previously detected problems with baseline intensities no longer pertain for the data set recorded at 403 nm. There exists a special form of rotational Raman scattering, corresponding to no change of the rotational levels of the gas molecules (i.e.  $\Delta J = 0$ ) but a change of the projection of the rotational angular momentum of the molecules on a space-fixed axis (i.e.  $\Delta m_J = \pm 2$ ) [85]. Such scattering pro-



**Figure 6.11** – Results on bulk viscosity values  $\eta_b$  as derived from Rayleigh-Brillouin scattering for air, N<sub>2</sub> and O<sub>2</sub> derived from this experiment at 403 nm and previous experiments at 366 nm [82; 68]. Only for the cases of RB-scattering in air the uncertainties are explicitly specified. In order to avoid congestion, the error bars for other measurements, being similar to those of air, are not shown.

cesses should reproduce the entire RB-profile, since no experimental distinction between Rayleigh-Brillouin and elastic Raman scattering can be made based on the spectral profile. Such elastic Raman contributions, however, produce depolarized light, a phenomenon which might be subject of future investigations. Additionally, it is worth noticing that the temperature fluctuations of gases, possibly contributing to some 2% of the scattering intensity, is neglected in making the step from Eq. (6.1) to Eq. (6.2). Also this effect should in first order affect the scattering intensity rather than the RB-spectra profile.

## 6.5 Bulk viscosity

Values of bulk viscosity for air, N<sub>2</sub>, and O<sub>2</sub>, derived by comparing the 3 bar measurements to the Tenti S6 model using Eq. (6.6), are plotted in black, blue, and green points in Fig. 6.11, respectively. A clear increasing trend of the bulk viscosity with respect to temperature is detected for all of the three species, which can be explained by the fact that at higher temperatures more degrees of freedom will participate in the internal motion of the molecules and the relaxation time of the internal motion are shorter as the collisions happen more frequently. Uncertainty of this determination includes statistical errors resulting from the noise in the measurements,  $\pm 0.9^{\circ}$  scattering angle uncertainty, 0.5% uncertainty in pressure reading, and 0.5 K uncertainty in temperatures. Since all the data are obtained from the same setup with the same systematic uncertainty and similar signal-to-noise ratio, the error margins for all the bulk viscosity determinations are in the same order of magnitude.  $\eta_b$  values for air and N<sub>2</sub> are compared with the ones derived previously from a 366 nm RB-scattering setup. Good agreement, within 1 $\sigma$  overlap, is found for both of the species, demonstrating that the bulk viscosities for air and N<sub>2</sub> are insensitive to the small change of hypersound frequency associated with the ~ 40 nm variation in scattering wavelength.

The temperature-dependency of the bulk viscosity can be empirically interpreted in terms of a linear function:

$$\eta_b = \eta_b^0 + \gamma \cdot T \tag{6.7}$$

Fitting of Eq. (6.7) to the values at 403 nm, as shown in Fig. 6.11, gives  $\eta_b^0 = (-3.15\pm0.22)\times10^{-5} \text{ kgm}^{-1}\text{s}^{-1}$  and  $\gamma = (1.58\pm0.07)\times10^{-7} \text{ kgm}^{-1}\text{s}^{-1}\text{K}^{-1}$  for air, and  $\eta_b^0 = (-3.30\pm0.26)\times10^{-5} \text{ kgm}^{-1}\text{s}^{-1}$  and  $\gamma = (1.59\pm0.09)\times10^{-7} \text{ kgm}^{-1}\text{s}^{-1}\text{K}^{-1}$  for N<sub>2</sub>. Values for oxygen are found to not differ significantly from those for air and N<sub>2</sub>. For N<sub>2</sub> we experimentally establish the ratio  $\eta_b/\eta = 0.79$  at room temperature, where experiments at ultrasound frequencies had yielded  $\eta_b/\eta = 0.73$  [22]. The good agreement between these values means that for the case of N<sub>2</sub> ultrasound and hypersound measurements deliver the same result.

Values of  $\eta_b$  for the gases at lower pressures, which are used as input parameters for the S6 simulations and listed in Table 6.2, are calculated according to Eq. (6.7) in combination with fitted values of the two coefficients,  $\eta_b^0$  and  $\gamma$ , given above. The good agreement between the measurements and the calculations at lower pressures (see Figs. 6.4 to 6.10) constitute a validation of the pressure-independence of the bulk viscosity, while the overall match between the measurements and the model demonstrates that the Tenti S6 model is valid to the same accuracy at the 403 nm wavelength as at 366 nm. Only the resulting values for  $\eta_b$  between the 403 nm and 366 nm data for air at 300 K are found to slightly deviate, but still agreeing within 1.5  $\sigma$  combined error margins.

The present study demonstrates that the values for the bulk viscosity  $\eta_b$  for nitrogen, oxygen and air agree within the stated error margins, and can hence be considered as effectively the same. Similarly, the values for shear viscosity  $\eta$  and thermal conductivity  $\kappa$  are also similar, while the internal specific heat capacity  $c_{int} = 1$  for these diatomic molecular species. This means that the macroscopic transport coefficients underlying the RB-scattering profiles for air closely resemble those of nitrogen and oxygen. Combined with the fact that the molecular masses of the atmospheric constituents are very close (28 u for N<sub>2</sub> and 32 u for O<sub>2</sub>), yielding an effective mass of 29 u for air particles, this makes that the RB-profiles of air closely resembles those of N<sub>2</sub> and O<sub>2</sub>, and that the treatment of air as a single species gas with effective particle mass and transport coefficients holds so well.



**Figure 6.12** – Calculated spectral profiles of Rayleigh-Brillouin scattering for air in a typical LIDAR back-scattering  $(180^{\circ})$  geometry probed with a 355 nm laser (black lines). The figure on the left represents the profile of air at p = 533 mbar and T = 255.6 K, the condition of 5 km altitude in the standard atmosphere, while the figure on the right represents the back-scattering profile at 3 km altitude level. The calculations are based on the Tenti S6 model with transport coefficients as calculated by Eqs. (6.3)-(6.4) and the value for the bulk viscosity presently determined. For comparison purely Gaussian Doppler profiles for the same conditions are plotted (red lines). 7% and 8.5% differences between Gaussian and Tenti calculations are found.

# 6.6 Simulations of RB-scattering for LIDAR applications

With the  $\eta_b$ -values determined in the previous section and the other gas transport coefficients that can be obtained independently, the Tenti S6 model is proven to be valid within 2% level in a wide range of temperatures, pressures and wavelengths including real atmospheric conditions. The spectral profiles and the comparison with model calculations, shown in Figs. 6.4 to 6.10, serve as an illustration. Hence, this model can be directly applied to LIDAR applications for exploring the properties of the atmosphere, such as wind speed profile retrieval or local temperature measurements. Scattering profiles of air at atmospheric conditions in the U.S. Standard Atmosphere model for 180° scattering angle and 355 nm, the often used scattering geometry and wavelength in LI-DAR applications, are simulated and compared with purely Gaussian profiles in Fig. 6.12. Here, some typical conditions of p = 533 mbar and T = 255.6 K, corresponding to an altitude of 5 km in the Standard Atmosphere model, and of p = 692 mbar and T = 268.7 K, corresponding 3 km altitude, are chosen. Fig. 6.12 clearly indicates that even at a height of 5 km in the atmosphere, a simple Gaussian assumption of the scattering profile would result in a 7% error in the peak intensity. Such deviations had been discussed in studies preparing for the ADM-Aeolus wind LIDAR satellite mission of the European Space Agency, and have now been detailed and further quantified [5; 6]. The Tenti

S6 model, invoking the temperature-dependent values for the macroscopic gas transport coefficients including the presently derived values for the bulk viscosity provide a much better algorithm for atmospheric retrieval procedures.

# 6.7 Conclusion

A comprehensive study on spontaneous Rayleigh-Brillouin scattering in diatomic gases N<sub>2</sub> and O<sub>2</sub>, and in air is reported. A large number of measurements recorded under different temperature-pressure conditions are compared with calculations based on the Tenti S6 model, yielding good agreement within 2% of peak level intensities. Values for the bulk viscosity are determined at 403 nm and compared with the ones obtained with a 366 nm setup [82; 68], demonstrating that a slight change in hypersound frequency, associated with a wavelength change of ~ 40 nm, does not affect the values of  $\eta_b$ .

An important conclusion of the present study is that the approximation of air as a single component species with effective transport coefficients and particle mass of 29 u holds well. This is understood from the fact that the gas transport coefficients, bulk viscosity, shear viscosity, thermal conductivity and internal specific heat capacity are all very much the same for air, N<sub>2</sub> and O<sub>2</sub>, while the particle masses are also very similar for the three species. In addition this explains why the Tenti S6 model, developed for single component species, is so well applicable to air.

The 2% deviations between the measurements and the calculations are presently not understood. They may derive from effects of scattering due to temperature fluctuations at constant density, which were not considered in the Tenti S6 model, or be associated with the Wang-Chang and Uhlenbeck linearization, which is a fundamental approximation to derive the Tenti S6 model. Effects of rotational Raman scattering are not likely to have an influence on the RB scattering profile, since it has been filtered out by the 1 nm bandwidth filter. It would be interesting to further investigate depolarization effects induced by Raman scattering.

This study, together with previous ones reported by our group for a different wavelength, verifies that the Tenti S6 model, with the values for the temperature-dependent bulk viscosities determined, is an appropriate basis for atmospheric LIDAR application studies based on Rayleigh-Brillouin scattering.

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# Chapter 7

# Temperature retrieval from Rayleigh-Brillouin scattering profiles measured in air

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In order to investigate the performance of two different algorithms for retrieving temperature from Rayleigh-Brillouin (RB) line shapes, RB scattering measurements have been performed in air at a wavelength of 403 nm, for a temperature range from 257 K to 330 K, and atmospherically relevant pressures from 871 hPa to 1013 hPa. One algorithm, based on the Tenti S6 line shape model, shows very good accordance with the reference temperature. In particular, the absolute difference is always less than 2 K. A linear correlation yields a slope of  $1.01 \pm 0.02$  and thus clearly demonstrates the reliability of the retrieval procedure. The second algorithm, based on an analytical line shape model, shows larger discrepancies of up to 9.9 K and is thus not useful at its present stage. The possible reasons for these discrepancies and improvements of the analytical model are discussed. The obtained outcomes are additionally verified with previously performed RB measurements in air, at 366 nm, temperatures from 255 K to 338 K and pressures from 643 hPa to 826 hPa [82]. The presented results are of relevance for future lidar studies that might utilize RB scattering for retrieving atmospheric temperature profiles with high accuracy.

# 7.1 Introduction

Temperature measurements in the Earth atmosphere are important both as input for atmospheric models and as input for retrievals of other atmospheric properties such as wind, relative humidity or trace gas concentrations. Currently, lidar (light detection and ranging) instruments enable the measurement of temperature with high accuracy (  $\approx 1K$ ), high resolution ( $\approx 100 \, m$ ) and long range (from ground up to 105 km) [86]. For temperature profiling between 0 km and 25 km it is common to make use of rotational Raman scattering on air molecules, whereby the temperature dependence of the intensities of rotational Raman lines is exploited [87–89]. However, although it was demonstrated that such lidars can measure temperature during daytime [89] and in the presence of clouds [87], they suffer from the low Raman scattering cross section. Thus, powerful lasers, sophisticated background filters or night-time operation are required to obtain reliable results. In particular, the rotational Raman scattering cross section (considering Stokes and anti-Stokes branches) is about a factor of 50 smaller than that of Rayleigh scattering. This marks the advantage of deriving atmospheric temperature profiles from Rayleigh-Brillouin (RB) scattering requiring high spectral resolution lidars.

Temperature is a measure of the average kinetic energy of molecules which has its imprint on the RB spectrum. Thus, atmospheric temperature can be derived by resolving the RB spectrum with high spectral resolution filters as for instance atomic vapor cells or Fabry-Pérot interferometers (FPI) and relating the measured spectrum to an appropriate line shape model. The narrow RB line width of a few GHz additionally enables the application of narrow band filters to suppress solar radiation and thus allows for daytime operation. This approach was already suggested and demonstrated in 1971 by Fiocco et al. [90], although their experimental data were severely contaminated by Mie scattering.

As further discussed by Young and Kattawar in 1983 [56], the accuracy of deriving temperature from RB spectra is strongly dependent on the quality of the RB line shape model. In 1974, Tenti et al. [8] developed a model the so-called Tenti S6 model - for describing RB spectra of light scattered in molecular gases of single species, which is since then considered as the best model available. In particular, they use macroscopic gas transport properties as shear viscosity, bulk viscosity and thermal conductivity for describing microscopic fluctuations within the scattering gas and with it the RB spectrum. However, as air is a mixture of gases, the applicability of the Tenti S6 model to air required validation. Although some laboratory studies on RB scattering have been performed in molecular gases and gas mixtures since the early 1970s, it was not before 2010 that the first RB measurements in air were published [46; 45]. The investigations showed that the Tenti S6 model describes the measured RB spectra in air with deviations smaller than 2% considering air as an "effective" medium, consisting of molecules with an effective mass whose collisions are parametrized by effective transport coefficients. Recently, the study was extended by Gu *et al.* [82] for a temperature range from 255 K to 340 K, leading to the same result. Thus, the applicability of the Tenti S6 model to RB spectra measured in air was confirmed with these experiments.

In order to retrieve temperature from measured RB profiles, they have to be analyzed with the line shape model in a certain optimization procedure as for instance a least-squares fit with temperature as free fitting parameter. As for such method it is an important issue how the 2% model deviation transfers into a temperature error. So as to deal with this issue, RB scattering measurements in air at a wavelength of 403 nm, at a scattering angle of  $91.7^{\circ}$ , for temperatures from 257 K to 330 K and pressures from 871 hPa to 1013 hPa were performed. After that, two different temperature retrieval algorithms, one based on the Tenti S6 model, and one on an analytical line shape model according to Witschas [42], are applied to the measured RB spectra.

# 7.2 Experimental details

#### 7.2.1 The instrumental setup

A simplified sketch of the experimental setup is shown in Fig. 7.1. A more detailed overview, also about the 366 nm experimental setup, can be found in [58].



**Figure 7.1** – Schematic diagram of the experimental setup. red: Ti:Sa laser beam (806 nm), dark blue: blue beam (403 nm), light blue: scattered radiation, green: reference beam, SC: scattering cell, PD: photo diode, PZT: piezo-electrical translator, FPI: Fabry-Pérot interferometer, PMT: photomultiplier, HCS: Hänsch-Couillaud stabilization, DAQ: data acquisition unit.

The laser source used in the experiment is a Ti:Sa laser which is pumped by a frequency doubled Nd:YVO<sub>4</sub> laser (Spectra Physics - Millennia), delivering single-mode continuous wave radiation at a wavelength of 806 nm and an output power of 1.5 W. The laser bandwidth is 1 MHz (at 806 nm) and the long-term frequency drift was measured with a wavelength meter (ATOS - LM-007) to be smaller than 10 MHz per hour (at 806 nm). To reach the desired wavelength of 403 nm, the frequency of the Ti:Sa laser light is doubled in a non-linear optical crystal. After second harmonic generation, laser light with a wavelength of 403 nm, 2 MHz line width and a power of 400 mW is obtained (Fig. 7.1, dark blue line).

The blue laser beam is split by a highly reflecting mirror such that most of the intensity is directed to the enhancement cavity where the scattering experiment is performed, whereas a small portion of the light leaking through the mirror is used as a reference beam (Fig. 7.1, green line), which is used to align the setup. The main beam is directed through a mode matching lens into the enhancement cavity, where the scattering cell is placed inside. The mode matching lens thereby ensures that the phase fronts of the laser beam match to the confocal cavity, which is held resonant by the Hänsch-Couillaud stabilization technique.

The scattering cell is sealed with Brewster-angled input and output windows which minimize reflection losses and ensure the amplification of the circulating power. The amplification reaches a factor of about 10, and hence a power level of 4 W is achieved. The photo diode (Fig. 7.1, PD), used to measure the intensity of the light leaking through one of the confocal cavity mirrors, delivers a signal which is proportional to the laser light intensity inside the cavity. The scattered light (Fig. 7.1, light blue line) is collected at an angle of 91.7° which is limited to be within the range of  $\pm 1.2^{\circ}$  by means of geometrical relations using sets of diaphragms and pinholes present in the optical setup. This scattering angle range is afterwards (section 7.3.2) used to estimate the upper limit of the uncertainty of the retrieved temperature. Considering that lidar measurements lead to a scattering angle of  $180^{\circ}$  per definition, it would be preferable to have the same angle also for the laboratory measurements. However, as spurious scattering on optical elements within the experimental setup would always lead to contamination of the measured RB line shape, it was decided to use a scattering angle different from 180°.

The frequency spectrum of the scattered light is resolved by means of a scanning FPI. The FPI is built as a hemispherical version of a confocal etalon, which means that it is composed of one spherical and one plane mirror. In order to scan the FPI plate distance, the spherical mirror is mounted on a piezo-electrical translator (Fig. 7.1, PZT) which is controlled by a computer (Fig. 7.1, DAQ). Despite the lower light gathering in comparison to a plane parallel FPI, the hemispherical configuration was chosen because of its insensitivity to small changes in tilt and orientation which can occur during scanning. The light that passes through the FPI is detected using a photomultiplier tube (PMT, Philips-XP2020/Q) that is operated in photon-counting mode and read out by the data acquisition unit.

In order to measure and monitor temperature and pressure of the gas under investigation, several measurement devices are mounted within the system. The pressure is measured with a baratron, in particular an active capacitive transmitter (Pfeiffer-CMR 271) for pressure values between 100 hPa and 1000 hPa, delivering an accuracy of 0.15% of the measured pressure value. The temperature is measured with a Pt100 thermo-resistor mounted on top of the scattering cell and delivering an accuracy of about  $\pm 0.25$  K (class A) for the temperatures measured within this study. The temperature of the gas sample is set and controlled by four Peltier elements, encased by a temperature controlled water cooling system and mounted below the scattering cell. This allows temperature settings of the gas sample from 250 K to 340 K.

### 7.2.2 Characterization of the instrument function

The instrument function of the experiment, which is principally given by the transmission function of the FPI, has to be determined accurately to avoid systematical errors in the data retrieval. In order to do so, the FPI is illuminated with light elastically scattered from a copper wire mounted within the scattering cell which warrants that the scattered light undergoes the same collecting angle as in RB scattering from the same interaction volume. First, the free spectral range (FSR) is determined by keeping the FPI plate distance constant and scanning the laser frequency over several FSR. Subsequently, the instrument function is acquired by keeping the laser frequency constant and scanning the PZT over several FSR. After that, the nonlinearity of the piezo extension is corrected and the piezo voltage is converted into a frequency scale by exploiting the information that the distance between each transmission peak equals one FSR. Furthermore, the signal to noise ratio of the measured instrument function is increased by averaging several transmission peaks. An exemplary measurement of the instrument function is shown in Fig. 7.2 (black dots). The step size of the processed data is 35 MHz.



**Figure 7.2** - (Top): Measured FPI instrument function (black dots) and best fit of an Airy function (red line) and and Airy function considering defects according to Eq. (7.1) (blue line). (Bottom): Respective residuals in % with respect to the transmission peak intensity.

Commonly, the intensity transmission  $\mathcal{T}(f)$  of an ideal FPI (i.e. axially parallel beam of rays, mirrors perfectly parallel to each other, mirrors of infinite size and mirrors without any defects) is described by an Airy function. However, in order to reach higher accuracy it is also necessary to consider defects on FPI mirrors [91]. As for instance shown in [92], this can be adequately done by adding a Gaussian distributed defect term to the Airy function leading to

$$\mathcal{T}(f) = \frac{1}{\Gamma_{\rm FSR}} \left( 1 + 2\sum_{k=1}^{\infty} R^k \cos\left(\frac{2\pi k f}{\Gamma_{\rm FSR}}\right) \exp\left(-\frac{2\pi^2 k^2 \sigma_g^2}{\Gamma_{\rm FSR}^2}\right) \right)$$
(7.1)

where  $\Gamma_{\text{FSR}}$  is the FSR, R is the mean mirror reflectivity and  $\sigma_g$  is the defect parameter. It is worth mentioning that Eq. (7.1) without the exp-term just represents the Fourier series of the pure Airy function.

A least-squares fit of Eq. (7.1) is used to characterize the instrument function as it is shown by the blue line in Fig. 7.2. For comparison, the best fit of an Airy function is also indicated (Fig. 7.2, red line) showing deviations of 4% with respect to peak intensity, whereas the deviations are smaller than 0.5% in case defects are considered. This demonstrates the necessity of considering defects for an accurate description of the FPI transmission function. In summary, the instrument function of the system is determined by Eq. (7.1) with R = 0.953,  $\sigma_g = 34.2$  MHz and  $\Gamma_{\rm FSR} = 7553$  MHz leading to a full width at half maximum (FWHM) of about 146 MHz. The instrument function of the 366 nm experiment is different as a different FPI was used [58]. In particular, it is determined by Eq. (7.1) with R = 0.916,  $\sigma_g = 35.7$  MHz and  $\Gamma_{\rm FSR} = 7440$  MHz leading to FWHM  $\approx 232$  MHz.

# 7.2.3 Measurement procedure for obtaining Rayleigh-Brillouin spectra

To avoid any contamination from gases of previous measurements, the scattering cell was evacuated and flushed with air, before being charged to the desired pressure. While charging the cell, particles larger than 500 nm were removed by an aerosol filter in the gas inlet line. For each measurement, the gas scattering cell is charged to a designated pressure  $p_{\rm amb}$  first and sealed at room temperature  $T_{\rm amb}$ . Afterwards, the temperature of the cell together with the gas inside is set and controlled to a user defined value  $T_{\rm meas}$  by four Peltier elements and a temperature-controlled water cooling system, and measured with a Pt100 sensor. The actual pressure  $p_{\rm meas}$  of each measurement is thus different from the initial pressure and can be calculated by means of the ideal gas law according to

$$p_{\rm meas} = \frac{p_{\rm amb} \cdot T_{\rm meas}}{T_{\rm amb}} \tag{7.2}$$

while the number density of the gas molecules in the scattering volume stays the same.

The RB spectrum of the scattered light is resolved by changing the FPI cavity length via applying a voltage ramp to the PZT on which the curved FPI mirror is mounted. Before detecting the photons of the scattered light, the PMT is kept optically closed to determine its dark counts, which have to be subtracted from the detected signal to obtain the desired measurement data. Apart from the PMT signal and the PZT scan voltage, a signal which is proportional to the intensity of the laser inside the scattering cell is recorded with a photo diode (Fig. 7.1, PD) to verify that no laser power fluctuations disturb the measured spectra. After finishing the measurement, the non-linearity of the piezo-extension is corrected, and the piezo voltage is converted into a relative frequency scale by utilizing the information that the distance between each measured RB spectrum equals one FSR. Subsequently, several peaks (20-50) are averaged to obtain a better signal to noise ratio. Furthermore, as the performed light-scattering experiments do not provide an absolute intensity, the integrated intensity of the RB spectra is normalized to unity after a background correction has been performed.

Examples of RB spectra measured at 403 nm ( $T_{\text{meas}} = 279.6 \text{ K}, p_{\text{meas}} = 870 \text{ hPa}$  (black),  $T_{\text{meas}} = 296.0 \text{ K}, p_{\text{meas}} = 1005 \text{ hPa}$  (red) and  $T_{\text{meas}} = 330.3 \text{ K}, p_{\text{meas}} = 1014 \text{ hPa}$  (blue)) and averaged for frequency intervals of 150 MHz are shown in Fig. 7.3. The error bars indicate the standard deviation obtained by the averaging procedure.



Figure 7.3 - RB spectra measured at 403 nm and different temperatures and pressures (see label), averaged for frequency intervals of 150 MHz and normalized to equal area. The error bars indicate the standard deviation of the respective data point resulting from the averaging procedure. Details about the respective measurement conditions can be found in Table 7.2.

### 7.3 Data and data analysis

### 7.3.1 The temperature retrieval algorithms

The goal of the retrieval algorithm is to obtain temperature from measured RB spectra as accurately as possible. This is done by analyzing and comparing the measured spectra with an appropriate RB line shape model. In recent studies [82; 46; 45] it was shown that the best RB line shape model for describing RB line shapes obtained in air is the Tenti S6 model [8]. In particular, it is shown that the deviation between model and measurement is less than 2% with respect to peak intensity. However, the Tenti S6 model appears in a mathematically complex, approximating the collision operator with 6 values and eigenfunctions, which makes the model complicated and less assessable for atmospheric operations. For that reason, Witschas [42] developed an analytical image of the Tenti S6 model which consists of three superimposed Gaussians and which is shown to mimic the Tenti S6 model with deviations of smaller than 0.85% with respect to peak intensity for y parameters varying from 0 to 1. Due to its analytical form, the analytical line shape model can be applied to measured spectra in ordinary fit procedures.

In this study, both the Tenti S6 as well as the analytical line shape model are used for temperature retrieval to verify their level of performance. Before being applied to the measured spectra, further details are considered.

Basically, the measured line shape  $\mathcal{M}$  is the convolution of the instrument function  $\mathcal{T}$  according to Eq. (7.1) and the spectral distribution of the scattered light  $\mathcal{S}$ 

$$\mathcal{M} = \mathcal{T}(f) * \mathcal{S}(T, p, f) \tag{7.3}$$

where \* denotes a convolution, f the optical frequency, and T and p the gas temperature and pressure.

In our experiments, the spectrum of the RB scattered light is mainly determined by the RB line shape  $S_{\text{RB}}(T, p, f)$ . However, it also contains an additional spectral component due to particle scattering or spurious reflections from optics and cell walls  $S_{\text{par}}(f)$ , which appears as an additional central peak as can be seen in the measured RB spectra shown in Fig. 7.3. Although the particle-scattering contribution is less than 1% of the intensity of the molecular scattered light for all measurements (see also Table 7.2) it is necessary to consider it in order to avoid systematic errors for the temperature retrieval. As only negligible spectral broadening occurs for particle scattered or reflected light,  $S_{\text{par}}(f)$  can be described by a Dirac-delta function  $\delta_{\text{par}}$  and the spectrum of the scattered light is calculated according to

$$\mathcal{S}(T, p, f) = I_{\rm RB} \cdot \mathcal{S}_{\rm RB}(T, p, f) + I_{\rm par} \cdot \delta_{\rm par}(f)$$
(7.4)

where  $I_{\text{RB}}$  and  $I_{\text{par}}$  are the RB signal intensity and the signal intensity of light scattered on particles or spurious reflections, respectively.
Eq. (7.3), together with Eq. (7.1) and Eq. (7.4) is now applied to the measured RB spectra in two different ways. On the one hand,  $S_{\rm RB}(T, p, f)$  is calculated with the Tenti S6 model [45] and considering air as an "effective" medium, consisting of molecules with an effective mass whose collisions are parametrized by effective and temperature dependent transport coefficients as summarized in Table 7.1. Subsequently, Eq. (7.3) is numerically calculated and compared

**Table 7.1** – Gas transport coefficients for air at temperature T used for Tenti S6 model calculations [65].

Mass number	$[g mol^{-1}]$	28.970
Bulk viscosity $\eta_b$	$[{\rm kg}~{\rm m}^{-1}{\rm s}^{-1}]$	$\eta_b = 1.61 \cdot 10^{-7} \cdot T - 3.1 \cdot 10^{-5}  [82]$
Shear viscosity $\eta$	$[{\rm kg}~{\rm m}^{-1}{\rm s}^{-1}]$	$\eta = \eta_0 \cdot \left(rac{T}{T_0} ight)^{3/2} \cdot rac{T_0 + T_\eta}{T + T_\eta}$
Thermal conductivity $\kappa$	$[{\rm W} \; {\rm m}^{-1} {\rm K}^{-1}]$	$\kappa = \kappa_0 \cdot \left(\frac{T}{T_0}\right)^{3/2} \cdot \frac{T_0 + T_A \cdot \exp[-T_B/T_0]}{T + T_A \cdot \exp[-T_B/T]}$
Heat capacity ratio $\gamma$		1.4
Internal specific heat $c_{\mathrm int}$		1.0

Here,  $\eta_0 = 1.846 \times 10^{-5}$  kg m<sup>-1</sup>s<sup>-1</sup> is the reference shear viscosity and  $\kappa_0 = 26.24 \times 10^{-3}$  W m<sup>-1</sup>K<sup>-1</sup> is the reference thermal conductivity at reference temperature  $T_0 = 300$  K;  $T_\eta = 110.4$  K,  $T_A = 245.4$  K, and  $T_B = 27.6$  K are characteristic constants for air [65].

to the measured line shape for several combinations of T and  $I_{\text{par}}$ , which are the remaining two free parameters considering that p is known (Eq. (7.2)) and  $I_{\text{par}} + I_{\text{RB}}$  equals unity as the measured spectra are normalized to unity before they are analyzed. It is worth mentioning that even for atmospheric measurements the pressure can be taken from the standard model atmosphere as simulations show that deviations between model pressure and real pressure of  $\pm 10$  hPa would lead to systematic errors of less than 0.1 K. The combination of T and  $I_{\text{par}}$  leading to optimum agreement between measured  $S_{\text{meas}}$  and modeled spectrum  $S_{\text{model}}$  is determined in a least-squares algorithm evaluating

$$\chi^2 = \sum_{i} \left( \mathcal{S}_{\text{meas, i}} - \mathcal{S}_{\text{model, i}} \right)^2 \tag{7.5}$$

The result is illustrated in Fig. 7.4, which shows in color-coding the calculated  $\chi^2$  according to Eq. (7.5) for several T and  $I_{par}$  on the left, and the comparison of the best-fit spectrum with the measurement on the right (blue line). The purple area in the middle of the color-plot indicates that the value of best accordance is for T = 294.6 K and  $I_{par} = 0.41\%$  of  $I_{RB}$ . The reference temperature was  $T_{Pt100} = 295.5$  K (see also Table 7.2). On the other hand,  $S_{RB}(T, p, f)$  is calculated by an analytical line shape model according to Witschas [42] which is composed of the superposition of three Gaussians. Again, the contribution of particle scattering is considered by adding an additional Dirac-delta function before convolving with the instrument function as depicted in Eq. (7.3). Using

this procedure, the measured signal can be calculated completely analytically according to

$$\mathcal{M} = \frac{I_{\rm RB}}{\Gamma_{\rm FSR}} \cdot \left[ \mathcal{A} \left( 1 + 2\sum_{k=1}^{\infty} R^k \cos\left(\frac{2\pi k \left(f - f_0\right)}{\Gamma_{\rm FSR}}\right) \exp\left(-\frac{2\pi^2 k^2 \left(\sigma_g^2 + \sigma_R^2\right)}{\Gamma_{\rm FSR}^2}\right) \right) + \frac{1 - \mathcal{A}}{2} \left( 1 + 2\sum_{k=1}^{\infty} R^k \cos\left(\frac{2\pi k \left(f - f_0 - f_B\right)}{\Gamma_{\rm FSR}}\right) \exp\left(-\frac{2\pi^2 k^2 \left(\sigma_g^2 + \sigma_B^2\right)}{\Gamma_{\rm FSR}^2}\right) \right) + \frac{1 - \mathcal{A}}{2} \left( 1 + 2\sum_{k=1}^{\infty} R^k \cos\left(\frac{2\pi k \left(f - f_0 + f_B\right)}{\Gamma_{\rm FSR}}\right) \exp\left(-\frac{2\pi^2 k^2 \left(\sigma_g^2 + \sigma_B^2\right)}{\Gamma_{\rm FSR}^2}\right) \right) \right] + \frac{I_{\rm par}}{\Gamma_{\rm FSR}} \cdot \left[ \left( 1 + 2\sum_{k=1}^{\infty} R^k \cos\left(\frac{2\pi k \left(f - f_0\right)}{\Gamma_{\rm FSR}}\right) \exp\left(-\frac{2\pi^2 k^2 \sigma_g^2}{\Gamma_{\rm FSR}^2}\right) \right) \right]$$
(7.6)

where  $f_0$  is the center frequency of the RB spectrum, and  $\mathcal{A}(x, y)$ ,  $f_B(x, y)$ ,  $\sigma_R(x, y)$  and  $\sigma_B(x, y)$  are quantities used to parameterize the line shape model and are given in [42].  $x = (2\pi f)/(\sqrt{2}kv_0)$  and  $y = (p)/(\sqrt{2}kv_0\eta)$  represent dimensionless parameters commonly used for parameterization in gas kinetic theory [8], where  $k = |\mathbf{k_s} - \mathbf{k_0}| = 4\pi/\lambda \sin(\theta/2)$  is the magnitude of the interacting wave vector (with  $\mathbf{k_0}$  and  $\mathbf{k_s}$  being the wave vectors of the incident and scattered light),  $\lambda$  is the wavelength of the incident light,  $\theta$  is the scattering angle, and  $v_0 = (k_{\rm B} T/m)^{(1/2)}$  the thermal velocity. Thus, Eq. (7.6), which is an analytical representation of Eq. (7.3), can now be applied to the measured spectra in a least-squares fit procedure, with  $f_0$ ,  $I_{par}$ ,  $I_{RB}$  and T (via  $\mathcal{A}(x, y)$ ,  $f_B(x, y)$ ,  $\sigma_R(x, y)$  and  $\sigma_B(x, y)$ ) being the free fit parameters and p is considered to be known. An example of a best-fit of Eq. (7.6) to a RB line shape measurement is shown in Fig. 7.4, right (red dashed line). The derived temperature is  $T_{anal.} = 292.8$  K and the reference temperature was  $T_{Pt100} = 295.5$  K.

# 7.3.2 Estimation of the uncertainty of the retrieved temperature values

In order to quantitatively evaluate the performance of the temperature retrieval algorithms, the uncertainties of the derived temperatures  $T_{model}$  as well as the one of the reference temperature  $T_{Pt100}$  have to be determined and considered.

The reference temperature  $T_{Pt100}$ , which is considered as the actual temperature of the air inside the scattering cell, was measured with a Pt100 sensor (class A) whose permissible deviation  $\Delta T_{Pt100}$  is caused by the resistance uncertainty and which is calculated according to  $\Delta T_{Pt100} = 0.15 \text{ K} + 0.002 \times |T_{Pt100} - 273.15 \text{ K}|$  (DIN IEC 751). Considering the temperature range of 255 K to 340 K used for the RB line shape measurements,  $\Delta T_{Pt100}$  varies between 0.19 K to 0.28 K.

For calculating the uncertainty  $\Delta T_{model}$  of the retrieved temperature values  $T_{model}$ , two main contributors are considered within this study, namely



Figure 7.4 – (left): Squared deviation between measured and model RB line shape depending on temperature and particle concentration calculated according to Eq. (7.5). (right, top): Measured RB spectrum ( $T_{Pt100} = 295.5$  K, p = 1010 hPa, black crosses) and best-fit according to the Tenti S6 model calculation ( $T_{Tenti} =$ 294.6 K,  $I_{par} = 0.41\%$  of  $I_{RB}$ , blue solid line) and the analytical model calculation ( $T_{anal.} = 292.8$  K,  $I_{par} = 0.34\%$  of  $I_{RB}$ , red dashed line). (right, bottom): Deviation between measured and model RB line shape in % with respect to peak intensity.

the noise on the measured data points and the uncertainty of the scattering angle caused by the geometrical structure of the optical setup. The noise contribution is estimated by applying a maximum likelihood estimator (MLE), considering solely Poisson noise on the measured data points, and assuming the RB spectrum to be Gaussian as it would be for very low pressures (Knudsen regime). As explicitly discussed by Hagen *et al.* [93], the width  $w_a$  ( $w_a =$  $FWHM/(8 \ln 2)^{1/2})$  of a Gaussian including Poisson noise can be determined with a standard deviation  $\sigma_{w_q} = w_q \times (2N)^{-1/2}$ , where N is the number of detected photons. As the RB spectrum is considered to be a Gaussian, its width is equivalently described according to  $w_a = 2/\lambda \times (k_{\rm B}T/m)^{1/2}$ , where  $\lambda$  is the wavelength of the scattered light, T is the air temperature,  $k_{\rm B}$  is the Boltzmann constant, and m the mass of a single air molecule. Using this relation,  $\Delta T_{noise}$  is calculated to be  $\Delta T_{noise} = T \times (2/N)^{1/2}$  by means of the partial derivative  $(\partial w_q/\partial T)$ . Within the presented measurements, N varied between  $1 \times 10^6 - 5 \times 10^6$  photons, and T was between 255 K - 338 K, thus,  $\Delta T_{\text noise} = 0.2 \text{ K} - 0.5 \text{ K}.$ 

The influence of the scattering angle uncertainty can be transferred to a temperature uncertainty by means of the x parameter used to parameterize RB line shapes and given before (section 7.3.1). Additionally, the RB spectrum is again assumed to be a Gaussian, and thus, the y parameter to be zero. As the x parameter depends on  $\theta$  as well as on T, the partial derivatives  $(\partial x/\partial \theta)$  and  $(\partial x/\partial T)$  can be used to calculate the temperature uncertainty caused by the scattering angle according to

$$\Delta T_{\text{angle}} = \frac{\partial \theta}{\tan(\theta/2)} \cdot T \approx 0.02 \cdot T \tag{7.7}$$

with  $\theta = 1.60 \text{ rad } (91.7^{\circ})$  and  $\partial \theta = 0.02 \text{ rad } (1.2^{\circ})$ . Now, both contributions are quadratically added yielding the overall uncertainty  $\Delta T_{\text{model}}$  of the retrieved temperature values as they are indicated by the error bars in Fig. 7.5

$$\Delta T_{\text{model}} = \sqrt{(\Delta T_{\text{noise}})^2 + (\Delta T_{\text{angle}})^2}$$
(7.8)

It can be seen that  $\Delta T_{angle}$  varies from 5.1 K to 6.8 K, and thus, it is the main contributor to the overall uncertainty  $\Delta T_{model}$ . However, it has to be mentioned that the estimate of  $\partial \theta = 0.02$  rad  $(1.2^{\circ})$  is quite conservative and gives the maximum possible error. As the laser beam was only slightly re-aligned between each measurement, it is very unlikely that the principally possible scattering angle range of  $\pm 1.2^{\circ}$  was exhausted. Thus, both  $\partial \theta$  and with it also  $\Delta T_{angle}$  are assumed to be smaller in reality. Anyway, this estimation demonstrates that RB spectra as well as the temperature retrieval from them are quite sensitive to the scattering angle itself. Regarding lidar measurements, which are usually restricted to a scattering angle of 180° and a small field of view of several hundred  $\mu$ rad, the scattering angle uncertainty will only play a minor role for a temperature retrieval from RB profiles.

### 7.4 Experimental results and discussion

In the following, RB line shape measurements performed at a wavelength of 403 nm in air (T = 257 K to 330 K, p = 871 hPa to 1013 hPa) are used to verify the performance of the two temperature retrieval algorithms explained in section 7.3.1. Furthermore, previously performed RB line shape measurements ( $\lambda = 366$  nm, T = 255 K to 335 K, p = 643 hPa to 826 hPa) published by Gu *et al.* [82] are used for additional verification. A summary of the respective experimental conditions for the measurements is given in Table 7.2.

In Fig. 7.5, the retrieved temperatures  $T_{\text{model}}$  are plotted as a function of the reference temperature  $T_{\text{Pt100}}$ . The left and right graph indicates the results for measurements performed at a wavelength of 366 nm and 403 nm, respectively. The blue dots denote the results from the temperature retrieval using the Tenti S6 model, the red dots the results obtained by using the analytical line shape model. The shown error bars indicate the uncertainty of the reference temperature  $\Delta T_{\text{Pt100}}$  and the one of the derived temperature  $\Delta T_{\text{model}}$  according to Eq. (7.8), respectively. The gray line represents the  $T_{\text{model}} = T_{\text{Pt100}}$ line.

For both data sets it is clearly obvious that there is very good accordance between temperatures retrieved with the Tenti S6 model and reference temperature. In particular, the absolute difference is less than 2 K for all measurements. A linear correlation of retrieved- and reference temperature (Fig. 7.5, blue dashed lines) yields a slope of  $1.00 \pm 0.03$  ( $\lambda = 366$  nm) and  $1.01 \pm 0.02$  ( $\lambda = 403$  nm), and thus clearly demonstrates the reliability of the retrieval procedure. The second algorithm using the analytical line shape model shows larger discrepancies of up to 9.9 K and is thus not useful at its present stage. The linear correlation of retrieved- and reference temperature (Fig. 7.5, red dashed lines) yields a slope of 0.89  $\pm$  0.03 ( $\lambda = 366$  nm) and  $0.87 \pm 0.02$  ( $\lambda = 403$  nm), and thus indicates that the model leads to larger discrepancies at higher temperatures. The statistical uncertainty of the retrieved temperature values varies between 5 K and 7 K. However, it is worth mentioning that the uncertainty caused by Poisson noise only varies between 0.2 K and 0.5 K. The larger contribution comes from the principally possible scattering angle uncertainty as prominent for the present experimental setup. As already explained, this estimation is conservative and gives the maximum uncertainty that can be caused due to a varying scattering angle. Considering that lidar measurements have a scattering angle of  $180^{\circ}$  due to geometrical reasons, only the Poisson noise uncertainty (0.2 K to 0.5 K) would contribute to such kind of atmospheric measurements.

The results shown above demonstrate that absolute temperature can be derived from RB spectra obtained in air with an accuracy of better than 2 K by utilizing the described temperature retrieval based on the Tenti S6 model. However, the retrieval based on the analytical model leads to larger deviations especially at higher temperatures. This behavior can be explained by a poor temperature-parameterization method within the analytical line shape



Figure 7.5 – Temperature values retrieved from RB spectra measured at 366 nm (left) and 403 nm (right) by using the Tenti S6 model (blue) and the analytical line shape model (red) compared to reference temperature measure with a Pt100 sensor. Detailed values are given in Table 7.2. The gray line indicates  $T_{model} = T_{Pt100}$  line.

model [42]. In particular, the analytical model is parameterized by the x- and y parameter and thus ensures versatility. However, in order to obtain different line shapes with different y parameters for the parameterization process, the temperature was kept constant to be 250 K and only the pressure values have been varied. Thus, the entire model is actually only valid for a temperature of T = 250 K. No temperature dependency of the gas transport coefficients (see Table 7.1) is considered. This explanation is also affirmed by the derived values at low temperatures which are  $T_{\text{anal.}} = 257.0$  K at a reference temperature of  $T_{\text{Pt100}} = 256.6$  K (at 403 nm) and  $T_{\text{anal.}} = 254.5$  K at a reference temperature of  $T_{\text{Pt100}} = 255.2$  K (at 366 nm). In both cases the deviation between derived-and reference temperature is less than 1 K. This means that the analytical model needs further development, in particular, the consideration of different temperature values before it is useful for any temperature retrievals.

### 7.5 Summary and conclusion

Rayleigh-Brillouin (RB) scattering measurements in air ( $\lambda = 403$  nm, T = 257 K to 330 K, p = 871 hPa to 1013 hPa) were performed and used to verify the performance of two different temperature retrieval algorithms, one based on the Tenti S6 line shape model [8], and one based on an analytical model [42]. Furthermore, previously performed RB measurements (air,  $\lambda = 366$  nm, T = 255 K to 335 K, p = 643 hPa to 826 hPa) [82] were used for additional validation. With both data sets it is demonstrated that absolute temperature can be derived from RB spectra obtained in air at atmospheric

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$\widehat{\mathbf{X}}$	(K)	(%)	(K)	$(\mathbf{K})$	(%)	(K)	(hPa)	$(\mathrm{nm})$
6.0	296.1	0.66	-0.1	292.5	0.68	+3.5	1005	402.987
6.6	254.7	0.41	+1.9	257.0	0.35	-0.4	880	402.995
5.5	294.6	0.41	+0.9	292.8	0.34	+2.7	1010	402.985
9.2	311.1	0.41	-1.9	305.5	0.38	+3.7	1011	402.995
0.3	328.4	0.75	+1.9	320.4	0.82	+9.9	1014	402.993
4.7	284.0	0.34	+0.7	282.6	0.41	+2.1	955	402.997
9.6	279.7	0.48	-0.1	279.7	0.43	-0.1	870	402.997
0.3	320.9	0.27	-0.6	313.9	0.24	+6.4	1013	402.996
5.2	254.9	0.34	+0.3	254.5	0.16	+0.7	643	366.840
6.8	278.6	0.34	-1.8	278.1	0.27	-1.3	703	366.840
7.2	297.6	0.48	-0.4	293.4	0.42	+3.8	726	366.650
7.7	317.0	0.41	+0.7	310.9	0.46	+6.8	776	366.650
8.2	339.1	0.55	-0.9	330.2	0.62	+8.0	826	366.650

conditions with high accuracy. In particular, it is shown that the accordance of the derived temperature to the reference temperature is better than 2 K in case of using the Tenti S6 model based retrieval algorithm. This outcome is of great relevance for future high spectral resolution lidar systems that might use RB spectra for deriving atmospheric temperature profiles with high accuracy over a long range also during daytime as it was recently shown by Witschas et al. [73]. The retrieval based on the analytical model leads to discrepancies between retrieved- and reference temperature of up to 9.9 K and is thus not useful at its present stage. It is discussed that these discrepancies are explained by a poor temperature-parameterization within the model which has to be improved for successful future use. Ma et al. [43; 44] recently developed a new analytical model based on the superposition of three Voigt-functions which partly shows even better performance than the analytical model of Witschas. However, due to the large number of free fit parameters, their fit routine runs not stable for pressures smaller or equal than 1000 hPa [43], which is the interesting pressure range for atmospheric applications.

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### Chapter 8

# Rayleigh-Brillouin scattering in binary gas mixtures

We present the result of precise measurements of spectral lineshapes of spontaneous Rayleigh–Brillouin scattering in mixtures of the noble gases Ar, Kr, and He. These experiments are in the kinetic regime, with largest non-uniformity parameter  $y \sim 5$ . It appears that the admixture of the light He results in marked changes of the spectra, although in all experiments He can be viewed as a spectator atom: it affects the relaxation of density fluctuations of the heavy constituent, but its contribution to the scattered light intensity is small. We compare these results to the model of Bonatto and Marques Jr. (J. Stat. Mech. P09014 (2005) [94], which has no adjustable parameters and reproduces the mixture spectra very well. This model is based on a BGK-type approach, which allows for a choice of the relevant physical phenomena included. For mixtures these should include the relaxation of temperature differences between the species. For a pure gas this choice no longer suffices and more moments of the distribution function must be considered.

### 8.1 Introduction

Rayleigh–Brillouin scattering in dilute gases offers a delicate probe of gas kinetics. Understanding the scattered light spectrum involves the linearized Boltzmann equation [14], and throughout the years intricate approximations to the collision integral have resulted in various kinetic models for the scattered light spectrum. These models may be viewed as a success of statistical physics. Still, discrepancies with experiments exist, and the kinetic models are generally restricted to simple gases. In this paper we will use a new experimental setup and concentrate on mixtures of noble gases. This setup provides spectra with unprecedented statistical accuracy [58]. Using it, we have previously documented spectra of  $N_2$ ,  $O_2$ , and  $CO_2$  gases, and compared them to a popular model for the spectral line shape: the Tenti model [45; 83].

The Tenti model model allows for kinetic and internal degrees of motion, and takes measured values of transport coefficients as parameters [7; 8]. The problem in the comparison to experiments is the value of one of them, the bulk viscosity, which is not known at GHz frequencies. Bulk viscosity is the relaxation of internal degrees of freedom to kinetic ones. Its value was measured at MHz frequencies, but not at the frequencies relevant for light scattering experiments. In fact, in all of our experiments, the bulk viscosity was used as an adjustable parameter, and its value was determined by the best fit to a measured spectrum.

In this paper, we measure scattered light spectra involving noble gases and mixtures of noble gases, and compare them to models with no adjustable parameters. Experiments on mixtures of He and Xe atoms were done by Clark [95], and the evolution of the spectrum from Gaussian to Lorentzian with increasing He pressure was observed, corresponding to the evolution of the extremely dilute Xe component from kinetic to diffusive behavior. Light scattering on He Xe mixtures in a range of pressures comparable to ours was studied by Laetamendia *et al.*[39], and sizable differences with a kinetic mixture model [96] were found.

For the models considered considered in the present paper the only parameter needed is the well-known value of the shear viscosity of the pure noble gas. All our experiments are in the kinetic regime, where the mean-free path between collisions is comparable to the scattered light wavelength. Interestingly, mixtures of gases with very different mass behave in a similar fashion as a gas of molecules with internal degrees of freedom. While the two components of the mixture briefly can have different temperatures, a molecular gas can have different temperatures associated with translational and internal degrees of freedom. It is the relaxation of these temperature differences that dermines the scattered line shape.

In the past decades, many ingenious efforts have been undertaken to arrive at approximate solutions of the Boltzmann equation which are relevant for light scattering. Light scattering involves density fluctuations, with the spectrum of scattered light the Fourier transform of the density-density correlation function. Van Leeuwen and Yip showed that this correlation function follows from the first moment of the solution of the linearized Boltzmann equation [14].

One such effort is based on the BGK model, which takes a simple relaxation form for the collision integral [97],

$$\frac{\partial f}{\partial t} + (\boldsymbol{c} \cdot \nabla) f = -\sigma \left( f - f_r \right),$$

with c the molecular velocity, f the position-velocity distribution function, and  $f_r$  a reference distribution function. The latter is determined from the requirement that N of its moments are the same as those of the complete collision integral for monatomic particles with a  $r^{-4}$  repulsive interaction potential. Through increasing N, increasingly accurate predictions of light scattering spectra can be computed.

A similar approach was used for a theory of light scattering in binary mixtures of noble gases, but now the moments of the reference distribution function were selected to be those relevant for the relaxation phenomena in mixtures. These moments reflect the relaxation of the velocity differences  $v_1 - v_2$ , of the constituents 1, 2, the relaxation of the temperature differences  $T_1 - T_2$ , but contributions due to the relaxion of (high-order) gradients, which are important for the description of scattered light spectra of *monatomic* gases, were not considered. In this sense, the BGK model with a judicious selection of the reference distribution  $f_r$  allows one to include the relevant physical phenomena in the kinetic description. This is a great advantage for the design of models, as the computation of these various contributions is a highly nontrivial task.

It is expected that a model that works well for mixtures, no longer works if the density of one of the constituents vanishes, and the gas becomes monatomic. This is because in the design of the mixture model the focus was on inter-species relaxation processes, and not on the physical mechanisms that determine the shape of the spectrum of light scattered from monatomic gases.

A gas of molecules with internal degrees of freedom may have two temperatures, related to the kinetic and internal motion. The relaxation time  $\tau_r$  of the associated temperature difference depends on the efficiency of collisions to alter the population of internal states. Similarly, a mixture of atomic gases with disparate masses,  $M_1$ ,  $M_2$ ,  $M_2 \gg M_1$ , may also have two temperatures, with the temperature relaxation time  $\tau_r \approx (M_2/M_1)^{1/2} \tau_{22}$ , where  $\tau_{22}$  is the self collision time of the heavy component. We will show the results of experiments on mixtures of noble gases with a large mass disparity. For a mixture of He and Ar, it is  $M_{\rm He}/M_{\rm Ar}$  = 0.1002, while for the He Kr mixture considered,  $M_{\rm He}/M_{\rm Kr} = 0.0478$ . With these different size atoms, it is only the the heavy ones that contribute to the scattered light intensity. The ratio of their polarizabilities is  $\alpha_{\rm He}/\alpha_{\rm Ar} = 0.1247$ , and  $\alpha_{\rm He}/\alpha_{\rm Kr} = 0.0772$ . Thus, the light atoms are *spectators*, and influence the spectral line shape only indirectly through collisions. We will show that, nevertheless, their influence can be large: adding light atoms to a gas of heavy ones significantly changes the shape of the scattered light spectrum.



**Figure 8.1** – Schematic diagram of the experimental setup for spontaneous Rayleigh– Brillouin scattering (not to scale). The UV laser beam (full black line) is reflected several times in the enhancement cavity to increase the scattering intensity. A reference beam (gray line), split off the main beam, is used for detector alignment. Scattered light is detected at 90° using a pinhole, a Fabry–Perot interferometer and a photomultiplier (PMT).

### 8.2 Experimental setup and results

A schematic view of the setup for spontaneous Rayleigh–Brillouin scattering is shown in Fig. 8.1. The light from a narrowband continuous–wave laser is scattered off a gas contained in a temperature–controlled gas cell. The laser is a frequency–doubled Ti:Sa laser delivering light at 403 nm, 2 MHz bandwidth and 400 mW of output power. The long–term frequency drift was measured with a wavelength meter to be smaller than 10 MHz per hour. The scattered light is collected at an angle of 90° from an auxiliary focus inside the enhancement cavity, in which a scattering–cell is mounted. The cell is sealed with Brewster windows. The circulation of the light inside the enhancement cavity amplifies the power by a factor of 10.

The scattering angle is calculated to be  $90 \pm 0.9^{\circ}$  by means of the reference laser beam and geometrical relations using sets of diaphragms and pinholes present in the optical setup. The scattered light is filtered by a diaphragm which covers an opening angle of 2°, collected by a set of lenses, further filtered by an extra pinhole ( $d = 50\mu$ m) and then directed into a hemispherical scanning Fabry–Perot interferometer, which is used to resolve the frequency spectrum of the scattered light. To scan the FPI plate distance, the spherical mirror is mounted on a piezo–electrical translator, which is controlled by a computer.

The spectral response S(f) of the Fabry–Perot spectrometer was measured in a separate experiment, and could be parametrized very well by the formula

$$S(f) = \left[1 + \left(\frac{2f_{\text{FSR}}}{\pi f_{\text{w}}} \sin \frac{\pi f}{f_{\text{FSR}}}\right)^2\right]^{-1}, \qquad (8.1)$$

where  $f_{FSR}$  is the free spectral range of the etalon,  $f_{FSR} = 7553$  MHz, and  $f_w = 139$  MHz is the Airy-width of the transmission peak. All computed model spectra were convolved with S(f), and since the free spectral range is relatively small, it is important to allow for the periodic nature of S(f).

The light that passes through the FPI is detected using a photo multiplier tube (PMT) which is operated in the photon–counting mode and read out by a computer. To prevent contamination on the mirrors that could lead to absorption of UV light, the enhancement cavity as well as the FPI is flushed with dry Nitrogen. Inside the cell the pressure is measured with an active piezo transmitter (Pfeiffer-APR). The temperature is measured with a thermo–resistor Pt100. Before performing a measurement, the scattering cell was evacuated and purged with the working gas, before being charged to the desired pressure, to a avoid any contamination from gases of previous measurements. The temperature for all measurements is 297 K.

The light scattering experiments do not provide an absolute intensity, therefore the experimental and computed spectra were normalized such that  $\int_{-f_b}^{f_b} I(f) \cdot df = 1$ , where the integral extends over one free spectral range (FSR),  $f_b = f_{FSR}/2$ . Ideally, the bounds  $f_b$  of the integration should be such that  $I(\pm f_b) = 0$ , however, the free spectral range of the etalon is not much larger than the width of the measured spectra ( $\approx 8 \times 10^9$  Hz, and it is important to realize how the spectra are normalized.

Another issue is the signal background  $I_{e_0}$  in the experiment, which must be subtracted from the raw measured spectrum  $I_{e_r}(f)$  before normalization of  $I_e(f) = I_{e_r}(f) - I_{e_0}$ . The background is mainly made up of dark counts of the photo multiplier; it was determined for each measurement and was subtracted from the subsequently measured spectrum. However, it turns out that  $I_{e_0}$ also contains a small contribution,  $I'_{e_0}$ , of broadband fluorescence of the cell windows. We discovered that this contribution also depends on the exposure history of the cell windows.

Therefore it was decided to correct the model spectra  $I_m(f)$  for this residual background contribution, by setting  $I_m(f) = a I_e(f) - I'_{e_0}$ , and determine  $I'_{e_0}$  and the proportionality constant a in a least squares procedure for the wings of the spectra, where the wings are defined as frequencies such that  $I_m(f) \leq \max(I_m)/4$ . The idea is that it is better to use the wings of a model spectrum rather than fitting a horizontal line to the background. If the measured spectra would have the correct background, a = 1 and  $I'_{e_0} = 0$ . The shifted model spectrum  $I'_m(f) = I_m(f) + I'_{e_0}$  was then normalized again such that  $\int_{-f_b}^{f_b} I'_m(f) df = 1$ . This procedure, which converges quickly, gave a small but perceptible shift of the background.

Let us now quantify the difference between the experiment and the computed model-spectra. Assuming Poissonian statistics of registered photon counts, an estimate of the statistical error  $\sigma(f_i)$  of measured spectra was obtained from the square root of the accumulated photon count  $N_i$  at each discrete frequency  $f_i$ . It was verified that the fluctuations  $N_i^{1/2}$  at each  $f_i$  were independent. We can then compute the normalized difference  $\Delta(f_i)$  between model  $I_m(f_i)$ and experimental  $I_e(f_i)$  spectrum as  $\Delta(f_i) = [I_m(f_i) - I_e(f_i)]/\sigma(f_i)$ , and the normalized error as  $\chi^2 = N^{-1} \sum_{i=1}^N \Delta^2(f_i)$ . If the computed line shape model  $I_m$  would fit the measurement perfectly, then only statistical errors remain and the minimum of  $\chi^2$  is unity. Rather than a percentage error, we will from now on quantify the difference between theory and experiment by  $\chi^2$ .

### 8.3 Results

The experiments on pure and mixed noble gases are documented in Table 8.1. They are characterized by the (partial) pressures and the (partial) nonuniformity parameters. The non-uniformity parameter of a simple gas is the ratio y of the scattering wavelength to the mean free path l between collisions, y = 1/(kl), where  $k = |\mathbf{k}_s - \mathbf{k}_p|$ , with incident- and scattered-light wavevectors  $\mathbf{k}_p$  and  $\mathbf{k}_s$ , respectively. In a mixture of hard-sphere atoms consisting of r components, we define the partial mean free paths  $l_i$  by

$$l_i = \left[\pi \sum_{j=1}^r n_j (a_i + a_j)^2 (1 + M_i/M_j)^{1/2}/4\right]^{-1}$$
(8.2)

with  $n_i$  the number density of component *i*,  $a_i$  its atomic radius and  $M_i$  its atomic mass, so that the partial nonuniformity parameter is  $y_i = 1/(k l_i)$ . With all nonuniformity parameters order of one, all experiments are in the kinetic regime. The comparison to spectral line shape models needs the hard– sphere radii, for which we have used the values  $a_{\text{H}e} = 2.16 \times 10^{-10}$  m and  $a_{\text{A}r} = 3.66 \times 10^{-10}$  m.  $a_{\text{K}r} = 4.20 \times 10^{-10}$  m, and atomic polarizabilities  $\alpha_{\text{H}e} = 0.227 \times 10^{-40} \text{ Cm}^2 \text{ V}^{-1}$ ,  $\alpha_{\text{A}r} = 1.82 \times 10^{-40} \text{ Cm}^2 \text{ V}^{-1}$ ,  $\alpha_{\text{K}r} = 2.94 \times 10^{-40} \text{ Cm}^2 \text{ V}^{-1}$ .

### 8.3.1 Pure noble gases

Let us first test the convergence of the N moment model for noble gases. This model needs a single experimental parameter, the shear viscosity (or the atomic radius a), which is well known. The result for N = 5, 13, 20 and 35 is shown in Fig. 8.2, with the convergence quantified by  $\chi^2$ . The results demonstrate that increasing the number of modes N leads to an increasingly precise reproduction of measured light scattering spectra, with the N = 35 model hardly distinguishable from the experiment. However, since the minimum  $\chi^2$  is still larger than 1, a significant difference between model and experiment remains, although on a relative scale it is smaller than  $\approx 1\%$ .

In fact, the agreement is so good that the model may be viewed as a benchmark testing for experiments. We must realize, however, that a monatomic ideal noble gas is the simplest system thinkable as there are no internal molec-

Figure	$p_{\mathrm{A}r}$	$p_{\mathrm{H}e}$	$y_{\mathrm{A}r}$	$y_{\mathrm{H}e}$	$\chi^2$
	pascal	pascal			
8.2(a)	2	0	1.14		4.5
8.3(a)	1	1	1.63	0.54	5.2
8.3(b)	2	2	3.28	1.08	13
8.3(c)	3	1	2.96	1.16	82
8.3(d)	1	3	3.59	1.00	7.6
	$p_{\mathrm{K}r}$	$p_{\mathrm{H}e}$	$y_{\mathrm{K}r}$	$y_{\mathrm{H}e}$	$\chi^2$
8.2(a)	1.3	0	0.96		12
8.3(e)	1.3	1.3	3.28	0.77	15
8.3(f)	2	2	5.01	1.17	62

**Table 8.1** – (Partial) pressures and (partial) non–uniformity parameters for the experiments on pure noble gases and mixtures of noble gases. The experimental results are shown in Figs.8.2 and 8.3. The last column shows the  $\chi^2$  discrepancy with the spectral line shape models.



**Figure 8.2** – Comparision of Ar and Kr spectra to the *N*-moment model. The spectra are shown for N = 35, while the convergence with increasing number of modes *N* is demonstrated in the inset of the figure. Since the minimum  $\chi^2$  is still larger than 1, there remains a significant difference between model and experiment, although on a relative scale it is smaller than  $\approx 1\%$ .

ular degrees of freedom. As a next step we will consider mixtures of noble gases.

### 8.3.2 Mixtures of noble gases

We have measured light scattering spectra mixtures of Ar and He and Kr and He. They were compared to the mixture model by Bonatto and Marquez [94]. The spectra are shown in Fig. 8.3 with the parameters listed in Table 8.1. The discrepancy between the model and the spectra is quantified with  $\chi^2$ . For

the equimolar He, Ar mixtures, the discrepacies are small. There is a large discrepancy in the asymmetric case with 1 bar He and 3 bars Ar. This is expected, as the mixture model is designed to capture the relevant interspecies relaxation processes, which become less important for asymmetric mixtures. Surprisingly, a similar large discrepancy is not seen for the reverse case, 3 bars He and 1 bar Ar. There is a slight difference in the importance of inter-species temperature relaxation for the two cases, as quantified by the ratio  $S_c = \nu_{\Delta}/\nu_s$ , with  $\nu_{\Delta}$  the relaxation frequency of the temperature difference, and  $\nu_s = p/\eta$  the stress relaxation frequency. This number is largest (temperature relaxation least important) for the 1 bar He, 3 bars Ar case ( $S_c = 0.40$ ), it is  $S_c = 0.37$  for the reverse case.

### 8.3.3 He-CO $_2$ mixture

Our mixture experiments are inspired by our experiments on air, which has great practical implications for LIDAR. Air is also a mixture, but now involving molecules with internal degrees of freedom. For a monomolecular gas, light scattering spectra have been reproduced approximately using the Tenti model, which allows for internal degrees of freedom, and takes experimental values of the transport coefficients, including the bulk viscosity, as parameters. When devising a theory for air one faces the formidable task of including both kinetic and internal degrees of freedom for at least two species.

As a slightly simpler system we consider the influence of a light spectator Helium atom in an equimolar mixture of CO<sub>2</sub> and He. As shown in Fig. 8.4, the influence is large. The addition of the light atoms dramatically reduces the sound peaks, which have a frequency  $v_s k/2\pi$ , with the velocity of sound  $v_s = (7k_{\rm B}T/5M)^{1/2}$ , with M the molecular mass.

It is tempting to view the influence of He collisions as helping the relaxation of the vibrational modes of the  $CO_2$  molecules, thus enhancing the bulk viscosity and suppressing the sound peaks. However, the addition of He not only influences the relaxation of the internal degrees of freedom, but also the translational modes. The proper way to explain these experiments is the design of a theory for light scattering off mixtures of monatomic and polyatomic gases. Such a theory exists, but it is only valid in the hydrodynamic regime, where the nonuniformity parameter y is much larger than one [98].

### 8.4 Conclusion

We have studied Rayleigh-Brillouin scattering in mixtures of noble gases, whose constituents have a very different mass. In all cases, the addition of the light He atomic gas has a large influence on the spectral line shapes, although He atoms hardly contribute to the scattered light intensity. These experiments, therefore, probe the influence of collision dynamics on the spectrum.

Density fluctuations in mixtures are dominated by the relaxation of temperature and velocity differences between the constituent gases. These relaxations



**Figure 8.3** – Comparing scattered light spectra of mixtures to the mixture model of [94]. (a) Equimolar mixture He p = 1 bar, Ar p = 1 bar, (a) equimolar mixture He p = 2 bar, Ar p = 2 bar, (c) asymmetric mixture He p = 1 bar, Ar p = 3 bar, (d) asymmetric mixture He p = 3 bar, Ar p = 1 bar, (a) equimolar mixture He p = 1.3 bar, Kr p = 1.3 bar, (a) equimolar mixture He p = 2 bar, Kr p = 2 bar. The lower line is the difference between experiment and model. Apart from the normalization of the spectra there are no adjustable parameters.

appear to be captured adequately in the six fields of the mixture model of [94]. This is the first time that these predictions are tested in the kinetic regime. The model ontains no adjustable parameters, and reproduces the experiments excellently, except in one case where the heavy atoms are a majority.

For the pure gas, the inter-species relaxation processes are no longer relevant and the three remaining fields no longer suffice and must be augmented by their gradients. As Fig. 8.2 illustrates, a minimum of 13 modes is necessary for a correct reproduction of the light scattering spectra.

Finally, we have studied the scattered light spectrum of a mixture of  $CO_2$  and He. Also here, the helium has a large influence on the spectrum. However,



**Figure 8.4** – The influence of He addition to CO<sub>2</sub>. (a) CO<sub>2</sub> gas at 1.5 bar. Also shown is the Tenti S7 model with bulk viscosity.  $\eta_b = 6.8 \times 10^{-6} \text{ kg m}^{-1} \text{s}^{-1}$ . The lower line is the difference between experiment and model. The gray lines indicate the frequency of sound,  $v_s k/2\pi$ , with the velocity of sound  $v_s = (7/5k_BT/M)^{1/2}$ , T the temperature and M the molecular mass. (b) Equimolar mixture of CO<sub>2</sub> 1.5 bar and He 1.5 bar. A large influence of the addition of He is observed. As there is no theory available, only the measurement is shown.

a model for such a mixture, where now one constituent has internal degrees of freedom, is still a far cry.

### Appendix A

## Derivation of S7 and S6 models

It is convenient to use Dirac notations to convert Eq. (1.8) to

$$\left(\frac{\partial}{\partial t} + \boldsymbol{v} \cdot \nabla\right) |h\rangle = n_0 \boldsymbol{J} |h\rangle, \qquad (A.1)$$

with

$$|h\rangle = \begin{pmatrix} h_1 \\ h_2 \\ \vdots \\ h_n \end{pmatrix} \quad \text{and} \quad \langle h| = (h_1^*, h_2^*, \dots, h_n^*) \quad (A.2)$$

J' is the collision operator that consists of the elastic one J' and the inelastic one J''. The eigenvectors and eigenvalues for the elastic collision operator J' have been studied by Wang-Chang and Uhlenbeck [17]:

$$\boldsymbol{J'} |\Psi_{s0}\rangle = (2k/m)^{1/2} \lambda_s |\Psi_{s0}\rangle, \quad \boldsymbol{J'} |\Psi_{sn}\rangle = (2k/m)^{1/2} \mu_s |\Psi_{sn}\rangle, \quad (A.3)$$

where  $\lambda_s$  and  $\mu_s$  are the eigenvalues (in the following part  $J_{rlmn}$  will be used for the eigenvalues), and  $\Psi_{sn}$  is the eigenfunction, which has the form:

$$|\Psi_{sn}\rangle = \begin{pmatrix} \Phi_{rlm}P_n(\varepsilon_1) \\ \Phi_{rlm}P_n(\varepsilon_2) \\ \vdots \end{pmatrix}$$
(A.4)

Here,  $\varepsilon_i = E_i/(k_B T_0)$  is the dimensionless energy, and  $P_n(\varepsilon_i)$  is a polynomial of the internal energy, which is given by

$$P_{0}(\varepsilon_{i}) = 1, \qquad P_{1}(\varepsilon_{i}) = \frac{\varepsilon_{i} - \langle \varepsilon \rangle}{\sqrt{\langle (\varepsilon - \langle \varepsilon \rangle)^{2} \rangle}}$$

$$P_{n}(\varepsilon_{i}) = K_{n} \left[ \varepsilon_{i} P_{n-1}(\varepsilon_{i}) - \sum_{m=0}^{n-1} \langle \varepsilon P_{n-1} P_{m} \rangle P_{n}(\varepsilon_{i}) \right], \qquad (A.5)$$

with  $K_n$  chosen to normalize  $\langle P_n^2 \rangle = 1$ .  $\Phi_{rlm}$  is the eigenfunction of the collision operator for an atomic gas, which can be further expressed as:

$$\Phi_{rlm} = \sqrt{\frac{2\pi^{3/2}r!}{(r+l+1/2)!}} S_{l+1/2}^{(r)}(c^2) c^l Y_{lm}(\hat{c}), \qquad (A.6)$$

where  $S_n^{(m)}(x)$  is the Sonine polynomial (Associated Laguerre Polynomial),  $\boldsymbol{c} = \boldsymbol{v}/v_0$  the dimensionless velocity (note that c is used as the dimensionless velocity only in this chapter), and  $Y_{lm}(\theta, \phi)$  the spherical harmonics for the direction angles  $\theta$ ,  $\phi$  of the dimensionless velocity  $\boldsymbol{c}$ . According to Eq. (A.4), scan be expressed as rlm.

Thus, we can diagonalize the elastic collision operator using the eigenvalues and eigenvectors. Following the method of Gross and Jackson [19], all of the eigenvalues except for a particular set are set equal to a common constant (degenerated), namely:

$$\mathbf{J'} |h\rangle = \sum_{r} J'_{r} |\Psi_{r}\rangle \langle \Psi_{r}|h\rangle 
\approx \sum_{r < R} J'_{r} |\Psi_{r}\rangle \langle \Psi_{r}|h\rangle + J'_{R} \sum_{r \ge R} |\Psi_{r}\rangle \langle \Psi_{r}|h\rangle 
= \sum_{r < R} (J'_{r} - J'_{R}) |\Psi_{r}\rangle \langle \Psi_{r}|h\rangle + J'_{R} |h\rangle$$
(A.7)

 $J'_{rlmn}$  denotes the eigenvalues of J':

$$J'_{rlmn} = \langle \Psi_{rlmn} | \mathbf{J'} | \Psi_{rlmn} \rangle, \qquad (A.8)$$

and

$$J'_{rln} = \frac{1}{2l+1} \sum_{m} J'_{rlmn}.$$
 (A.9)

Boley et al. [7] selected 7 non-degenerate eigenvectors for the elastic collision operator:  $\Psi_{0000}$  the fraction of particles in different internal states,  $\Psi_{01m0}$ the momentum,  $\Psi_{1000}$  the translational energy,  $\Psi_{11m0}$  the translational heat flux,  $\Psi_{0001}$  the internal energy,  $\Psi_{01m,1}$  the internal heat flux, and  $\Psi_{02m,0}$  the traceless pressure tensor. The corresponding eigenvalues are  $J'_{000}$ ,  $J'_{010}$ ,  $J'_{100}$ ,  $J'_{110}$ ,  $J'_{001}$ , and  $J'_{011}$ . For the other eigenvectors we assume they have the same eigenvalue  $J'_{030}$ . Hence, the resulting elastic collision model is

$$(J'h)_{i} = -J'_{030} \left[ \nu_{i} + 2\mathbf{c} \cdot \mathbf{u} + \left(c^{2} - \frac{3}{2}\tau_{tr}\right) \right] + \left(-J'_{030} + J'_{110}\right) \frac{4}{5}\mathbf{c} \left(c^{2} - \frac{5}{2}\right) \cdot \mathbf{q}_{tr} + \left(-J'_{030} + J'_{011}\right) \frac{\varepsilon_{i} - \langle \varepsilon \rangle}{c_{int}} 2\mathbf{c} \cdot \mathbf{q}_{int} + \left(-J'_{030} + J'_{020}\right) \left(c_{\alpha}c_{\beta} - \frac{1}{3}\delta_{\alpha\beta}c^{2}\right) \pi_{\alpha\beta} + J'_{030}h_{i}$$
(A.10)

Similarly, according to the theory by Hanson and Morse [18], Boley *et al.* [7] wrote the seven moment inelastic collision model as:

$$\begin{split} (J''h)_{i} &= -J''_{030} \left[ \nu + 2\mathbf{c} \cdot \mathbf{u} + \left( c^{2} - \frac{3}{2} + \varepsilon_{i} - \langle \varepsilon \rangle \right) \tau \right] \\ &+ \left( J''_{100} - \frac{c_{int}}{3/2 + c_{int}} J''_{030} \right) \left[ c^{2} - \frac{3}{2} - \frac{3}{2c_{int}} \left( \varepsilon_{i} - \langle \varepsilon \rangle \right) \right] \left( \tau_{tr} - \tau_{int} \right) \\ &+ \left( -J''_{030} + J''_{011} \right) \frac{\varepsilon_{i} - \langle \varepsilon \rangle}{c_{int}} 2\mathbf{c} \cdot \mathbf{q}_{int} \\ &- J''_{011} \frac{2\sqrt{2}}{\sqrt{5c_{int}}} \left[ \left( \varepsilon_{i} - \langle \varepsilon \rangle \right) \mathbf{c} \cdot \mathbf{q}_{tr} + \mathbf{c} \left( c^{2} - \frac{5}{2} \right) \cdot \mathbf{q}_{int} \right] \\ &+ \left( J''_{110} - J''_{030} \right) \frac{4}{5} \mathbf{c} \left( c^{2} - \frac{5}{2} \right) \cdot \mathbf{q}_{tr} \\ &+ \left( J''_{020} - J''_{030} \right) \left( c_{\alpha} c_{\beta} - \frac{1}{3} \delta_{\alpha\beta} c^{2} \right) \pi_{\alpha\beta} + J''_{030} h_{i}, \end{split}$$
(A.11)

where

$$J_{r'l'n'}^{\prime\prime rln} = \frac{1}{2l+1} \sum_{m} \langle \Psi_{rlmn} | J'' | \Psi_{r'l'mn'} \rangle.$$
 (A.12)

Therefore, the entire collision model is  $(J^{(7)}|h\rangle)_i = (J'h)_i + (J''h)_i$ , which is referred to as the S7 model. Since the number of non-degenerate eigenvectors for elastic and inelastic collision operators is 7, the model is regarded as S7 model.

As a result, the linearized WCU equation (A.1) is written as:

$$\left(\frac{\partial}{\partial t} + \boldsymbol{v} \cdot \nabla\right) |h\rangle = n_0 \boldsymbol{J}^{(7)} |h\rangle, \qquad (A.13)$$

Applying a Fourier transform to Eq. (A.13), followed by taking the inner product of the transformed equation and each of the 7 eigenvectors, a set of seven linear equations is obtained, which can be written in the form of AX = B:

$$\boldsymbol{A} = \begin{bmatrix} -J_{030} I_{00}^{00} - \frac{kv_0}{in_0} & -J_{030} I_{01}^{00} & (J_{030} - J_{110}) I_{10}^{00} & (J_{020} - J_{030}) I_{20}^{00} \\ -J_{030} I_{01}^{00} & -J_{030} I_{01}^{01} - \frac{kv_0}{in_0} & (J_{030} - J_{110}) I_{11}^{01} & (J_{020} - J_{030}) I_{02}^{01} \\ -J_{030} I_{00}^{01} & -J_{030} I_{01}^{01} & (J_{030} - J_{110}) I_{11}^{11} + \frac{kv_0}{in_0} & (J_{020} - J_{030}) I_{02}^{01} \\ -J_{030} I_{00}^{02} & -J_{030} I_{01}^{02} & (J_{030} - J_{110}) I_{11}^{11} + \frac{kv_0}{in_0} & (J_{020} - J_{030}) I_{02}^{02} - \frac{3kv_0}{i2n_0} \\ -J_{030} I_{00}^{00} & -J_{030} I_{01}^{00} & (J_{030} - J_{110}) I_{11}^{10} & (J_{020} - J_{030}) I_{02}^{02} - \frac{3kv_0}{i2n_0} \\ 0 & 0 & -J_{011}^{011} I_{01}^{00} & 0 \\ 0 & 0 & -J_{011}^{011} I_{01}^{00} & 0 \\ (J_{030} - J_{100}) I_{10}^{00} & J_{000}^{001} I_{00}^{00} & J_{011}^{011} I_{11}^{01} \\ (J_{030} - J_{100}) I_{10}^{10} & J_{100}^{001} I_{10}^{01} & J_{110}^{110} I_{11}^{11} \\ (J_{030} - J_{100}) I_{10}^{10} & J_{100}^{001} I_{10}^{10} & J_{011}^{110} I_{11}^{11} \\ (J_{030} - J_{100}) I_{10}^{10} & J_{100}^{001} I_{10}^{10} & J_{011}^{110} I_{11}^{11} \\ (J_{030} - J_{100}) I_{10}^{10} & J_{100}^{001} I_{10}^{10} & J_{011}^{110} I_{11}^{11} \\ (J_{030} - J_{100}) I_{10}^{10} & J_{100}^{001} I_{10}^{10} & J_{011}^{110} I_{11}^{11} \\ (J_{030} - J_{100}) I_{10}^{10} & J_{100}^{001} I_{10}^{10} & J_{011}^{110} I_{11}^{11} \\ (J_{030} - J_{100}) I_{10}^{10} & J_{100}^{001} I_{10}^{10} & J_{011}^{110} I_{11}^{11} \\ (J_{030} - J_{100}) I_{10}^{10} & J_{100}^{001} I_{10}^{10} & J_{011}^{110} I_{11}^{11} \\ -J_{000}^{001} I_{00}^{00} & (J_{001} - J_{030}) I_{00}^{00} - \frac{kv_0}{in_0} & (J_{011} - J_{030}) I_{00}^{00} \\ J_{100}^{011} I_{00}^{11} & (J_{001} - J_{030}) I_{00}^{00} & (J_{001} - J_{030}) I_{01}^{01} - \frac{kv_0}{in_0} \end{bmatrix} \right]$$

$$\boldsymbol{X} = \begin{bmatrix} \nu(\boldsymbol{k}, \omega) \\ \sqrt{2}u_{z}(\boldsymbol{k}, \omega) \\ (2/\sqrt{5})q_{tr,z}(\boldsymbol{k}, \omega) \\ (1/\sqrt{3})\pi_{zz}(\boldsymbol{k}, \omega) \\ \sqrt{3/2}\tau_{tr}(\boldsymbol{k}, \omega) \\ \sqrt{2/c_{int}}\tau_{int}(\boldsymbol{k}, \omega) \\ \sqrt{2/c_{int}}q_{int,z}(\boldsymbol{k}, \omega) \end{bmatrix} \quad \text{and} \quad \boldsymbol{B} = -\frac{1}{k^{2}v_{0}} \begin{bmatrix} I_{00}^{00} \\ I_{00}^{01} \\ I_{00}^{01} \\ I_{00}^{00} \\ I_{00}^{00} \\ 0 \\ 0 \end{bmatrix} \quad (A.14)$$

where z is the direction of the acoustic wave and

$$I_{r'l'}^{rl} = \langle \Psi_{rlm,n} | \frac{1}{\omega/(kv_0) - i \cdot n_0 J_{030}/(kv_0) - c_z} | \Psi_{r'l'm,n} \rangle$$
(A.15)

Applying a Chapman-Enskog analysis [18], the matrix elements of J in Matrix A can be expressed in terms of the transport coefficients, i.e. the shear viscosity  $\eta$ , the bulk viscosity  $\eta_b$ , and the thermal conductivity  $\kappa$ :

$$\eta = -\frac{k_B T}{J_{020}}, \quad \eta_b = -\frac{2}{3} \left(\frac{c_{int}}{\frac{3}{2} + c_{int}}\right)^2 \frac{k_B T}{J_{100}},$$

$$\kappa = -\frac{k_B^2 T}{m} \frac{\frac{5}{2} J_{011} + c_{int} J_{110} + (10c_{int})^{1/2} J_{011}^{110}}{J_{011} J_{110} - (J_{011}^{110})}$$
(A.16)

Together with the identities:

$$J_{110} = -\frac{2k_BT}{3\eta} - \frac{5\gamma_{int}^2 k_BT}{9\eta_b}, \quad J_{011}^{110} = -\frac{\sqrt{5/8c_{int}}\gamma_{int}^2 k_BT}{\eta_b},$$

$$J_{011} = -\frac{2\gamma_{int} k_BT}{3(3/2 + c_{int})\eta_b}$$

$$\cdot \frac{2\eta_b/(5\eta)(3/2 + c_{int})^2 + c_{int}(1 + c_{int}/3) + \gamma_{int}^2 m\kappa/(6k_B\eta_b)}{-1 + 4m\kappa/(15k_B\eta) + 2\gamma_{int}^2 m\kappa/(9k_B\eta_b)},$$

$$J_{100} = \sqrt{\frac{2c_{int}}{3}} J_{100}^{001} = \sqrt{\frac{2c_{int}}{3}} J_{001}^{100} = \frac{2c_{int}}{3} J_{001},$$
(A.17)

all the elements of J in Eq. (A.14) can be expressed in terms of these three transport coefficients, the atomic mass m of the particles, the internal specific heat capacity per molecule  $c_{int}$ , and  $\gamma_{int} = c_{int}/(3/2 + c_{int})$ .

Now the only work is to establish the connection between the densitydensity correlation function  $G(\mathbf{r}, t)$ , and the solutions of the model in Eq. (A.14). By definition,  $G(\mathbf{r}, t)$  describes the correlation between the presence of a particle in position  $\mathbf{r'} + \mathbf{r}$  at time t' + t and the presence of a particle in position  $\mathbf{r'}$  at time t'. Setting a particle initially at the origin, i.e. r' = 0 at t' = 0,  $G(\mathbf{r}, t)$  describes the space-time evolution of density correlations in the system. Since it is clear that a microscopic density disturbance arises as a result of the localization of a particle, while the correlation function describes the location of a particle given that the other particle is found at r' = 0 when t' = 0. Boley *et al.* [7] identified  $G(\mathbf{r}, t)$  to the deviation of the total number density:  $G(\mathbf{r}, t) = n_0\nu(\mathbf{r}, t)$ , where  $n_0\nu(\mathbf{r}, t)$  was defined in Eq. (1.9).

Therefore, the RB scattering profile, which is proportional to  $S(\mathbf{k}, \omega)$ , the time-space Fourier-transform of the density-density correlation function  $G(\mathbf{r}, t)$ , can be written as:

$$I(\boldsymbol{k},\omega) \propto S(\boldsymbol{k},\omega) = n_0 \nu(\boldsymbol{k},\omega), \qquad (A.18)$$

where  $\nu(\mathbf{k}, \omega)$  is a solution of Eq. (A.14).

The difference between the S6 and S7 models is that the S6 model treats  $\Psi_{02,0}$ , the eigenvector related to the traceless pressure tensor, degenerated. Therefore, the matrix equation for the S6 model is very similer to the one for the S7 model, i.e. Eq. (A.14): only the fourth row and the fourth column of matrix A and the fourth element of X and B are deleted. Also, the common degenerated eigenvalue for the S6 model is  $J_{020}$  instead of  $J_{030}$ . A complete matrix equation for the S6 model is, therefore, written as:

$$\boldsymbol{A} = \begin{bmatrix} -J_{020}I_{00}^{00} - \frac{kv_0}{in_0} & -J_{020}I_{01}^{01} & (J_{020} - J_{110})I_{11}^{01} \\ -J_{020}I_{00}^{01} & -J_{020}I_{01}^{01} - \frac{kv_0}{in_0} & (J_{020} - J_{110})I_{11}^{01} \\ -J_{020}I_{00}^{10} & -J_{020}I_{01}^{11} & (J_{020} - J_{110})I_{11}^{11} + \frac{kv_0}{in_0} \\ -J_{020}I_{00}^{10} & -J_{020}I_{01}^{10} & (J_{020} - J_{110})I_{11}^{10} \\ 0 & 0 & -J_{011}^{110}I_{01}^{01} \\ 0 & 0 & -J_{011}^{110}I_{01}^{01} \\ (J_{020} - J_{100})I_{10}^{00} & J_{100}^{001}I_{10}^{00} & J_{011}^{110}I_{11}^{10} \\ (J_{020} - J_{100})I_{10}^{10} & J_{001}^{001}I_{10}^{10} & J_{011}^{110}I_{11}^{11} \\ (J_{020} - J_{100})I_{10}^{10} & J_{100}^{001}I_{10}^{10} & J_{011}^{110}I_{11}^{11} \\ (J_{020} - J_{100})I_{10}^{10} & J_{100}^{001}I_{10}^{10} & J_{011}^{110}I_{11}^{11} \\ (J_{020} - J_{100})I_{10}^{10} & +\frac{kv_0}{in_0} & J_{000}^{001}I_{10}^{10} & J_{011}^{110}I_{11}^{11} \\ (J_{020} - J_{100})I_{10}^{10} & (J_{001} - J_{020})I_{00}^{00} - \frac{kv_0}{in_0} & (J_{011} - J_{020})I_{01}^{00} \\ -J_{100}^{001}I_{00} & (J_{001} - J_{020})I_{00}^{00} - \frac{kv_0}{in_0} & (J_{011} - J_{020})I_{01}^{00} \\ -J_{100}^{001}I_{00}^{00} & (J_{001} - J_{020})I_{00}^{00} & (J_{011} - J_{020})I_{01}^{00} - \frac{kv_0}{in_0} \end{bmatrix}$$

$$\boldsymbol{X} = \begin{bmatrix} \boldsymbol{\nu} \\ \sqrt{2}u_z \\ \sqrt{3/2}\tau_t \\ \sqrt{3/2}\tau_t \\ \sqrt{3/2}\tau_tr \\ \sqrt{2/c_{int}}q_{int,z} \end{bmatrix} \quad \text{and} \quad \boldsymbol{B} = -\frac{1}{k^2v_0} \begin{bmatrix} I_{00}^{00} \\ I_{00}^{10} \\ I_{00}^{10} \\ I_{00}^{10} \\ I_{00}^{10} \\ I_{00}^{10} \end{bmatrix}$$

$$(A.19)$$

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## List of publications

This thesis is based on the following publications:

### Chapter 2:

A Rayleigh-Brillouin scattering spectrometer for ultraviolet wavelengths Z. Y. Gu, M. O. Vieitez, E.-J. van Duijn, and W. Ubachs Rev. Sci. Instrum. **83**, 053112 (2012).

### Chapter 3:

Temperature-dependent bulk viscosity of nitrogen gas determined from Rayleigh-Brillouin scattering Z. Y. Gu, and W. Ubachs Opt. Lett. **38**, 1110-1112 (2013).

### Chapter 4:

Rayleigh-Brillouin scattering profiles of air at different temperatures and pressuresZ. Y. Gu, B. Witschas, W. van de Water, and W. UbachsAppl. Opt. 52, 4640-4651 (2013).

### Chapter 5:

Rayleigh-Brillouin scattering of carbon dioxide Z. Y. Gu, W. Ubachs, and W. van de Water Opt. Lett. **39**, 3301-3304 (2014).

#### Chapter 6:

A systematic study of Rayleigh-Brillouin scattering in air, N<sub>2</sub> and O<sub>2</sub> gases Z. Y. Gu, and W. Ubachs J. Chem. Phys. **141**, 104320 (2014).

### Chapter 7:

Temperature retrieval from Rayleigh-Brillouin scattering profiles measured in air gases

B. Witschas, Z. Y. Gu, and W. Ubachs

accepted.

### Chapter 8:

Rayleigh-Brillouin scattering in binary gas mixtures Z. Y. Gu, W. Ubachs, W. Marques Jr, and W. van de Water in preparation. A.0

Publications that have not been reproduced in this thesis:

- Analysis of Rayleigh-Brillouin spectral profiles and Brillouin shifts in nitrogen gas and air
  Y. Ma, H. Li, Z. Y. Gu, W. Ubachs, Y. Yu, J. Huang, B. Zhou, Y. Wang, and K. Liang
  Opt. Express 22, 2092-2104 (2014).
- Further validation and refinement of the Tenti model for atmospheric lidar backscatter
  Z. Y. Gu, and W. Ubachs
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- Rotational diffusion and alignment of short gold nanorods in an external electric field
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## Summary

A major problem to achieve the accuracy of Rayleigh-Brillouin scattering experiments in gases, required by European Space Agency's satellite-based lidar mission (ADM-Aeolus), is that the RB scattering cross-section is very low: for 1 bar air and 532 nm light it is as small as  $10^{-27}$  cm<sup>2</sup>. In order to overcome this challenge, as detailed in Chapter 2, two methods have been used: 1, amplifying the effective power of incident light by placing the scattering samples inside an enhancement cavity; 2, stabilizing the entire setup in terms of temperatureand frequency-drift and recording the scattered photons for hours. In such a setup scattering line shapes could be measured at better than ever-achieved signal-to-noise ratios. This allows for an accurate test of the Tenti S6 model, which is considered to provide the best description of the Rayleigh-Brillouin scattering line shape. It had so far only been verified for a few cases. In the present study this Tenti S6 model has been tested in a wide parameter space and for a number of atmospheric gases. Chapter 3, 4, and 5 of this thesis show 366 nm measurements in N<sub>2</sub>, air, and CO<sub>2</sub>, respectively. The bulk viscosity, a macroscopic gas transport coefficient describing the energy exchange between the translational and internal motions of molecules is not well known at frequencies related to light scattering experiments. It has been intensively studied and its temperature- and pressure-dependency have been determined.

With optimized values of the bulk viscosity the Tenti S6 model is accurate to the 2% level for N<sub>2</sub> and air (diatomic gases) under the specific measurement conditions, providing evidence that the Tenti S6 model is a good representation of scattering profiles for conditions of lidar experiments on realistic atmospheres. For CO<sub>2</sub> (polyatomic gas), the Tenti S6 model works well at low pressures, while at high pressures a relatively large discrepancy between the model and the measurements has been observed, suggesting that the Tenti S6 model may need to be improved for polyatomic gases.

After the initial verification of the Tenti S6 model by series of measurements at 366 nm we have investigated the wavelength dependence of the main model for RB-scattering. We have chosen a second wavelength at 403 nm, where the combination of Ti:Sa laser and second harmonic generation cavity delivers the highest output power. As detailed in Chapter 6, a new experimental setup has been established and RB scattering measurements in air, N<sub>2</sub> and O<sub>2</sub> at 403 nm have been performed and compared with the Tenti S6 calculations. The same

level of difference (2%) between the model predictions and the experiments at 403 nm as that at 366 nm demonstrates that the Tenti S6 model is valid for a wide range of wavelengths. Also, values of the bulk viscosity derived from these measurements have been proven to be identical (with combined error margins) to the ones obtained from the measurements at 366 nm, indicating that the bulk viscosity is insensitive to the small change of hypersound frequency associated with the  $\sim 40$  nm variation in scattering wavelength.

With accurate knowledge of scattering profiles, not only the velocity profile, but also the temperature of the atmosphere can be measured by lidar techniques. It has been demonstrated in Chapter 7 that by comparing the measured RB scattering profiles of air to the Tenti S6 calculations, temperatures can be determined with less than 2 K discrepancies in a range of atmospheric conditions.

Finally, we have extended our RB scattering experiment to binary gas mixtures with significantly different masses and/or molecular structures, and have shown inapplicability of the Tenti S6 model in predicting their scattering profiles. In the last chapter of this thesis, results of RB scattering have been compared to a kinetic model recently developed explicitly for binary gas mixtures. In this preliminary study, good agreement is found between measurements and calculations.

## Samenvatting

## Spontane Rayleigh-Brillouinverstrooiing in de aardse atmosfeer

Dit proefschrift beschrift Rayleigh-Brillouin (RB) verstrooiingsmetingen, die verricht zijn, in opdracht van de Europese ruimtevaartorganisatie ESA in verband met de ADM-Aeolus missie. Een centraal probleem bij het bereiken van grote nauwkeurigheid bij de bepaling van spectrale verstrooiingsprofielen is de geringe waarde van de werkzame doorsnede voor RB-verstrooiing: voor een druk van 1 atmosfeer, bij een golflengte van 532 nm meet die  $10^{-27}$  cm<sup>2</sup>. Om toch nauwkeurige profielen te meten, als beschreven in hoofdstuk 2, zijn twee technieken toegepast: 1, versterking van de effectieve lichtintensiteit door de gascel in een optische trilholte te plaatsen; 2, de meetopstelling is zodanig gestabiliseerd voor temperatuur- en frequentie-drift dat data collectie over perioden van meerdere uren mogelijk was. In een dergelijke meetopstelling werden verstrooiingslijnvormen gemeten met een betere signaal-ruisverhouding dan tot nu toe gerealiseerd. Dit maakt het mogelijk om nauwkeurige testen uit te voeren op het zogenaamde Tenti S6 model, dat beschouwd wordt als de beste beschrijving van de Rayleigh-Brillouin lijnvorm. Dit model werd tot dusver slechts in een klein aantal gevallen geverifieerd. In de voorliggende studie is het Tenti S6 model getest voor een aantal atmosferische gassen in verschillende meetcondities. Hoofdstukken 3, 4, en 5 van dit proefschrift beschrijven metingen bij een golflengte van 366 nm voor  $N_2$ , lucht en  $CO_2$  gas.

De 'bulk viscositeit' is een gas transport coefficiënt, die de energie uitwisseling representeert tussen de translationele en interne bewegingsvrijheidsgraden in moleculen. De waarde van deze grootheid is niet goed bekend voor frequenties die van belang zijn in lichtverstrooiingsexperimenten. In deze studie is het effect van bulk viscositeit intensief bestudeerd en zijn waarden afgeleid bij verschillende temperaturen en drukken van het gas. Met de gemeten waarden voor de bulk viscositeit is de beschrijving met het Tenti S6 model nu nauwkerig op het 2% niveau voor N<sub>2</sub> en lucht, dus voor gassen bestaand uit twee-atomige moleculen. Dit bewijst dat het Tenti S6 model een goede beschrijving levert voor verstrooiingslijnvormen, die ook vigeren in lidarexperimenten aan realistische atmosferen. Voor CO<sub>2</sub> (een polyatomair gas), werkt het Tenti S6 model goed bij lage drukken, terwijl voor hoge drukken een aanmerkelijk verschil tussen metingen en model blijft bestaan. Dit suggereert dat het Tenti S6 model nog verbetering behoeft voor poly-atomaire gassen. Na een eerste verificatie van het Tenti S6 model voor metingen bij 366 nm hebben we de golflengte-afhankelijkheid bestudeerd bij de beschrijving van RB-lijnvormen. We hebben daartoe een tweede golflengte gekozen bij 403 nm, waar de combinatie van titaan-saffierlaser en het frequentieverdubbelingssysteem het hoogste uitgangsvermogen levert. Als beschreven in hoofdstuk 6, is een nieuwe experimentele opstelling gebouwd om RB-verstrooiingsmetingen te verrichten in lucht, N<sub>2</sub> en O<sub>2</sub> gas bij 403 nm. Resultaten van deze metingen zijn weer vergeleken met berekingen volgens het Tenti S6 model. Eenzelfde overeenstemming, op het 2 % niveau, is weer bereikt. Van belang daarbij is dat de waarden voor de bulk viscositeit, afgeleid uit beide data sets voor 366 en 403 nm, dezelfde zijn binnen de foutenmarges. Hieruit mag geconcludeerd worden, dat het model toepasbaar is voor een breed golflengtebereik.

Op basis van de nauwkeurige kennis van verstrooiingslijnvormen kan zowel het snelheidsprofiel als de temperatuur van een atmosfeer bepaald worden, via lidartechnieken. In hoofdstuk 7 is aangetoond dat vergelijkingen van RB lijnvormen met Tenti S6 modelberekeningen voor lucht, de atmosferische temperatuur bepaald kan worden binnen 2 °C voor verschillende hoogtelagen in de atmosfeer.

Tot slot hebben we een begin gemaakt met metingen aan binaire gasmengsels, bestaand uit atomen/moleculen met uiteenlopende massa. Voor deze condities blijkt dat het Tenti S6 model tekort schiet bij de beschrijving van de verstrooiingslijnvorm. In het laatste hoofdstuk van dit proefschrift zijn de resultaten van RB verstrooiingsmetingen vergeleken met een kinetisch model, dat recentelijk werd ontwikkeld specifiek voor binaire gasmengsels. Onze resultaten blijken goed over te komen met dit alternatieve model.