## VRIJE UNIVERSITEIT AMSTERDAM

## Spontaneous Rayleigh-Brillouin Scattering in Molecular Gases

## ACADEMISCH PROEFSCHRIFT

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## Chapter I

## Introduction

## 1.1 Prologue

The fascinating question why the sky is blue had puzzled many people for a very long time until Lord Rayleigh (John William Strutt) came up with an explanation based on Maxwell's theory of electromagnetism [1, 2]. He stated that particles in air with sizes much smaller than the wavelength of visible light scatter blue light more efficiently than at longer wavelengths. This marked the birth of the scientific study of light scattering. Subsequently, Einstein related the scattered light to the refractive index fluctuations in the scattering media 3 and found that the scattering intensity is proportional to the square of the fluctuation amplitude of the dielectric constant. In particular, if the scattering medium is a gas, the determining factor for the refractive index change is the gas density variation, which is the main focus for study of the Rayleigh scattering profile and their calculation. The modulation of scattered light caused by adiabatic fluctuations was later investigated by Mandel'shtam in 1918, although the corresponding publication appeared only in 1926 [4], and in 1922 Brillouin had independently found and published part of the results [5]. This resulted in the finding of a fine structure in the Rayleigh scattering profile, which was later referred to as Brillouin scattering, although in the Russian literature it is often referred to as Mandel'shtam scattering. The research of Rayleigh-Brillouin (RB) scattering has drawn more and more attention since then [6-9].

After the invention of the laser in 1960 the study of Rayleigh scattering was revived, and several detailed studies were performed that had not been possible with classical light sources. Such as:

• Precise study of Rayleigh cross sections. The intensity and polarization

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of the RB-scattering light as well as the refractive index of the medium are directly related to Rayleigh cross section [10-13].

- Investigation of RB-scattering spectral profiles. Through calculating the RB-profile and comparing with the experimental data the interaction between molecules as well as the interaction between molecules and light can be understood. [14–20].
- Application of RB-scattering in lidar (light detection and ranging) and remote sensing for Earth observation. Molecular motion is related to the properties of gases such as bulk viscosity, thermal conductivity, temperature, pressure. These properties can be extracted from the RB-scattering profile based on some models. Therefore the RB-scattering can be used for real application such as weather forecasts, climate studies and oceanography based on lidar remote sensing [21–23].

The goal of this thesis is to measure the RB-scattering spectral lineshapes of different molecular gases like  $SF_6$ ,  $N_2O$ ,  $CO_2$  at different conditions (pressure, temperature, scattering angle), and compare those to different RB-scattering models in order to obtain the intrinsic relation between the properties of the gas and the profiles. In addition, the RB-spectra of binary mixture gases are measured to study the interaction between molecules. Furthermore, the transport coefficients derived from RB-scattering experiments can be used for future application like lidar remote sensing. In the remainder of this chapter, the basic theories in this field will be introduced briefly to lay a basis for the rest of the thesis, comprising the theory of Rayleigh-Brillouin scattering in subsection 1.2, Rayleigh-Brillouin lineshape in subsection 1.4. This chapter will end with an outline of this thesis.

## 1.2 Theory of Rayleigh-Brillouin scattering

Although we are primarily interested in Rayleigh-Brillouin scattering, it is necessary to appreciate the competing molecular scattering processes. In the early 1980s, Young [24] gave a review about the history of discoveries concerning molecular light scattering and suggested the terminology sketched in Fig. 1.1. According to Young, Rayleigh scattering not only covers elastic light scattering, as it is often mentioned in literatures, but it also contains the inelastic rotational Raman scattering and the Cabannes line, which is commonly regarded as the result of Rayleigh-Brillouin scattering [25].

Rayleigh-Brillouin scattering can be understood on the basis of the electromagnetic (EM) interaction between light and matter [2]. When an

## 1.2. Theory of Rayleigh-Brillouin scattering



Figure 1.1: Overview of different scattering mechanisms in molecular gases suggested by Young [24].

incident wave passes through an atom or a molecule, the electrons inside the atom or molecule will be influenced by the electric field of the wave [26]. The negative charge tends to be pushed to the side of the molecule which orients towards the opposite direction of the electric field direction, while the positive charge migrates to the other side, thus inducing a dipole moment in the atom or molecule [27], as shown in Fig. 1.2. For spherical particles with radius much smaller than the incident light wavelength  $\lambda_i$ , the light field  $E_i$  inside the particle can be considered to be homogeneous and the induced electric moment can be expressed as  $P = \alpha E_i$ , in which  $\alpha$  is the dynamic polarizability of the molecule which is frequency dependent. The dipole moment will oscillate as the incident electric field changes and radiates light like a Hertzian dipole [28]. The amplitude and intensity of the scattered field are [12]:

$$|\mathbf{E}_{\mathbf{s}}(r,\varphi)| = \frac{\omega^2 P \sin\varphi}{4\pi \ \epsilon_0 \ r \ c^2} \tag{1.1}$$

and

$$I_{\rm s}(r,\varphi) = \frac{\epsilon_0 \ c \ \left| \boldsymbol{E}_{\rm s}(r,\varphi) \right|^2}{2} \tag{1.2}$$

where  $\omega$  is the oscillation frequency, P is the amplitude value of the dipole with  $P^2 = \alpha^2 |\mathbf{E}_i|^2 = \alpha^2 2I_i/c \epsilon_0$  and  $I_i$  is the intensity of the incident light. The parameter  $\varphi$  is the angle between the axis of the dipole and the direction of observation, r is the distance from the radiating dipole to the point of observation,  $\epsilon_0$  is the permittivity of vacuum and c is the light speed in vacuum. This is the source of RB-scattered light. The total power of the scattered light  $I_{\rm sc}$  from a single atom or molecule can be obtained by integrating Eq. (1.2)



Figure 1.2: Scattered light from the induced dipole of molecule due to the incident wave.

over the surface of a sphere of radius r:

$$I_{\rm sc} = \int_0^{\pi} I_{\rm sc}(r,t) \, 2\pi \, r^2 \, \sin\varphi \, d\varphi = \frac{\omega^4}{6 \, \pi \, c^2 \, \epsilon_0^2} \, \alpha^2 \, I_{\rm i} \tag{1.3}$$

The polarizability can be related to the index of refraction n by the Lorentz-Lorenz equation [29]:

$$\alpha = \frac{3\epsilon_0}{N} \left(\frac{n^2 - 1}{n^2 + 1}\right) \tag{1.4}$$

where N is the number density of the gas. Then the scattering cross section  $\sigma_{\rm ss} = I_{\rm sc}/I_{\rm i}$  can be written as:

$$\sigma_{\rm ss} = \frac{3}{2\pi} \frac{\omega^4}{c^4} \frac{1}{N^2} \left(\frac{n^2 - 1}{n^2 + 1}\right)^2 = \frac{24\pi^3}{\lambda_{\rm i}^4 N^2} \left(\frac{n^2 - 1}{n^2 + 1}\right)^2 \tag{1.5}$$

Eq. (1.5) is the scattering cross section for a spherically symmetric scatterer. As the molecular polarizability depends on the orientation of the molecule, for non-spherical molecules the Rayleigh cross section  $\sigma$  can be corrected by adding a correction King factor  $F_{\rm k}$  [12, 30]:

$$\sigma = \sigma_{\rm ss} \ F_{\rm k} \tag{1.6}$$

and

$$F_{\rm k} = \frac{6+3\rho_0}{6-7\rho_0} \tag{1.7}$$

in which  $\rho_0$  is the ratio of the horizontally-to-vertically polarized scattered light. It can be expressed as:

$$\rho_0 = \frac{6\gamma^2}{45\bar{\alpha}^2 + 7\gamma^2} \tag{1.8}$$

with  $\bar{\alpha}$  the mean polarizability and  $\gamma$  the anisotropy. This depolarization factor $\rho_0$  can be determined from studies of the rotational Raman effect [31, 32]. In general the scattering cross section is very small, for example,  $\sigma_{Ar} =$  $4.45 \times 10^{-27}$  cm<sup>2</sup>,  $\sigma_{CO_2} = 12.4 \times 10^{-27}$  cm<sup>2</sup>, and  $\sigma_{SF_6} = 32.3 \times 10^{-27}$  cm<sup>2</sup> for Ar, CO<sub>2</sub> and SF<sub>6</sub> at an incident laser wavelength of 532 nm [13]. So the King factor,  $F_k$  as defined in Eqs. (1.6) and (1.7) enhances the Rayleigh cross section with an amount of depolarized light. It is understood that this addition is represented by the amount of rotational Raman light, which is depolarized. The Raman branches O ( $\Delta J = -2$ ) and S ( $\Delta J = 2$ ) are displaced from the central Cabannes line, but add to the amount of depolarized light included in the Rayleigh-Brillouin cross section. Overlapped with the central Cabannes line is a fraction of rotational Raman light, the Q branch with  $\Delta J = 0$  but with  $\Delta M = \pm 2$ . This gives rise to a depolarized fraction of the central Cabannes peak, which has been experimentally quantified [33].

In a gaseous medium, the molecular thermal motion leads to the fluctuations of the density as well as of the orientation of the molecular anisotropy, and finally gives rise to fluctuations of the dielectric constant, which can be described by the elements of the dielectric tensor:

$$\epsilon_{ik} = \epsilon_0 \,\,\delta_{ik} + \Delta \epsilon_{ik} \tag{1.9}$$

in which i, k are the indices of the tensor, and  $\delta_{ik}$  is the Kronecker delta. The first term of Eq. (1.9) determines the value of  $\epsilon$  in the homogeneous medium which only exhibits forward scattering. The effect of light scattering is determined only by the second part which can be further separated:

$$\Delta \epsilon_{ik} = \Delta \epsilon \ \delta_{ik} + \Delta \epsilon'_{ik} \tag{1.10}$$

The fluctuations  $\Delta \epsilon$  are isotropic and related to the fluctuations of pressure  $\Delta p$ , entropy  $\Delta S$ , density  $\Delta \rho$  as well as temperature  $\Delta T$ , and scattered light from this part is polarized, meaning that the polarization of the scattered light is the same as that of the incident light. The fluctuations  $\Delta \epsilon'_{ik}$  determine the anisotropy of the medium that results from the thermal motion, giving rise to the Rayleigh-wing and Raman scattering, and scattered light from this part is depolarized.

For RB-scattering, only the fluctuations of the dielectric constant  $\Delta \epsilon$  are considered. This scalar fluctuation can be separated into two parts: the

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Figure 1.3: The scattering vector diagram.  $\mathbf{k}_{i}$ ,  $\mathbf{k}_{s}$ ,  $\omega_{i}$ ,  $\omega_{s}$  are the incident and scattered light wave vectors and frequencies respectively.  $\mathbf{q} = \mathbf{k}_{s} - \mathbf{k}_{i}$  is the scattering wave vector.

density fluctuations at constant temperature and the temperature fluctuations at constant density, as:

$$\Delta \epsilon(\rho, T) = \left(\frac{\partial \epsilon}{\partial \rho}\right)_{\rm T} \ \Delta \rho + \left(\frac{\partial \epsilon}{\partial T}\right)_{\rho} \ \Delta T \tag{1.11}$$

The second part of Eq. (1.11) is usually ignored as it contributes very little to the fluctuations [3, 34, 35], that is  $(\partial \epsilon / \partial T)_{\rho} = 0$  and the intensity of scattered light is proportional to the density fluctuations  $\Delta \rho$  alone. The thermodynamic calculation of  $\Delta \rho$  can be expressed as a function of two independent thermodynamic variables, the pressure p and the entropy S:

$$\Delta\rho(p,S) = \left(\frac{\partial\rho}{\partial p}\right)_{\rm S} \ \Delta p + \left(\frac{\partial\rho}{\partial S}\right)_{\rm p} \ \Delta S \tag{1.12}$$

In the right of Eq. (1.12), the first part is the pressure fluctuation at constant entropy corresponding to Brillouin scattering and this part shows the equation of motion of a damped acoustic wave. The second part is the entropy fluctuation at constant pressure leading to Rayleigh-center scattering and the entropy fluctuations can be described by a diffusion equation [36].

## 1.3 Rayleigh-Brillouin lineshape

A single RB-scattering light process is shown in Fig. 1.3. The scattering wave vector q is defined as the difference between incident and scattered propagation vectors,  $k_i$  and  $k_s$ . The angle  $\theta$  between the  $k_s$  and  $k_i$  vectors is the scattering

angle. In light scattering experiments,  $k_s \approx k_i = 2\pi n/\lambda_i$ , where n is the refractive index of the medium and  $\lambda_i$  the incident wavelength. The magnitude of the scattering wave vector can be obtained as:

$$q = 2k_{\rm i}\,\sin\frac{\theta}{2} = \frac{4\pi\,n}{\lambda_{\rm i}}\,\sin\frac{\theta}{2}\tag{1.13}$$

This is the Bragg condition.

Rayleigh scattering is quasi-elastic. The frequency of the scattered wave is almost the same as the incident wave and its spectrum is broadened by the molecular random thermal motion. Each of these scattered frequencies can be considered separately as a monochromatic wave propagating to the observer, and the observed frequency components can be considered as being part of an interference pattern, the spatial wavelength of which imposes a spatial scale  $\lambda_s = 2\pi/q$  on the scattering volume. When the spatial structures of density variations in the sample volume are on the same scale as the interference pattern, they strongly contribute to the detected signal [37]. For the RB-profile, the Brillouin side peaks will appear.

Under different physical conditions, the RB-profile will be different. Fig. 1.4 displays the variation of RB-scattering profiles for different temperature, pressure, scattering angle and incident wavelength. This figure shows that the broadening of the RB-profile may be caused by increasing the temperature, increasing the scattering angle and decreasing the incident wavelength.

To describe the spectral distribution of RB-scattering at different conditions, a dimensionless parameter y —the ratio of the scattering wave length  $(2\pi/q)$  to the mean free path, which is the reciprocal of Knudsen number— is used as a scaling parameter. The parameter y, also known as the uniformity parameter, can be expressed as:

$$y = \frac{p}{q \ v_0 \ \eta_{\rm s}} \tag{1.14}$$

where p is the pressure, the thermal velocity  $v_0 = (2k_{\rm B}T/m)^{1/2}$ ,  $k_{\rm B}$  is the Boltzmann constant, T is the temperature, m is the molecular mass and  $\eta_{\rm s}$  is the shear viscosity, which is ratio of the shearing stress to the velocity gradient.

When  $y \ll 1$ , that is the mean free path is much larger than the scattering wavelength, the density wave will be spread out too far to contribute significantly to the scattering signal. This is the Knudsen regime, where molecules are collisionless and collective effects are absent. For molecules radiating light with frequency  $\nu_0$  which is the same as the incident frequency and moving with a speed v along the bisectrix of the scattering angle, the observer detects radiation of frequency:

$$\nu = \nu_0 + v \, \frac{q}{2\pi} = \nu_0 + \frac{v}{c} \, 2 \, \nu_0 \, n \, \sin(\frac{\theta}{2}) \tag{1.15}$$

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Figure 1.4: The RB-profiles at different conditions. (a), (b), (c) and (d) show the RB-profile change with temperature T, pressure p, scattering angle  $\theta$  and incident wavelength  $\lambda_i$ , respectively. All profiles represent the simulation spectra of N<sub>2</sub> using the Tenti-S6 model described in Sec. 1.4. (a) p = 1 bar,  $\theta = 90^{\circ}$  and  $\lambda_i = 532$  nm (b)  $T = 23.6 \ ^{\circ}C$ ,  $\theta = 90^{\circ}$  and  $\lambda_i = 532$  nm (c)  $T = 23.6 \ ^{\circ}C$ , p = 1 bar and  $\lambda_i = 532$  nm (d)  $T = 23.6 \ ^{\circ}C$ , p = 1 bar and  $\theta = 90^{\circ}$ .

Molecules move in all directions and the observer detects the corresponding spectral line profile which reflects the distribution of molecular velocities along the line of detection. The velocity distribution can be expressed by the Maxwell distribution function  $\phi(v)$ :

$$P_v(v)dv = \phi(v)dv = \sqrt{\frac{m}{2 k_{\rm B} T}} \exp\left(-\frac{m v^2}{2 k_{\rm B} T}\right)dv$$
 (1.16)

 $P_v(v) dv$  is fraction of particles with velocity component v to v+dv.

Combining Eq. (1.15) and Eq. (1.16) yields an expression for the distribution of the frequencies as function  $\nu$ :

$$P_{\nu}(\nu)\mathrm{d}\nu = P_{v}(\nu)\frac{\mathrm{d}v}{\mathrm{d}\nu}\mathrm{d}\nu = \sqrt{\frac{4\,\ln 2}{\pi}}\frac{1}{\Delta\nu_{D}}\,\exp\left(-4\,\ln 2\,\frac{(\nu-\nu_{0})^{2}}{\Delta\nu_{D}^{2}}\right)\mathrm{d}\nu \quad (1.17)$$

where:

$$v = \frac{\nu - \nu_0}{\nu_0} \frac{c}{2 n \sin(\frac{\theta}{2})}$$



Figure 1.5: The RB-scattering spectra of N<sub>2</sub> at different scattering angles as indicated in the legend. The spectra are calculated using the Tenti-S6 model with  $\lambda_i = 532 \text{ nm}, T = 23.6 \text{ }^{\circ}\text{C}$  and p = 1 mbar.

and:

$$\Delta \nu_D = \frac{2\nu_0}{c} n \, \sin(\frac{\theta}{2}) \, \sqrt{\frac{2 \, \ln 2 \, k_{\rm B} \, T}{m}}$$

is the full width at half maximum of the distribution.

Eq.(1.17) shows that the RB-spectrum is characterized as a Gaussian profile. This is the usual Doppler profile observed in light scattering and this profile will be different at different scattering angles as shown in Fig. 1.5.

For  $y \gg 1$  the mean free path is very short and the scattering is in the hydrodynamic regime. The molecular gas can be treated as a continuum, and the sound wave is obviously taking effect. For the RB-profile, the Brillouin side peaks will be completely separated from the central Cabannes peak. The density fluctuations of the gas can be calculated using the Navier-Stokes equations. Note that in the fully hydrodynamic regime the effect of inhomogeneous broadening, leading to a Gaussian profile, no longer exists and is replaced by the effect of collisions dominating, yielding Lorentzians. The whole RB-scattering spectrum can be expressed by three Lorentzians. The widths of these Lorentzians are then connected to relaxation phenomena [38].

When the mean free path is on the same scale as the grating wavelength, for  $y \approx 1$ , the gas is in the kinetic regime. Within this regime, the density fluctuations caused by the acoustic waves begin to take effect. The density fluctuations move at the acoustic propagation speed (the speed of sound) making the acoustic sidebands appear. For the scattering profile, the Rayleigh peak and two side-peaks (Brillouin peaks) become distinctly observable. Here,

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the sound wave can be treated as a periodic multi-layer stack with periodicity  $\Lambda$  and the reflected light interferes on the detector, as seen in Fig. 1.6. The reflected intensity reaches its maximum when the interference is constructive, which means that the sound waves with vector equal to the scattering wave vector will be detected. Therefore, we have  $\Lambda = 2\pi/q$ . For the same incident wave  $\lambda_i$ , at different angle  $\theta$ , the q will be different and the corresponding sound wave will be probed. In this regime, neither the individual particle approach nor the continuum approach applies. The line shape description cannot be expressed by a Gaussian nor by the sum of three Lorentzian functions.

Fig 1.7 shows the RB-scattering profile of  $N_2$  varing for increasing the values of y.



Figure 1.6: Brillouin scattering diagram.  $k_i$ ,  $k_s$ ,  $\omega_i$ ,  $\omega_s$  are the incident and scattered light wave vectors and frequencies respectively.

## 1.4 Models for the Rayleigh-Brillouin lineshape

As discussed in section 1.2, the dielectric constant fluctuations  $\epsilon$  are responsible for the generation of scattering light. These fluctuations are caused, in turn, by the fluctuations in the density, in the temperature, and in the orientation of the molecules. The intensity of the scattered light is [8]:

$$I(\mathbf{R},\omega) = I_0 \left[ \frac{Nk_1^4}{16\pi^2 R^2} \right] \sin^2\theta \langle [\epsilon(\mathbf{q},\omega)]^2 \rangle$$
  
=  $I_0 \left[ \frac{Nk_1^4}{16\pi^2 R^2} \right] \sin^2\theta \left( \frac{\partial\epsilon}{\partial\rho} \right)_{\mathrm{T}}^2 \langle [\rho(\mathbf{q},\omega)]^2 \rangle$   
=  $I_0 \left[ \frac{Nk_1^4}{16\pi^2 R^2} \right] \sin^2\theta \left( \frac{\partial\epsilon}{\partial\rho} \right)_{\mathrm{T}}^2 S(\mathbf{q},\omega)$  (1.18)

#### 1.4. Models for the Rayleigh-Brillouin lineshape



Figure 1.7: The simulation of spontaneous RB-scattering profiles of N<sub>2</sub> using the Tenti-S6 model (see Sec. 1.4). Pressure values are varied for y = [0.08-8] (wavelength = 532 nm, scattering angle = 90°, temperature = 20 °C).

Eq. (1.18) shows polarized incident light of intensity  $I_0$ , scattered at the origin and observed at  $\mathbf{R}$ , where  $\omega$  is the angular frequency shift of the scattered light, N is the molecular number in the scattering volume,  $\theta$  is scattering angle,  $\mathbf{k}_i$ and  $\mathbf{q}$  are the incident and scattering wave vector, respectively.  $(\partial \epsilon / \partial \rho)_T$ is the dielectric constant derivatives of density at constant temperature, and  $\rho(\partial \epsilon / \partial \rho)_T \approx 2(n-1)$  with n the refractive index [39]. The angular brackets  $\langle \ldots \rangle$  indicate an ensemble average over the initial states of the system. The fluctuation characteristics of the gases are all contained in the structure factor:

$$S(\boldsymbol{q},\omega) = \int_{-\infty}^{+\infty} e^{-i\omega t} \mathrm{d}t \int G(\boldsymbol{r},t) \ e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \mathrm{d}\boldsymbol{r}$$
(1.19)

Eq. (1.19) shows that the structure factor  $S(q, \omega)$  is the space time Fourier transform of  $G(\mathbf{r}, t)$ .  $G(\mathbf{r}, t)$  is the classic time-dependent density Van Hove's correlation function [40], which can be expressed as [8, 41]:

$$G(\mathbf{r},t) = \frac{1}{\rho_0} \langle \rho(0,0) \ \rho(\mathbf{r},t) \rangle$$
(1.20)

and the power spectrum as:

$$S(\boldsymbol{q},\omega) = \langle \rho(\boldsymbol{q},\omega)\rho(-\boldsymbol{q},0) = \langle |\rho(\boldsymbol{q},\omega)|^2 \rangle \rangle$$
(1.21)

## 1.4.1 The dilute regime

The dilute regime is described by the microscopic velocity-position distribution function  $f(\mathbf{r}, \mathbf{v}, t)$ , which is a solution of the Boltzmann equation. In equilibrium f becomes the Maxwellian function  $\phi(v)$  in term of the deviation  $h(\mathbf{r}, \mathbf{v}, t)$ . The distribution h satisfies the linearized Boltzmann equation subject to the initial condition:

$$h(\boldsymbol{r}, \boldsymbol{v}, 0) = \delta(\boldsymbol{r}) \tag{1.22}$$

in which  $\delta(\mathbf{r})$  is the Dirac delta function at position  $\mathbf{r}$ . The power spectrum  $S(\mathbf{q}, \omega)$  is the space time Fourier transform of  $G(\mathbf{r}, t)$ , and Yip and Nelkin [42] gave the  $G(\mathbf{r}, t)$  as:

$$G(\mathbf{r},t) = \rho_0 \left( 1 + \int \phi(v) \ h(\mathbf{r},\mathbf{v},t) \mathrm{d}^3 v \right)$$
(1.23)

Usually, in the Knudsen and hydrodynamic scattering regime, the scattering profile is simple and it is easy to establish the relationship between RB-scattering characteristics (e.g. Rayleigh and Brillouin linewidth, Brillouin shift) and the transport coefficients. However in the kinetic regime, the Rayleigh peak and Brillouin peaks overlap, and the RB-profile cannot be simply expressed by Gaussian or Lorentzian functions. Also, as it is difficult to distinguish the Rayleigh peak and Brillouin peaks, the underlying transport coefficients cannot be extracted in a direct manner from the observed line profile. For the scattering profile in the kinetic regime, many mathematical models have been proposed and some of them will be used in this thesis such as the Tenti-S6 model [15], the rough-sphere model [17], the Grad's six-moment kinetic model [19] to enable a computational simulation. These models will be described here in some details.

**The Tenti-S6 model.** For diluted gases in the kinetic regime of spontaneous RB-scattering, where two-body collisions dominate,  $G(\mathbf{r}, t)$  can be expressed by the normalized phase-space distribution function  $f(\mathbf{r}, \mathbf{v}, t)$  obtained via the Boltzmann equation in absence of external forces [15, 43]:

$$\frac{\partial f(\boldsymbol{r}, \boldsymbol{v}, t)}{\partial t} + \boldsymbol{v} \cdot \nabla f = -\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}$$
(1.24)

where r is the space position and v is the velocity of the particle at time t. The collision term  $-(\partial f/\partial t)_{\text{coll}}$  captures the interactions – or collisions – of the particles. For two-body collisions:

$$-\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = \int |\boldsymbol{v} - \boldsymbol{v}_1| \ \sigma \ (f_1'f' - f_1f) \ d\Omega \ d^3v_1 \tag{1.25}$$

where  $\boldsymbol{v}$ ,  $\boldsymbol{v_1}$  are the velocities of the first and second particles before the collision,  $\sigma$  is the scattering cross section,  $d\Omega$  is the solid angle, f and  $f_1$  are the phase space distribution functions of the two particles before the collision, and conversely, f' and  $f'_1$  are those after the collision.

Wang Chang and Uhlenbeck [44] first presented the kinetic equation for gases with internal degrees of freedom as the WCU equation:

$$\frac{\partial f(\boldsymbol{r}, \boldsymbol{v}, t)}{\partial t} + \boldsymbol{v} \cdot \nabla f_i = \sum_{jkl} \int |\boldsymbol{v} - \boldsymbol{v}_1| \ \sigma_{ij}^{kl} \left( f'_k f'_l - f_i \ f_j \right) d\Omega \ d^3 v_1 \quad (1.26)$$

where i, j, k, and l are the internal states of molecules. This equation considers the effects of elastic collisions (k = j and l = j) as well as inelastic collisions. The WCU equation satisfies the conservation of mass, momentum, and total energy.

As the collisions between molecules only cause small deviations from equilibrium, the distribution function of the  $i^{\text{th}}$  internal level  $f_i(\mathbf{r}, \mathbf{v}, t)$  can be linearized from the overall equilibrium via:

$$f_i(\boldsymbol{r}, \boldsymbol{v}, t) = n_0 \ x_i \ \phi(v) \ [1 + h_i(\boldsymbol{r}, \boldsymbol{v}, t)]$$
(1.27)

where  $n_0$  is the average number density,  $\phi(v)$  is the Maxwell distribution function,  $x_i$  is the averaged fraction of molecules in the internal state and  $h_i(\mathbf{r}, \mathbf{v}, t)$  is the dimensionless deviation from equilibrium. Insertion of Eq. (1.27) into Eq. (1.26) yields:

$$\frac{\partial \boldsymbol{h}}{\partial t} + \boldsymbol{v} \cdot \nabla \boldsymbol{h} = n_0 \boldsymbol{J} \boldsymbol{h}$$
(1.28)

where the collision operator J is a  $N \times N$  matrix, and each element of this matrix is an integral operator. This equation is used to generate a linear system of equations, by expanding h into eigenfunctions of J.

Boley et al. [14] selected 7 non-degenerate eigenvectors to describe the collision operator and this model is named the S7 model. These 7 eigenvectors are related to 7 physical vectors: (1) the fraction of particles in different internal states, (2) the momentum, (3) the translational energy, (4) the translational heat flux, (5) the internal energy, (6) the internal heat flux, and (7) the traceless pressure tensor. The Fourier transform of Eq. (1.28) can be written in the form of AX = B. A, B can be found in Ref. [14], and X is a vector representing the Fourier transform of deviation of the total number density  $n_0\psi(\mathbf{r},t)$ , the flow velocity  $u(\mathbf{r},t)$ , the translational heat flux  $q_{tr}(\mathbf{r},t)$ , the traceless pressure tensor  $\pi(\mathbf{r},t)$ , the translational temperature  $\tau_{tr}(\mathbf{r},t)$ , the internal temperature  $\tau_{int}(\mathbf{r},t)$  and internal heat flux  $q_{int}(\mathbf{r},t)$ . Among them,

$$n_0\psi(\mathbf{r},t) = n_0 \sum_i x_i \int \phi(v) h_i(\mathbf{r},\mathbf{v},t) \mathrm{d}^3 v \qquad (1.29)$$

Boley et al. [14] identified the density correlation function  $G(\mathbf{r}, t) = n_0 \psi(\mathbf{r}, t)$ . Then based on Eq. (1.19), the RB-scattering profile which is proportional to  $S(\mathbf{q}, \omega)$  can be written as:

$$I(\boldsymbol{q},\omega) \propto S(\boldsymbol{q},\omega) = n_0 \Phi(\boldsymbol{q},\omega) \tag{1.30}$$

where  $\Phi(\boldsymbol{q}, \omega)$  is the Fourier transform of  $\psi(\boldsymbol{r}, t)$ . The matrix elements of  $\boldsymbol{J}$  in matrix  $\boldsymbol{A}$  can be expressed in terms of three transport coefficients (the shear viscosity  $\eta_s$ , bulk viscosity  $\eta_b$ , and the thermal conductivity  $\lambda_{\rm th}$ ), the atomic mass m of the particles, and the internal specific heat capacity per molecule  $c_{\rm int}$ .

Later, Tenti et al. [15] truncated the S7 model by neglecting one of the eigenvectors related to the traceless pressure tensor and produced a new model known as the S6 model or the Tenti-S6 model. The Tenti-S6 model has proven to constitute a superior model description for experimentally observed RB-lineshapes [12, 45, 46]. This model needs transport coefficients, and many of them except the bulk viscosity  $\eta_{\rm b}$  are directly known from other experiments. So the bulk viscosity can be fitted as a variable. The FORTRAN code of this model can be found in Pan [47], and a converted MATLAB code is provided in the Appendix A of this thesis.

**The rough-sphere model.** The rough-sphere model was proposed by Marques Jr [17] to treat an ideal gas of polyatomic molecules exhibiting a spherical structure and having rotational energy. This model is also based on the Boltzmann equation, in which the collision term is expressed by a single relaxation-time term (the vibrational relaxation is not considered):

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = \sigma \ (f - f_{\text{r}}) \tag{1.31}$$

where  $\sigma$  is the stress relaxation frequency and  $f_r$  is a reference distribution function. Based on the collisional invariant conditions of the collision term and taking the collisional transfer of momentum and energy to be same as that of the Boltzmann equation for polyatomic gases of rough spherical molecules, the  $f_r$  can be generated. Set the distribution function  $f(\mathbf{r}, \mathbf{v}, \mathbf{w}, t)$ 

$$f(\boldsymbol{r}, \boldsymbol{v}, \boldsymbol{w}, t) = n_0 \phi(\boldsymbol{v})(1 + h(\boldsymbol{r}, \boldsymbol{v}, \boldsymbol{w}, t))$$
(1.32)

in which r, v, w denote the position, velocity and angular velocity of the particle in a volume. The Boltzmann equation can be expressed as:

$$\frac{\partial h}{\partial t} + v_i \cdot \nabla h = \sigma \ F(\bar{n}, \bar{u}_i, \bar{T}, \bar{\varpi}, \bar{p}_{\langle ij \rangle}, \bar{q}_i, \bar{h}_i, \kappa)$$
(1.33)

in which F is a function of the fluctuation of number density n, flow velocity  $u_i$ , temperature T, dynamic pressure  $\varpi$ , pressure deviator  $p_{\langle ij \rangle}$ , translational heat flux  $q_i$ , rotational heat flux  $h_i$  and  $\kappa$  is the dimensionless moment of inertia. These variables are used in a Grad's 17-moment approximation for a macroscopic state of a polyatomic ideal gas [48].

By solving the Fourier–Laplace transforms of Eq. (1.33) for h, substituting it into the Fourier–Laplace transform of the perturbed variable expressions, this leads to a matrix form:

$$(\boldsymbol{M} - \boldsymbol{I}) \ \boldsymbol{X} = -\frac{i}{v_0} \boldsymbol{q} \boldsymbol{X}_0 \tag{1.34}$$

M and  $X_0$  can be found in Ref. [17].  $X = (\bar{n}; \bar{u}_z; \bar{T}; \bar{\varpi}; \bar{p}_z; \bar{q}_z)$  with the disturbance propagating in the z direction, q is the magnitude of the scattering wave vector, and  $v_0$  is the thermal velocity. The matrix Eq. (1.34) can be solved numerically for the number density perturbation  $\bar{n}(q, \omega)$ . With the help of the auto-correlation function:

$$G(\boldsymbol{r},t) = \int f_0 \ h(\boldsymbol{r},\boldsymbol{v},\boldsymbol{w},t) \mathrm{d}\boldsymbol{v} \mathrm{d}\boldsymbol{w} = \bar{n}(\boldsymbol{r},t)$$
(1.35)

the RB-scattering spectrum  $S(\boldsymbol{q},\omega) = \bar{n}(\boldsymbol{q},\omega)$  can be obtained, where  $\bar{n}(\boldsymbol{q},\omega)$  is the Fourier transform of  $\bar{n}(\boldsymbol{r},t)$ .

For this model, the moment of inertia of the sphere  $\kappa = 4I/(m d^2)$  is the unique freely adjustable parameter, with m, I and d representing the mass, the moment of inertia and the diameter of the spherical molecule, respectively. This model can be applied (1) for gaseous molecules of spherical symmetry and (2) for conditions where the specific heat capacity ratio  $\gamma$  is close to 4/3. Note that the value  $\gamma = 4/3$  ignores the vibrational degrees of freedom for spherical polyatomic molecules. The MATLAB code for this model can be found in Appendix B.

The Grad's six-moment kinetic model. This model was put forward by Fernandes and Marques Jr [19] based on a specific evaluation of the Boltzmann equation. Similarly as in the rough-sphere model, the collision term in this model is replaced by a single relaxation-time term with the form as:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = \frac{p}{\eta_{\text{s}}} \left(f - f_{\text{r}}\right) \tag{1.36}$$

where p is the gas pressure and  $\eta_s$  is the shear viscosity,  $f_r$  is a reference distribution function to be determined by preserving some of the main physical properties of the collision operator.

#### 1. INTRODUCTION

The difference with the rough-sphere model is that this kinetic model description is compatible with Grad's six-moment approximation for polyatomic gases [49]. In such a six-moment approximation the macroscopic state of a dilute polyatomic gas is characterized by the fields of mass density  $\rho$ , bulk velocity  $v_{\rm bi}$ , translational temperature  $T_{\rm tr}$  and internal temperature  $T_{\rm int}$ . Balance equations of these fields can be defined as in Fernandes and Marques Jr [19]:

$$\begin{pmatrix} \rho \\ \rho v_{\mathrm{b}i} \\ \frac{3}{2} n k_{\mathrm{B}} T \\ \rho \varepsilon \end{pmatrix} = \sum_{s} \int \begin{pmatrix} mf \\ mv_{i}f \\ \frac{mC^{2}}{2}f \\ \xi_{s} \end{pmatrix} \mathrm{d}\boldsymbol{v}$$
(1.37)

where  $C_i = v_{\rm bi} - v_i$  is the peculiar velocity,  $k_{\rm B}$  is the Boltzmann constant,  $n = \rho/m$  is the particle number density,  $\varepsilon$  is the specific energy of the internal degrees of freedom and s is the quantum state. Based on Eq. (1.37) and the Boltzmann equation, new balance equations, which are expressed by the pressure tensor  $p_{ij}$ , the translational heat flux vector  $q_i$ , the internal heat flux vector  $h_i$  and the collision terms  $\Delta(mC^2/2)$  could be obtained. The quantities  $p_{ij}, q_i, h_i$  and  $\Delta(mC^2/2)$ , can be determined by considering the fact that the energy exchange between translational and internal degrees of freedom is slow, but not negligible. With the help of the new balance equations, a kinetic model equation for polyatomic gases with internal quantum-mechanical degrees of freedom can be obtained. For further details of these equations and descriptions we refer to Ref. [19].

In this model, the distribution function is written as:

$$f = n_0 \phi_0 (1+h) \tag{1.38}$$

 $n_0$  is the average number density,  $\phi_0$  is Maxwellian distribution,  $h = h(\mathbf{r}, \mathbf{v}, s, t)$  is the solution of the linear Boltzmann equation. Inserting  $h(\mathbf{r}, \mathbf{v}, s, t)$  to the Fourier transforms of the perturbation of density  $\delta n(n = \rho/m)$ , bulk velocity  $\delta v_{bi}$ , translational temperature  $\delta T_{tr}$ , and internal temperature  $\delta T_{int}$ , a matrix form can be derived:

$$\left[\frac{p}{\eta_{\rm s} \ q \ v_0} \mathbf{M}^{(0)} + i(\mathbf{I} - \mathbf{M}^{(1)})\right] \mathbf{X} = -\frac{\mathbf{X}_0}{q \ v_0} \tag{1.39}$$

where  $\mathbf{X} = (\delta n; \delta v_{bi}; \delta T_{tr}; \delta T_{int}), \mathbf{M}^{(0)}, \mathbf{M}^{(1)}$  and  $\mathbf{X}_0$  can be found in Ref. [19]. The solution of the Eq. (1.39) for the number density perturbation provides  $S(\mathbf{q}, \omega)$  based on Eq. (1.35):

$$S(\boldsymbol{q},\omega) = \langle \delta n(\boldsymbol{q},\omega) \delta n^*(\boldsymbol{q},\omega) \rangle$$
(1.40)

For the Grads six-moment model, only the specification of the ratio of heat capacities  $\gamma$ , the relaxation time of the internal degrees of freedom  $\tau_{\text{int}}$  and the numerical factor  $u'_{11} = 3\Omega^{(2,2)}/5\Omega^{(1,1)}$  which depends on the law of interaction between molecules through the Chapman-Cowling collision integrals  $\Omega^{(l,r)}$  [50] are needed. This model has a similar performance as the Tenti-S6 model, as will be demonstrated in **chapter 4**. Also, the MATLAB code of this model is shown in Appendix C.

## 1.4.2 The continuum regime

In the continuum regime density fluctuations are described by the hydrodynamic equations [8, 38, 51] which obey the conservation of mass, moment and energy, as

(1) the continuity equation:

$$\frac{\partial \rho_1}{\partial t} + \rho_0 \nabla \cdot \boldsymbol{v} = 0 \tag{1.41}$$

(2) the Navier-Stokes moment equation:

$$\rho_0 \frac{\partial \boldsymbol{v}}{\partial t} + \frac{C_0^2}{\gamma} \nabla \rho_1 + \frac{C_0^2 \beta \rho_0}{\gamma} \nabla T_1 - (\frac{4}{3}\eta_{\rm s} + \eta_{\rm b}) \nabla (\nabla \cdot \boldsymbol{v}) = 0$$
(1.42)

(3) the energy transport equation:

$$\rho_0 c_{\rm v} \frac{\partial T_1}{\partial t} - \frac{c_{\rm v}(\gamma - 1)}{\beta} \frac{\partial \rho_1}{\partial t} - \lambda_{\rm th} \nabla^2 T_1 = 0$$
(1.43)

Here  $\rho_1$  is the deviation of the number density from its equilibrium value  $\rho_0$ ,  $T_1$  is the deviation of the temperature from its equilibrium value  $T_0$ ,  $\boldsymbol{v}$  is the average local velocity. The ratio of heat capacity is  $\gamma = c_{\rm p}/c_{\rm v}$ , while  $\eta_{\rm s}$  and  $\eta_{\rm b}$  are shear and bulk viscosities,  $\lambda_{\rm th}$  is the thermal conductivity,  $\beta$  is the thermal expansion coefficient and  $C_0$  is the low frequency limit of the sound velocity. The Fourier-Laplace transform of Eqs. (1.41), (1.42), (1.43) can be used to derive the dynamic structure factor  $S(q) = \langle \rho_1^*(\boldsymbol{q}), \rho_1(\boldsymbol{q}) \rangle$  based on Eq. (1.21).

The Hammond–Wiggins hydrodynamic model. Hammond and Wiggins [16] extended the hydrodynamic equations by including the Burnett corrections to translational motion and the effect of diffusion on the rotational relaxation time as well as treating the vibrational contribution with a formulation parallel to that of rotation, devising a new model which we will refer to as the Hammond–Wiggins model. This model gives a good description for RB-scattering from the kinetic regime to the hydrodynamic

#### 1. INTRODUCTION

regime. In this model, the hydrodynamic equations are based on the balance equations of mass density  $\rho$ , momentum  $\rho v$  and energy density including translational  $\rho C_{\rm tr} T_{\rm rot}$ , rational  $\rho C_{\rm rot} T_{\rm rot}$  and vibrational  $\rho C_{\rm vib} T_{\rm vib}$  energies, where  $C_{i(i={\rm tr,rot,vib})}$  reflects the heat capacity. The Fourier transform of these balance equations combined with the linear fluctuations for mass density  $\rho$ , translational temperature  $T_{\rm tr}$ , momentum of velocity density v, vibrational temperature  $T_{\rm vib}$  and rotational temperature  $T_{\rm rot}$  can be used to evaluate this hydrodynamic model by:

$$\frac{\partial \boldsymbol{X}}{\partial t} = -\boldsymbol{M}(q) \; \boldsymbol{X} \tag{1.44}$$

where 
$$\mathbf{X} = [\hat{\rho}/\rho_0; T/T_0; \hat{v}/v_0; T_{\text{vib}}/T_0; T_{\text{rot}}/T_0]$$
 and  
 $\mathbf{M}(q) = \begin{pmatrix} 0 & 0 & -iqv_0 & 0 & 0 \\ 0 & M_{23} & M_{24} & -C_{\text{vib}}/C_{\text{tr}}\tau_{\text{vib}} & -C_{\text{rot}}C_{\text{tr}}\tau_{\text{rot}} \\ M_{31} & M_{32} & 4\eta_{\text{s}}q^2/3\rho_0 & 0 & 0 \\ 0 & -1/\tau_{\text{vib}} & 0 & 1/\tau_{\text{vib}} + D_{\text{vib}}q^2 & 0 \\ 0 & -1/\tau_{\text{rot}} & 0 & 0 & 1/\tau_{\text{rot}} + D_{\text{rot}}q^2 \end{pmatrix}$ 
with

with

$$M_{23} = \frac{5}{2} \frac{\eta_{s} q^{2}}{\rho_{0}} + \frac{C_{\text{vib}}}{C_{\text{tr}} \tau_{\text{vib}}} + \frac{C_{\text{rot}}}{C_{\text{tr}} \tau_{\text{rot}}}$$

$$M_{24} = -iqv_{0} \left(\frac{2}{3} - \frac{2}{3}(\epsilon_{1} + \epsilon_{2})\frac{\eta_{s}^{2} q^{2}}{\rho_{0}^{2} C_{\text{tr}} T_{0}}\right)$$

$$M_{31} = -iqv_{0} \left(\frac{1}{2} + \frac{2}{3}\epsilon_{3}\right)\frac{\eta_{s}^{2} q^{2}}{\rho_{0}^{2} v_{0}^{2}}$$

$$M_{32} = -iqv_{0} \left(\frac{1}{2} - \frac{2}{3}(\epsilon_{2} - \epsilon_{3})\right)\frac{\eta_{s}^{2} q^{2}}{\rho_{0}^{2} v_{0}^{2}}$$

In Matrix M(q),  $\eta_s$  is the shear viscosity,  $v_0$  is the thermal speed,  $\tau_{vib}$  and  $\tau_{rot}$  are vibrational and rotational relaxation times, respectively.  $D_{i(i=rot,vib)}$  are self-diffusion coefficients,  $\epsilon_{i(i=1,2,3,4)}$  are values of dimensionless coefficients.

The auto-correlation density function  $G(\mathbf{r}, t) = \hat{\rho}(\mathbf{r}, t)$ , the RB-scattering spectrum can then be computed again via the structure factor:

$$S(q,\omega) \propto Re[(s\mathbf{I} + \mathbf{M}(q))_{11}^{-1}|_{s=i\omega}]$$
(1.45)

that is, the (1,1) element of the reciprocal of the matrix (sI + M(q)). The MATLAB code of this model can be found in Appendix D.

## 1.5 Outline of this thesis

This thesis describes RB-scattering experiments performed in a variety of gases such as  $SF_6$ ,  $N_2O$ ,  $CO_2$  and a comparison is made with the different models

presented in section 1.4. In addition, RB-scattering profiles of binary mixtures are investigated. The thesis is structured as follows:

chapter 2: The experimental set up is described, including an existing setup for RB-scattering measurements at a laser wavelength of 403 nm and a new simpler setup using a laser at 532 nm. Also, the methods of measuring some key parameters as scattering angle, free spectral range, instrument function, etc are introduced. In addition, the method for obtaining high signal-to-noise experimented data, including signal averaging over measurement times of several hours, are explained.

**chapter 3:** The 90° RB-scattering spectra of  $SF_6$  gas are measured at a wavelength of 403 nm and in a pressure range of 0.2 - 5 bar in the kinetic regime. These spectra are compared with the Tenti-S6 model, the rough-sphere model and the HW hydrodynamic model to address the effects of rotational and vibrational relaxation. The bulk viscosity for  $SF_6$  is obtained based on these different models.

**chapter 4:** The RB-scattering spectra of the linear molecule  $N_2O$ , for which the linear N-N-O structure does not provide a symmetry point, are measured at an incident wavelength of 403 nm, at 90°, at room temperature and at pressures from 0.5 - 4 bar. Four models, the Tenti-S6 model, the rough-sphere model, the Grad's six-moment model and the HW hydrodynamic model are compared with these experimental spectra to study the collisional dynamics and relaxation of this polyatomic molecular species. The applications of these models, in some cases also involving fitting of some parameters, are discussed. **chapter 5:** RB-scattering spectra of another linear but symmetric molecule  $CO_2$  are investigated at pressures in the range of 0.5 - 4 bar, and temperatures in the range 257 - 355 K using laser radiation at wavelength of 532 nm. These spectra were compared to two lineshape models, the Tenti-S6 model and the HW hydrodynamic model with the bulk viscosity taken as a parameter. Also, the connection between the bulk viscosity and shear viscosity is investigated.

**chapter 6:** The RB-scattering spectra of binary mixture gases are measured with the green RB-scattering setup at room temperature. A variety of binary mixtures,  $SF_6$ -He,  $CO_2$ -He,  $SF_6$ -D<sub>2</sub>,  $CO_2$ -D<sub>2</sub>,  $SF_6$ -H <sub>2</sub>,  $SF_6$ -CH<sub>4</sub> as well as  $CO_2$ -CH<sub>4</sub>, are investigated with the heavy mass set at 1 bar, and the pressure of the lighter collision partner increasing.



## ${\rm Chapter}\; 2$

# Experimental Setup and Procedures

### 2. Experimental Setup and Procedures

The typical way to measure the RB-scattering profile is the employment of a frequency separation device such as a Fabry-Perot etalon (FPE) or a Fabry-Perot interferometer (FPI) to resolve the functional form of the spectrum and using a photo-detector such as charge-coupled device (CCD) or photon-multiplier tube (PMT) to obtain the intensity of the spectral function. Here, our experimental setup is adopted with a scannable FPI and PMT. In this chapter, the experimental apparatus with a continuous wave (CW) laser of 403 nm as the excitation source is first described and, secondly a setup with an excitation laser of 532 nm is described. Also, the data processing methods are discussed.

## 2.1 Rayleigh-Brillouin scattering setup with 403 nm

This experimental apparatus for measuring the RB-scattering light with scattering angle of  $90^{\circ}$  is sketched in Fig. 2.1. This system contains three parts: the source unit, the scattering unit and the detection unit. For the source unit, a tunable Ti:Sapphire laser pumped by a Verdi-10 laser produces CW light at 806 nm and bandwidth less than 1 MHz. This red light then goes into an external frequency-doubling cavity for the production of UV-light at a wavelength of 403 nm and power approximately 0.5 Watt. The UV-light is split into two beams, one beam propagates into the scattering unit for producing the scattered light and the other one is used for aligning the light path and the FPI. In the scattering unit, the enhancement cavity will enhance the power of the UV-light about 10 times. The scattering gas cell was designed such that scattered light is collected at a  $90^{\circ}$  scattering angle with a low background. For the detection unit, a plano-concave FPI with mirrors specifically coated for 403 nm is used for analyzing the spectral profile of the scattered light. In addition, a single photon counting module which consists of a PMT, a discriminator and a counter is adopted to measure the RB-spectral profiles. This setup was used for the scattering measurements of  $SF_6$  (chapter 3) and  $N_2O$  (chapter 4) and more details about this apparatus can be found in Refs. [52, 53].

## 2.2 Rayleigh-Brillouin scattering setup with 532 nm

As the UV-setup is complex, a simpler one was built as sketched in Fig. 2.2. For the source unit, this new green-setup just uses a Verdi-5 CW laser, which produces green light of 532.22 nm at a bandwidth less than 5 MHz. As this laser can provide enough power and narrow bandwidth, the source unit is simplified significantly in particular and there is no need for using an enhancement cavity. This provides flexibility in choosing the scattering angle. For the scattering unit, another gas cell is chosen and the scattering light with scattering angle



#### 2.2. Rayleigh-Brillouin scattering setup with 532 nm

Figure 2.1: Schematic of the experimental apparatus. The Ti:Sa laser, pumped by a 10 W Verdi-10 CW pump laser, produces red light at 806 nm which then enters into a frequency-doubling cavity and produces CW UV-light of 403 nm with power around 500 mW. The UV-light is then split into two beams. One is directed into an enhancement cavity for amplification by a factor of 10. The RB-scattering cell is set at the focus of the UV-beam in the cavity. The 90° scattered light from the cell is directed to a Piezo-scannable Fabry-Perot Interferometer (FPI) with instrumental linewidth of 126  $\pm$  3 MHz. The photons transmitted by the FPI are detected by a photo-multiplier tube (PMT). The other beam transmitted through M<sub>5</sub> is used as a reference beam for aligning beam paths. Mirrors, lenses and diaphragms are indicated with M<sub>i</sub>, L<sub>i</sub> and D<sub>i</sub>.

 $\theta = (55.7 \pm 0.3)^{\circ}$  can be collected. This scattering angle is smaller than that of the UV-light setup, and the Brillouin side peaks will be more pronounced. As seen in Fig. 1.1, the scattered light contains the Raman scattering light and RB-scattering light. Before the scattered light goes into the detection unit, it first propagates through a bandpass filter (Materion, T > 90% at  $\lambda_i = 532$  nm, bandwidth  $\Delta \lambda = 2.0$  nm) to get rid of the most part of the Raman scattering light except the special part of rotational Raman scattering, named rotational Q-branch ( $\Delta J = 0, J$  is the magnitude of the rotational angular momentum),

### 2. Experimental Setup and Procedures

corresponding to no frequency shift. The detection unit is similar to the one used in the UV-setup, although the mirrors and the FPI geometry changed yielding a different instrument resolution. More details about the scattering unit and detection unit are described in the following subsections.



Figure 2.2: Schematic diagram of the experimental setup for spontaneous Rayleigh-Brillouin scattering at 532 nm. A Verdi-V5 laser provides continuous wave light at 532.22 nm, at a power of 5 Watt and bandwidth less than 5 MHz. The laser light is split into two beams. The pump beam crosses the RB-scattering gas cell producing scattered light that is captured under an angle  $\theta = (55.7 \pm 0.3)^{\circ}$ . A small fraction of the power, retained in a reference beam transmitted through M<sub>4</sub>, is used to align the beam path after the gas cell towards the detector. The scattered light after an bandpass filter (F<sub>BW</sub>) is analyzed in a Fabry-Perot interferometer (FPI), with free spectral range of 2.9964 GHz and an instrument linewidth of  $(58 \pm 3)$  MHz, and is collected on a photo-multiplier tube (PMT). Mirrors, lenses and diaphragm pinholes are indicated as M<sub>i</sub>, L<sub>i</sub> and D<sub>i</sub>, and B is the barotron used for the pressure measurement. A slit of 500 µm is inserted to limit the opening angle for collected scattering light, therewith optimizing the resolution.

## 2.2.1 Scattering unit

The geometry and design of the gas cell, as displayed in Fig. 2.3, is of great importance for RB-light scattering experiments. The design is focused on minimizing the detection of background photons. On the gas cell two Brewster-angled windows are mounted at entrance and exit ports, and black paint covers the inside walls to reduce stray light. A baratron with range of 0-10 bar is added to measure and monitor the pressure. In addition, a



2.2. Rayleigh-Brillouin scattering setup with 532 nm

Figure 2.3: The scattering gas cell.

temperature control system consisting of two temperature sensors PT-100, a thermoelectric Peltier element connected to a water cooling system and a proportional-integral-derivative controller are installed to keep the gas at constant temperature.

**Scattering angle.** The scatting angle is defined by the design and construction of the gas cell at the scattering unit. To measure the scattering angle, a home-built rotation goniometer is designed, see Fig. 2.4.

For the rotation goniometer, a needle is set at the center of the cylinder with an arm extended. The arm is about 100 mm and at the end a slit is mounted with width of 1 mm. For a precise measurement of the scattering angle  $\theta$ , the reference beam and pump beam, as shown in Fig. 2.2, are used. When measuring this scattering angle, first it is ensured that the needle of the rotation stage sits at the crossing point of the two beams. Then the arm is rotated until the reference beam passes though the slit, using a power meter to monitor the power of the beam behind the slit, and read the angle  $\theta_1$  from the goniometer tick marks at optimum power. The same procedure is followed by using pump beam to detect the angle  $\theta_2$ . The scattering angle is the value of the difference between  $\theta_1$  and  $\theta_2$ .

The scattering angle is a critical parameter for the scattering experiment as

### 2. Experimental Setup and Procedures



Figure 2.4: Home-built goniometer setup for measuring the scattering angle  $\theta$ .

an angle difference of 1° will bring about 1 percent amplitude deviation [52]. With the home-built goniometer, the scattering angle is finally obtained as  $\theta = 55.7 \pm 0.3^{\circ}$ .

For the RB-scattering experiment, the scattered light is collected by the lens  $M_2$  over a range of angles, defined as the opening angle, around the center value of the scattering angle  $\theta$ . This opening angle will broaden the spectrum and enlarge the amplitude of the scattering spectrum. As shown in Fig. 2.5, an opening angle of  $0.5^{\circ}$  can lead to about 0.5 percent amplitude deviation, while an opening angle of  $1^{\circ}$  will bring 0.9 percent amplitude difference. In our experiment, a slit with width of 0.5 mm is mounted behind the gas cell to limit the scattered light of other scattering angles, as displayed in Fig. 2.6. The geometry of the slit, and the distance to the gas cell define the scattering opening angle  $2\Delta\theta$  of  $0.48 \pm 0.12^{\circ}$ .

## 2.2.2 Detection unit

**Fabry-Perot interferometer (FPI).** The FPI is an optical cavity including two mirrors fixed at a certain distance with one mirror is fixed and the other is movable. Incident light entering into the FPI will produce multiple reflections from one mirror to the other, and the light between the mirrors undergoes successive destructive and constructive interferences based on the relationship of the distance of the two mirrors and the incident light wavelength. The transmitted light passes through the second mirror when the constructive interference happens. Therefore, the FPI can be used as a frequency-selective element for analysing the RB-spectra.

As displayed in Fig. 2.7, the FPI we used is composed of a flat mirror (in-coupling mirror,  $M_{in}$ ) and a concave mirror (out-coupling mirror,  $M_{out}$ ), which is glued onto a piezo-electric tube. The substrate of the  $M_{in}$  has a wedge



**Figure 2.5:** (a) Area-normalized Rayleigh-Brillouin scattering profiles for 1 bar N<sub>2</sub> at 20 °C simulated with the Tenti-S6 model. Red is the simulation with scattering angle at 55.7°, light blue is the integration simulation with scattering angle from  $(55.7 - 0.25)^{\circ}$  to  $(55.7 + 0.25)^{\circ}$ , and blue is the integration simulation with scattering angle from  $(55.7 - 0.5)^{\circ}$  to  $(55.7 + 0.5)^{\circ}$ . (b) Calculated deviations of RB-scattering profiles measured with opening angle of  $0.5^{\circ}$  and 1° from that measured at scattering angle of  $55.7^{\circ}$ . The deviation are shown in percentages of the peak amplitude at  $55.7^{\circ}$ .

of 30' to avoid the interference between its two surfaces as well as between  $M_{\rm in}$  and  $M_{\rm out}$ . For the UV-light setup (Sec. 2.1), the radius of the curvature (ROC) of  $M_{\rm out}$  was chosen as 10 mm, resulting in a free spectral range of about 7.5 GHz, which can cover a complete spectrum for many gases, like air, SF6, CO<sub>2</sub>, at the scattering angle of 90°. In this green setup, the ROC of  $M_{\rm out}$  is chosen as 25 mm considering the scattering angle of 55.7°. The distance of  $M_{\rm in}$  and  $M_{\rm out}$  is set L = 12.5 mm, which means that the focal point of  $M_{\rm out}$  coincides with the rear surface of  $M_{\rm in}$ . In this geometry the plano-concave FPI acts as a stable resonator.

The reflectivity of  $M_{in}$  and  $M_{out}$  determines the in-coupling efficiency and the finesse of the FPI. As Refs. [53, 54] stated, the amount of light coupled into a cavity depends on the impedance matching (reflectivity of the in-coupling

2.2. Rayleigh-Brillouin scattering setup with 532 nm

#### 2. Experimental Setup and Procedures



Figure 2.6: The geometry of the opening angle at top view of slit and gas cell.

mirror) and on the cavity mode matching (choice of incoupling lens). If the cavity mode matching is perfect, the in-coupling efficiency can be calculated by 1-P with:

$$P = \frac{\sqrt{R} - \sqrt{V}}{1 - \sqrt{RV}} \tag{2.1}$$

where R is the reflectivity of the in-coupling mirror, and 1-V are the losses per round trip without taking into account the in-coupling mirror reflectivity. The losses of the light inside a cavity contains the transmission losses which is decided by the reflectivity of out-coupling mirror and the dissipative losses which are caused by the imperfections on the surface of the mirrors, or fluorescence on the mirror surfaces. The finesse F is calculated by:

$$F = \frac{\text{FSR}}{\text{FWHM}} = \frac{\pi(\sqrt{RV})^{\frac{1}{2}}}{1 - \sqrt{RV}}$$
(2.2)

where FWHM is the linewidth of the instrument function of the FPI. The finesse is related to the frequency resolution of the FPI. From Eq. (2.2), it can be seen that the higher refractivities of the mirrors, the larger finesses and for a certain FSR, the larger finesses, the smaller FWHM, which means a higher frequency resolution. For the frequency resolution, we need it as high as possible which indicates the need of a large finesse and high refractivities of the mirrors. However, the high refractivities of the mirrors will cause a lower in-coupling efficiency. For example, if we choose  $M_{in} = M_{out} = 0.9999$  and dissipative losses 0.5%, the finesses is 1205 while the in-coupling efficiency is 7.5%. For this plano-concave FPI, the reflectivity of  $M_{in}$  and  $M_{out}$  are 99%. The in-coupling lens  $L_{FP}$ , with a confocal length of 75 mm, is put in front of  $M_{in}$  and its focal point is set at the rear surface of  $M_{in}$ . Therefore, the collimated scattered light can be mode–matched to couple into the FPI.



#### 2.2. Rayleigh-Brillouin scattering setup with 532 nm

Figure 2.7: The design and operation of the plano-concave Fabry-Perot interferometer.

For the analysis of RB-spectral profiles two characteristics of the FPI are decisive: the free spectral range and instrument function.

Free spectral range (FSR). The RB-scattering spectra are obtained by scanning the voltage of the FPI. When comparing with the RB-scattering model, the voltage needs to be transformed to frequency based on the FSR. The detailed procedure of FSR measurement will be discussed in section 2.3.

For a plano-plano cavity, the FSR is calculated by:

$$FSR = \frac{c}{2 n L}$$
(2.3)

where c is the speed light in vacuum, n is the refractive index of the material in between mirrors, and L the distance between the mirrors. In the plano-plano FPI, the self interference of light between round trips is 2L. For a plano-concave FPI with the distance between the two mirrors equals to L, the half radius of curvature of the concave mirror, the self interference of light between round trips is 8L, then the effective FSR is four times smaller based on:

$$FSR = \frac{c}{8 \ n \ L} \tag{2.4}$$

This plano-concave FPI can be considered as a confocal FPI with the distance of the two concave mirrors ( $M_{out}$ , image of  $M_{out}$ ) as 2L, as seen in Fig. 2.7. However, if the incident beam is spatially coherent, like the laser beam, there will be additional interferences between different light rays in the confocal cavity. As example, after two reflections, the ray indicated in red arrow in Fig. 2.7 will follow the same path as the ray indicated in black arrow,

#### 2. Experimental Setup and Procedures



Figure 2.8: The spectrum of the transmitted reference laser beam measured by a piezo-scan.

and interference can occur. This phenomenon effectively enlarges the FSR of the confocal FPI by a factor of 2. In addition, if the incident beam is extremely paraxial, the plano-concave FPI almost works as a plano-plano FPI, the FPI transmission pattern shows that the major fringes with separations of  $c/2nL \approx 12$  GHz corresponding to the paraxial alignment of the reference beam as shown in Fig. 2.8 and between two adjacent major fringes there are four modes, spaced by  $\sim 3$  GHz. The central mode between two adjacent major fringes is caused by the wave-vector mismatch of the additional interferences in the plano-concave FPI, and the other two smaller peaks are due to the incomplete coherence of the reference beam [55]. For incoherent light like RB-scattered light, all four modes produce an effective resonance, as seen in Fig. 2.12. This phenomena of mode-doubling was observed for both the UV-FPI and the green FPI.

An accurate value of the FSR is required for the frequency calibration of the RB-spectral profiles. The FSR can be calibrated by measuring the maxima of the transmission fringes of the FPI, on a photodiode, while scanning the frequency of a tunable laser. Since the frequency of the Verdi-5 cannot be varied, a tunable dye laser was used for this purpose. Note that this laser runs at a wavelength of 580 nm, where the finesse of the FPI is rather low. A measurement of the broad transmission fringes under these conditions, shown in Fig. 2.9, can nevertheless be used for determining the transmission maxima at sufficient accuracy. The accurate calibration of the FSR then depends on the measurement of a large span of frequency markers, following a stepwise procedure (also documented in Table. 2.1).


#### 2.2. Rayleigh-Brillouin scattering setup with 532 nm

Figure 2.9: Transmission fringes of FPI viewed from an oscilloscope. It is measured by a piezo-scan with laser light around 580 nm.

- 1. record two adjacent resonant frequency,  $f_1$  and  $f_2$ , and in all cases the frequencies are determined via a measurement by the wavemeter;
- 2. calculate the difference  $FSR_{21} = f_2 f_1$ ;
- 3. based on FSR<sub>21</sub>, estimate the third resonant frequency  $f'_3$ ,  $f'_3 = f_2 + n_* \text{FSR}_{21}$ , where  $n_*$  is a positive integer;
- 4. change the laser frequency, record the resonant frequency  $f_3$  which is around  $f'_3$  and the difference of  $f_3$  and  $f'_3$  should be only a small fraction of 1 FSR;
- 5. calculate the average value  $FSR_{32} = (f_3 f_2)/n_*$ ;
- 6. repeat the Steps 3 5 and change the value of  $n_*$  to  $n_*^2$ ,  $n_*^3$ ,  $n_*^4$ ...;
- 7. finally record the resonant frequency  $f_i$ , the average value is  $\text{FSR}_{ii-1} = (f_i f_{i-1})/n_*^{i-2}$  which is the final value of the FSR. *i* is the number of repeating steps.

The accuracy of the FSR depends on the number of transmission fringes  $n_*$ and number of steps *i*. In our experiment, we chose  $n_* = 4$  and *i* could reach to 7, which means the distance between the last two resonant frequencies is 1024 FSR, giving finally value of the FSR = 2.9964 GHz with an uncertainty less than 1 MHz.

#### 2. Experimental Setup and Procedures

**Table 2.1:** The procedure of measuring the FSR. The  $f_i$  is the *i*th recorded resonance frequency,  $f'_i$  is the *i*th estimated resonance frequency based on the  $f_{i-1}$  and the mean value between  $f_{i-2}$  and  $f_{i-1}$ ,  $n_*$  is a positive integer.

measured	$f_1$	$f_2$		$f_3$		$f_4$		 $f_{i-1}$	$f_i$	
mean			$f_2 - f_1$		$(f_3 - f_2)/n_*$		$(f_4 - f_3)/n_*^2$			$(f_i - f_{i-1})/n_*^{i-2}$
estimated				$f'_3$		$f'_4$			$f'_i$	



Figure 2.10: The averaged spectrum of the transmitted reference laser beam and Airy function fitting.

function. Instrument The scattered light is broadened  $\mathbf{b}\mathbf{v}$ the interferometer instrument function after it transmits from the FPI and the measured spectrum can be considered as the convolution of the spectrum of the scattered light and the interferometer instrument function [56]. Therefore, to obtain the actual line shape of the scattered light and compare with RB-scattering models, the instrument function should be known. For this purpose, the reference laser beam is directly transported into the FPI to measure the instrument function. Through scanning the voltage of the piezo the transmitted function can be recorded, see Fig. 2.8. After calibrating the spectrum (from voltage to frequency) and averaging, the instrument linewidth can be fitted by a Airy function (or Lorentzian profile function), as shown in Fig. 2.10. Here, the linewidth is measured as  $\sigma_{\nu_{\text{instr}}} = 58 \pm 3$  MHz (FWHM).

The instrument function is primarily determined by the finesse of the FPI as the laser bandwidth is small (less than 5 MHz). Also light elastically scattered from a needle mounted within the scattering cell is used to measure the instrument function, see Fig. 2.11. This scattered light is supposedly explores the same collecting angle as the RB-scattered light. The instrument function measured by reflection from a needle is in agreement with that by using the reference beam.

#### 2.3. Experimental data processing



Figure 2.11: The spectrum of the reflected light from a needle mounted in the cental of the scattering volume measured by a piezo-scan.

#### 2.3 Experimental data processing

RB-spectroscopic data are collected by scanning the FPI analyzer in a voltage step fashion at integration times of 1 s for each position, and each step usually over 18 MHz. A full spectrum covering a sequence of consecutive RB-peaks and 10,000 data points was obtained in about 3 h. As an example, the RB-scattering spectrum of  $CO_2$  at pressure of 2 bar and temperature of 20 °C is shown in Fig. 2.12. In this figure, the first 300 points are measured while blocking the pump beam. They allow an estimate of the background. This background contains the light from the environment and the thermal noise from the PMT, and it will be first subtracted from the whole spectrum before further processing.

The process of transferring the raw measurement data into an RB-scattering profile with a calibrated frequency axis is divided into the following steps:

- 1. Denoising. If the signal-to-noise ratio of the measured data is too low, denoising needs to be done to make the data more smooth. A moving average filter can be used to reduce the noise. However, this step is only needed in case of a very weak signal.
- 2. Find the approximate center position, in terms of voltage, of each individual RB-spectral feature, as shown in Fig 2.13, the c'\_1, c'\_2, c'\_3....

#### 2. Experimental Setup and Procedures



Figure 2.12: The spectrum of  $CO_2$  at pressure of 2 bar and temperature of 20 °C when scanning the piezo in the FPI with voltage from 0 V to 400 V and interval of 0.04 V.

- Based on the approximate center position, calculate the middle position between each two spectra, as
   d'<sub>1</sub> = (c'<sub>1</sub>+c'<sub>2</sub>)/2, d'<sub>2</sub> = (c'<sub>2</sub>+c'<sub>3</sub>)/2....
- 4. Define all individual RB spectra for ranges  $[d'_1, d'_2]$ ,  $[d'_2, d'_3]$ ..., using one Gaussian function or three Gaussian functions to fit each spectrum to calculate the accurate central position  $c_2, c_3$ ....
- 5. The distance between each two neighbouring peaks is one FSR. Then we <u>obtain:</u>

corresponding frequency (Hz) $0$ FSR $1 \times$ FSR $2 \times$ FSR	

and the relationship between the voltage and the frequencies on an FSR scale can be obtained.

6. Use the voltage-frequency relationship to convert the voltage range  $[d_2, d_3]$ ,  $[d_4, d_5]$ ..., with  $d_2 = (c_2+c_3)/2$ ,  $d_3 = (c_3+c_4)/2$ ..., onto a frequency scale.

7. Set the central frequency of each spectrum to zero, add all the individual RB-spectra and average to obtain the final spectrum.



Figure 2.13: The diagram of RB scattering spectrum with three consecutive peaks.

It is noted that for the piezo the voltage to length conversion is nonlinear and this in turn will also cause a nonlinear voltage to frequency conversion of the FPI, as displayed in Fig. 2.14. The nonlinearity will cause an inaccuracy in the calibration of the frequency scale that spans one FSR. This will always be the case, even for single peak spectra. Then, the above data processing method is not suitable. An improved accuracy is obtained when steps 4 - 7are modified.

4. Define each spectrum over the ranges,  $[d'_1, d'_2]$ ,  $[d'_2, d'_3]$ ..., using three Gaussian functions to fit each spectrum to calculate the central positions  $c_1, c_2, c_3$  ..., the left side position  $a_1, a_2$ ... and the right side positions  $b_1, b_2$ .... When using one Gaussian to fit, positions of the side peaks will not be considered. Based on these values, the modified central positions are calculated:

$$\begin{split} c_{m1} &= ((a_1 + b_1)/2 + c_1)/2, \\ c_{m2} &= ((a_2 + b_2)/2 + c_2)/2, \\ \dots; \\ as well as the modified left peak positions: \\ a_{m2} &= c_{m2} - \frac{((b_3 + b_1)/2 + b_2)/2 - ((a_3 + a_1)/2 + a_2)/2}{2}, \\ a_{m3} &= c_{m3} - \frac{((b_4 + b_2)/2 + b_3)/2 - ((a_4 + a_2)/2 + a_3)/2}{2}, \end{split}$$

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#### 2. Experimental Setup and Procedures



Figure 2.14: The voltage to frequency conversion of the FPI reflecting the nonlinearity of the piezo.

- 5. Calculate the voltage difference of each spectrum with the first spectrum skipped. Then the second spectrum covers  $L_2 = (c_3 c_1)/2$ , the third  $L_3 = (c_4 c_2)/2$  .... After that, obtain the begin and end voltage of each spectrum. For the second spectrum:  $d_{begin2} = c_{m2} - L_2/2$ ,  $d_{end2} = c_{m2} + L_2/2$ , for the third spectrum:  $d_{begin3} = c_{m3} - L_3/2$ ,  $d_{end3} = c_{m3} + L_3/2$ , .... The range of each spectrum can then be set to  $\alpha_2 \rightarrow d_{begin2} : (d_{end2} - d_{begin2})/N : d_{end2}$ ,  $\alpha_3 \rightarrow d_{begin3} : (d_{end3} - d_{begin3})/N : d_{end3}$ , ..., and all corresponding frequencies are -FSR/2 : FSR/N : FSR/2, where N is an integer.
- 6. The corresponding voltage-voltage relation between the fitting part (here

named old area) and the modified part (here named new area) is:

 $\{d_{begin2}, a_2, c_2, b_2, d_{end2}\} \leftrightarrow \{d_{begin2}, a_{m2}, c_{m2}, b_{m2}, d_{end2}\},\$ 

 $\{d_{begin3}, a_3, c_3, b_3, d_{end3}\} \leftrightarrow \{d_{begin3}, a_{m3}, c_{m3}, b_{m3}, d_{end3}\}...$ 

If we say the ranges  $\alpha_2$ ,  $\alpha_3$ ... as shown in step 5, belong to the new area, then their corresponding ranges of old area  $\beta_2$ ,  $\beta_3$ ... can be obtained by using spline interpolation method based on these corresponding voltage-voltage relations,  $\alpha_i$  and  $\beta_i$  have the same number of data points. Now, we have original voltage points and their corresponding intensity of each spectrum as well as the corresponding range  $\beta_i$ . Through linear interpolation, the intensity of  $\beta_2$ ,  $\beta_3$ ... can be obtained as I<sub>2</sub>, I<sub>3</sub>..., and these intensity is corresponding to the frequencies -FSR/2 : FSR/N : FSR/2.

7. Add intensity  $I_2$ ,  $I_3$ ... and average to get the final spectrum.

This modification method can reduce the spectral dispersion and decrease the standard deviation of intensity of each frequency, making the average final spectrum more accurate. Fig. 2.15 shows a comparison of the results of the two methods with the RB-spectra of Fig. 2.12. It may be concluded that this additional linearization procedure provides an improved RB-scattering profile.



Figure 2.15: Each spectrum of the measured data (blue) and their average (red). (a) using the first method; (b) using the additional linearization method.



## Chapter 3

# Rayleigh-Brillouin scattering in $SF_6$ in the kinetic regime

#### Abstract

Rayleigh-Brillouin spectral profiles are measured with a laser-based scatterometry setup for a 90 degrees scattering angle at a high signal-to-noise ratio (r.m.s. noise below 0.15 % w.r.t. peak intensity) in sulphur-hexafluoride gas for pressures in the range 0.2 - 5 bar and for a wavelength of  $\lambda = 403.0$ nm. The high quality data are compared to a number of light scattering models in order to address the effects of rotational and vibrational relaxation. While the vibrational relaxation rate is so slow that vibration degrees of freedom remain frozen, rotations relax on time scales comparable to those of the density fluctuations. Therefore, the heat capacity, the thermal conductivity and the bulk viscosity are all frequency-dependent transport coefficients. This is relevant for the Tenti-S6 model that depends on the values chosen for these transport coefficients. This is not the case for the other two models considered: a kinetic model based on rough-sphere interactions, and a model based on fluctuating hydrodynamics. The deviations with the experiment are similar between the three different models, except for the hydrodynamic model at pressures  $p \leq 2$  bar. As all models are in line with the ideal gas law, we hypothesize the presence of real gas effects in the measured spectra.

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#### 3.1 Introduction

Quasi-elastic light scattering is a powerful technique for probing collisional dynamics and relaxation phenomena in gases and liquids. Its theory is based in the description of light in terms of electromagnetism by Lord Rayleigh [2], and the scattering process can be explained in terms of fluctuations, either of density or of entropy. Brillouin [5] and Mandelstam [4] explained that collisions of the gaseous particles inducing acoustic modes in the medium will affect the line shape of the scattering spectral profile. Rayleigh-Brillouin (RB) scattering in various gases has been studied since the 1960s [16, 57–60] using the method of spontaneous RB-scattering, which will be followed in the present study. Later, alternative methods were developed, such as stimulated gain Brillouin scattering [61], laser-induced gratings [62], coherent RB-scattering [63, 64] and superheterodyne optical beating Brillouin spectroscopy [65, 66].

At low densities the spectral profile reflects the Maxwellian velocity distribution of the gas particles. At larger pressures density fluctuations also involve collective particle motion: sound. The key parameter is the ratio y of the scattered light wavelength over the mean free path  $l_{\rm mfp}$  between collisions. More precisely, the uniformity parameter y is defined in terms of the scattered light wavenumber q as  $y = 1/q l_{\rm mfp}$ , and taking for the mean free path the kinetic approximation  $l_{\rm mfp} = v_{\rm th} \eta_s / p$ , with the thermal velocity  $v_{\rm th} = (2k_{\rm B}T/m)^{1/2}$ ,  $\eta_s$  the shear viscosity, p the pressure, and m the molecular mass. The length of the scattering wave vector is

$$q = \frac{4\pi \ n}{\lambda} \ \sin(\theta/2),$$

with  $\lambda$  the wavelength in vacuum, n the refractive index, and  $\theta$  the scattering angle. At large values of y, the density fluctuations are described by the equations of the continuum regime, the Navier-Stokes equations. At intermediate values of  $y, y = \mathcal{O}(1)$ , where the mean free path between collisions is comparable to 1/q, light scattering is in the kinetic regime, and density fluctuations must be described by the Boltzmann equation. Therefore, whether a kinetic or a hydrodynamic approach is needed to explain the scattered light spectrum, not only depends on the density of the gas, but also on the scattered light wavelength, and thus on the scattering geometry.

Light scattering not only depends on the translational modes of motion of a gas, but also on internal degrees of freedom: rotations and vibrations. Each mode of motion has its own relaxation rate. These relaxation frequencies must be compared to a typical frequency of the density fluctuations: the frequency  $f_s$  of sound with wavelength equal to the scattered wavelength,  $f_s = c_s q/2\pi$ , with  $c_s$  the speed of sound. When  $f_s$  is much larger than the relaxation rate of internal degrees of freedom, internal motion remains frozen on the timescale of the density fluctuations, and only translational degrees of freedom remain. Most light scattering experiments involve translations and rotations only, unlike experiments at ultrasound frequencies, where molecular vibrations may come into play.

A kinetic model of scattered light spectra needs information about the collision properties of the gas molecules, which enters the collision integral in the Boltzmann equation. Such information may be based on explicit molecular interaction parameters. In one of the kinetic models discussed in this paper, collisions are between hard rough spheres that can spin, and thus have internal energy. These collisions are parameterized by the hard-sphere radius and the moment of inertia of the spheres. The roughness allows for the exchange between translational and rotational energy.

On the other hand for the well-known Tenti model [14, 15], the collision integral is approximated using the known values of the transport coefficients of a gas. Of these transport coefficients, the heat capacity, the heat conductivity and the bulk viscosity depend on the relaxation of internal degrees of freedom.

If transport coefficients are taken as the input of line shape models, it is important to know if the values used should or should not allow for the relaxation of internal degrees of motion. For example, the bulk viscosity of CO<sub>2</sub> used in light scattering with frequencies  $f_s = \mathcal{O}(10^9)$  Hz is three orders of magnitude smaller than the one measured at ultrasound frequencies [67, 68]. The reason is that the vibrational relaxation time  $\tau_{\rm vib} = 6 \times 10^{-6}$  s (for a pressure of 1 bar and scaling with  $\propto 1/p$ ) is comparable to the period of ultrasound, but slow compared to  $1/f_s$ .

Line shape models that take the transport coefficients of macroscopic gas dynamics as input are attractive because they can be used to measure these transport coefficients at very large frequencies by comparing measured scattered light spectra to models. In this manner we have recently studied Spontaneous Rayleigh-Brillouin scattering-profiles of N<sub>2</sub> [69] and CO<sub>2</sub> [68], while it was also used to describe RB-scattering in air, where air was treated as a mono-molecular species [46, 70]. In the same fashion, the bulk viscosity of several polar and non-polar polyatomic gases was studied using Coherent Rayleigh-Brillouin scattering [71]. The bulk viscosity is an effective parameter that quantifies the relaxation of internal degrees of motion in collisions of molecules. Clearly, the bulk viscosity is frequency dependent, and this dependency could be measured as a function of frequency in experiments where light is scattered at different angles.

In this paper we present measurements of Rayleigh scattering involving sulphur hexafluoride (SF<sub>6</sub>) molecules. For SF<sub>6</sub> the vibrational relaxation time is  $\tau_{\rm vib} = 2.22 \times 10^{-7}$  s, while the rotational relaxation time is  $\tau_{\rm rot} = 6 \times 10^{-10}$  s (both values defined for pressures of 1 bar) [72]. In our scattering geometry, the typical Doppler and Brillouin shifts are  $f_{\rm s} = \mathcal{O}(10^9 \text{ Hz})$  so that the time scale

#### 3. Rayleigh-Brillouin scattering in $SF_6$ in the kinetic regime

of measured density fluctuations is approximately two orders of magnitude larger than  $\tau_{\rm vib}$ , but it is of the same order as  $\tau_{\rm rot}$ . Therefore, vibrational modes of motion can be ignored, and the high-frequency values of the transport coefficients should be chosen. In addition, rotational relaxation may only be partial at the sound frequencies in our experiment.

In this particular case, models that do not depend explicitly on values of the transport coefficients may perform better. In this paper we will compare two such models to measured SF<sub>6</sub> spectra. Marques Jr [17] has designed a kinetic theory based on a rough-sphere interaction model between rotations and translations. As parameters it takes the moment of inertia of the molecule and the momentum relaxation rate  $\sigma = \eta_s/p$ , with  $\eta_s$  the shear viscosity and p the pressure. It replaces the linearized collision operator with a simple relaxation term  $\propto \sigma(f - f_r)$ , where the reference distribution function  $f_r$  is designed such that collisional transfers of momentum and energy agree with those of the full Boltzmann collision operator. The SF<sub>6</sub> molecule is ideally suited for application of this model as it is nearly spherically symmetric, while with frozen vibrations its heat capacity ratio  $c_p/c_v$  is close to 4/3,  $c_p$  is the heat capacity at constant pressure and  $c_v$  is the heat capacity at constant volume.

The other theory by Hammond and Wiggins [16] is based on fluctuating hydrodynamics, explicitly involves rotational (and vibrational) relaxation, and takes measured relaxation rates,  $\tau_{\rm vib}^{-1}$  and  $\tau_{\rm rot}^{-1}$  and as input. In order to accommodate more rarified gases, Burnett terms are added to the continuum equations [16], but the applicability is still restricted to values of the uniformity parameter  $y \gtrsim 1$ . However, for light scattering off a CH<sub>4</sub> gas at y = 2.70, the two models, one kinetic, and the other one hydrodynamic, are hardly distinguishable [17].

The importance of the frequency dependence of the transport coefficients in explaining light scattering spectra of SF<sub>6</sub> was already recognized by Clark et al. [9], who compares experiments at 2 < y < 55 with continuum models. Lao et al. [58] propose to change rotational specific heats from their zero-frequency value  $c_{\rm rot}$  to  $c_{\rm rot}/(1 + 2\pi i f_{\rm s} \tau_{\rm rot})$ , which results in a frequency dependence of the thermal conductivity  $\lambda_t$  through Eucken's formula. Weinberg et al. [73] propose transport coefficients which not only depend on frequency, but also on the wavenumber of sound. In general, if the product  $2\pi f_s \tau$  is much larger than 1, the internal degrees of freedom, while relaxing on a time scale  $\tau$ , do not partake in light scattering. For vibrations of SF<sub>6</sub>  $2\pi f_s \tau_{\rm vib} \approx 10^3$ , while for rotations  $2\pi f_s \tau_{\rm rot} \approx 4$ , where we used the sound frequency  $f_s = 10^9$  Hz.

Using a recently constructed sensitive light scattering setup [52] with operates at 403 nm and a 90° scattering angle we will revisit Clark's experiments, but with a very high signal-to-noise ratio. Much as in Clark et al. [9] we will address the frequency dependence of transport coefficients, but now in the context of both kinetic and hydrodynamic models: (a) a well-known

kinetic model [14, 15] which takes transport coefficients as input, (b) a kinetic model which takes collision parameters, and (c) a continuum model that uses known relaxation times of the internal degrees of freedom.

#### 3.2 Experimental

Rayleigh-Brillouin scattering profiles of SF<sub>6</sub> gas were measured with a sensitive RB-scattergometry setup described previously [52]. A cell equipped with Brewster windows is placed inside a folded optical cavity to enhance the circulating power effectively used for inducing RB-scattering to 5 Watt. The incident laser wavelength was set to  $\lambda = 403.00$  nm [46] for which a narrowband transmission bandpass filter (Materion, T = 90% at  $\lambda = 403$  nm and  $\Delta \lambda = 1.0$  nm) was available to reject most of the Raman-scattered light. The RB-spectra were recorded by scanning a plano-concave Fabry-Perot interferometer (FPI) by tuning its piezo voltage. The four sub-modes supported in the FPI have a free spectral range of FSR = 7.498 GHz, which was calibrated independently by scanning the laser over some 20 full modes of the FPI with mirror spacings of 5 mm. The instrument linewidth was measured by imposing a reference laser beam to the FPI yielding  $\sigma_{\nu_{instr}} = 126.7 \pm 3.0$  MHz (FWHM).

An important parameter for comparing the measured RB-profiles with theory is that of the scattering angle  $\theta$ . A first determination is obtained by measurements on the geometrical lay-out of the setup, where narrow pinholes are used to determine beam paths (see Fig. 1 in [52]). Subsequently a test RB-scattering measurement was performed for 1 bar of argon. Analysis of the spectrum, on the basis of a Tenti code adapted for argon (including the macroscopic transport coefficients, while neglecting an effect of a bulk viscosity) yielded a value of the scattering angle  $\theta = 89.6 \pm 0.29$  degrees. While care was taken to not rearrange the alignment of the setup, this value is used throughout the present study for measuring an analyzing the spectral profiles for SF<sub>6</sub>.

RB-spectroscopic data were collected by scanning the FPI analyzer in a stepwise fashion at integration times of 1 s for each position. A full spectrum covering typically 40 RB-peaks in 10,000 data points was obtained in some 3 hrs. The scanning axis was linearized and converted into a frequency scale by computerized interpolation and matching to the FSR value. Finally the consecutive RB-peaks were overlaid and added to an averaged RB-spectrum, following procedures as discussed by Gu et al. [52].

The data collection rate of 7,000 counts/sec leads to a noise-to-background ratio of 0.15% (w.r.t. peak height) for a typical spectrum recorded at 1 bar. All experiments were conducted at room temperature. Eight measurements (I to VIII) were performed in a sequence of pressures ranging from 0.2 to 5 bar for which conditions and gas transport coefficients listed in Table 3.1.

**Table 3.1:** Values for pressure (p) and temperature (T) for the eight different measurements of RB-scattering in SF<sub>6</sub>. In the last column the calculated non-uniformity parameter y is given. Other relevant parameters of the present study are the scattering wavelength  $\lambda = 403.00$  nm and the scattering angle  $\theta = 89.6^{\circ}$ .

Data	p (bar)	T (°C)	y-parameter
Ι	0.215	25.59	0.35
II	0.500	23.36	0.82
III	0.754	24.66	1.22
IV	1.002	23.36	1.64
V	2.002	23.36	3.26
VI	3.002	23.87	4.88
VII	4.000	23.87	6.49
VIII	5.017	23.36	8.14

#### 3.3 Results

The experimental results are shown in Figs. 3.1 and 3.2 for the eight different experimental pressure conditions as listed in Table 3.1. Due to the larger RB-scattering signals at higher gas pressures, some form of normalization must be invoked for a consistent comparison between experiment and model spectra. For this normalization a scale of equal integrated intensity  $I_{\rm int}$  over the spectral profile was chosen. As a result the different peak intensities in the eight experimental spectra, as displayed in the top rows of Figs. 3.1 and 3.2 reflect the unity integration over the spectral profile. The scaling implies that the large pressure dependence of the RB-scattering of  $SF_6$  [13] is divided out from the experimental data. A comparison is made with the results of various models, which will be detailed below. For this purpose residuals are determined between experimental intensities  $I_e(f_i)$  and modelled spectral intensities  $I_m(f_i)$ , and these are plotted on the same scale of equal integrated intensity in the second, third and fourth rows in Figs. 3.1 and 3.2. We note that we compare in the present study the experimental data with physics-based models, not relying on ad hoc mathematical functional formulas [74, 75], to describe the scattering profiles.

As a final figure of merit for the comparison between experiment and the models a summed and normalized root-mean-square deviation is quantified for the spectral profile:

$$\Sigma_{\rm nRMS} = \frac{\sqrt{\frac{1}{N} \sum_{i=1}^{N} [I_e(f_i) - I_m(f_i)]^2}}{I_{\rm int}}$$
(3.1)

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3.3. Results



Figure 3.1: Data on RB-scattering in SF<sub>6</sub>, measured under pressure and temperature conditions as listed in Table 3.1, indicated by corresponding Roman numerals I-IV, and at  $\lambda = 403.00$  nm and  $\theta = 89.6^{\circ}$ . Top-line: experimental data on a scale of normalized integrated intensity. Second line: deviations of the Tenti-S6 model description including a frequency dependence of the thermal conductivity and the bulk viscosity  $\eta_{\rm b}$  determined from a least-squares fit. Third line: deviations from a rough-spheres model (with  $\kappa = 0.227$ ). In the fourth row, the deviations from the extended hydrodynamic model by Hammond and Wiggins [16] are plotted. Residuals are plotted on a scale of normalized integrated intensity for each profile.

which is again normalized to the integrated area of the spectral profile. Results of such comparisons are displayed in Fig. 3.3 for the eight different pressure and y-parameter conditions and the three models discussed below.

#### 3.3.1 Comparison with the Tenti-S6 model

All models need a value of the shear viscosity, for which we took  $\eta_{\rm s} = 1.52 \times 10^{-5} \,\rm kgm^{-1}s^{-1}$  [76, 77]. For all models we also assumed that vibrations do not partake in the exchange of translational and internal degrees of freedom, and that the molecules are spherically symmetric, so that the heat capacity of internal motion is  $c_{\rm int} = 3/2$ .

In addition, the Tenti-S6 model needs two possibly frequency-dependent transport coefficients as input: the thermal conductivity  $\lambda_{\rm th}$  and the bulk viscosity  $\eta_{\rm b}$ . The zero-frequency value is  $\lambda_{\rm th} = 1.30 \times 10^{-2} \ {\rm Wm^{-1}K^{-1}}$  [78], but at the GHz frequencies of this light scattering experiment the value should





**Figure 3.2:** Continued from Fig. 3.1 for data sets V-VIII for pressures in the range 2-5 bar. The expression of all the rows are the same as Fig. 3.1 (Experimental spectra, Tenti-S6 model with frequency dependent gas coefficients, rough-sphere model, and the extended hydrodynamic model).

be smaller as vibrational degrees of freedom remain frozen. At these frequencies we estimate the reduction of  $\lambda_{\rm th}$  using Eucken's formula [50]

$$\lambda_{\rm th} = \frac{5}{2} \eta_s c_{\rm t} / m + \rho D (c_{\rm vib} + c_{\rm rot}) / m, \qquad (3.2)$$

where the heat capacities of translations and vibrations are  $c_{\rm t} = c_{\rm rot} = \frac{3}{2}k_{\rm B}$ , and the mass diffusion coefficient is  $\rho D = 20.21 \times 10^{-6} \,\rm kgm^{-1}s^{-1}$ , with  $\rho$ the mass density [79]. The heat capacity of vibrations  $c_{\rm vib} = 7.66 \,\rm k_B$  follows from the heat capacity at room temperature  $c_{\rm p} = 0.664 \,\rm Jg^{-1}K^{-1}$  [80], which contains both a rotational and vibrational contribution. The zero-frequency value of  $\lambda_{\rm th}$  is then reduced by the factor  $(\frac{5}{2}\eta_{\rm s}c_{\rm t} + \rho Dc_{\rm rot})/(\frac{5}{2}\eta_{\rm s}c_{\rm t} + \rho D(c_{\rm vib} + c_{\rm rot}))$ , with the result  $\lambda_{\rm th} = 4.72 \times 10^{-3} \,\rm Wm^{-1}K^{-1}$ . In view of the approximate character of Eucken's formula, we ignore a slight pressure dependence of  $\lambda_{\rm th}$ [78].

The kinetic gas model parameters were implemented in a RB-scattering code for calculating the spectral profiles within a framework of the Tenti-S6 model and based on the code by Pan [47]. In the program the bulk viscosity  $\eta_{\rm b} = 1.6 \times 10^{-5} \,\mathrm{kg} \,\mathrm{m}^{-1} \mathrm{s}^{-1}$  was determined in a least squares procedure using the p = 5 bar data. This value for the bulk viscosity was used in the description

of spectral profiles at lower pressures as well. Following a similar procedure as in Vieitez et al. [81], where a value of  $\eta_{\rm b} = 3.5 \times 10^{-5} \,\mathrm{kg} \,\mathrm{m}^{-1} \mathrm{s}^{-1}$  was derived. We attribute the changed value to an improved instrument resolution, with respect to the SF<sub>6</sub> measurements in previous experiments [81]. The bulk viscosity  $\eta_{\rm b} = 1.6 \times 10^{-5} \,\mathrm{kg} \,\mathrm{m}^{-1} \mathrm{s}^{-1}$  is 300 times smaller than that at low frequencies [82].

The calculated spectral profiles, obtained with the RB-scattering code for the Tenti-S6 model implementing frequency-dependent transport coefficients and  $\eta_{\rm b} = 1.6 \times 10^{-5} \,\mathrm{kg} \,\mathrm{m}^{-1} \mathrm{s}^{-1}$  are convolved with the instrument width and compared with the experimental profiles measured for eight different pressures. Residuals of such comparison are displayed in Figs. 3.1 and 3.2.

#### 3.3.2 Comparison with the rough-sphere model

Apart from the momentum relaxation rate  $\sigma = \eta_s/p$ , the rough-sphere model needs one additional parameter, the dimensionless moment of inertia  $\kappa$  of the SF<sub>6</sub> molecule,  $\kappa = 4I/md^2$ , where m, I, and d are the mass, moment of inertia and the effective diameter of the molecule. The rough-sphere model assumes that the spherical surfaces of two colliding molecules have no relative tangential velocity during a collision. This leads to a solvable model for the interaction between translational and rotational motion of the molecules [50]. The moment of inertia I can be assessed directly via spectroscopic investigation of the rotational level structure of SF<sub>6</sub> [83], or via a direct measurement of the bond length  $R_{SF}$  via X-ray diffraction [84, 85], both yielding a value of  $R_{SF} =$ 1.561 Å. Via  $I = 4M_S R_{SF}^2$  this corresponds to a value of  $I = 3.088 \times 10^{-45}$  kg m<sup>2</sup> for the moment of inertia for the SF<sub>6</sub> molecule.

It should be realized that the effective diameter of the SF<sub>6</sub> molecule is not simply  $2R_{SF}$  but has a value d which can be determined via experiments on gases. In experiments measuring the viscosity a value of d = 4.73 Å was determined [86], which then results in a value of  $\kappa = 0.227$ . Using the rough-sphere relation between shear- and bulk viscosity,  $\eta_b = \eta_s (6 + 13\kappa)/60\kappa$  [50], a value of the bulk viscosity results:  $\eta_b = 1.00 \times 10^{-5}$  kg m<sup>-1</sup>s<sup>-1</sup>. Alternatively, experiments on molecular sieves and zeolites [87, 88] a slightly larger value for the effective diameter of SF<sub>6</sub> molecules was determined, d =4.90 Å, yielding a value of  $\kappa = 0.211$  and  $\eta_b = 1.05 \times 10^{-5}$  kg m<sup>-1</sup>s<sup>-1</sup>. The effect of this difference in effective diameter, resulting in a slightly higher value for the bulk viscosity, was quantified in a model calculation. It results only in a 0.15% difference in peak intensity of the spectral profile, which is negligible.

The formalism used for transforming the rough-sphere model into a RB-scattering spectrum has been described by Marques [17]. Again, the calculated profile was convolved with the instrument function and compared

with the experimental data in Figs. 3.1 and 3.2, with the normalized root-mean-square deviations of the comparisons presented in Fig. 3.3.

#### 3.3.3 Comparison with the hydrodynamic model

Finally, for the hydrodynamic model by Hammond and Wiggins [16] we ignored vibrations, used the rotational relaxation time at p = 1 bar,  $\tau_{\rm rot} = 6 \times 10^{-10}$  s, and mass diffusion coefficient  $\rho D = 20.21 \times 10^{-6} \,\rm kgm^{-1}s^{-1}$  [79]. The diffusion of rotational energy  $D_{\rm rot}$  was assumed equal to D. The bulk viscosity derived from the rotational relaxation time is  $\eta_{\rm b} = 1.00 \times 10^{-5} \,\rm kg \,m^{-1}s^{-1}$  [50], while Eucken's relation leads to a thermal conductivity for translational degrees of freedom  $\lambda_{\rm th \ tr} = 3.25 \times 10^{-3} \,\rm Wm^{-1}K^{-1}$ .

The hydrodynamic model used is the one described by Hammond and Wiggins [16] involving a five-dimensional linear system. It distinguishes kinetic and rotational temperatures, with the associated heat flows. Therefore, it is consistent with a frequency-dependent heat conductivity [16]. This hydrodynamic model evaluates an equation

$$\partial \psi(k_{sc}, t) / \partial t = -M(k_{sc})\psi(k_{sc}, t) \tag{3.3}$$

where  $\psi(k_{sc}, t)$  spans a 5-component vector with as dimensionless elements the Fourier spatial transforms of the fluctuations of mass density  $\bar{\rho}/\rho_0$ , translational temperature  $\bar{T}/T_0$ , momentum or velocity density  $\bar{v}/v_0$ , vibrational temperature  $\bar{T}_{vib}/T_0$ , and rotational temperature  $\bar{T}_{rot}/T_0$ . The 5×5 coefficient matrix  $M(k_{sc})$  involves functions of the transport coefficients [16]. The spectrum of the scattered light is then computed via

$$S(k_{sc},\omega) = \operatorname{Re}[(sI + M(k_{sc}))_{11}^{-1}|_{s=i\omega}]$$
(3.4)

evaluating the real part of the (1,1) matrix element of  $\psi(k_{sc}, s)$ , which is the Laplacian of  $\psi(k_{sc}, t)$ . Hence the scattering profile is derived from the density fluctuations in the medium. Via this procedure a model spectrum is calculated, which is then convolved with the instrument width and compared with the experimental spectra in Figs. 3.1 and 3.2.

#### **3.3.4** Difference between experiment and models

The normalized root-mean-square differences  $\Sigma_{nRMS}$  between experiment and the three models introduced and discussed in the above is summarized in Fig. 3.3. At low pressures, corresponding to  $y \leq 3$ , the hydrodynamic model, understandably, fails. Otherwise the residues of all models with the experiments are very similar: within the experimental accuracy it is impossible



Figure 3.3: Normalized root-mean square deviations  $\Sigma_{nRMS}$  as obtained from comparison between experimental spectra and the various line shape models (Tenti-S6, the rough-sphere model, and the extended hydrodynamic model), with data points as indicated in the legend. Along the top axis the dimensionless uniformity parameter y is plotted.

to decide in favor for one of the models. This is remarkable as the various models are based on very different physical principles.

However, all models considered share the assumption of  $SF_6$  as an ideal gas. It is well known that scattered light spectra are sensitive to real gas effects, i.e. to the deviation from ideal gas law behaviour. The two kinetic models considered in this paper are derived from the linearized Boltzmann equation, which is consistent with the ideal gas law [60]. Similarly, the hydrodynamic model assumes the ideal gas law. We believe that the residual spectra of Figs. 3.1 and 3.2 whose amplitudes increase with increasing pressure, point to real gas effects.

#### 3.4 Conclusion

Light scattering opens a new window on the properties of SF<sub>6</sub> gas, as relaxation phenomena involve rotational degrees of freedom only, while acoustic measurements are dominated by vibrational relaxation. Consequently, the values of the bulk viscosity that we find  $\eta_{\rm b} = (1.0 - 1.6) \times 10^{-5} \,\mathrm{kg \, m^{-1} s^{-1}}$ are 300 times smaller than those at low frequencies [82]. All three models investigated here to describe the Rayleigh-Brillouin line shape, indicate that the three rotational modes are involved in light scattering.

#### 3. Rayleigh-Brillouin scattering in ${\rm SF}_6$ in the kinetic regime

A surprising finding is the small but significant residues that for  $y \gtrsim 3$  are very similar for the three models considered. As the two kinetic models and the hydrodynamic model all assume that SF<sub>6</sub> is an ideal gas, we hypothesize that the deficiency of all models points to real gas effects.

## Chapter 4

# Rayleigh-Brillouin light scattering spectroscopy of nitrous oxide $(N_2O)$

#### Abstract

High signal-to-noise and high-resolution light scattering spectra are measured for nitrous oxide  $(N_2O)$  gas at an incident wavelength of 403.00 nm, at 90° scattering, at room temperature and at gas pressures in the range 0.5 - 4bar. The resulting Rayleigh-Brillouin light scattering spectra are compared to a number of models describing in an approximate manner the collisional dynamics and energy transfer in this gaseous medium of this polyatomic molecular species. The Tenti-S6 model, based on macroscopic gas transport coefficients, reproduces the scattering profiles in the entire pressure range at less than 2% deviation at a similar level as does the alternative kinetic Grad's six-moment model, which is based on the internal collisional relaxation as a decisive parameter. A hydrodynamic model fails to reproduce experimental spectra for the low pressures of 0.5-1 bar, but yields very good agreement (< 1%) in the pressure range 2 - 4 bar. While these three models have a different physical basis the internal molecular relaxation derived can for all three be described in terms of a bulk viscosity of  $\eta_{\rm b} \sim (6 \pm 2) \times 10^{-5}$ Pas. A 'rough-sphere' model, previously shown to be effective to describe light scattering in  $SF_6$  gas, is not found to be suitable, likely in view of the non-sphericity and asymmetry of the N-N-O structured linear polyatomic molecule.

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#### 4.1 Introduction

Spontaneous Rayleigh and Brillouin scattering arises from fluctuations in the dielectric constant of gases and its spectral profiles have been studied since the early  $20^{th}$  century [2, 4, 5]. The density fluctuations associated with molecular thermal motion takes the form of entropy fluctuations at constant pressure causing a central elastic Rayleigh scattering peak. Pressure fluctuations in the form of acoustic waves, at constant entropy, cause inelastic side-peaks referred to as Brillouin scattering [35]. In the decade after the invention of the laser numerous studies have been performed measuring the spectral profile of Rayleigh-Brillouin (RB) scattering with the goal to derive collisional properties of gaseous media [57–60]. More recently the field of RB-scattering has been revived with the goal to monitor gas flow and the conditions of the Earth's atmosphere [22, 46, 89, 90]. Independently, in addition to conventional spontaneous RB-scattering, methods of coherent RB-scattering have been developed for the investigation of collisional phenomena in gases [64, 71, 91, 92].

Typically, at different gas densities, the spectral lineshape of the scattered light intensity will be different, thereby reflecting the collisional phenomena occurring in the gas. A key scaling parameter is the uniformity parameter y, which compares the reciprocal of the scattering wave vector q to the mean free path between collisions  $l_{\rm mfp}$ , hence  $y = 1/q l_{\rm mfp}$ . When y becomes large with respect to unity, such as for dense gases, the effect of acoustic modes will become apparent as side peaks in the spectra profile. The frequency shift of these Brillouin side features is  $f_s = v_s q/2\pi$ , with  $v_s$  the speed of a sound wave in the dense gas. The density fluctuations in this hydrodynamic regime can be described by the Navier-Stokes equation. The broadening effects are homogeneous and the central and both Stokes peaks adopt a Lorentzian functional form. In the opposite case, of the Knudsen regime for values  $y \ll 1$ , the spectral line shape adopts the character of a pure Gaussian, as a result of the inhomogeneous effect of molecular random thermal motion, or the Doppler effect. In the intermediary or kinetic regime, as  $y \approx 1$ , the analysis is most difficult and the spectral scattering line shape can be derived by solving the Boltzmann equation, for which approximate methods must be employed.

The Tenti-S6 model, proposed in the 1970s [14, 15], is such a model which has become a standard approach for Rayleigh-Brillouin scattering in the kinetic regime. In this model, the collision integral of Boltzmann equation is replaced by seven or six matrix elements, which can be expressed in terms of the macroscopic transport coefficients, pressure p, temperature T, shear viscosity  $\eta_{\rm s}$ , thermal conductivity  $\lambda_{\rm th}$ , bulk viscosity  $\eta_{\rm b}$  and the internal molar heat capacity  $C_{\rm int}$ . An alternative kinetic approach deals with the Boltzmann equation in replacing the collision operator with a single relaxation-time term [19]. This model builds on the Chapman-Enskog model for solving the Boltzmann equation [50] and the Grad's six-moment approximation is employed for calculating the light scattering spectral function [49].

As a third approach, the model by Hammond and Wiggins [16] based on hydrodynamics involves the vibrational and rotational relaxation,  $\tau_{\rm vib}$  and  $\tau_{\rm rot}$ , as signatures of non-ideal gas effects. The Burnett correction is also added to the Navier-Stokes equation to approximately extend it to the rarified regime [93]. This model is valid in the higher pressure regime where the a gaseous medium can be envisioned as a fluid continuum. As was indeed shown [16, 94] the Hammond-Wiggins model has an extended application in the realm toward lower pressures, thus forming a bridge between the full hydrodynamic and kinetic regimes.

A rough-sphere model, proposed by Marques [17], was recently applied to describe the RB-light scattering spectra in SF<sub>6</sub> gas [94], in which the molecules exhibit the structure of a regular octahedron with a sulfur atom in the center and six fluorine atoms at vertexes, hence taking the form of a spherical molecule. In such model a dimensionless moment of inertia  $\kappa$  is an important and uniquely adjustable parameter.

In the present study the Rayleigh Brillouin scattering profile of nitrous oxide, or dinitrogen monoxide ( $N_2O$ ), is investigated experimentally and results are compared to profiles calculated from the four models mentioned. Here, the  $N_2O$  molecule is chosen as a scattering species, partly in view of its favorable cross section [13]. Goal is to investigate how the various models can describe the spectral profile for RB-scattering off a linear polyatomic molecule, of a shape strongly deviating from sphericity.

#### 4.2 Experiment

RB-scattering from N<sub>2</sub>O gas (Praxair, purity 99.7%) is measured at right angles from a scattering cell with an incident laser beam at  $\lambda = 403.00$  nm. For this, infrared light at 806.00 nm is produced with a Nd:VO<sub>4</sub> laser (Millennia-X) pumping a continuous wave Titanium:Sapphire laser (Coherent-699). Its output is converted to the second harmonic in an external frequency-doubling cavity producing power levels of 400-500 mWatt. The spectral bandwidth of the blue laser beam is ~ 2 MHz, thus negligible for the analyses in the present study.

The scattering cell, equipped with Brewster-angled windows at entrance and exit ports, is placed inside an enhancement cavity in which the blue light beam is amplified by a factor of ten to reach power levels of 4-5 Watt in the scattering volume. During operation both the frequency-doubling and enhancement cavities are locked by Hänsch-Couillaud opto-electronics [95].

#### 4. RB-light scattering spectroscopy of nitrous oxide

Scattered light propagates through a bandpass filter (Materion, T = 90%at  $\lambda = 403$  nm, bandwidth  $\Delta \lambda = 1.0$  nm) onto a Fabry-Perot interferometer (FPI) via an optical projection system consisting of a number of lenses and pinholes to reduce stray light and contributions from Raman scattering. The geometry is such that the opening angle for in-plane scattering is limited to 0.5 degree to not compromise the instrument resolution. Scattered photons are finally collected on a photomultiplier tube. The FPI is half-confocal and has an effective free spectral range (FSR) of 7.498 GHz, which is determined through scanning the laser frequency over more than 80 modes of the FPI while measuring the laser wavelength by a wavelength meter (ATOS). The instrument width is obtained in two different ways yielding a value of  $\sigma_{\nu_{\text{instruct}}}$  $= 126.0 \pm 3.0$  MHz (FWHM). First an auxiliary reference beam from the frequency-doubled laser is propagated through the scattering cell at right angles and through the optical system. Subsequently scattered light obtained from a metal needle placed in the scattering center is measured while scanning the laser frequency or the piezo-actuated FPI. This instrument function is verified to exhibit the functional form of an Airy function which may well be approximated by a Lorentzian function. Further details of the experimental setup and the calibration of the RB-spectrometer haven been described in a technical paper [52].

The scattering angle is an important parameter in RB-scattering since it determines the effective width of the spectral profile through the Doppler condition. From measurements on the geometrical lay-out of the setup, where narrow pinholes determine the beam path, the angle  $\theta$  is precalibrated at  $\theta = 90 \pm 1^{\circ}$ . Calibration measurements on argon gas at 1 bar and comparison with Tenti-S6 model calculations were used to assess a precise value for the scattering angle yielding  $\theta = 89.6 \pm 0.3^{\circ}$  by fitting to the recorded spectral profile. During the measurements on N<sub>2</sub>O the angular alignment of the setup was kept fixed.

RB-scattering spectral profiles were recorded by piezo-scanning the FPI at integration times of 1 s for each step. Typical detection rates were ~ 2000 count/s for conditions of 1 bar pressure. A full spectrum covering 100 consecutive RB-peaks and 10,000 data points was obtained in about 3 h. The piezo-voltage scans were linearized and converted to frequency scale by fitting the RB-peak separations to the calibrated FSR-value. Finally, a collocated spectrum was obtained by cutting and adding all individual recordings over ~ 100 RB-peaks [52]. This procedure yields a noise level of ~ 0.4% (with respect to peak height) for the 1 bar pressure case. Measurements of the RB-scattering profile were performed for conditions of 0.5-4 bar pressure and room temperatures as listed in Table 4.1.

Data set	p(bar)	$T(\mathbf{K})$	y
Ι	0.560	297.81	0.51
II	1.035	296.25	0.95
III	2.074	297.28	1.90
IV	3.052	297.28	2.79
V	4.194	297.28	3.84

**Table 4.1:** Data sets for RB-scattering measurements in  $N_2O$  gas recorded under conditions as indicated. y represents the uniformity parameter.

#### 4.3 Results

The experimental data of the RB-scattering measurements performed on gaseous  $N_2O$  at five different pressures and all at room temperature are displayed in Fig. 4.1. The spectral profiles demonstrate the superior quality of the RB-spectrometer in achieving high signal-to-noise reaching a value of > 100 even at the lowest pressure (0.5 bar) and better at the higher pressures. While the spectral intensities scale with the familiar factor  $(n-1)^2$  in the Rayleigh scattering cross section, with n the index of refraction [13], the profiles are plotted on a normalized scale of unit area. In the following model calculations of the spectral profile are carried out, in the context of (i) the Tenti-S6 model [14, 15], (ii) the Grad's six-moment kinetic model optimizing a single relaxation time constant [19], (iii) a hydrodynamic model as developed in the past for methane gas [16], and (iv) a 'rough-spheres' model as recently developed for poly-atomic molecules [17] and successfully applied to describe RB scattering in  $SF_6$  gas [94]. Before making the comparison of the model data with the experimental data, the results from the theoretical profiles are folded with a Lorentzian of 126 MHz (FWHM) representing the instrument function of the RB spectrometer. The comparison is made by calculating the root mean square error (RMSE) expressed as:

$$R_{\rm rmse} = \frac{\sqrt{\frac{1}{N} \sum_{i=1}^{N} (I_e(i) - I_m(i))}}{\sum_{i=1}^{N} I_e(i)}$$
(4.1)

where  $I_e$  is the intensity of the experimental spectrum,  $I_m$  the intensity of modeled spectra and the sum is taken over N data points. While making the comparison between observed and modeled spectra in several cases one or more physical constants (such as the bulk viscosity parameter  $\eta_b$ ) were included in a fitting routine. In the fitting procedures a background zero level was included to account for slight levels of stray light and dark counts on the detector [52].

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#### 4. RB-light scattering spectroscopy of nitrous oxide



Figure 4.1: Data on RB-scattering in N<sub>2</sub>O, measured at the five different pressures and temperature conditions (indicated by corresponding Roman numerals I to V as listed in Table 4.1) at wavelength of  $\lambda = 403.00$  nm and a scattering angle  $\theta = 89.6^{\circ}$ . Top-row: experimental data on a scale of normalized integrated intensity. Second row: deviations of the Tenti-S6 model description (TS6) as discussed in section 4.3.1. Third row: deviations of the six-moment kinetic model as discussed in section 4.3.2. Fourth row: deviations from the extended hydrodynamic model (HW) [16] as discussed in section 4.3.3. Fifth row: deviations from a 'rough spheres model' (RS) as discussed in section 4.3.4. Residuals are plotted on a scale of normalized integrated intensity for each profile. 56

**Table 4.2:** Values for the bulk viscosity parameters obtained by fitting the experimental spectra to various model calculations where intramolecular relaxation is included as a free parameter, which is then linked to  $\eta_{\rm b}$ . The parameter  $\eta_{\rm b}^T$  is the value obtained by applying the Tenti-S6 model with the bulk viscosity as a single fitting parameter. In the Grad's 6-moment model [19] the relaxation time  $\tau_{\rm int}^{6G}$  is derived as a fitting parameter, and the bulk viscosity  $\eta_{\rm b}^{6G}$  is then derived via Eq. (4.5). In the hydrodynamic model a rotational relaxation time  $\tau_{\rm rot}^H$  is derived from a fit to the data and the bulk viscosity  $\eta_{\rm b}^H$  is derived via Eq. (4.5). Values in brackets represent the uncertainties derived in a fit.

Data set	$\eta_b^T \ (\times 10^{-5} \ \mathrm{Pa} \cdot \mathrm{s})$	$\tau_{int}^{6G} \; (\times 10^{-10} \; \mathrm{s})$	$\eta_{\rm b}^{6G} \; (\times 10^{-5} \; {\rm Pa}{\cdot}{\rm s})$	$\tau_{\rm rot}^{H} \; (\times 10^{-10} \; {\rm s})$	$\eta_{\rm b}^H \ (\times 10^{-5} \ {\rm Pa}{\cdot}{\rm s})$
Ι	1.06(0.24)	6.95(0.18)	0.62(0.02)		
II	2.63(0.37)	2.49(0.15)	0.41(0.02)		
III	6.18(2.06)			17.18(1.39)	5.70(0.46)
IV	5.19(0.57)	15.87(2.92)	7.75(1.43)	13.13(0.66)	6.41(0.32)
V	6.66(0.56)	11.53(1.24)	7.74(0.83)	13.82(0.80)	9.28(0.54)

#### 4.3.1 The Tenti-S6 model

The Tenti-model was developed in the 1970s to describe the RB-scattering profile of diatomic molecules, in particular for molecular hydrogen [14, 15]. Later this model was revived after investigations were performed involving coherent RB-scattering for which RB-scattering codes were developed by Pan [47], Pan et al. [91]. Those codes were applied to describe both coherent RB scattering [81] and spontaneous RB-scattering in  $CO_2$  [68] and in nitrogen, oxygen and air [46]. In those studies it was established that the S6-version of the Tenti model yields a better agreement with experiment than an alternative S7-version.

The Tenti-model invokes molecular properties in terms of macroscopic transport coefficients and thermodynamic properties, which are usually known or can be measured in a variety of experiments. The shear viscosity and thermal conductivity of N<sub>2</sub>O are reported in the literature:  $\eta_s = 1.48 \times 10^{-5}$  Pa·s and  $\lambda_{\rm th} = 17.47 \times 10^{-3}$  W/mK [96]. Alternatively, a value for the thermal conductivity can be estimated by Eucken's formula [50]:

$$\lambda_{\rm th} = \frac{5}{2} \eta_{\rm s} C_{\rm t} / M + \rho D (C_{\rm vib} + C_{\rm rot}) / M \tag{4.2}$$

where  $C_{\rm t}$ ,  $C_{\rm rot}$ , and  $C_{\rm vib}$  are the translational, rotational and vibrational molar heat capacities in units of J/mol·K, respectively, M is the molar mass (M =44.01 g/mol),  $\rho$  is mass density and D is the diffusion coefficient [79, 96]. This leads to a mass diffusion coefficient of  $\rho D = 2.09 \times 10^{-5}$  kg/m·s. If  $C_{vib}$  is set to zero in Eq. (4.2) then a value of  $\lambda_{\rm th} = 14.5 \times 10^{-3}$  W/mK would result,

#### 4. RB-light scattering spectroscopy of nitrous oxide

which is in good agreement with the measured value. This illustrates that indeed vibrational relaxation can be ignored as an effective relaxation process. A measurement of vibrational relaxation yielding  $\tau_{\rm vib} = 0.87 \times 10^{-6}$  s [97] (for a pressure of 1 bar and scaling with  $\propto 1/p$ ) corresponds to a relaxation rate at the MHz level, hence much smaller than the sound frequency, which is at the GHz level. Therefore, here and also below in the other model descriptions, only the rotational relaxation is considered as an internal degree of freedom and the internal molar heat capacity for N<sub>2</sub>O is  $C_{\rm int} = R$ , where R is the universal gas constant.

Here we adopt the procedure to regard the final macroscopic transport coefficient, the bulk viscosity  $\eta_{\rm b}$  as a parameter that can be derived via a least-squares algorithm when comparing the experimental and model spectral profiles. This procedure was followed and documented in studies on the determination of bulk viscosities in N<sub>2</sub> [69], in O<sub>2</sub> and air [69] and in CO<sub>2</sub> [68]. For each data set I-V (Table 4.1)  $\eta_{\rm b}$  is fitted and results are shown in Table 4.2. The deviations between experimental and calculated RB-scattering profiles, for the optimized values of  $\eta_{\rm b}$  for each pressure case, are presented in Fig. 4.1. For the low pressures of p = 0.5 - 1 bar near-perfect agreement is found, while for the higher pressures of p = 2 - 4 bar still very good agreement is found from the Tenti-S6 model with deviations being smaller than 3%.

It is found that in this application of the Tenti-S6 model the value of  $\eta_{\rm b}$  appears to be pressure dependent (see Table 4.2). For the data recorded for p = 0.5 and p = 1 bar the  $\eta_{\rm b}$  values are in range  $(1-2) \times 10^{-5}$  Pa·s, while for the pressures p = 2-4 bar the  $\eta_{\rm b}$  values level off at  $(5-6) \times 10^{-5}$  Pa·s. This effect might be considered as a measurement artifact since at the lower pressures collisional relaxation effects are expected to be small and the deviations from a Gaussian profile are also small (see Fig. 4.1). However, in numerical terms the fits return values with < 10% uncertainties in all cases, so the derivation of bulk viscosities at low pressures should be considered significant.

Interestingly, in the case of  $\text{CO}_2$  an opposite behaviour was found at low pressures, displaying a decreasing trend in  $\eta_b$  with respect to pressure [68]. In the pressure range p = 2 - 4 bar a value of  $6 \times 10^{-6}$  Pa·s was found for  $\text{CO}_2$ , hence an order of magnitude smaller than is presently found for N<sub>2</sub>O. This is remarkable in view of the similar size and chemical composition of the two molecules.

#### 4.3.2 The Grad's six-moment kinetic model

Subsequently we use the kinetic model equation proposed by Fernandes and Marques Jr [19] to describe the RB-scattering profiles measured for  $N_2O$ . In this model, the collision operator of the Boltzmann equation is replaced by a

single relaxation-time term of the form

$$\mathcal{C}(f,f) = -\frac{p}{\eta_{\rm s}}(f - f_{\rm r}),\tag{4.3}$$

where  $f_r$  is a reference distribution function. The determination of the distribution function follows by requiring that the Chapman-Enskog solution of the model equation to be compatible with Grad's six-moment approximation for polyatomic gases. In the six-moment approximation, the balance equations governing the dynamical behavior of mass density, flow velocity, translational temperature and internal temperature are supplemented with constitutive relations for the pressure tensor, translational heat flux vector and internal heat flux vector. In their approach, Fernandes and Marques Jr [19] used Navier-Stokes-Fourier constitutive relations which are valid for the case that the energy exchange between translational and internal degrees of freedom is slow, but not negligible.

The application of Grad's six-moment model equation to describe light scattering experiments in polyatomic gases requires only the specification of the ratio of heat capacities  $\gamma$ , the relaxation time of the internal degrees of freedom  $\tau_{\text{int}}$  and the numerical factor  $u'_{11} = 3\Omega^{(2,2)}/5\Omega^{(1,1)}$  which depends on the law of interaction between molecules through the Chapman-Cowling collision integrals  $\Omega^{(\ell,r)}$  [50]. For the ratio of heat capacities  $\gamma$  (as in the previous model) we take the value 1.4, while for the numerical factor  $u'_{11}$  we adopt the value 1.32, which follows by assuming that the nitrous oxide molecules interact according to the Lennard-Jones (6 – 12) model (for details, see Hirschfelder et al. [98]).

In the model description the relaxation time  $\tau_{\rm int}$  is then the only unknown variable when comparing with the experimental data, hence this internal relaxation time is then optimized in a least-squares fitting process. Results of the fitted values are included in Table 4.2 and the calculated RB-scattering profiles are included in Fig. 4.1 in terms of deviations from the experimental spectra. For data set III the model calculation does not converge while performing a least-squares fit to deduce the relaxation parameter. However, in the full range of physically possible relaxation times, hence in range  $(3 - 15) \times 10^{-10}$  s, similar  $\chi^2$  and  $R_{\rm rmse}$  values are determined, and the comparison with the spectrum itself is rather well behaved (see Fig. 4.1).

The relaxation phenomena in a gas can be described by a single parameter, the bulk viscosity  $\eta_b$ , which may be related to relaxation times for the degrees of freedom [50]:

$$\eta_{\rm b} = \frac{2}{(3+f_{\rm int})^2} p \left( f_1 \tau_1 + f_2 \tau_2 + \dots \right) \tag{4.4}$$

where  $f_{\text{int}}$  denotes the internal degrees of freedom of a molecule,  $f_1, f_2, \dots$  are the contributions to  $f_{\text{int}}$  from the separate parts of the internal energy and

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#### 4. RB-light scattering spectroscopy of nitrous oxide

 $f_1 + f_2 + \ldots = f_{\text{int}}$ . The value 3 in the denominator refers to the three degrees of freedom associated with translational motion and is added to the number of internal degrees of freedom. The values  $\tau_1$ ,  $\tau_2$ ,  $\ldots$  are the corresponding relaxation times.

In our case we only have rotational degrees of freedom ( $f_{\rm rot} = 2$  for a linear molecule) as the vibrational modes are frozen. Consequently, Eq. (4.4) reduces to

$$\eta_b^G = \frac{2}{(3+f_{\rm rot})^2} p f_{\rm rot} \tau_{\rm rot} = \frac{4}{25} p \tau_{\rm rot}.$$
(4.5)

Then, the corresponding bulk viscosity  $\eta_{\rm b}^G$  for data sets III-V can be calculated and values are listed in Table 4.2.

#### 4.3.3 The Hammond-Wiggins hydrodynamic model

In a third approach, the hydrodynamic model of Hammond and Wiggins [16] was used to compare with the RB scattering spectral profiles measured for N<sub>2</sub>O. In this model, vibrational and rotational relaxation times  $\tau_{\rm vib}$  and  $\tau_{\rm rot}$  are key parameters in the description. Again vibrational relaxation is a too slow process and only rotational relaxation is considered as effectively contributing.

The same code, implemented in a previous analysis on RB-scattering in SF<sub>6</sub>, was used here to evaluate the 5-component matrix equations of the Hammond-Wiggins (HW) model involving fluctuations of the mass density  $\bar{\rho}/\rho_0$ , translational temperature  $\bar{T}/T_0$ , momentum or velocity density  $\bar{v}/v_0$ , vibrational temperature  $\bar{T}_{\rm vib}/T_0$ , and rotational temperature  $\bar{T}_{\rm rot}/T_0$ . Again a value for the thermal conductivity  $\lambda_{\rm th}$  was included following Eucken's relation.

In the analysis a fit was made, comparing the experimental and model spectra, in which the rotational relaxation was adopted as a free parameter. The values for  $\tau_{\rm rot}$  resulting from the fits are listed in Table 4.2. At the lowest pressure p = 0.5 bar the fit did not converge, while for the spectrum recorded at p = 1 bar an unphysical value was found. Hence these entries are left out of Table 4.2. In Fig. 4.1 the deviations between experimental and modeled spectra are presented in graphical form. For the data sets III-V, for pressures p = 2-4 bar, good agreement is found from the HW-model yielding deviations of less than 1%. This may be considered an excellent result, keeping in mind that an hydrodynamic model focusing on relaxation phenomena is in principle not suited to model dynamics under conditions where collisions play less of a role, like at low pressures. The present study provides a demarcation point, between p = 1 and p = 2 bar, where the application of the HW hydrodynamic model becomes relevant. Quantitatively the study provides a value for the rotational relaxation at  $\tau \sim 1.5$  ns, which is commensurate with the relaxation found in the Grad's six-moment model.



Figure 4.2: Geometrical structure of the linear  $N_2O$  molecule (in its electronic ground state) with nitrogen atoms depicted as the smaller (blue) balls and the oxygen atom as the larger (red) ball. Internuclear separations for the ground state are displayed as resulting from spectroscopy [99, 100].

Again, from the obtained relaxation times the bulk viscosity  $\eta_{\rm b}^{\rm H}$  can be derived via Eq. (4.4). Values are listed in Table 4.2.

#### 4.3.4 The 'rough-sphere' model

The rough-sphere model proposed by Marques Jr [17], is also a kinetic theory describing the density fluctuation in polyatomic gases. In this model, a simple relaxation term  $\delta(f - f_r)$  is used to replace the collision operator in Boltzmann equation with  $f(\vec{r}, \vec{v})$  the six-dimensional position-velocity distribution and  $f_{\rm r}$ representing a reference distribution function. Here the coefficients satisfy the conservation laws, while the collisional transfer of momentum and energy agree with the full Boltzmann description. The rough sphere model considers the interaction between the translational and rotational degrees of freedom and regards the collisions between molecules as hard spheres, thereby ignoring the effect of vibrational relaxation. This model is built on a dimensionless moment of inertia  $\kappa = 4I/m d^2$ , with m the mass, I the moment of inertia and d an effective diameter of the molecule. The moment of inertia I may be derived from the rotational constant as obtained in microwave spectroscopy of the molecule for which a value of B = 12561 MHz was reported [101], corresponding to a moment of inertia of  $I = 66.7 \times 10^{-47}$  kg m<sup>2</sup> for N<sub>2</sub>O [99, 100]. In Fig. 4.2 the geometrical structure of the N<sub>2</sub>O molecule is depicted with internuclear separations between nitrogen and oxygen atoms. The distance between outer atoms is 2.3 Å, but the effective diameter d of the molecule is determined in a number of studies to be higher: d = 3.85 Å [102] and d = 3.828 Å [103]. This results in a value of  $\kappa = 0.246$ .

With a value for the shear viscosity of  $\eta_s = 1.48 \times 10^{-5}$  Pa·s the rough-sphere model derives a value for internal relaxation effects, represented as a bulk

#### 4. RB-light scattering spectroscopy of nitrous oxide

viscosity via the relation [50]

$$\eta_{\rm b} = \eta_{\rm s} \frac{6+13\kappa}{60\kappa} \tag{4.6}$$

resulting in a value of  $\eta_{\rm b} = 0.92 \times 10^{-5}$  Pa·s. Model spectra for RB-scattering in N<sub>2</sub>O were subsequently calculated using the formalism presented by Marques Jr [17], Marques Jr and Kremer [104]. Results are displayed in Fig. 4.1 in terms of deviations between experimental and modeled spectral profiles. Large discrepancies arise in particular at the high pressure values where relaxation phenomena play an important role. Numerically the rough sphere model delivers a value for the bulk viscosity  $\eta_{\rm b}$  that is significantly smaller than the values obtained from the kinetic Tenti-S6 model, by a factor of six. Hence relaxation phenomena are not well described by the assumptions made for collisions to occur between object of spherical nature. In view of the geometrical structure of the N<sub>2</sub>O molecule as displayed in Fig. 4.2 this is not surprising.

Lastly, it is mentioned that the discrepancy resulting from the rough sphere model is not just based on the non-sphericity of the N<sub>2</sub>O geometrical structure. The model predicts a value for the heat capacity ratios of  $\gamma = 4/3$ , which is slightly smaller than the value  $\gamma = 7/5$  for nitrous oxide. Therefore, the rough sphere model predicts a wrong value for the speed of sound and this is crucial in producing good agreement with experiments.

#### 4.4 Discussion and Conclusion

In this study spontaneous Rayleigh-Brillouin scattering spectra of  $N_2O$  gas of high signal-to-noise are experimentally recorded, allowing for detailed comparison with models describing the phenomena underlying the scattering profiles. RB-scattering is a complex phenomenon as it entails all intramolecular and intermolecular interactions of molecules in a dense gaseous environment. Hence, the scattering profiles involve information on the spectroscopy, internal vibrational and rotational relaxation, coupling with translational motion, quantum state-to-state energy transfer, velocity-changing collisions, etcetera. The entirety of the behavior can in principle be described by the Boltzmann equation. Since the full six-dimensional information on position-velocity coordinates and involving all state-to-state collisional cross sections in a medium are not known, approximate methods must be invoked to model the RB-light scattering process.

In the present study four of such prevailing models are applied to the scattering of the nitrous oxide molecule which is special for a number of reasons. N<sub>2</sub>O is a polyatomic molecule for which the linear N-N-O structure (see also

4.4. Discussion and Conclusion



Figure 4.3: The root-mean-square error based on the deviation of experimental spectra and the models (Tenti-S6, the Grad's six-moment kinetic model, the HW-hydrodynamic and the rough sphere models) after folding with the instrument function. The top-axis shows the scale converted to the uniformity parameter y.

Fig. 4.2) does not provide a symmetry point as is the case for  $CO_2$  [68]. While a number of recent studies were performed to model RB-scattering in diatomic molecules [14, 15, 46, 59] the quest is now to investigate RB-scattering in polyatomic molecules of different symmetry and sizes. N<sub>2</sub>O is a convenient target in view of its large scattering cross section [13].

The deviations between the experimental spectra and the modeled spectra, for the models discussed in the present study, are presented in condensed form in terms of a normalized root-mean-square error  $R_{\rm rmse}$  value of each model at the five pressure conditions is shown in value Fig. 4.3. The Tenti-S6 model provides overall a good description of RB-scattering, now also for the polyatomic N<sub>2</sub>O molecule. For the lowest pressures, where the spectral profile is close to Gaussian,  $R_{\rm rmse}$  deviations are below the 1% level. For the higher pressure ranges deviations grow to the 2% level, but in view of the quality of the spectra, deviations are significant. The value for the bulk viscosity  $\eta_{\rm b}$  is found to be pressure dependent, as expected from general considerations on relaxation phenomena [50], while leveling off to a value of  $6 \times 10^{-5}$  Pa·s. This is an order of magnitude larger than the bulk viscosity of CO<sub>2</sub>, a molecule of comparable size and composition.

The Grad's six-moment kinetic model shows a similarly good performance in the comparison with experimental data as does the Tenti-S6 model. In fact the spectral comparisons in Fig. 4.1 as well as the values for the root-mean-square deviations, as in Fig. 4.3 are virtually identical. As for the underlying physical parameter, the bulk viscosity as deduced from the internal relaxation number Z, some difference is found with the values derived in the Tenti-S6 model. However this is mainly the case for the low pressures p = 0.5-1 bar, where collisional relaxation does not play a decisive role, and the value of  $\eta_{\rm b}$  barely affects the spectra profile. For the higher pressures, p = 3 - 4 bar, where collisional relaxation is more decisive the differences between bulk viscosities  $\eta_{\rm b}^{\rm T}$  and  $\eta_{\rm b}^{\rm 6G}$  are some 20-30%.

The Hammond-Wiggins hydrodynamic model is well applicable to the spectra measured at pressures at 2-4 bar, where agreement is found below the 1% level. In fact, at pressures p = 2 - 4 bar this model yields the best description of RB-light scattering in N<sub>2</sub>O gas. This hydrodynamic model is not applicable at the low pressures  $p \leq 1$  bar, where extremely large deviations are found between modeled and experimental spectra, even when a rotational relaxation parameter is adapted in a fit. However, the non-applicability of a hydrodynamic model in a low-pressure regime is well understandable. Also in the context of this hydrodynamic model the relaxation phenomenon can be connected to a bulk viscosity parameter, values for which are listed in Table 4.2.

Although the three models, Tenti-S6, Grad's six-moment and HW-hydrodynamic, have very different physical basis and show differing deviations between model and experimental data, in the range p = 2 - 4 bar the internal relaxation is described by a gas transport coefficient that is bounded within some limits. The value for the bulk viscosity pertaining to all three descriptions is bound by  $\eta_{\rm b} \sim (6 \pm 2) \times 10^{-5}$  Pa·s.

The rough-sphere model turns out to be not applicable to describe RB-light scattering in  $N_2O$  gas. Even in the near-collisionless regime of p = 0.5 bar deviations are evident, but they grow to large proportions for increasing pressures. This is, after all, not surprising, in view of the non-spherical geometrical structure of the  $N_2O$  molecule.

### Chapter 5

## Bulk viscosity of CO<sub>2</sub> from Rayleigh-Brillouin light scattering spectroscopy at 532 nm

#### Abstract

Rayleigh-Brillouin scattering spectra of  $CO_2$  were measured at pressures ranging from 0.5 to 4 bar, and temperatures from 257 to 355 K using green laser light (wavelength 532 nm, scattering angle of 55.7°). These spectra were compared to two lineshape models, which take the bulk viscosity as a parameter. One model applies to the kinetic regime, i.e. low pressures, while the second model uses the continuum, hydrodynamic approach and takes the rotational relaxation time as a parameter, which translates into the bulk viscosity. We do not find a significant dependence of the bulk viscosity with pressure or temperature. At pressures where both models apply we find a consistent value of the ratio of bulk viscosity over shear viscosity  $\eta_{\rm b}/\eta_{\rm s} = 0.41 \pm 0.10$ . This value is four orders of magnitude smaller than the common value that is based on the damping of ultrasound, and signifies that in light scattering only relaxation of rotational modes matters, while vibrational modes remain 'frozen'.

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#### 5.1 Introduction

The light scattering properties of carbon dioxide remain of interest, both from a fundamental perspective studying the relaxation in molecular gases and for determining their thermodynamic properties, as well as from an applied perspective. Details of Rayleigh-Brillouin (RB) phenomena, scattering spectral profiles of  $CO_2$  gas at differing pressures and temperatures [58, 67, 68] as well as its cross section [13], are of relevance for current and future remote sensing exploration of the planetary atmospheres where  $CO_2$  is the main constituent, either under high-pressure and high-temperature conditions as on Venus [105] or under low pressure and low-temperature conditions as on Mars [106]. The fact that carbon dioxide is the prime greenhouse gas has spurred large-scale activity in the transformation of this gaseous species [107, 108], through catalytic hydrogenation [109], electrochemical conversion into renewable energy [110], as well as in plasma-driven dissociation for the synthesis of fuel from CO<sub>2</sub> [111, 112]. Apart from issues of capture, fixation and transformation of Teratons of carbon dioxide, its storage and transport, either in the liquid or gas phase, forms an important challenge [113, 114]. For these purposes study of the transport coefficients of  $CO_2$  gas, such as thermal conductivity [96], heat capacity, and shear viscosity [76, 115], is of practical importance. Light scattering is an elegant way to determine the thermodynamic properties of a gas, because the Rayleigh scattering phenomenon resulting in the elastic peak is connected to entropy fluctuations [2], while the Brillouin-side peaks are associated with density fluctuations or sound [4, 5]. The macroscopic gas transport coefficients govern the scattering spectral profiles and can in turn be deduced from measurement of such profiles [98]. This holds for both spontaneous RB-scattering [60, 81, 104] as well as for coherent RB-scattering [71, 91].

The bulk viscosity  $\eta_{\rm b}$  [82, 116], is the most elusive transport coefficient. It is associated with the relaxation of internal degrees of freedom of the molecule, i.e. rotations and vibrations. The bulk viscosity is commonly measured from the damping of ultrasound at frequencies in the MHz domain [51]. It can also be retrieved from the light scattering spectrum of molecular gases. This was demonstrated by Pan et al. [67] and recently for N<sub>2</sub>, O<sub>2</sub> and air by Gu and Ubachs [46], and for N<sub>2</sub>O gas by Wang et al. [117]. In light scattering, the frequencies  $f_{\rm s}$  involved are those of sound with wavelengths comparable to that of light, three orders of magnitude larger than the frequencies used to measure  $\eta_{\rm b}$  from ultrasound experiments. The bulk viscosity of CO<sub>2</sub> from light scattering is found to be four orders of magnitude smaller than that from ultrasound experiments[58, 67, 68]. A simple explanation is that at high (hypersound) frequencies the relaxation of vibrational modes of the CO<sub>2</sub> molecule no longer plays a role, i.e. the vibrational energy stays frozen in.
The bulk viscosity can be expressed in terms of relaxation times of intra-molecular degrees of freedom,

$$\eta_{\rm b} = p \frac{2}{\left(3 + \sum_{i} N_i\right)^2} \sum_{i} N_i \,\tau_i \tag{5.1}$$

where p is the pressure,  $N_i$  is the number of degrees of freedom of mode i (rotations, vibrations), and  $\tau_i$  is the relaxation time  $(\tau_{\rm rot}, \tau_{\rm vib})$  [50]. A frequency-dependent version of this formula, depending on the product  $f_{\rm s}\tau_i$  was given by Meijer et al. [71]. Carbon dioxide is a linear molecule with 2 rotational degrees of freedom. In case of frozen vibrations  $(f_{\rm s}\tau_{\rm vib} \gg 1)$ , Eq. (5.1) reduces to

$$\eta_{\rm b} = \frac{4}{25} p \,\tau_{\rm rot} \tag{5.2}$$

The vibrational relaxation time strongly decreases with temperature, and so does the bulk viscosity. In a simple model Landau and Teller proposed an exponential dependence of the chance of relaxation on the ratio of the collision interaction time and the vibration period [51]. This leads to a scaling prediction for the temperature dependence of the bulk viscosity which agrees with experiment [82]. On the other hand, a classical analysis of collisions of rigid rotators by Parker [118] results in a scaling expression for  $\tau_{\rm rot}$  which predicts an *increase* of  $\tau_{\rm rot}$  with increasing temperature.

That the bulk viscosity changes with temperature motivated the present study in which laser-based light scattering measurements in CO<sub>2</sub> gas are carried out in a pressure regime of 0.5 – 4 bar and in a temperature regime of 257 – 355 K. Accurate, highly spectrally resolved and high signal-to-noise scattering line profiles are measured at a scattering angle of 55.7 degrees and a scattering wavelength of  $\lambda_i = 532$  nm, a wavelength commonly used in lidar applications. Under these conditions of a longer wavelength and a smaller scattering angle than in a previous study [68], the Brillouin-side peaks become more pronounced in the scattering spectrum.

Experimental data are analyzed in the context of two models for the spectral lineshape. One model applies at low pressures, the kinetic regime where the mean free path between collisions is comparable to the wavelength of light [14, 15], while the other one is valid in the hydrodynamic regime [16]. Values of the bulk viscosity are determined in a least squares method by comparing model spectra to measured ones.

The remainder of the article consists of an experimental section, a section discussing the bulk viscosity and model descriptions for RB-scattering, a presentation of results in the context of applicable models to describe the scattering spectrum, followed by a conclusion.

# 5.2 Experiment



Figure 5.1: Schematic of the experimental apparatus. A Verdi-V5 laser provides continuous wave light at 532.22 nm at a power of 5 Watt and bandwidth less than 5 MHz. The laser light is split into two beams: The pump beam crosses the RB-scattering gas cell producing scattered light that is captured under an angle  $\theta = (55.7 \pm 0.3)^{\circ}$ . The small fraction reference beam transmitted through M<sub>4</sub> is used to align the beam path after the gas cell towards the detector. The scattered light is analyzed in a Fabry-Perot Interferometer (FPI), with free spectral range of 2.9964 GHz and an instrument linewidth of  $(58 \pm 3)$  MHz, and is collected on a photo-multiplier tube (PMT). Mirrors, lenses and diaphragm pinholes are indicated as M<sub>i</sub>, L<sub>i</sub> and D<sub>i</sub>. A slit of 500  $\mu$ m is inserted to limit the opening angle for collected scattering light, therewith optimizing the resolution.

The experimental apparatus for measuring the RB-scattering spectral profiles of CO<sub>2</sub> is displayed in Fig. 5.1. The laser source provides continuous wave radiation at  $\lambda_i = 532.22$  nm at a bandwidth of less than 5 MHz. RB-scattered light is produced from the laser beam of 5 Watt intensity traversing a gas cell equipped with a gas inlet valve and a pressure sensor. Brewster-angled windows are mounted at entrance and exit ports, and black paint covers the inside walls, to reduce unwanted scatter contributions. A temperature control system equipped with Peltier elements is employed for heating, cooling and keeping the cell at a constant temperature with uncertainty less than 0.1 °C. RB-scattered light is captured at a scattering angle  $\theta = (55.7 \pm 0.3)^\circ$  defined by the setting of a slit in the scatter beam path (see Fig. 5.1), that also limits the opening angle for collecting RB-scattered light to less than  $0.5^{\circ}$ . The exact scatter angle and uncertainty are determined with a rotatable stage operated as a goniometer. A reference beam as depicted in Fig. 5.1 is used for aligning the collection and detection system. The scattering angle determines the scattered light wave vector q,

$$q = \frac{2\pi}{\lambda_{\rm i}} \, 2 \, n \, \sin(\theta/2)$$

with n the index of refraction.

The scattered light propagates through a bandpass filter (Materion, T > 90% at  $\lambda_i = 532$  nm, bandwidth  $\Delta \lambda = 2.0$  nm) onto a Fabry-Perot interferometer (FPI) via an optical projection system consisting of a number of lenses and pinholes to reduce stray light and contributions from Raman scattering. Finally the scattered photons are detected on a photomultiplier tube (PMT), processed and stored in a data acquisition system. The FPI is half-confocal, the curved mirror having a radius of curvature of r = -12.5mm. Mirror reflectivities are 99%.~ The FPI has an effective free spectral range (FSR) of 2.9964 GHz, which is determined through frequency-scanning a laser (a narrowband tunable cw-ring dye laser) over more than 1000 modes of the FPI while measuring the laser wavelength by a wavelength meter (Toptica HighFinesse WSU-30), hence yielding an uncertainty in the FSR below 1 MHz. The instrument width, yielding a value of  $\sigma_{\nu_{\text{instr}}} = 58.0 \pm 3.0 \text{ MHz}$  (FWHM), is determined by using the reference beam while scanning the piezo-actuated FPI, following methods discussed by Gu et al. [52]. It includes the bandwidth of the incident laser. The instrument function is verified to exhibit the functional form of an Airy function, which may be well approximated by a Lorentzian function during data analysis.

RB-scattering spectral profiles were recorded by piezo-scanning the FPI at integration times of 1 s for each step, usually over 18 MHz. Typical detection rates were ~ 2000 count/s for conditions of 1 bar pressure. A full spectrum covering lots of consecutive RB-peaks and 10,000 data points was obtained in about 3 h. The piezo-voltage scans were linearized and converted to frequency scale by fitting the RB-peak separations to the calibrated FSR-value. The linearization procedure also corrects for frequency drifts of the laser, which were measured to amount to 10 - 100 MHz/hour, depending on temperature drifts in the laboratory. Finally, a collocated spectrum was obtained by cutting and adding all individual recordings over ~ 60 RB-peaks [52]. In a final step the RB-scattering profiles were averaged to improve the signal to noise ratio. This procedure yields a noise level of ~ 0.4% (with respect to peak height) for the 1 bar pressure case. A single typical light scattering spectrum recorded at 1 bar and room temperature, measured in a typical recording time of ~ 3 h, is



Figure 5.2: (a) Experimental data for the RB-light scattering spectrum of CO<sub>2</sub> measured at  $\lambda_i = 532 \text{ nm}, \theta = 55.7^{\circ}$  and (p, T) conditions as indicated, corresponding to a uniformity parameter y = 1.88; the spectrum on the right shows en enlargement of the central part indicated in grey; (b) Residuals from comparison with Tenti-S6 model by using thermal conductivity  $\lambda_{\text{th}}$  from Eq. (5.3) and a fitted value for  $\eta_{\text{b}}$ ; (c) Residuals with  $\lambda_{\text{th}}$  from Uribe et al. [96].

displayed in Fig. 5.2. This figure and its inset demonstrate the signal-to-noise ratio attainable in the present setup.

# 5.3 RB-scattering and line shape models

In light scattering the key quantity is the uniformity parameter y, which -up to a constant- is defined as the ratio of the scattering wavelength over the mean free path between collisions, which can be shown to equal

$$y = \frac{p}{k_{\rm sc} \, v_0 \, \eta_{\rm s}}$$

with thermal velocity  $v_0 = (2k_{\rm B}T/m)^{1/2}$ , where  $k_{\rm B}$  is the Boltzmann constant, m the molecular mass and  $\eta_{\rm s}$  the shear viscosity.

Values  $y = \mathcal{O}(1)$  pertain to the kinetic regime, and models must be based on the Boltzmann equation. There, spectra do not deviate strongly from the Rayleigh (Maxwellian) line shape. At larger values of y many mean free paths fit in a wavelength, and a hydrodynamic, continuum, approach applies. The Brillouin-side features become more and more prominent with increasing y, and occur at frequency shifts  $f_s = \pm v_s k_{sc}/2\pi$ , with  $v_s$  the speed of sound. Our data are in the interval y = [0.7 - 9], and, therefore range from the kinetic into the hydrodynamic regime.

#### 5.3.1 The Tenti model

The Tenti model, originally developed for analyzing RB-scattering in molecular hydrogen and diatomic molecules [14, 15], is a widely used model for light scattering spectra in the kinetic regime. It uses the Wang Chang–Uhlenbeck eigentheory which takes known values of the macroscopic transport coefficients as input [44]. This input consist of values for the shear viscosity  $\eta_s$ , thermal conductivity  $\lambda_{th}$ , the molar heat capacity  $C_{int}$  of internal modes of motion (rotations, vibrations), and the bulk viscosity  $\eta_b$ . The model agrees well with experiment [68, 81, 91], where it was established that the six-mode version of the Tenti model (hereafter called the Tenti-S6 model) yields a better agreement with experiment than the seven-mode variant.

We use the values for a temperature dependent shear viscosity  $\eta_{\rm s}(T)$  for CO<sub>2</sub> from Boushehri et al. [79]. Of the transport coefficients needed in the model,  $\lambda_{\rm th}$  and  $C_{\rm int}$  and  $\eta_{\rm b}$  depend on the participation of intra-molecular modes of motion. We assume that at the frequencies associated with light scattering, only rotations participate in the exchance of internal and kinetic energy, so that  $C_{\rm int}$ , for the linear CO<sub>2</sub> molecule becomes  $C_{\rm int} = 2/2 R$  with R the gas constant.

 $\lambda_{\rm th}$ , Uribe [96]For the thermal conductivity  $\operatorname{et}$ al. list temperature-dependent values. As in the present study only the thermal conductivity associated with rotational relaxation is considered, these values are not straightforwardly applicable to RB-scattering data. We need a value that reflects rotational internal energy only. For polyatomic gases, a high-frequency value for  $\lambda_{\rm th}$  was estimated from the Eucken relation, which expresses  $\lambda_{\rm th}$  as a function of the shear viscosity  $\eta_{\rm s}$ , the diffusivity D and the heat capacity  $C_{int}$  of internal motion:

$$\lambda_{\rm th} = \frac{5}{2} \eta_{\rm s} \, C_{\rm t} + \rho \, D \, C_{\rm int} \tag{5.3}$$

with  $C_t = 3/2 R$ , the heat capacity of kinetic motion,  $C_{int} = 2/2 R$ , and the temperature-dependent diffusivity D taken from Boushehri et al. [79]. At

temperature T = 296.55 K, the low-frequency value is  $\lambda_{\rm th} = 1.651 \times 10^{-2}$  W/m·K (Ref. [96]), whereas Eq. (5.3) predicts a high-frequency value  $\lambda_{\rm th} = 1.452 \times 10^{-2}$  W/m·K. As will be demonstrated below, the smaller value indeed produces a better fit of the kinetic model. The bulk viscosity  $\eta_{\rm b}$ , our prime quantity of interest, is determined in a least-squares procedure.

#### 5.3.2 The Hammond–Wiggins model

At the other end of the uniformity scale we seek confrontation with a hydrodynamic, continuum, model by Hammond and Wiggins [16]. Unlike the Tenti model, which is built on (tensorial) eigenvectors of the linearized collision operator, the hydrodynamic model is built on (tensorial) moments of the space-time distribution function, i.e. hydrodynamic quantities. The hydrodynamic model takes the shear viscosity  $\eta_s$ , the diffusivity D and the heat capacity of internal motion  $C_{int}$  as parameters. The rotational relaxation time  $\tau_{rot}$  is determined in a least squares procedure, from which the bulk viscosity  $\eta_b$  is computed using Eq. (5.2). Allowance for rotational relaxation only is done through the choice for  $C_{int} = 2/2 R$ .

The evaluation of both kinetic and hydrodynamic models can be done extremely quickly. Where their range of validity overlaps, the derived values of the bulk viscosity should agree.

#### 5.4 Results and Discussion

In this section we will first present experimental data on light scattering in  $CO_2$ , followed by an analysis in terms of two complementary spectral line models. We finally summarize the results of the temperature-dependent bulk viscosity.

#### 5.4.1 Measurements: Light scattering in CO<sub>2</sub>

Measurements of the RB-scattering spectral profile of  $CO_2$  gas were performed for conditions of 0.5-4 bar pressure and temperatures in the range between 258 and 355 K, as listed in Table 5.1. In this table the accurately measured p and T conditions for 29 (p, T) measurement combinations are listed as well as the temperature-dependent transport coefficients: shear viscosity  $\eta_s$  and thermal conductivity  $\lambda_{th}$ . For all measurements a value for the internal molecular heat capacity of  $C_{int} = 2/2 R$  is adopted.

In Fig. 5.3 the RB-light spectra for the 29 different (p, T) combinations are graphically displayed. A qualitative inspection shows, when comparing profiles from the top- row down, the pressure p is increased and therewith the *y*-parameter is increased as well, and hence the spectra show more **Table 5.1:** Data sets for RB-scattering measurements in CO<sub>2</sub> gas recorded under conditions as indicated. The uniformity parameter is y. For values of the temperature-dependent  $\eta_{\rm s}$  and  $\lambda_{\rm th}$  we use Boushehri et al. [79] and Eq. (5.3), respectively. The bulk viscosity and the ratios  $\eta_{\rm b}/\eta_{\rm s}$  are derived in a fit to the experimental data. The bulk viscosity  $\eta_{\rm b}^T$  is based on the Tenti-S6 model, while  $\eta_{\rm b}^H$  is based on the Hammond–Wiggins hydrodynamic model. The parameter  $C_{\rm int} = 2/2R$ , for all cases is the heat capacity of rotational motion.

Data set	p	Т	$\eta_{\rm s}(\times 10^{-5})$	$\lambda_{\rm th}(\times 10^{-3})$	$\eta_{\rm b}^T(\times 10^{-5})$	$\eta_{\rm b}^T/\eta_{\rm s}$	$\eta_{\rm b}^{H}(\times 10^{-5})$	$\eta_{\rm b}^H/\eta_{\rm s}$	y
Unit	bar	Κ	Pa·s	$W/m \cdot K$	Pa·s		Pa·s		
	0.500	273.2	1.37	13.4	0.64	0.47			1.03
	0.500	293.2	1.47	14.3	0.72	0.49			0.93
0 5 har	0.505	313.2	1.56	15.3	0.91	0.58			0.85
0.5 bar	0.508	333.2	1.66	16.2	1.65	0.99			0.78
	0.503	353.2	1.75	17.1	1.79	1.02			0.71
	1.033	258.1	1.30	12.7	0.50	0.38	0.30	0.23	2.32
	1.038	274.3	1.38	13.4	0.46	0.33	0.24	0.18	2.13
	1.011	293.2	1.47	14.3	0.54	0.37	0.28	0.19	1.88
1 bar	1.055	312.9	1.56	15.2	0.69	0.45	0.31	0.20	1.79
	1.048	330.8	1.65	16.1	0.77	0.47	0.33	0.20	1.62
	1.028	353.2	1.75	17.1	0.67	0.38	0.34	0.19	1.46
	2.012	257.4	1.29	12.6	0.47	0.37	0.49	0.38	4.54
	2.037	274.5	1.38	13.4	0.46	0.34	0.45	0.33	4.18
	2.000	293.2	1.47	14.3	0.40	0.27	0.37	0.25	3.71
2 bar	2.047	312.9	1.56	15.2	0.60	0.38	0.47	0.30	3.47
	2.050	331.8	1.65	16.1	0.70	0.42	0.51	0.31	3.15
	2.042	354.8	1.76	17.1	0.64	0.36	0.40	0.23	2.89
	3.012	257.1	1.29	12.6	0.66	0.51	0.73	0.57	6.80
	2.996	273.2	1.37	13.4	0.65	0.47	0.63	0.46	6.18
	3.037	295.7	1.48	14.4	0.66	0.45	0.68	0.46	5.59
3 bar	3.050	313.7	1.56	15.3	0.77	0.49	0.75	0.48	5.15
	3.064	332.4	1.65	16.1	0.98	0.59	0.89	0.54	4.76
	3.021	354.4	1.76	17.1	0.75	0.43	0.61	0.35	4.28
	4.026	258.1	1.29	12.6	0.98	0.76	1.07	0.83	9.04
	4.052	274.9	1.34	13.5	0.70	0.51	0.79	0.57	8.29
	4.048	295.2	1.48	14.4	0.61	0.41	0.70	0.47	7.46
4 bar	4.041	313.1	1.56	15.3	0.73	0.47	0.78	0.50	6.84
	4.042	332.7	1.65	16.2	0.86	0.52	0.86	0.52	6.27
	4.000	353.5	1.75	17.1	0.94	0.54	0.89	0.51	5.68

pronounced Brillouin-side peaks. Indeed at higher uniformity parameters y the hydrodynamic regime is approached resulting in well-isolated acoustic side modes. Similarly, while going from left to right along the columns, the temperature T is increased, associated with a lowering of the y-parameter, and hence the Brillouin-side peaks become less pronounced. In the following the experimental profiles will be compared to the Tenti-S6 model and the Hammond–Wiggins hydrodynamic model.



Figure 5.3: Experimental data for RB–scattering in  $CO_2$  as measured for the various pressure and temperature conditions as indicated. The data is on a scale of normalized integrated intensity over one FSR. The 29 spectra pertain to the entries in Table 5.1.

#### 5.4.2 Comparison with the two models

For a quantitative analysis of the data a comparison is made with the Tenti-S6 model, that was developed into a code [47, 91] that was included in fitting routines for analyzing both spontaneous and coherent RB-scattering [71, 81]. In comparing model and experiments, the bulk viscosity  $\eta_{\rm b}$  was determined in a least-squares procedure, minimizing the mean squared deviation

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

where  $I_e(f_i)$  and  $I_m(f_i)$  are the experimental and modeled amplitude of the spectrum at (discrete) frequency  $f_i$ , and N is total number of the experimental data. The error  $\delta(f_i)$  of  $I_e(f_i)$  is estimated as the square root of the number of collected photons.

First an analysis is made of the spectrum presented in Fig. 5.2.

Least-squares fits are performed for the value of the bulk viscosity  $\eta_{\rm b}$  invoking two values for the thermal conductivity, first  $\lambda_{\rm th} = 14.3 \text{ mW/m}\cdot\text{K}$  as resulting from the modified Eucken approach and, second the value obtained from a direct measurement at acoustic frequencies  $\lambda_{\rm th} = 16.2 \text{ mW/m}\cdot\text{K}$  [79]. The residuals plotted in Fig. 5.2 show that in the first approach a peak residual of 3% is found, where in the latter approach the peak deviation amounts to 5%. This supports validity of the treatment of thermal conductivity following the modified Eucken relation in this study conducted at hypersound frequencies. In such an approach focusing on hypersound the internal heat capacity is set at  $C_{\rm int} = 2/2 R$ , signifying that two rotational degrees of freedom are involved and vibrational relaxation is 'frozen'.

Least-squares fitting procedures based on the Tenti-S6 model were applied to the large body of 29 data sets on CO<sub>2</sub> for (p, T) values as displayed in Fig. 5.3. With inclusion of values for the transport coefficients as listed in Table 5.1 optimized values for  $\eta_b^T$  were derived. Resulting values are listed in Table 5.1. Based on these fits and optimized  $\eta_b^T$  values, residuals between experimental data and the Tenti-S6 model description are calculated and displayed in Fig. 5.4. These residuals provide insight in the quality of the fit, its accuracy and the applicability of the model.

Similarly, the hydrodynamic model is used to compare the experimental and model spectra for the data of pressures above 1 bar. Here, the rotational relational time  $\tau_{\rm rot}$  was adopted as a free parameter, from which the bulk viscosity was calculated using Eq. (5.2). Fig. 5.5 displays the residual between the experimental data and this model.

#### 5.4.3 Bulk viscosities

Our main result, the ratio  $\eta_{\rm b}/\eta_{\rm s}$  as a function of temperature and pressure is summarized in Fig. 5.6. At p = 0.5 bar the spectral lineshape is not very sensitive to variation of  $\eta_{\rm b}$ , at the highest pressure the models deviate significantly from the experiment. At p = 1 bar (corresponding to y =[1.4 - 2.3]), the hydrodynamic model does not yet apply, and the values of  $\eta_{\rm b}/\eta_{\rm s}$  of the two models differ significantly.

Fig. 5.6 also shows the prediction of the Landau–Teller scaling, which captures low-frequency experimental data [82]. However, with a crucial proviso: *it is scaled down by a factor* 10<sup>4</sup>. This vividly illustrates the dramatic effect of high frequencies on the ratio  $\eta_{\rm b}/\eta_{\rm s}$ . At these high frequencies, only rotational relaxation remains. Based on the analysis of classical trajectories, Parker [118] derived a scaling expression for the ratio  $\eta_{\rm b}/\eta_{\rm s}$ ,

$$\eta_{\rm b}/\eta_{\rm s} \propto \left[1 + \frac{\pi^{3/2}}{2} \left(\frac{T^*}{T}\right)^{1/2} + \left(\frac{\pi^2}{4} + \pi\right) \frac{T^*}{T}\right]^{-1}$$



#### 5. Bulk viscosity of $CO_2$ from RB-spectroscopy at 532 nm

Figure 5.4: Plot of calculated residuals between experimental data and spectral profiles obtained from a fit to the Tenti-S6 model with transport coefficients as listed in Table 5.1 and optimized values for  $\eta_{\rm b}$  as derived in the fit. Note the one-to-one correspondence with the 29 graphs of spectra in Fig. 5.3.

with  $T^* = 82.6$  K the temperature associated with the well depth of the O-O interaction potential [119]. This prediction, scaled on  $\eta_{\rm b}/\eta_{\rm s} = 0.5$  at T = 250K, is also shown in Fig. 5.6.

We find no significant dependency on pressure or temperature. At pressures where both kinetic and hydrodynamic models apply, we find an average  $\eta_{\rm b}/\eta_{\rm s} =$  $0.33 \pm 0.06$  at p = 2 bar and  $\eta_{\rm b}/\eta_{\rm s} = 0.48 \pm 0.06$  at p = 3 bar. These averages, together with their uncertainty, are also indicated in Fig. 5.6. Our present numbers are consistent with the finding obtained from the light scattering experiments on CO<sub>2</sub> in the UV-range ( $\lambda_{\rm i} = 366.8$  nm) covering the parameter space y = [0.9 - 3.7], and yielding  $\eta_{\rm b} = (5.7 \pm 0.6) \times 10^{-6}$  Pa·s [68], which gives rise to  $\eta_{\rm b}/\eta_{\rm s} = 0.39 \pm 0.04$ . These values should be compared to  $\eta_{\rm b} = 4.6 \times 10^{-6}$ Pa·s (for y = [3.3 - 8.2]) by Lao et al. [58], corresponding to  $\eta_{\rm b}/\eta_{\rm s} = 0.31$ , and  $\eta_{\rm b} = 3.7 \times 10^{-6}$  Pa·s for y = [0.44 - 3.54] by Pan et al. [67], for which the ratio  $\eta_{\rm b}/\eta_{\rm s} = 0.25$ .



Figure 5.5: Plot of calculated residuals between experimental data and spectral profiles obtained from a fit to the Hammond-Wiggins model with transport coefficients as listed in Table 5.1 from 1bar to 4 bar. The optimized values for  $\tau_{\rm rot}$  as derived in the fit and the corresponding  $\eta_{\rm b}^{\rm H}$  as derived using Eq. (5.2) when setting the vibrational relaxational time as 0. Note the one-to-one correspondence with the 24 graphs of spectra in Fig. 5.3.

# 5.5 Discussion and conclusion

In this paper we study Rayleigh-Brillouin scattering over a range of pressures with the aim of determining the bulk viscosity using two different types of models for the spectral lineshape. Where the range of applicability of these two models overlaps, we find consistent values of the bulk viscosity.

At low frequencies the bulk viscosity depends strongly on temperature, which is caused by the temperature dependence of the vibrational relaxation rate. We do not find a significant temperature dependence, not even the one predicted for the increase of the bulk viscosity with temperature due to the increase of the *rotational* relaxation time. We find  $\eta_{\rm b}/\eta_{\rm s} = 0.41 \pm 0.10$  at





Figure 5.6: Summary of results: the ratio of bulk to shear viscosity  $\eta_{\rm b}/\eta_{\rm s}$  of CO<sub>2</sub> as a function of temperature *T*. Open circles: as estimated from the experimental data using the Tenti-S6 model, closed dots: using the Hammond–Wiggings hydrodynamic model. Red line in (c): Landau–Teller theory scaled down by a factor 10<sup>4</sup>. Blue dashed line in (c): prediction of Parker model [118] for rotational relaxation. Violet bars in (c), (d): estimate of mean  $\eta_{\rm b}/\eta_{\rm s}$ .

pressures of 2 and 3 bar.

For N<sub>2</sub>, a measurement of sound absorption at low pressure yielded a value of the bulk viscosity, expressed relative to the shear viscosity as  $\eta_{\rm b}/\eta_{\rm s} = 0.73$ (Ref. [120]). Cramer [82] showed that this ratio should increase from 0.4 to 1 as the temperature changes from 100 K to 420 K. Indeed Gu and Ubachs [69] experimentally determined a ratio of  $\eta_{\rm b}/\eta_{\rm s} = [0.46 - 1.01]$  from RB-scattering for the temperature range 254.7 – 336.6 K. Hence, for measurements at lower sound frequencies ( $f_{\rm sl}$ ) and at hypersound frequencies ( $f_{\rm sh}$ ), this ratio yields a similar value. The vibrational relaxation time of N<sub>2</sub> is larger than 10<sup>-4</sup> seconds at room temperature [121], thus  $f_{\rm sl}\tau_{\rm vib} \gg 1$  as well as  $f_{\rm sh}\tau_{\rm vib} \gg 1$ . In other words, the vibrational degrees remain frozen under both conditions [122].

For CO<sub>2</sub> a different situation is encountered. At atmospheric pressure, the vibrational relaxation time is  $\tau_{\rm vib} = 6 \times 10^{-6}$  s, while the rotational relaxation time is  $\tau_{\rm rot} = 3.8 \times 10^{-10}$  s (Ref. [68, 123]). Hence, for sound frequency measurements (at the MHz scale),  $f_{\rm sl}\tau_{\rm vib} \approx 1$  and  $f_{\rm sl}\tau_{\rm rot} \ll 1$ , which means that both rotation and vibration are excited and take effect during energy exchange

with translation in collisions. The method of sound absorption delivers an experimental ratio of bulk viscosity to shear viscosity  $(\eta_{\rm b}/\eta_{\rm s})$  of  $\mathcal{O}(10^4)$  (Ref. [120, 124, 125]). For hypersound frequencies (at the GHz scale),  $f_{\rm sh}\tau_{\rm vib} \gg 1$ , causing the vibrational modes not to take effect.

In order to describe macroscopic flow phenomena on time scales ranging from microseconds to nanoseconds, the used value of the bulk viscosity will range over four orders of magnitude. An example of such a flow phenomenon is a shock in a high Mach number flow. The comparison of scattered light spectra to kinetic and hydrodynamic models in this paper shows that this dramatic frequency dependence of the bulk viscosity is due to the (gradual) cessation of vibrational relaxation.



# Chapter 6

# Rayleigh-Brillouin scattering of binary mixture gases

The Rayleigh-Brillouin scattering spectra of binary mixture gases were measured at 532 nm at room temperature including the mixtures of  $SF_6$ -He,  $CO_2$ -He,  $SF_6$ -D<sub>2</sub>,  $CO_2$ -D<sub>2</sub>,  $SF_6$ -H<sub>2</sub>,  $SF_6$ -CH<sub>4</sub> as well as  $CO_2$ -CH<sub>4</sub>. In these measurements, the pressure of the gases with heavy molecular mass is set at 1 bar, and the pressure of the lighter collision partner was increasing. A relaxation hydrodynamic model based on linearized hydrodynamic equations for mixture gases is briefly described. The complex relaxation phenomena in gas mixtures, not only including energy exchange between translational an internal modes of motion, but also energy exchange between the two components are quantified with a single relaxation parameter z. The model is compared with experimental Rayleigh-Brillouin scattering data of  $SF_6$ -He,  $SF_6$ -H<sub>2</sub>,  $SF_6$ -D<sub>2</sub> mixtures as well as  $CO_2$ -He,  $CO_2$ -D<sub>2</sub> mixtures. The value of z is determined in a least-squares procedure.

<sup>\*</sup>The author acknowledges Prof. Dr. Wilson Marques Junior for developing the RB-scattering model as described in section 6.2.

# 6.1 Introduction

Spontaneous Rayleigh-Brillouin (RB) scattering spectra of gaseous/fluidic media contain information on the thermodynamics and the transport properties of the gases/fluids such as thermal diffusivity, speed of sound, relaxation times of various dynamical processes. Besides, it can also provide a way to test a given theory of light scattering.

Theories of RB-scattering for fluids in the kinetic and hydrodynamic regimes have been devised based on the linearized Boltzmann equation and on linearized hydrodynamic equations, respectively. Many models have already successfully explained the scattered light spectra [8, 15, 42, 126]. Some models have been able to reproduce the spectra very well, even though some discrepancies with experiments still exist, while their validity is often restricted to certain pressure regimes. Similarly, the study of RB-scattering for mixtures was also undertaken.

The hydrodynamic theory of light scattering in binary fluid mixtures was first developed by Mountain and Deutch [127], who described the local dielectric constant fluctuations by several linear hydrodynamic equations including the continuity equation for mass conservation, the Navier-Stokes equation for momentum conservation, the diffusion equation and the energy transport equation. Later, Cohen et al. [128] corrected some correlation functions by adding the 'non-Lorentzian' term based on the original paper of Mountain and Deutch [127] which improved the light scattering models.

The Rayleigh-Brillouin scattering spectra of helium-xenon mixtures were measured by Letamendia et al. [129] at different pressures, compositions, and scattering angles. The data were compared with a complete two-component hydrodynamic theory and good agreement was found at low molar fractions of He and at molar fractions of He higher than a 'critical' value which depends on the partial pressure of Xe. In addition, since the spectral shape in He–Xe mixtures is very sensitive to the presence and magnitude of thermal-diffusion effects, the thermal diffusion coefficient could be derived.

A kinetic model was formulated by Letamendia et al. [130] based on the generalized Enskog equations for a binary mixture of hard-sphere fluids. This model gives an improvement over an existing model derived by Boley and Yip [131], which is based on the linearized Boltzmann equations for Maxwell molecules and which was successful in explaining light scattering spectra of He–Xe mixtures at very low Xe pressure and small Xe molar fraction, conditions under which imperfect-gas effects and thermal diffusion can be ignored.

Bonatto and Marques Jr. [18] proposed a model to describe the spontaneous density fluctuations in a binary mixture of monatomic ideal gases based on the Boltzmann equation, the collision operators of which are replaced by simple

$CO_2$	He		SF <sub>6</sub>	He	
p (bar)		T (K)	p (bar)		$T(\mathbf{K})$
1.014		295.0	1.032		295.0
1.014	0.509	295.1	1.033	0.512	295.1
1.014	1.009	295.0	1.037	1.029	295.1
1.007	2.019	295.0	1.037	2.146	295.1
1.008	3.016	295.0	1.035	2.993	295.1
			1.037	4.084	295.1

 Table 6.1: The conditions of mixture gases experimentally investigated.

Table 6.2: The conditions of mixture gases experimentally investigated.

$\rm CO_2$	$D_2$		$SF_6$	$D_2$	
p (t	par)	$T(\mathbf{K})$	p (bar)		$T(\mathbf{K})$
1.003		293.2	1.007		293.2
1.002	0.500	293.2	1.001	0.506	293.2
1.002	1.020	293.2	1.002	1.001	293.2
1.002	2.003	293.2	1.002	2.003	293.2
1.002	2.999	293.2	1.002	3.002	293.2
1.002	4.001	293.2	1.002	4.002	293.2

relaxation-time terms. For this model, the description of kinetic equations for a mixture of monatomic ideal gases is characterized by the fields of partial number density, partial flow velocity and partial temperature and assuming that the particles of the mixture interact according to the Lennard-Jones (6-12) potential. This model shows that it can be applied to the light scattering spectrum of a binary gas mixture passing over from a hydrodynamic to a kinetic regime. Based on this model, Gu et al. [132] measured the RB-spectra mixtures of Ar–He and Kr–He, and obtained excellent agreement with the model. Clearly, since noble gas atoms do not have the internal degrees of motion that molecules have, this model is not suited for mixtures including molecular gases.

To study the molecular relaxation during the collision for different kinds of molecules, the mixture gases with  $CO_2$ -He,  $SF_6$ -He,  $CO_2$ -D<sub>2</sub>,  $SF_6$ -D<sub>2</sub>,  $SF_6$ -H<sub>2</sub>,  $CO_2$ -CH<sub>4</sub> and  $SF_6$ -CH<sub>4</sub> are measured under different conditions as listed in Tables 6.1-6.4. In addition, a relaxation hydrodynamic model based on a generalized hydrodynamic description will be introduced and compared with the experimental data.

$SF_6$	$H_2$	
p (t	bar)	$T(\mathbf{K})$
1.004		293.2
1.002	0.510	293.2
1.002	1.004	293.2
1.002	2.007	293.2
1.002	3.002	293.2
1.004	4.001	293.2

 Table 6.3:
 The conditions of mixture gases experimentally investigated.

Table 6.4: The conditions of mixture gases experimentally investigated.

$\rm CO_2$	$CH_4$		$SF_6$	CH <sub>4</sub>	
p (bar)		$T(\mathbf{K})$	p (bar)		$T(\mathbf{K})$
0.999		293.2	1.007		295.2
1.007	0.495	293.2	1.007	0.497	295.2
1.007	0.998	293.2	1.007	0.995	295.2
1.007	1.999	293.2	1.007	1.997	295.2
1.007	2.999	293.2	1.007	2.997	295.2
			1.007	4.009	295.2

# 6.2 Model description

The intensity of the Rayleigh-Brillouin scattered light is related to the fluctuations of the dielectric constant  $\Delta \epsilon$  caused by the random thermal motion of molecules in a fluid. For mixture gases, these fluctuations can be expressed by dynamic quantities as pressure p, temperature T and mass concentration of the light constituent c:

$$\Delta \epsilon(\boldsymbol{r},t) = \left(\frac{\partial \epsilon}{\partial p}\right)_{T,c} \Delta p(\boldsymbol{r},t) + \left(\frac{\partial \epsilon}{\partial T}\right)_{p,c} \Delta T(\boldsymbol{r},t) + \left(\frac{\partial \epsilon}{\partial c}\right)_{T,p} \Delta c(\boldsymbol{r},t) \quad (6.1)$$

and the dynamic structure factor can be expressed by:

$$S(\boldsymbol{q},\omega) = 2\operatorname{Re}\langle\Delta\epsilon(\boldsymbol{q},i\omega)\Delta\epsilon(-\boldsymbol{q},0)\rangle$$
(6.2)

Compared with Eq. (1.9), an important new ingredient in Eq. (6.1) is the fluctuating composition c of the binary mixture. Let us now briefly describe the light scattering model for binary gas mixtures. Compared to a simple (molecular) gas, there are many more dynamic processes in gas mixtures, and the challenge is to obtain the associated transport coefficients. The model

applies to the continuum case, which deals with the following fields: density  $\rho$ , velocity  $\boldsymbol{v}$ , composition c and energy  $\varepsilon$ . The fluxes of these fields: mass  $\boldsymbol{J}$ , energy  $\boldsymbol{\kappa}$ , stress  $\boldsymbol{\sigma}$  satisfy the continuum equations:

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} + \rho \nabla \cdot \boldsymbol{v} = 0$$

$$\rho \frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} + \nabla \cdot \boldsymbol{\sigma} = 0$$

$$\rho \frac{\mathrm{d}c}{\mathrm{d}t} + \nabla \cdot \boldsymbol{J} = 0$$

$$\rho \frac{\mathrm{d}\varepsilon}{\mathrm{d}t} + \nabla \cdot \boldsymbol{\kappa} + \boldsymbol{\sigma} : \nabla \boldsymbol{v} = 0$$
(6.3)

Constitutive relations express the fluxes J,  $\kappa$ , and  $\sigma$  in terms of composition c, energy  $\varepsilon$  (or temperature T) and velocity strain field  $\nabla v$ . For example, the expression for components of the stress [133]:

$$\sigma_{mn} = p \,\,\delta_{mn} - 2\eta_{\rm s} \,\,S_{mn} - \eta_{\rm b} \,\,\nabla \cdot \boldsymbol{v} \,\,\delta_{mn} \tag{6.4}$$

where  $\delta_{mn}$  is the Kronecker delta,  $S_{mn}$  is the off-diagonal part of  $\nabla \boldsymbol{v}$  and p is the pressure, and this equation involves the shear viscosity  $\eta_s$  and the bulk viscosity  $\eta_b$ . Similarly, the mass flux  $\boldsymbol{J}$  is proportional to the concentration gradient  $\nabla c$  through the diffusion coefficient  $D_{12}$ , but in a mixture  $\boldsymbol{J}$  also depends on the pressure p and temperature gradients  $\nabla T$ . Finally, the heat flux  $\boldsymbol{\kappa}$  is proportional to the temperature gradients  $\nabla T$ , but in a mixture also depends on the mass flux  $\boldsymbol{J}$ .

The challenge of the model involves the introduction of a large number of transport coefficients, many of which are not known very well experimentally. In the model tested in this chapter, all transport coefficients were computed theoretically assuming Lennard-Jones interaction between the molecules with potential function:

$$U_{ij}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right]$$
(6.5)

where r is the distance between the centres mass of the two molecules,  $\epsilon_{ij}$  the maximum depth of the potential well and  $\sigma_{ij}$  is the distance at which  $U_{ij}(r)=0$ .

Table 6.5 documents the well depths and size parameters for the binary mixtures considered in this chapter. Since polarizabilities of the two components may differ, they are listed in Table 6.6. For simple gases, this information is irrelevant as we do not measure absolute cross sections.

In this model, a large unknown is the bulk viscosity  $\eta_{\rm b}$ , which involves the exchange of energy between translational motion of the components and internal motion, and between translational motion of the two components. This bulk viscosity is left as a free parameter,  $z = \tau_b/\tau_s$ , where  $\tau_s$  is the relaxation time associated with the shear viscosity  $\eta_s = p\tau_s$  and  $\tau_b$  involves the classic relation [50]:

$$\eta_{\rm b} = \frac{3}{2} (\gamma_{mix} - 1) (\frac{5}{3} - \gamma_{mix}) p \tau_b \tag{6.6}$$

Incidentally, the association of  $\eta_{\rm b}$  to a relaxation time, as in Eq. (6.6) was proven for binary mixtures with disparate mass by Monchick et al. [134]. In Eq. (6.6),  $\gamma_{mix}$  is the heat capacity ratio  $\gamma_{mix} = c_{\rm p}/c_{\rm v}$  given by

$$\gamma_{\rm mix} = 1 + \frac{1}{\sum_{i=1}^{2} \frac{x_i}{\gamma_i - 1}} \tag{6.7}$$

where  $\gamma_i$  is the heat capacity ratio of the *i*-component, respectively. It is also a parameter in the model. For He, which only has translational degrees of freedom,  $\gamma_{He} = 5/3$ .

In this model, the parameter z, which describes on average the number of molecular collisions required for internal and translational degrees of freedom to reach thermal equilibrium, is an unknown parameter and set as the only variable in this model. In the comparison of the model with the experimental data of light scattering in binary mixtures, this parameter is fitted.

#### 6.3 Experimental setup and results

A schematic view of the setup for spontaneous Rayleigh-Brillouin scattering is shown in Fig. 6.1. The laser light with wavelength of 532.22 nm, power of 5 Watts, and bandwidth less than 5 MHz travels through the scattering gas cell. For the scattering cell, two Brewster-angled windows are mounted at entrance and exit ports to reduce the loss of incident light and the inside walls were painted black to reduce stray light. A pressure gauge is connected to the cell to monitor the pressure change and a temperature control system consisting of PT-100 sensor, Peltier elements as well as water cooling are used to keep the cell at a constant temperature with uncertainty less than 0.1  $^{\circ}$ C.

The scattering angle determines the scattering wave vector

$$q = \frac{2\pi}{\lambda_{\rm i}} \, 2 \, n \, \sin(\theta/2)$$

with  $\lambda_i$  the incident wavelength and *n* the index of refraction. Here, the scattering angle  $\theta = 55.7 \pm 0.3^{\circ}$ C is measured by a homemade rotation stage and the opening angle is less than  $0.5^{\circ}$  which is calculated by the geometric relationship of the scattering gas cell and a slit is set behind the gas cell. The scattered light propagates through a bandpass filter (Materion, T> 90%)

#### 6.3. Experimental setup and results

			$\sigma_{ij} (nm)$	)		
	$SF_6$	$\rm CO_2$	He	$D_2$	$CH_4 v$	$H_2$
$SF_6$	$0.5252^{\rm a}$		$0.4298^{\rm a}$	$0.4420^{c}$	$0.4530^{a}$	$0.4396^{\circ}$
$\rm CO_2$		$0.3769^{\rm a}$	$0.3339^{\rm a}$	$0.3339^{c}$	$0.3745^{\rm a}$	$0.3453^{c}$
He			$0.2576^{\rm b}$			
$D_2$				$0.2948^{\mathrm{b}}$		
$CH_4$						
$H_2$						$0.2968^{\mathrm{b}}$
			$\epsilon_{ij}/k_{\rm B}$ (K	I)		
	$SF_6$	$\rm CO_2$	He	$D_2$	$CH_4$	$H_2$
$SF_6$	$207.7^{\rm a}$		$19.24^{\rm a}$	$42.65^{c}$	$161.6^{\mathrm{a}}$	$39.77^{c}$
$CO_2$		$245.3^{\rm a}$	$34.14^{\rm a}$	$34.14^{c}$	$198.5^{\rm a}$	$75.58^{c}$
He			$10.12^{b}$			
$D_2$				$39.3^{\mathrm{b}}$		
$CH_4$						
$H_2$						$33^{\mathrm{b}}$
<sup>a</sup> Ref.	[135].					
<sup>b</sup> Ref.	[129].					

**Table 6.5:** Effective spherical scaling parameters  $\sigma_{ij}$  and  $\epsilon_{ij}$ .

`

<sup>c</sup> Calculated based on Kong rule [136].

**Table 6.6:** The dynamic polarizability  $\alpha$  at wavelength of 532.22 nm and heat capacity ratio  $\gamma$  for the molecular species.

molecule	polarizability $(\times 10^{-40} \text{ C} \cdot \text{m}^2/\text{V})^{c}$	$\gamma$
$SF_6$	$5.029^{a}$	$1.10^{\rm e}$
$\rm CO_2$	$2.932^{\rm a}$	$1.30^{\mathrm{f}}$
He	$0.231^{\rm b}$	$1.66^{\mathrm{f}}$
$D_2$	$0.900^{\circ}$	1.4
$H_2$	0.911 <sup>c</sup>	$1.41^{f}$
$CH_4$	$2.946^{\mathrm{d}}$	$1.31^{\mathrm{f}}$

<sup>a</sup> Calculated based on the static polarizability, the dynamic polarizability function [137] and Ref. [138].

<sup>b</sup> Calculated based on the static polarizability, the dynamic polarizability function [137] and Ref. [139].

<sup>c</sup> Calculated based on the static polarizability, the dynamic polarizability function [137] and Ref. [32].

<sup>d</sup> Calculated based on Ref. [140].

 $^{\rm e}$  Ref. [100].

<sup>f</sup> Ref. [141].

#### 6. RAYLEIGH-BRILLOUIN SCATTERING OF BINARY MIXTURE GASES



Figure 6.1: The schematic diagram of the experimental setup for spontaneous Rayleigh Brillouin scattering. The green light (532.22 nm, full green line) propagates the scattering gas cell and produces the scattered light. The scattered light at scattering angle  $\theta = 55.7^{\circ}$  is analyzed by a FPI (Fabry-Perot interferometer) and detected on a PMT (photomultiplier tube). Symbols  $\mathbf{k}_{\rm s}$ ,  $\mathbf{k}_{\rm i}$ ,  $\mathbf{q}$  are scattered, incident and scattering wave vectors, respectively.

at  $\lambda_i = 532$  nm, bandwidth  $\Delta \lambda = 2.0$  nm) onto a half-confocal Fabry-Perot interferometer (FPI).

The FPI is optimized by using a reference laser beam. The radius of the curved mirror is r = -12.5 mm with reflectivity of 99%. The FPI has an effective free spectral range (FSR) of 2.9964 GHz, which is determined through frequency-scanning a laser (a narrowband tunable cw-ring dye laser) over more than 1000 modes of the FPI while measuring the laser wavelength by a wavelength meter (Toptica HighFinesse WSU-30), hence yielding an uncertainty in the FSR below 1 MHz. The instrument width, yielding a value of  $\sigma_{\nu_{\text{instr}}} = 58.0 \pm 3.0$  MHz (FWHM), is determined by using the reference beam while scanning the piezo-actuated FPI, following methods discussed in chapter 2. The instrument function is verified to exhibit a functional form of an Airy function, which may be well approximated by a Lorentzian function during data analysis.

RB-scattering spectral profiles were recorded by piezo-scanning the FPI at integration times of 1 s for each step, usually over 18 MHz. A full spectrum covering a large number of consecutive RB-peaks and 10,000 data points were obtained in about 3 h. The piezo-voltage scans were linearized and converted to frequency scale by fitting the RB-peak separations to the calibrated FSR-value.

#### **6.3.1** $SF_6$ and He

Comparing with He,  $SF_6$  has a much larger Rayleigh cross section and plays the decisive role in the scattering, making the He component a 'spectator'. However, the presence of the He essentially influences the hydrodynamics and the light scattering. In this mixture, RB-scattering spectra were recorded at the  $SF_6$  pressure of 1 bar and He changing from 0.5 bar to 4 bar at room temperature. Results are shown in Fig. 6.2. As the pressure of He increases, the Brillouin side peaks disappear gradually. Fig. 6.2 also gives the comparison between the experimental spectra and the mixture model. In this model, the depth of the potential well  $\epsilon_{ij}$  and the distance  $\sigma_{ij}$  are listed in Table 6.5. Table 6.6 provides the polarizabilities and ratios of specific heats of SF<sub>6</sub> and He. The experimental value of  $\gamma_{SF_6} = 1.10$  is shown in Table 6.6 at 1 bar for room temperature. Here  $\gamma_{SF_6} = 1.14$  is chosen, as with this value the root mean square errors (RMSE) of the fitting for the five spectra is lowest, as shown in Fig. 6.3. It appears that the model spectra sensitively depend on  $\gamma_{SF_6}$ . This 'best value' is very different from the nominal  $\gamma_{SF_6} = 4/3$ . This clearly signifies a problem in applying our model. We emphasize that the experimental value for  $\gamma$  in Table 6.6 represents a value pertaining to zero frequency, while it involves vibrational degrees of freedom as well as rotational ones. At the frequencies associated with light scattering, vibrational relaxation is too slow, and  $\gamma$  should involve rotations only.

Fig. 6.4 shows that the fitting value of z decreases as the component of He increases, which meaning that the bulk viscosity  $\eta_{\rm b}$  rapidly decreases with increasing He pressure.

#### **6.3.2** $SF_6$ and $D_2$

The molecule  $D_2$  has the same mass as the He atom but it exhibits a different structure and different Lennard-Jones parameters as well as different polarizability. Moreover,  $D_2$  has internal degrees of freedom. The RB-scattering spectra of SF<sub>6</sub> and  $D_2$  were measured at fixed 1 bar SF<sub>6</sub> and the pressure of  $D_2$  increases as shown in Fig. 6.5. The spectral profiles of these mixtures exhibit similar characteristics as that of the mixture of SF<sub>6</sub>-He. The effect of the linear structure of  $D_2$  is not obvious, possibly because of the large mass disparity of SF<sub>6</sub> and  $D_2$ . Fig. 6.5 also shows the comparisons between these spectra and the relaxation hydrodynamic model. Tables 6.5 and 6.6 display the depth of the potential well  $\epsilon_{ij}$ , the distance  $\sigma_{ij}$ , polarizability as well as the ratio of specific heats of  $D_2$ . Remarkably, the best value of  $\gamma_{D_2}$  is now close to its nominal value  $\gamma_{D_2} = 7/5$ . Usually, for diatomic molecules (where there is only one pure stretch vibrational mode), the vibrational contribution to  $c_v$  is very small [142] at room temperature.



Figure 6.2: Comparisons between the mixture model (red) and the experimental Rayleigh-Brillouin scattering profiles (black) of binary mixtures of SF<sub>6</sub>-He as measured for the various conditions as indicated. Bottom graphs display the corresponding residuals. The experimental data were measured at wavelength of  $\lambda_i = 532.22$  nm and scattering angle of  $\theta = 55.7^{\circ}$ , and these spectra are on a scale of normalized integrated intensity over one FSR.

Fig. 6.4 shows the fitting value of z changes as the component of  $D_2$  increases, which agrees that of He at corresponding conditions.

#### **6.3.3** $SF_6$ and $H_2$

The RB-scattering spectra of  $SF_6-H_2$  mixture are also measured at 1 bar  $SF_6$ while the pressure of the H<sub>2</sub> component increases. H<sub>2</sub> has the same structure as D<sub>2</sub> but its mass is only half that of D<sub>2</sub>. Fig. 6.6 shows the experimental data for these mixtures at different conditions. Similarly, the comparisons between these spectra and the relaxation hydrodynamic model are also displayed in Fig. 6.6. The depth of the potential well  $\epsilon_{ij}$ , the distance  $\sigma_{ij}$ , polarizability as well as the ratio of specific heats of H<sub>2</sub> are displayed in Tables 6.5 and 6.6.

Fig. 6.4 shows the fitting value of z as the component of H<sub>2</sub> increases, which is little larger than that of D<sub>2</sub> at corresponding conditions.

#### 6. RAYLEIGH-BRILLOUIN SCATTERING OF BINARY MIXTURE GASES

6.3. Experimental setup and results



**Figure 6.3:** The root-mean-square error for  $\gamma_{SF_6} = 1.14$  and  $\gamma_{SF_6} = 1.10$  when comparing the model with the spectra of SF<sub>6</sub>-He, SF<sub>6</sub>-D<sub>2</sub> and SF<sub>6</sub>-H<sub>2</sub>.



**Figure 6.4:** The value of z changes as the pressure of the lighter component varies for the mixture of SF<sub>6</sub>-He, SF<sub>6</sub>-D<sub>2</sub> and SF<sub>6</sub>-H<sub>2</sub>. Note that here the  $\gamma_{SF_6} = 1.14$  was adopted.



#### 6. RAYLEIGH-BRILLOUIN SCATTERING OF BINARY MIXTURE GASES

Figure 6.5: Comparisons between the mixture model (red) and the experimental Rayleigh-Brillouin scattering profiles (black) of binary mixtures of  $SF_6-D_2$  as measured for the various conditions as indicated. Bottom graphs display the corresponding residuals. The experimental data were measured at wavelength of  $\lambda_i = 532.22$  nm and scattering angle of  $\theta = 55.7^{\circ}$ , and these spectra are on a scale of normalized integrated intensity over one FSR.

#### **6.3.4** CO<sub>2</sub> and He

Compared with SF<sub>6</sub>, the CO<sub>2</sub> molecule is lighter and has a linear structure, implying that it only has 2 rotational degrees of freedom. Fig. 6.7 shows the RB-spectra of the mixture of CO<sub>2</sub> and He. Similar to the mixture of SF<sub>6</sub> and He, the Brillouin side peaks disappear gradually for increasing He pressure. Also the comparisons between the experimental data and the relaxation hydrodynamic model were made. The polarizability of CO<sub>2</sub> is shown in Table 6.6. In this case,  $\gamma_{CO_2}$  is a true fitting parameter which greatly differs from its nominal value  $\gamma_{CO_2} = 7/5$  as well as the experimental value in Table 6.6.



6.3. Experimental setup and results

Figure 6.6: Comparisons between the mixture model (red) and the experimental Rayleigh-Brillouin scattering profiles (black) of binary mixtures of  $SF_6-H_2$  as measured for the various conditions as indicated. Bottom graphs display the corresponding residuals. The experimental data were measured at wavelength of  $\lambda_i = 532.22$  nm and scattering angle of  $\theta = 55.7^{\circ}$ , and these spectra are on a scale of normalized integrated intensity over one FSR.

#### **6.3.5** $\mathbf{CO}_2$ and $\mathbf{D}_2$

The RB-spectral of CO<sub>2</sub> and D<sub>2</sub> were measured with 1 bar of CO<sub>2</sub> and increasing D<sub>2</sub> pressure, as shown in Fig. 6.8. Compared to the previous cases (SF<sub>6</sub>-He, CO<sub>2</sub>-He), the side peaks in the spectra do not disappear with increasing D<sub>2</sub> pressure. Also compared to the previous cases where it exceeded  $\approx 12$ , the ratio of polarizabilities now becomes  $\alpha_{CO_2}/\alpha_{D_2} \approx 3$ , which implies that D<sub>2</sub> becomes less of a 'spectator' molecule. However, it is difficult to disentangle the role of spectator from that of collision partner. Again, the best values of  $\gamma_{CO_2}$  depend on the mixtures composition and differ strongly from the nominal value  $\gamma_{CO_2} = 7/5$ .



#### 6. RAYLEIGH-BRILLOUIN SCATTERING OF BINARY MIXTURE GASES

Figure 6.7: Comparisons between the mixture model (red) and the experimental Rayleigh-Brillouin scattering profiles (black) of binary mixtures of  $CO_2$ -He as measured for the various conditions as indicated. Bottom graphs display the corresponding residuals. The experimental data were measured at wavelength of  $\lambda_i = 532.22$  nm and scattering angle of  $\theta = 55.7^{\circ}$ , and these spectra are on a scale of normalized integrated intensity over one FSR.

#### 6.3.6 Mixtures with CH<sub>4</sub>

Another heavier molecule  $CH_4$  is considered as a collision partner for  $SF_6$ and  $CO_2$ . The RB-scattering spectra of the mixtures gases  $SF_6-CH_4$  and  $CO_2-CH_4$  are measured with increasing pressure of  $CH_4$ , with results shown in Fig. 6.9 and Fig. 6.10. In these measurements  $CH_4$  also contributes to the scattering as the polarizabilities of the two components are now comparable. From the experimental figure it can be seen that the side peaks first decrease and then increase, and the shift of the side peaks becomes larger, especially for the mixtures with  $CO_2$ . As the relaxation hydrodynamic model does not show a good behaviour for the mixture with two big molecules, the comparison is not made, awaiting further development of the model.



Figure 6.8: Experimental data for RB-scattering in binary mixtures of  $CO_2-D_2$  as measured for the various conditions as indicated. The experimental data were measured at wavelength of  $\lambda_i = 532.22$  nm and scattering angle of  $\theta = 55.7^{\circ}$ , and these spectra are on a scale of normalized integrated intensity over one FSR.

### 6.4 Conclusion

For these mixture gases, the scattering is mainly coming from the heavy molecule, the He just influences the collision dynamics. Both Fig. 6.2 and Fig. 6.7 show that as soon as some amounts of He are added, the Brillouin lines become strongly damped and disappear gradually with higher He mole fraction. A possible explanation is that collisions of the fast He atoms with  $SF_6$  molecules that move coherently in a pressure wave, destroy this coherence.

Fig. 6.5 and Fig. 6.8 show that  $D_2$  exhibits a similar influence as He, as was expected because these two molecules have the similar mass. However, as the  $D_2$  pressure increases, the Brillouin side peaks persist and increase in size, seen in Fig. 6.8. The light scattering spectra of mixtures of the polyatomic molecules of  $SF_6-CH_4$  and  $CO_2-CH_4$  are qualitatively different from the spectra of mixtures with disparate masses. A striking observation in Fig. 6.9 and Fig. 6.10 is that the Brillouin side peaks are always present. Perhaps this is related to



RAYLEIGH-BRILLOUIN SCATTERING OF BINARY MIXTURE GASES

Figure 6.9: Experimental data for RB-scattering in binary mixtures of  $SF_6-CH_4$  as measured for the various conditions as indicated. The experimental data were measured at wavelength of  $\lambda_i = 532.22$  nm and scattering angle of  $\theta = 55.7^{\circ}$ , and these spectra are on a scale of normalized integrated intensity over one FSR.

the comparable polarizabilities of the components. In these cases, the model could not reproduce the spectra.

6.



Figure 6.10: Experimental data for RB-scattering in binary mixtures of  $CO_2-CH_4$  as measured for the various conditions as indicated. The experimental data were measured at wavelength of  $\lambda_i = 532.22$  nm and scattering angle of  $\theta = 55.7^{\circ}$ , and these spectra are on a scale of normalized integrated intensity over one FSR.



# Appendix A

# Matlab code for Tenti-S6 model

1 % This is the code for Tenti-S6 model, translated from the thesis of 2 %Pan (2003). With this code, a spontaneous RB-scattering spectrum 3 %can be obtained. Here, the N2O is taken as an example. If choosing 4 %other molecules, the corresponding parameters should be changed. 5 % The unknown parameters can be set as variables for fitting. 6 clc;clear all; close all; 7 %-----N2O as an example----8 gas = 'N20';% selecting gas species 9 M = 44.0128; % molar mass, unit g/mol 10 p = 1.000 \* 10<sup>5</sup>; % pressure, unit Pa 11 T = 20 + 273.15; %temperature, unit K 12 eta\_s = 1.48 \* 10^(-5);% shear viscosity, unit Pa s 13 bulk\_vis = 2.63 \* 10<sup>(-5)</sup>;% bulk viscosity, unit Pas 14 thermal\_cond = 14.4\*1e-3; % thermal conductivity, unit W/(m K) 15 lambda = 532.22e-9; % The wavelength of the laser unit m 16 17 kb = 1.380649e-23; % Boltzmann constant, unit J/K 18 R = 8.314462618;% gas constant, unit J/(mol K) 19 m\_m = M\*1.66053906660e-27; % Molecular weight, unit kg 20 v0 = sqrt(2\*kb\*T/m\_m); % thermal speed, unit m/sec 21 n0 = p/(T\*kb); % Numerical density, unit 1/m<sup>3</sup> 22 23 %-----scattering angle-----24 scattering\_angle = 55.7; % scattering angle 25 angle = scattering\_angle/2\*(pi/180); % scattering angle in radians 26 q = sin(angle) \*4\*pi/lambda; % wave number, unit m^-1 27 y = n0\*kb\*T/(q\*v0\*eta\_s); % Ratio of mean free path and laser 28 % wavelength, dimensionless unit 29 8----

#### A. MATLAB CODE FOR TENTI-S6 MODEL

```
30 n_xi = 2001; % Number of frequency points, dimensionless unit
31 xi_lef = -2.6; % Minimum frequency point, dimensionless unit
32 xi_rgt = 2.6; % Maximum frequency point, dimensionless unit
33 dxi = (xi_rgt-xi_lef)./(2.0.*(n_xi-floor(n_xi_/2)-1));
34 for i = 1:n_xi
       xi(i) = xi_lef+dxi.*(i-1); % Calculate the frequency points,
35
36
             % dimensionless unit
37 end
38 c_tr = 3/2; % Translational heat capacity, unit J/(mol K)
39 c_int = 1; % internal heat capacity, unit J/(mol K)
40 gamma_int = c_int/(c_tr+c_int); % Internal heat capacity ratio,
41 c_int = 3/2*gamma_int/(1-gamma_int);
42 y6 = y;
43 rlx_int = 1.5*bulk_vis/(eta_s*gamma_int); % Internal relaxation
44 eukenf = m_m*thermal_cond/(eta_s*kb*(c_tr+c_int)); % Eucken factor
45 v1 = xi'.*q.*v0./(2.*pi)./1e9;% The relative frequency, unit GHz
46 %-----
47 %% The spectrum calculation from WCU equation
48 cpxunit = 1i; % Unit imaginary part of complex
49 one = 1; % One
50 zero = 0; % Zero
51
52 % Calculate matrix j
53 \quad j020 = -y;
54 j100 = -gamma_int*y/rlx_int;
55 j001 = j100*c_tr/c_int;
56 j100001 = j100*sqrt(c_tr/c_int);
57 j110 = j100*5/6+j020*2/3;
58 j011110 = j100*sqrt(5/(8*c_int));
59
60 j_nu = 0.4*(1.5+c_int)+(3+c_int)/(2*rlx_int)+...
           9*eukenf/(16*rlx_int^2);
61
62 j_de = -1+(4/15)*eukenf*(1.5+c_int)+(c_int/3)*eukenf/rlx_int;
63 j_co = -y*(2*gamma_int/3);
64 j011 = j_co*j_nu/j_de;
65
66 % Initialization for the area of spontaneous RBS spectrum
67 %and coherent RBS spectrum
68
69 sptarea = 0; % Area of spontaneous RBS spectrum
70 coharea = 0; % Area of coherent RBS spectrum
71
72 % calculate the matrix equation ax = b.
73 % The x here is the target variable.
74 for i = 1:n_xi
       % Calculate w
75
76
       z = xi(i)+cpxunit.*y6;
       F = @(x) exp(-x.^2)./(z-x);
77
78
       w0 = integral(F,-inf,inf);
79
       w1 = -sqrt(pi) + z. * w0;
80
81
       w^2 = z \cdot * w^1;
```

```
w3 = -0.5.*sqrt(pi)+z.*w2;
 82
 83
        w4 = z \cdot * w3;
 84
        w5 = -3.*sqrt(pi)./4+z.*w4;
        w6 = z.*w5;
 85
 86
        % Calculate i
 87
        i0000 = w0./(sqrt(pi));
 88
        i0100 = (z.*w0-sqrt(pi)).*sqrt(2./pi);
 89
        i0001 = i0100;
 90
        i0010 = (2.*w2-w0)./(sqrt(6.*pi));
 91
        i1000 = i0010;
 92
        i0011 = (2.*w3-3.*w1)./(sqrt(5.*pi));
 93
        i1100 = i0011;
 94
        i0101 = 2.*w2./sqrt(pi);
 95
        i0110 = (-w1+2*w3)./sqrt(3.*pi);
 96
        i1001 = i0110;
97
        i0111 = (-3.*w2+2.*w4).*sqrt(2./(5.*pi));
98
99
        i1101 = i0111;
        i1111 = (13.*w2-12.*w4+4.*w6)./(5.*sqrt(pi));
100
        i0002 = (-w0+2.*w2)./sqrt(3.*pi);
101
102
        i0200 = i0002;
        i0211 = (-w1+8.*w3-4.*w5)/sqrt(15.*pi);
103
104
        i1102 = i0211;
        i0202 = 2.*(w0-2.*w2+2.*w4)./(3.*sqrt(pi));
105
        i0210 = (w0+4.*w2-4.*w4)./(3.*sqrt(2.*pi));
106
        i1002 = i0210;
107
108
        i0102 = (-w1+2.*w3).*sqrt(2./(3.*pi));
109
        i0201 = i0102;
        i1010 = (5.*w0-4.*w2+4.*w4)./(6.*sqrt(pi));
1110
        i1110 = (7.*w1-8.*w3+4.*w5)./sqrt(30.*pi);
111
112
        i1011 = i1110;
113
114
        % Calculate matrix A
115
        a_factor = one;
        a(1,1) = -j020.*i0000+cpxunit;
116
117
        a(2,1) = -j020.*i0001;
        a(3,1) = -j020.*i0011;
118
119
        a(4,1) = -j020.*i0010;
120
        a(5,1) = zero;
121
        a(6,1) = zero;
122
123
        a(1,2) = -j020.*i0100;
124
        a(2,2) = -j020.*i0101+cpxunit;
        a(3,2) = -j020.*i0111;
125
        a(4,2) = -j020.*i0110;
126
127
        a(5,2) = zero;
128
        a(6,2) = zero;
129
130
        a(1,3) = (j020-j110) \cdot i1100;
131
        a(2,3) = (j020-j110) \cdot i1101;
        a(3,3) = (j020-j110).*i1111-cpxunit;
132
133
        a(4,3) = (j020-j110).*i1110;
```

#### A. MATLAB CODE FOR TENTI-S6 MODEL

```
134
         a(5,3) = -j011110.*i0100;
        a(6,3) = -j011110. \star i0101;
135
136
        a(1,4) = (j020 - j100) \cdot i1000;
137
        a(2,4) = (j020-j100) . \star i1001;
138
        a(3,4) = (j020-j100).*i1011;
139
140
        a(4,4) = (j020-j100).*i1010-cpxunit;
        a(5,4) = -j100001.*i0000;
141
        a(6,4) = -j100001.*i0001;
142
143
144
        a(1,5) = j100001. \star i1000;
        a(2,5) = j100001. \star i1001;
145
        a(3,5) = j100001.*i1011;
146
        a(4,5) = j100001.*i1010;
147
        a(5,5) = (j001-j020).*i0000+cpxunit;
148
        a(6,5) = (j001-j020) . * i0001;
149
150
151
        a(1,6) = j011110.*i1100;
        a(2,6) = j011110.*i1101;
152
        a(3,6) = j011110.*i1111;
153
        a(4,6) = j011110.*i1110;
154
        a(5,6) = (j011-j020) . * i0100;
155
156
        a(6,6) = (j011-j020).*i0101+cpxunit;
157
158
        % calculate matrix B
        % For coherent RBS
159
        b(1,1) = -i0100;
160
        b(2,1) = -i0101;
161
        b(3,1) = -i0111;
162
163
        b(4,1) = -i0110;
        b(5,1) = zero;
164
165
        b(6, 1) = zero;
166
        % For spontaneous RBS
167
        b(1,2) = -i0000;
168
        b(2,2) = -i0001;
169
        b(3,2) = -i0011;
170
        b(4,2) = -i0010;
171
        b(5,2) = zero;
172
173
        b(6,2) = zero;
174
175
        % solve the equation for X
176
        X=a\b;
         cohsig(i) = X(1,1).*conj(X(1,1));
177 %
178
        sptsig(i) = 2.*real(X(1,2));
179 end
180 % area normalization
181 TentiSpectrum = sptsig./...
182
                 polyarea([min(v1) v1' max(v1)],[0 sptsig 0]);
183
184 FSR = 2.9929;% the value of FSR, unit GHz
185 FWHM = 0.058;% the linewidth of the instrument function, unit GHz
```
```
186 % Calculate the instrument function
187 Airy = 1./(1+(2.*FSR./(pi.*FWHM)).^2.*sin(pi./FSR.*v1).^2);
188
189 % convolve with instrument function
190 TentiSpectrum.conv = conv(Airy,TentiSpectrum,'same');
191
192 % area normalization
193 TentiSpectrum.conv = TentiSpectrum.conv./...
194 polyarea([min(v1) v1' max(v1)],[0 TentiSpectrum.conv' 0]);
195 % plot figure;
196 figure;
197 plot(v1,TentiSpectrum.conv)
```



### Appendix B

# Matlab code for rough-sphere model

1 % This is the code for rough-sphere model, publised by Marques Jr 2~ %(1999). With this code, a spontaneous RB-scattering spectrum can be  $3\,$  % obtained. Here, SF6 is taken as an example. If chosing other 4 % molecues, the corresponding parameters should be changed. 5 % The unknown parameters can be set as variables for fitting. 6 clc;clear all; close all; 7 %-----8 gas = 'SF6'; 9 k = 0.227; % dimensionless moment of inertia, kappa = 4I/ma^2 10 p = 1.000\*10^5; % pressure, unit Pa 11 T = 20 + 273.15; % temperature, unit K 12 eta\_s = 1.5193\*10^(-5);% shear viscosity, unit Pa s 13 lambda= 402.996\*10^(-9);% incident wavelength, unit m 14 M = 44.0128; % molar mass, unit g/mol 1516 m = M\*1.66053906660e-27;% mass 17 kb = 1.380649e-23; % Boltzmann constant, unit J/K 18 v0 = sqrt(2\*kb\*T/m);% thermal velocity, unit m/s 19 R = 8.314462618;% gas constant unit, J/(mol K) 20 %-----scattering angle-----21 scattering\_angle = 55.7; 22 angle = scattering\_angle/2\*(pi/180); % scattering angle in radians 23 q = sin(angle)\*4\*pi/lambda; % wave number, unit m^-1 24  $y = p/eta_s/v0/q;$ 25 %--26 = (6 - 7.\*k) . / (6 + 13.\*k);27 b =  $(2 - 4.*k) \cdot / (6 + 13.*k);$ 28 c = 20.\*k./(18 + 39.\*k); 29 d =  $(1 + 3.*k - 10.*k^2)/(6 + 13.*k);$ 

#### B. MATLAB CODE FOR ROUGH-SPHERE MODEL

```
30 %-----
                   -----frequency----
31 n_xi = 2001; % Number of frequency points, dimensionless unit
32 xi_lef = -1.5; % Minimum frequency point, dimensionless unit
33 xi_rgt = 1.5; % Maximum frequency point, dimensionless unit
34 % frequency space
35 dxi = (xi_rgt-xi_lef)./(2.0.*(n_xi-floor(n_xi./2)-1));
36 for i = 1:n_xi
37
        xi(i) = xi_lef+dxi.*(i-1); % Calculate the frequency points,
38
              % dimensionless unit
39 end
40 xi = xi';
41 v1 = 2*pi*xi*1e9/(q.*v0);% frequency, unit GHz
42 for index = 1:length(xi)
43 z = v1(index) - 1i \cdot v;
       F = Q(x) 1/sqrt(pi) *exp(-x.^2)./(x - z);
44
       w = integral(F, -inf, inf);
45
       A1 = z \cdot * w + 1;
46
       A2 = (z \cdot 2 - 1/2) \cdot w + z;
47
       A3 = z \cdot (z \cdot 2 - 3/2) \cdot w + z \cdot 2 - 1;
48
       A4 = (z.^4 - z.^2 + 11/4).*w + z.^3 - 1/2*z;
49
       A5 = z \cdot (z \cdot 4 - 2 \cdot z \cdot 2 + 7/4) \cdot w + z \cdot 4 - 3/2 \cdot z \cdot 2 + 3/2;
50
51
       M11 = 1i.*y.*w - 1;
52
       M12 = 2.*1i.*y.*A1;
53
       M13 = 1i.*y.*A2;
54
       M14 = a.*M13;
55
       M15 = 4/5*1i.*y.*b.*A3;
56
       M16 = 1i.*y.*c.*A3;
57
58
       M21 = 1/2 \star M12;
59
       M22 = z. * M12 - 1;
60
       M23 = z.*M13;
61
       M24 = z.*M14;
62
       M25 = z.*M15;
63
       M26 = z.*M16;
64
65
       M31 = 1/3.*M13;
66
       M32 = 2/3.*z.*M13;
67
       M33 = 1/3.*1i.*y.*A4 - 1;
68
       M34 = a.*(M33 - M11);
69
       M35 = 4/15.*1i.*y.*b.*A5 + 1/4.*c.*M12;
70
       M36 = 1/3.*1i.*y.*c.*A5 + 1/3.*d.*M12;
71
72
73
       M41 = 1/3. \star M13;
       M42 = 2/3.*z.*M13;
74
       M43 = M33 - M11;
75
76
       M44 = a. * M33 - 1;
       M45 = M35 - 1/2 * c. * M12;
77
       M46 = M36 - 2/3.*d.*M12;
78
79
       M51 = 1i*y.*A3;
80
       M52 = 2.*z.*M51;
81
```

```
82
         M53 = 1i*y.*A5;
         M54 = a. * M53;
83
84
         M55 = 4/5 \times 1i \times y \times b \times z \times (A5 - A3) - 1;
         M56 = li*y.*c.*z.*(A5 - A3);
85
86
87
        M61 = 0;
        M62 = 0;
88
         M63 = 3/4 \star M12;
89
90
         M64 = -a.*M63;
        M65 = 3/4.*c.*z.*M12;
91
92
         M66 = d. *z. *M12 - 1;
93
94
         N11 = -1i * w;
        N21 = -1i * A1;
95
         N31 = -1i/3 * A2;
96
        N41 = -1i/3 \star A2;
97
        N51 = -1i * A3;
98
99
        N61 = 0;
100
         XM = [M11, M12, M13, M14, M15, M16;...
101
               M21, M22, M23, M24, M25, M26;...
102
103
               M31, M32, M33, M34, M35, M36; ...
104
               M41, M42, M43, M44, M45, M46; ...
               M51, M52, M53, M54, M55, M56; ...
105
               M61, M62, M63, M64, M65, M66];
106
           XN = [N11;N21;N31;N41;N51;N61];
107
           xr = XM \setminus XN;
108
109 %
              xr = inv(XM) *XN;
110
           spectrum(index) = real(xr(1,1));
111 end
112 spectrum = spectrum';
113 % area normalized
114 RSspectrum =spectrum./...
1115
             polyarea([min(v1) v1' max(v1)],[0 spectrum' 0]);
116
117 FSR = 2.9929;% the value of FSR, unit GHz
118 FWHM = 0.058;% the linewidth of the instrument function
119 % Calculate the instrument function, unit GHz
120 Airy = 1./(1+(2.*FSR./(pi.*FWHM)).^2.*sin(pi./FSR.*v1).^2);
121
122 % convolve with instrument function
123 RSspectrum_conv = conv(Airy,RSspectrum,'same');
124
125 % area normalization
126 RSspectrum_conv = RSspectrum_conv./...
         polyarea([min(v1) v1' max(v1)], [0 RSspectrum_conv' 0]);
127
128 figure;
129 plot(v1,RSspectrum_conv)
```



## Appendix C

# Matlab code for Grad's six-moment model

1 % This is the code for Grad's six-moment model, published by  $2\,$  % Fernandes and Marques Jr (2007). With this code, a spontaneous 3~ % RB-scattering spectrum can be obtained. Here, CO2 is taken as an 4 % example. If choosing other molecules, the corresponding parameters 5 % should be changed. The unknown parameters can be set as variables 6 % for fitting. 7 clc;clear all;close all; 8 %----- CO2----9 gas = 'CO2'; 10 M = 44.0095; %Relative molecular weight, g/mol 11 p = 1.000 \* 10<sup>5</sup>; % pressure, unit Pa 12 T = 20 + 273.15; %temperature, unit K 13 eta\_s = 1.47e-05;% shear viscosity, unit Pa s 14 t\_tao = 5.08e-10;% internal relaxational time, unit s 15 lambda= 532.22\*1e-9; % The wavelength of the laser, unit m 16 17 kb = 1.380649e-23; % Boltzmann constant, unit J/K 18 R = 8.314462618;% gas constant, unit J/(mol K) 19 m = M\*1.66053906660e-27;% mass 20 v0 = sqrt(2\*kb\*T/m); % thermal speed, unit m/s 21 n0 = p/(T\*kb); % Numerical density, unit 1/m<sup>3</sup> 22 %-----scattering angle-----23 scattering\_angle = 55.7; 24 angle = scattering\_angle/2\*(pi/180); % scattering angle in radians 25 q = sin(angle) \*4\*pi/lambda; % wave number, unit m^-1 26 y = p/eta\_s/v0/q; 27 28 r = 1.4;% heat capacity ratio 29 Z = 3/2\*(r-1)\*p\*t\_tao/eta\_s;%internal relaxation number

C. MATLAB CODE FOR GRAD'S SIX-MOMENT MODEL

```
30 v1 = (-1.5:0.01:1.5)';% frequency, unit GHz
31 xi = v1*1e9*2*pi/q/v0;
32 for index = 1:length(v1)
        z = xi(index) - 1i * y;
33
34
        F = Q(x) \frac{1}{\operatorname{sqrt}(pi)} \exp(-x.^2)./(x - z);
        Wz = integral(F,-inf,inf);
35
36
        8----
        Az = z * Wz + 1;
37
        Bz = (z^2 - 1/2) * Wz + z;
38
        Cz= z*(z^2-3/2)*Wz + z^2 -1;
39
        Dz = (z^4 - z^2 + 5/4) * Wz + z^3 - z/2;
40
        Fz = z * (z^4 - 2 * z^2 + 7/4) * Wz + z^4 - 3/2 * z^2 + 3/2;
41
42
        8---
        ull = 1.32;% ull = 3*Omgega22/5/Omgegall;
43
       M011 = Wz;
44
       M012 = 2 * Az;
45
       M013 = (1-3/2 * (5/3-r)/Z) *Bz;
46
       M014 = 3/2 * ((5/3-r)/Z) *Bz;
47
48
       M021 = Az;
49
       M022 = z * M012;
50
       M023 = z * M013;
51
       M024 = z \star M014;
52
53
       M031 = 2/3 * Bz;
54
       M032 = 2 * z * M031;
55
       M033 = 2/3 * (1-3/2 * (5/3-r)/Z) * Dz;
56
       M034 = (5/3-r)/Z*Dz;
57
58
       M041 = 0;
59
       M042 = 0;
60
       M043 = 3/2*(r-1)/Z*Wz;
61
        M044 = (1 - 3/2 * (r-1)/Z) * Wz;
62
63
        8----
       M111 = 0;
64
       M112 = 0;
65
       M113 = (1-3/2*(1-15/8*(5/3-r)/Z))*Cz;
66
       M114 = -9/8 \star ((5/3-r)/Z) \star u11 \star Cz;
67
68
       M121 = 0;
69
       M122 = 0;
70
       M123 = z * M113;
71
       M124 = z * M114;
72
73
74
       M131 = 0;
       M132 = 0;
75
       M133 = 2/3*(1-3/2*(1-15/8*((5/3-r)/Z)))*Fz;
76
       M134 = -3/4*((5/3-r)/Z)*u11*Fz;
77
78
       M141 = 0;
79
       M142 = 0;
80
       M143 = -15/8 \star (r-1)/Z \star u11 \star Az;
81
```

```
82
        M144 = (1 - u11 * (1 - 3/4 * (r - 1)/Z * u11)) * Az;
 83
 84
        M0 = [M011, M012, M013, M014;...
               M021, M022, M023, M024;...
 85
 86
               M031,M032,M033,M034;...
 87
               M041,M042,M043,M044];
 88
        M1 = [M111, M112, M113, M114;...
 89
               M121, M122, M123, M124;...
 90
               M131,M132,M133,M134;...
 91
 92
               M141,M142,M143,M144];
 93
 94
         I = eye(4, 4);
        XM = y \star MO + 1i \star (I-M1);
 95
        X0 = [Wz;...
 96
               z*Wz+1;...
97
               2/3*((z^2-1/2)*Wz + z);...
98
               0];
99
        X = XM \setminus (-X0);
100
       spectrum(index) = real(X(1,1));
101
102 end
103 % area normalized
104 Grad6spectrum =spectrum'./...
             polyarea([min(v1) v1' max(v1)],[0 spectrum 0]);
105
106
107 FSR = 2.9929;% the value of FSR, unit GHz
108 FWHM = 0.058;% the linewidth of the instrument function
109 % Calculate the instrument function, unit GHz
110 Airy = 1./(1+(2.*FSR./(pi.*FWHM)).^2.*sin(pi./FSR.*v1).^2);
111
112 % convolve with instrument function
113 Grad6spectrum_conv = conv(Airy,Grad6spectrum,'same');
1114
115 % area normalization
116 Grad6spectrum_conv = Grad6spectrum_conv./...
        polyarea([min(v1) v1' max(v1)], [0 Grad6spectrum_conv' 0]);
117
118 figure;
119 plot(v1,Grad6spectrum_conv);
```



## Appendix D

# Matlab code for HW-hydrodynamic model

1 % This is the code for Hammond-Winggs hydrodynamic model, provided 2~ % by Wilson Marques Jr.. With this code, a spontaneous RB-scattering  $3\,$  % spectrum can be obtained. Here, CO2 is taken as an example. If 4 % choosing other molecules, the corresponding parameters should be 5 % changed. The unknown parameters can be set as variables for 6 % fitting. 7 clc;clear all;close all; 8 %----- CO2----9 gas = 'CO2'; 10 M = 44.0095; %Relative molecular weight, g/mol 11 p = 1.000 \* 10<sup>5</sup>; % pressure, unit Pa 12 T = 20 + 273.15; %temperature, unit K 13 eta\_s = 1.47e-05;% shear viscosity, unit Pa s 14 t\_rot = 1.71e-10;% rotational relaxational time, unit s 15 t\_vib = 6\*1.01325\*10^-1/(p);% vibrational relaxational time, unit s 16 lambda= 532.22\*1e-9; % The wavelength of the laser, unit m 17 18 kb = 1.38e-23; % Boltzmann constant, unit J/K 19 R = 8.3144598;% gas constant, unit J/(mol K) 20 m\_m = M\*1.66e-27; % Molecular weight, unit kg 21 v0 = sqrt(2\*kb\*T/m\_m); % thermal speed, unit m/s 22 n0 = p/(T\*kb); % Numerical density, unit 1/m<sup>3</sup> 23 %-----scattering angle-----24 scattering\_angle = 55.7; % scattering angle 25 angle = scattering\_angle/2\*(pi/180); % scattering angle in radians 26 q = sin(angle) \*4\*pi/lambda; % wave number, unit m^-1 27 y = n0\*kb\*T/(q\*v0\*eta\_s); % Ratio of mean free path and laser 28 % wavelength, dimensionless unit 29 rou = p/(T\*kb)\*M\*1.66e-27; the density of the gas, unit kg/m<sup>3</sup>

#### D. MATLAB CODE FOR HW-HYDRODYNAMIC MODEL

```
30 %-----
31 n_xi = 2001; % Number of frequency points, dimensionless unit
32 xi_lef = -1.5; % Minimum frequency point, dimensionless unit
33 xi_rgt = 1.5; % Maximum frequency point, dimensionless unit
34 % frequency space
35 dxi = (xi_rgt-xi_lef)./(2.0.*(n_xi-floor(n_xi./2)-1));
36 for i = 1:n_xi
37
       xi(i) = xi_lef+dxi.*(i-1); % Calculate the frequency points,
38
             % dimensionless unit
39 end
40 %----
41 D = 6.24*1e-6;%diffusion coefficient
42 D_vib = D; %the vibrational diffusion coefficient
43 D_rot = D; %the rotational diffusion coefficient
44 %-----
45 upsilon1 = -45/8 \times 1.014;
46 upsilon2 = 3 \times 0.806;
47 upsilon3 = 2*1.014;
48 %-----
49 C_v = 1.5*R/M*1000; %the transform specific heat, unit J/(K kg)
50 C_rot = 1*R/M*1000; the rotational specific heat, unit J/(K kg)
51 C_vib = 0;%the vibrational specific heat
52 %------
53 for index = 1:length(xi)
     M13 = -1i*q*v0;
54
     M22 = \frac{5}{2 \cdot eta_s \cdot q^2} / rou + C_vib / (C_v \cdot t_vib) + C_rot / (C_v \cdot t_rot);
55
    M23 = -1i * q * v0 * (2/3 - 2/3 * (upsilon1 + upsilon2) * eta_s^2 * q^2/...
56
57
           (rou^2*C_v*T));
    M24 = -C_vib/(C_v \star t_vib);
58
    M25 = -C_rot/(C_v*t_rot);
59
    M31 = -1i*q*v0*(0.5+2/3*upsilon3*eta_s^2*q^2/rou^2/v0^2);
60
    M32 = -1i * q * v0 * (0.5 - 2/3 * (upsilon2 - upsilon3) * eta_s^2 * q^2/...
61
           rou^2/v0^2);
62
    M33 = 4/3*eta_s*q^2/rou;
63
    M42 = -1/t_vib;
64
    M44 = 1/t_vib+D_vib*q^2;
65
    M52 = -1/t_{rot};
66
    M55 = 1/t_rot+D_rot*q^2;
67
    Matrix = [0 0 M13 0 0;...
68
               0 M22 M23 M24 M25;...
69
               M31 M32 M33 0 0;...
70
                0 M42 0 M44 0;...
71
                  M52 0 0 M55];
72
                0
73
    InvM = inv(1i*xi(index)*1e9*2*pi*eye(5,5)+Matrix);
74
     spectrum(index) = real(InvM(1,1));
75 end
76 v1 = xi';
77 HWspectrum =spectrum'./...
78
                polyarea([min(v1) v1' max(v1)], [0 spectrum 0]);
79
80 FSR = 2.9929;% the value of FSR, unit GHz
81 FWHM = 0.058;% the linewidth of the instrument function
```

```
82 % Calculate the instrument function, unit GHz
83 Airy = 1./(1+(2.*FSR./(pi.*FWHM)).^2.*sin(pi./FSR.*v1).^2);
84
85 % convolve with instrument function
86 HWspectrum.conv = conv(Airy, HWspectrum, 'same');
87
88 % area normalization
89 HWspectrum.conv = HWspectrum_conv./...
90 polyarea([min(v1) v1' max(v1)],[0 HWspectrum_conv' 0]);
91 figure;
92 plot(v1, HWspectrum_conv);
```

-



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## Summary

In this thesis it is shown that high signal-to-noise ratio Rayleigh-Brillouin scattering profiles can be measured at high spectral resolution. The RB-spectra, obtained under a variety of measurement parameters, such as pressure, temperature, incident wavelength and scattering angle, form a powerful tool for studying the thermal dynamic and gas transport properties associated with the collective motion and relaxation phenomena in the gas. Different models have been proposed to describe this complex motion involving acoustic excitation and relaxation. Four different models, application in certain conditions, are experimentally tested and relevant gas transport parameters are derived. In particular the bulk viscosity, one of the elusive parameter is determined.

In chapter 2, two measurement setups are described: a complex one using UV-light and simpler one using green light. The optical components and their characteristics are described in detail and the method of data acquisition and processing are explained.

In chapter 3, the bulk viscosity of  $SF_6$  is obtained through comparing the measured RB-scattering data under varying conditions with three models: the Tenti-S6 model, the rough-sphere model and Hammond-Wiggins hydrodynamic model. For the scattering approach Knudsen regime, the hydrodynamic model is not suitable, and we suppose the residuals between these three models and experimental data are caused by the ideal gas law.

In chapter 4, RB-scattering spectra of  $N_2O$  are compared with the Tenti-S6 model, the Grad's six-moment model, the Hammond-Wiggins hydrodynamic model and the rough-sphere model. From the results, the bulk viscosity is found to be pressure dependent. The Grad's six-moment model has a similarly good performance as the Tenti-S6 model. The rough-sphere model is demonstrated to not be applicable in view of the non-spherical and non-symmetrical geometric structure of the  $N_2O$  gas.

**Chapter 5** shows another study of RB-scattering of a linear structure of the symmetric molecule,  $CO_2$ . The spectra of  $CO_2$  are measured at different pressures and temperatures. The bulk viscosity of  $CO_2$  obtained

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from an RB-scattering experiment is found to be four orders of magnitude smaller than that obtained using the method of sound absorption. The comparison of scattered light spectra to kinetic and hydrodynamic models shows that this dramatic frequency dependence of the bulk viscosity is due to the (gradual) cessation of vibrational relaxation. There is no significant temperature dependence.

In chapter 6, the RB-scattering of binary mixture gases is investigated. A large amount of data has been collected for mixtures of gases, where one component is a strong scatterer, while a second component acts as 'spectator', only influencing the collisional dynamics. In case of SF<sub>6</sub>-He and CO<sub>2</sub>-He binary mixtures, the RB-scattering intensity is entirely produced by the strongly polarizable SF<sub>6</sub> and CO<sub>2</sub>. Nevertheless, the spectral profiles are strongly influenced by the additional of the atoms, that influence the motion and collisional dynamic of the SF<sub>6</sub> and CO<sub>2</sub> molecules. In addition, SF<sub>6</sub>-D<sub>2</sub>, CO<sub>2</sub>-D<sub>2</sub>, SF<sub>6</sub>-H<sub>2</sub>, SF<sub>6</sub>-CH<sub>4</sub> as well as CO<sub>2</sub>-CH<sub>4</sub> mixtures are also studied. A full quantitative treatment and modeling the data is presently under way.

The primary perspective of the present investigations was to measure high quality Rayleiigh-Brillouin scattering spectra with the twofold aim to (i) produce scattering profiles to compare with light scattering media under realistic conditions, and (ii) to determine thermodynamic gas transport coefficients. As for the applicability of the data the investigation of RB scattering in  $CO_2$  is to be mentioned. Carbon dioxide is a prominent greenhouse gas and its capture, transport, storage, and conversion is of relevance for a sustainable environment. Accurate knowledge of the thermal dynamic properties of  $CO_2$  gas, and of gas mixtures containing  $CO_2$ , is therefore of relevance. In addition, measurement of its light scattering properties can later support the detection and quantification of  $CO_2$ -gas during transport and processing. Light scattering might be applied as an alternative for absorption or emission spectroscopy for detecting species. Also the measured profiles might be of relevance for lidar detection of planetary atmospheres where  $CO_2$  is a major component, like on Venus and Mars. Possibly such light scattering results may be of future relevance for the study of explants. For the measurements on other gases or mixtures thereof the relevance leans more toward finding proper descriptions of thermodynamic and statistical mechanics properties of complex ensembles of particles. The study of gas mixtures has been explored in the past but it is for the first time that systematic studies yielding such accurate data are performed. The acquired experimental data form a starting point for extended modeling, perhaps opening up a new direction in statistical mechanics.

## 结论

本论文阐述了在一个较高频谱分辨率情况下的高信噪比的瑞利-布里渊散射光 谱的测量。在不同实验条件下(不同气压,温度,入射光波长,散射角),基 于气体分子集体运动与弛豫现象,瑞利-布里渊散射谱成为一种研究热运动、 气体输运特性的重要工具。相应地,多种用于描述包括声激励与弛豫的分子的 复杂运动的瑞利-布里渊散射理论模型已经被提出。基于实验数据,本论文测 试了四种适应于不同实验条件下的理论模型并得到了一些相关的气体输运参 数,尤其是难以得到体粘滞系数。

第一章引言主要介绍了瑞利-布里渊散射理论、散射光谱的线型以及理论模型。第二章描述了两套不同的瑞利-布里渊实验设备:基于紫色光源的较为复杂的实验设备以及基于绿色光源的比较简单的实验设备。其中,详细描述了设备的组成、设备的特性以及相关的实验数据的采集及处理方法。

在第三章中,我们通过比较三种不同的散射模型: Tenti-S6 模型、近似球 模型以及Hammond-Wiggins 流体模型和六氟化硫气体(SF<sub>6</sub>)的瑞利-布里渊 实验散射光谱来获得SF<sub>6</sub>的体粘滞系数。实验结果表明Hammond-Wiggins流 体模型并不适用于努森区域,并且我们认为由于这些模型是基于理想气体状态 方程使得了模型与实验数据产生了差别。

第四章比较了Tenti-S6 模型、近似球模型、Grad's six-moment 模型以及Hammond-Wiggins 流体模型与一氧化二氮发( $N_2O$ )的散射光谱。结果表明 $N_2O$ 的体粘滞系数跟气压有关,Grad's six-moment 模型和Tenti-S6 模型表现相似,并且由于 $N_2O$ 是一个线性的非对称分子,近似球模型此时并不适用。

在第五章中,我们测量了另一种线性对称的气体分子——二氧化碳 (CO<sub>2</sub>)在不同温度、气压下的瑞利-布里渊散射光谱。通过这些散射光谱 与Tenti-S6 模型、Hammond-Wiggins 流体模型的拟合,我们得到的CO<sub>2</sub>的体 粘滞系数比通过使用声波吸收的方法得到的体粘滞系数小四个数量级,并且振 动松弛的逐渐停止使得体粘滞系数表现出显著频率依赖性。我们并没有发现体 粘滞系数随温度变动而产生较大的变化。

第六章探索了二元混合气体的瑞丽-布里渊散射。我们测量了一些二 元混合气体的瑞丽-布里渊散射光谱。在这些二元混合气体中,一种分子 用来产生散射光,而另一种分子则起着"观众"的作用,它只对分子碰 撞产生影响。例如对于SF<sub>6</sub>-He和CO<sub>2</sub>-He的混合气体,散射光主要来源

#### SUMMARY (CHINESE)

于SF<sub>6</sub>和CO<sub>2</sub>,但是He(氦)影响SF<sub>6</sub>和CO<sub>2</sub>的运动及碰撞从而改变散射频光 谱的线型。本章中,我们还研究了其它二元混合气体的瑞丽-布里渊散射光 谱如SF<sub>6</sub>-D<sub>2</sub>,CO<sub>2</sub>-D<sub>2</sub>,SF<sub>6</sub>-H<sub>2</sub>,SF<sub>6</sub>-CH<sub>4</sub>以及CO<sub>2</sub>-CH<sub>4</sub>。同时,相应 的理论模型的也正在研究中。

目前研究高质量瑞丽-布里渊散射光谱主要有两个目的:(i)获得理论上的 散射光谱并与实际气体介质的光谱做比较;(ii)获得气体介质的输运系数。对 于瑞丽-布里渊散的实际应用,我们以CO<sub>2</sub>来说明。CO<sub>2</sub>是一种主要的温室气 体,它的获取、运输、转化对于环境的可持续发展至关重要。因此对于CO<sub>2</sub>或 者含有CO<sub>2</sub>气体的热运动特性的研究是非常必要的。除此之外,CO<sub>2</sub>的光谱测 量对于以后CO<sub>2</sub>在运输及处理中的检测和量化都能提供帮助。通过吸收光谱或 者发射光谱,光散射或许能够成为一种应用在物质检测方面上的替代方法。散 射光谱测量也是使用雷达来测量如金星和火星等行星大气的关键,对于这些行 星,其大气的主要成分是CO<sub>2</sub>,而我们的测量结果或许能够应用于将来相关行 星的探测。对于其它气体或者混合气体的测量,我们主要侧重于找到一种对于 复杂粒子群热力学和统计力学性质的合适描述。虽然过去已经有了对于混合气 体的探索,但是这里也是首次基于精确的实验数据对其进行系统性地研究。这 些实验数据对于模型研究来说是一个起点,或许在统计学方面能够开启一个新 的方向。

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