Probing gases and flames by Coherent Rayleigh Brillouin Scattering and Two Lines Atomic Fluorescence

PROEFSCHRIFT

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Summary

Laser diagnostic techniques in combustion are employed to measure various gas kinetic parameters in a non-intrusive way. This is performed by temporally and spatially mapping of desired parameters with high accuracy. The main challenges are to circumvent the optical accessibility limitations, and scattering and interference from unwanted fluorescence from other molecules. Among other parameters, temperature is one of the key parameters which has a strong influence on ignition and flame speed and it determines the operation of the combustion device. It also influences the pollutant production because of its central role in controlling reaction rates during the combustion. In this thesis, we describe the development and employment of a thermometry setup based on two lines atomic fluorescence. Our technique makes benefit of saturation regime which provides a better signal, lower sensitivity to laser fluctuations and easier temperature estimation. The high signal feature offers the possibility of single shot temperature measurement with higher accuracy in comparison to conventional TLAF experiments. We also study the gaseous medium with Coherent Rayleigh Brillouin Scattering. CRBS is a versatile technique which provides the possibilities to measure different gas parameters like flow speed, gas temperature and viscosity which doesn’t require seeding inside the flame.

Chapter 1 provides a survey on different optical thermometry techniques and it investigates the advantages and disadvantages of different approaches. These methods rely on different parameters which are subject to change with temperature and by measuring those parameters (e.g. total number density, population distribution over the rotational, vibrational or electronic states or Doppler shift) we can estimate the temperature indirectly.

Coherent Rayleigh-Brillouin scattering is one of the techniques which is not limited to temperature measurement and that is a method which
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has great potential to measure various gas kinetic parameters. It is a coherent technique which allows a background free measurement with high signal to noise ratio, but it requires a more complex setup, which needs more alignment effort and elaborate data analysis.

In chapter 2 we make an introduction on Rayleigh-Brillouin scattering providing an outline on theoretical concepts and measurement techniques. We present a brief history on light scattering followed by a timeline on Rayleigh-Brillouin scattering. The momentum and energy conversation laws by scattering are investigated and spontaneous and stimulated scatterings are shortly discussed.

In chapter 3 we investigate the spectral narrowing of scattered light in coherent Rayleigh-Brillouin scattering; we provide experimental data on the scattered spectrum as a function of the coherence between the two pump beams, and we show the fourth order coherence effect on scattered light. We also demonstrate that orders of magnitude in scattering efficiency are to be expected when the experiments are performed with bandwidth-limited picosecond laser pulses. In chapter 4 we investigate the TLAF in saturation. By assuming a three level system and a temporal Gaussian profile for excitation we calculate the temporal behavior of the levels and the generated signal. Based on this simulation and our experimental observation we can investigate the effect of different unknown parameters in level kinetics like quenching and relaxation rates. To date the ground levels are assumed to be steady state over excitation. In higher excitation intensity this assumption is not valid and we calculate the error that might rise due to this assumption. Based on this assumption we propose a model to calculate the temperature in saturation regime and we show that in a flame with an average temperature of 1500K our model can calculate the temperature with a maximum error of 2% over the temperature variation of 200K. The experimental verification of our model is performed in chapter 5. We demonstrate a TLAF setup which employs a novel PIV based seeding system which operates at saturation regime. A new method has been developed, in which salt is deposited on the surface of micron-size metal oxide particles (Al₂O₃) and then fed them into the flame with a modified PIV seeding system. This method provides fast salts decomposition at small particle seeding rates, making this methodology non-intrusive and al-
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allows obtaining strong TLAF signals without flame disturbing even for very lean flames. The saturation curves are extracted and we determined the required pulse energy to operate at saturation level. The single shot temperature images are generated which show a better accuracy over traditional TLAF measurement.
1 Introduction
Combustion devices ranging from gas turbines and automobile engines, to airplanes and power plants are playing an important role in daily life. The development and optimization of these devices have been the subject of numerous studies in recent years. Different approaches have been employed to improve their performance in relation to achieve sustainable usage of non-renewable fossil energy sources, or to reduce the emission of the pollutants such as NO\textsubscript{x}, SO\textsubscript{x} or soot particles which are potentially harmful for human health [1].

Combustion is a complex process in which several phenomena like chemical reactions, fluid dynamics, heat and mass transfer are involved and are interacting with each other. These phenomena need to be known in detail to achieve a deeper understanding of the entire process. In order to accomplish this, various techniques have been utilized to quantify, for instance, the spatial and temporal distributions of various combustion species, which can help to study the chemical reactions during the combustion in more detail.

For instance, the NH radicals can be found in only the reaction zone of particular flames; they are an important intermediate in the production of NO [2]. Another example is OH which is distributed in all flame regions, and its spectrum is studied to extract information about the flame temperature [3]. Apart from concentration maps, the temperature measurement in combusting media is of crucial importance because of its central role in controlling reaction rates during the combustion.

The rate constant \( k \) of many chemical reactions depends on temperature \( T \) through some kind of Arrhenius reaction rate, generally expressed as \( k = AT^b \exp\left(-E_{\text{act}}/k_b T\right) \) in which \( A \) is a constant, \( b \) is a constant of order unity (positive or negative), \( k_b \) is the boltzmann constant and \( E_{\text{act}} \) is the activation energy. The \( A, E_{\text{act}} \) and \( b \) all vary with reaction.

The operation of combustion devices depends to a large extent on the exact control of the fuel/air mixture. The concentration of fuel determines the total available energy of combustion, and the chemical process is determined by the ratio of fuel and oxygen. For any particular mixture the temperature has a strong influence on ignition and flame speed.

Among the various thermometry techniques, optical methods have
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drawn a lot of attention because of their non-intrusive properties and because they provide accurate information about temporal and spatial distributions. However, implementation of laser-based optical techniques in combustion is not trivial. Along with difficulties of optical accessibility, in strongly sooting media the strong absorption, scattering, spectral interference from other species and unwanted fluorescence from large molecules are all potentially reflected in the measured signal, and complicate the analysis of measured data.

In all of the laser diagnostics and optical thermometry methods, the crucial parameters are accuracy, spatial resolution and the ability to measure on small time scales to study turbulent flames. This thesis focuses on two such diagnostic techniques, that potentially can fulfill at least some of these requirements: Two-line atomic fluorescence (TLAF) and Coherent Rayleigh Brillouin Scattering (CRBS).

TLAF meets both requirements by forming the exciting laser beam into a sheet to image the temperature distribution with an acceptable spatial resolution and by employing two cameras to capture sequentially the two fluorescence images in less than 100 ns to provide enough time resolution. Moreover, the temperature uncertainty of better than 100 K [4] makes it suitable for temperature estimation in flames.

TLAF is in principle a linear method, that is, the intensity of the signal is a linear function of excitation intensity. There are also non-linear methods where the output signal is proportional to the second, third or higher power of incident laser intensity. In this category, an additional aspect concerns the directionality of the signal. In linear techniques the generated signal is divergent and more or less isotropically distributed in all directions, but the signal from many non-linear methods is coherent and beam-like, with a low divergence. This property facilitates the detection by the fact that the signal can be recorded a long distance away from the source region, which reduces the scattering or background noise. In some cases, even collisional effects can be avoided by the fact that the signal generation is faster than collision time scales [5].

Coherent Rayleigh-Brillouin scattering is one of the non-linear techniques which is not limited to temperature measurement and that is a method which has great potential to measure various gas kinetic pa-
1.1 Laser Diagnostics of Flame Temperature

Temperature is the measure of the molecular activity of a substance and it is the quantity that becomes equal when two systems are allowed to exchange energy with one another. The concept of temperature plays a central role in thermodynamics and combustion, in which it influences the velocity distribution of particles, chemical reaction rates, and the population of atomic and molecular energy levels.

Optical thermometry techniques are based on the measurement of one of three distinct parameters by means of atomic or molecular probes:

a) Total number density, which is related to temperature through the ideal gas law. This is used in techniques such as Rayleigh scattering [6], spontaneous Raman scattering [7], or Single line LIF [8]. In this category, the total number density as a function of pressure and temperature is measured. Assuming a spatially homogeneous pressure, the temperature can be obtained from the ideal gas law.

b) The distribution of the population over ro-vibrational or electronic states, which is implemented in Excitation scanning LIF [2], THAF (Thermally assisted fluorescence) [9], or TLAF (Two lines atomic fluorescence) [10]. These methods are based on the temperature-dependent Boltzmann fraction. Temperature modifies the population distribution over the energy levels, which (in thermal equilibrium) is described by the Boltzmann distribution.

c) Doppler shift, where temperature is derived from the spectral
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broadening of fluorescence signal, arriving from the temperature dependent velocity of the particles. A good example is the atomic line shape method [11].

d) Indirect methods such as toluene LIF, in which the temperature dependence of another property is used to derive temperature [12].

1.2 Spontaneous Rayleigh scattering

Spontaneous Rayleigh scattering is an experimentally straightforward technique that is based on the measurement of elastically and non-resonantly scattered light. In a typical implementation, the medium of interest is irradiated by quasi-monochromatic laser light, the wavelength of which is far detuned from any absorption by the medium. The intensity of the scattered light is recorded, typically (but not necessarily) in a direction perpendicular to both the propagation direction and the polarization direction of the incident light. For random media, the scattering efficiency can be shown to be proportional to the total molecular number density, but the determination of the proportionality factor is complicated, certainly for gas mixtures. Temperature information follows from application of the ideal gas law, to relate number density to temperature. Typically, then, the scattered light intensity originating from a specific location in the medium is inversely proportional to the local temperature, and the setup is calibrated by a measurement on the medium at a known temperature, e.g. room temperature. The method can easily be extended to planar (2-D) measurements, using a laser light sheet for excitation and a camera to collect the scattered light, and it does not pose serious requirements on the laser wavelength, beyond it being far from resonance. In practice, the contribution of Raman-scattered light (see below) is neglected, Raman scattering being much less efficient than Rayleigh scattering.

In this method, the laser light is focused into the combustion medium and the scattered light is recorded by a detector. Apart from the total number of components the signal is a function of the effective scattering cross section which is in general independent of temperature: it varies 1~2% [13] over a large range of temperature. To estimate the temperature from the total number of species and ideal gas law, the pressure needs to be measured separately. Because of the relatively strong signal
1.2 Spontaneous Rayleigh scattering

it is possible to employ this method as single shot technique [14].

However, there are several complications. This technique suffers from Mie scattering interference which is basically produced from larger particles which their size are in the order of wavelength of the excitation light. The cross section of Mie scattering is higher than that of Rayleigh scattering, and in practice the (unfiltered) Rayleigh scattering method is restricted to clean situations where large particles are absent [15].

Another problem is background scattering from walls or soot particles. To overcome this problem, filtered Rayleigh scattering is used [6]. Because of thermal motion of gas molecules, the Rayleigh scattered light is spectrally broader than scattering from walls, particles or droplets. By using a single longitudinal mode laser with a very narrow line width and a suitable filter, the elastic scattering from quasi-stationary particles can be rejected [fig. 1.1]. The average thermal velocity of molecules in a gas, however, is approximately equal to the speed of sound in the gas. The light scattered by these molecules is Doppler-broadened, and the wings of the spectrum will bypass the narrow-band filter and result in detectable intensity. The contribution of the wing increases with increasing line width, and this imparts temperature sensitivity to the method.

![Figure 1.1: The spectral line shape of Rayleigh scattering and the filter transmission curve.](image)

Figure 1.1: The spectral line shape of Rayleigh scattering and the filter transmission curve.
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1.3 Raman scattering

In Rayleigh scattering the molecules scatter without energy exchange. In Raman scattering a net energy exchange causes an increase or decrease of the rotational and/or vibrational molecular energy, and due to energy conservation scattered photons have energies equal to $\hbar (\omega_0 \pm \omega_k)$, in which $\hbar \omega_0$ is the energy of the incident photons and $\hbar \omega_k$ is the energy difference between states that are involved in the scattering process. The red shifted photons, of energy $\hbar (\omega_0 - \omega_k)$, are referred to as Stokes photons, and blue-shifted photons, with energy $\hbar (\omega_0 + \omega_k)$, are referred to as anti-Stokes photons.

In Raman scattering the frequency shifts are species-dependent, which becomes obvious if the scattered light is dispersed before detection. The dispersed spectrum includes all information needed for thermometry, but due to the small amount of energy exchange the spectral shifts are small and the scattered wavelengths reside very close to the laser line. In multicomponent flames the spectra overlap, which makes it difficult to unmix the components. The measurement can be performed by a single laser that can operate at almost any wavelength, but the scattering cross section scales with $\lambda^{-4}$. Comparing to Rayleigh scattering the cross sections are much lower, which needs to be overcome by higher energy flux. It should be mentioned that the Raman scattering cross section is not intensity dependent, and focusing of light is usually performed to achieve higher spatial resolution, and not to obtain a larger signal. The method is usually point-wise and provides spatial distributions only by scanning, and in practice can be applied only up to 1-D.

There are three different methods to estimate temperature from Raman scattering [16]: given enough Raman lines, it is possible to fit a simulated Raman spectrum to the measured spectra. This spectrum is temperature-dependent and the pressure and Doppler broadening of the lines need to be considered. The second way is to determine the number density of each component present in the combustion medium from dispersed Raman spectra and adding them to find the overall number density. Then it is possible to determine the temperature via the ideal gas law, as in Rayleigh scattering thermometry. The third method is to
1.4 LIF-based thermometry

measure the Stokes and anti-Stokes lines simultaneously. The intensity ratio of these two lines is given by [13]:

\[
\frac{S_\text{stokes}}{S_\text{anti-stokes}} = \left( \frac{\omega_0 - \omega_k}{\omega_0 + \omega_k} \right)^3 \exp \left( \frac{\hbar \omega_k}{kT} \right)
\]  

(1.1)

Against all of these advantages stands the drawback that the Raman signal is usually very weak, its cross section typically being three orders of magnitude smaller than those of Rayleigh scattering. As a result the method is restricted to point-wise (0-D) and 1-D [17] measurements.

1.4 LIF-based thermometry

Aside from non-resonant scattering, Laser-Induced Fluorescence (LIF) can be used to find temperatures. LIF is the spontaneous emission of photons by molecules that were brought into an (electronically) excited state by means of absorption of laser photons. It can be used to determine (absolute or relative) densities of molecules in specific energy states, and the temperature is derived from several of these densities by means of Boltzmann statistics. Since there is species selectivity in both the absorption and the emission step, LIF is a highly species-selective method. The large cross sections typically involved in both the absorption and the emission step allows detection using a large variety of native species in combustion, like OH, O\textsubscript{2}, NO and CH. The emitted photons are typically red-shifted relative to the excitation laser wavelength. This property facilitates easy separation of fluorescence and elastic scattering.

The emission step relies on spontaneous emission. The lifetime of the excited state is finite, and typically amounts to about 1 – 100 ns. During this so-called natural lifetime, the molecule is susceptible to its surroundings: intermolecular collisions may cause the excited state to decay without emission of a (detectable) photon, so-called quenching. The quenching efficiency depends on local temperature, density and chemical composition, and, certainly at above-atmospheric pressure, the quenching rate is generally competitive with the spontaneous emission rate. Thus, unlike the situation in Rayleigh and Raman scattering, the effective fluorescence intensity becomes environment-dependent, and this is
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undoubtedly the major drawback of LIF.

1.5 Thermally assisted fluorescence

Thermally assisted fluorescence (THAF) is one of the techniques which are based on the temperature-dependent population distribution over electronic levels in probe atoms [18, 19]. Usually atomic Gallium is employed, and the ground state atoms are excited by means of a single laser. The excited state population is distributed over the available excited states due to collisions. This distribution depends on temperature, and the resulting spectrally resolved fluorescence intensities reflect the population ratio, which can be used to estimate the temperature. One major problem with this technique is that collision cross sections between species must be known. In addition to this the transition rates of involved levels are also needed. On the other hand due to low signal levels only time-averaged temperature measurements of laminar combustion events could be performed [20].

1.6 Atomic line shape thermometry

Atomic line-shape based temperature measurements have been used in low pressure environments, where collisional broadening is negligible, and the transition width depends only on Doppler broadening and the natural line widths [21]. In this technique Indium is used as a seeded atom for excitation and a tunable extended-cavity diode laser is used to probe the lower electronic state of Indium atoms. This state has hyperfine levels, and the net spectral shape of the transition is temperature dependent. After excitation all of the fluorescence is collected with a photo-multiplier tube (PMT). The relative spectral positions and relative intensities of the four lines are well known and it is possible to make a theoretical spectrum. By fitting this function to the experimental spectrum it is possible to extract the temperature. This is a time consuming process where only point-wise measurements are reported. Also, the method is limited to clean situations; in sooting flames elastic scattering can induce errors in the measurements.
1.7 Coherent anti-Stokes Raman scattering (CARS)

Discovered by Maker and Terhune [22], CARS is one of the non-linear techniques which has become a major tool in laser diagnostics. Compared to spontaneous Raman scattering, CARS provides stronger signal, and as the name implies it is a coherent process. It means that the signal is beam-like, which facilitates the collecting of a background-free signal.

Nitrogen is extensively used for CARS measurements to estimate the temperature in flames over a broad range, from room temperature to 2000 K flame temperature, with an accuracy of 24 - 100 K.[23]

CARS is a four-wave mixing process, for which two lasers are required, which are referred to as pump and Stokes lasers. The pump laser is usually a frequency-doubled Nd:YAG laser and the Stokes laser is usually a tunable source which can be pumped by splitting off a portion of the pump laser. The probe beam is also split off from the pump laser. The schematic diagram of the CARS experiment is shown in figure 1.2. When the difference between the pump and Stokes frequencies ($\omega_1 - \omega_2$) matches the molecular vibrational frequency, $\Omega_{vib}$, the anti-Stokes signal is generated at a frequency $\omega_s = 2\omega_1 - \omega_2$

![Figure 1.2: The schematic diagram of four wave mixing in a CARS experiment.](image)

The CARS spectrum can be obtained by scanning a narrow-band
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Stokes laser where the resolution is limited by the line-width of the laser. This approach does not need a spectrometer but it can be used in stationary laminar flames only. In turbulent flames, due to the short time scale of fluctuations, the scanning approach is not appropriate and broadband CARS is used. In this method a broad-band laser source is used to establish resonance for all available transitions simultaneously, and thereby instantaneously generate the entire CARS spectrum. CARS is one of the most accurate optical techniques for temperature measurements, but the setup is complicated and it needs high-intensity pulsed lasers to provide statistically significant signals. Moreover, the measurement is point-wise, although in some cases it can be extended to 1-D [24].

1.8 Two lines atomic fluorescence (TLAF)

TLAF is realized by sequentially pumping two closely spaced ground state populations to a same excited state and collecting the fluorescence at Stokes and anti-Stokes transitions. The method was first used as two-line atomic absorption method on Indium, Gallium and Thallium by Browner [25], and later as a fluorescence measurement by Haragichi et al. [26]. They used an arc lamp together with a monochromator to choose the excitation wavelengths for Indium and Thallium. After that Dec [27] provided a theoretical frame work using rate equations and they verified the theory experimentally. Kaminski et al. [28] used this technique to measure the temperature in two dimensions in a Volvo N1P engine.

Due to excitation to the same level the quenching is canceled out during the calculation of temperature. The method can be easily extended to a 2D scheme and by employing two cameras to capture the Stokes and anti-Stokes signals independently, there is a possibility to measure the temperature in a short time scale to study turbulent flames. This technique will be discussed in more detail in chapter 4.
2 Rayleigh Brillouin Scattering
2.1 A brief history of light scattering

Phenomena associated with light scattering have always attracted the attention of physicists. Early investigations on scattering brought basic knowledge to explain the blue color of the clear sky and the red sunset on the basis of light scattering off molecules in the air.

After Newton’s experiments on scattering with sunbeams, which explained the process in an elementary fashion, in 1871 Lord Rayleigh [29] provided more insight by introducing the well-known $\lambda^{-4}$ law for scattering of light by particles with size up to about a tenth of the wavelength of the light. The theory described the molecular origin of atmospheric scattering and it explained the observed effects, like the blue color of the sky. Moreover, it provided a quantitative expression for the amount of light scattered. Rayleigh scattering is a quasi-elastic scattering process and it can take place when the distance between the particles is larger than the wavelength of light. In an experiment in which monochromatic light is scattered by a (gas phase) medium that is macroscopically at rest, the mean frequency of the scattered light is not shifted, but a broadening of its spectral distribution can be observed, due to the Doppler shift imposed onto the scattered light by the thermal translational motion of the scattering molecules. The frequency distribution of the scattered light has a Gaussian shape, and its width is in the order of a few GHz for air at a temperature of 300 K. The velocity profile of the atoms and molecules in the gas is given by the Maxwell-Boltzmann distribution and the scattered light spectrum $S(\nu)$ is therefore given by a Gaussian line shape function (see e.g. [30]):

$$S(\nu) \propto F_g(\nu) \equiv \frac{1}{\sqrt{2\pi}\delta} \exp\left(-\frac{(\nu - \nu_0)^2}{2\delta^2}\right)$$  \hspace{1cm} (2.1)

with $\delta = \nu_0\sqrt{\frac{k_B T}{M c^2}}$. Here $k_B$ is the Boltzmann constant. For larger particles, Mie in 1908 [31] and Debye in 1909 [32] independently provided a solution for scattering of light by isotropic spheres embedded in a homogeneous medium; this has become known as Mie scattering. In spite of big particle sizes, geometrical optics can not fully describe the observed phenomena, and Mie theory is employed to explain the interaction of an electromagnetic wave with a particle that is large compared to the
2 Rayleigh Brillouin Scattering

wavelength.

The (quasi-)elastic Rayleigh and Mie scattering processes do not involve energy exchange with the internal degrees of freedom of the scattering particles. In 1928, Raman [33] explained the effect of atomic and molecular structure on light scattering, for which he was awarded the 1930 Nobel Prize in physics. In non-resonant molecular scattering processes, Rayleigh scattering, whereby the light is emitted at essentially the same frequency as the incident light (elastic scattering), is the dominant phenomenon. A small fraction of the incident light, however, is scattered at other frequencies due to an energy exchange between the electromagnetic radiation and the scattering molecules. In this way, the scattered photons either gain or lose energy relative to the incident photon, and a frequency shift in the scattered spectrum will be observed. This frequency shift is characteristic for the energy level structure of the scattering molecules; it typically is in the order of 1-50 THz (for vibrational Raman scattering). In Raman scattering, as it is illustrated in Figure 2.1, the incident photon with frequency of $\nu_L$ is scattered at another frequency $\nu_s$. The difference corresponds to an energy difference $h(\nu_b - \nu_a)$ in the scattering molecule. The levels involved can be electronic levels, but typically they are vibrational or rotational energy levels of a molecule. The scattered frequency is denoted by $\nu_s$.

Figure 2.1: Diagrams of (a) spontaneous and (b) stimulated Raman scattering.
and it is called Stokes-shifted when $\nu_s < \nu_L$, and anti-Stokes shifted when $\nu_s > \nu_L$. The energy difference between incident and scattered photon, $\Delta E = h(\nu_L - \nu_s)$, called the Raman shift, must be accommodated by the scattering molecule. Then, an anti-Stokes shift can occur when the system is in an excited state before the scattering process. It can then make a downward transition, and the scattering frequency is shifted to values larger than the incident frequency. In stimulated Raman scattering, illustrated in figure 2.1(b), light with frequency of $\nu_s$ is incident on the molecules simultaneously with a light wave at $\nu_L$. During the scattering process a quantum of light is added to the incident light wave at $\nu_s$, which thus is amplified.

Considering the fact that scattering occurs only in a non-homogeneous medium, it might be surprising that nominally homogeneous media like air or water scatter light anyway. Scattering from such media results from time-dependent thermal fluctuations which give rise to small fluctuations in density and therefore in refractive index. Two kinds of thermal fluctuations can be considered as a source of scattering in these media. Besides thermal sound waves, fluctuations in entropy can give rise to scattering. These fluctuations don’t propagate but only diffuse and they scatter light with no frequency shift. This is the origin of Rayleigh scattering. Debye, in his theory of specific heat, described thermal fluctuations which propagate with sound velocity. Scattering off these waves imparts a positive or negative frequency shift onto the scattered light, depending on the direction of the sound wave propagation.

Studies by Brillouin [34] in 1914 showed a double peak in the spectrum of scattered light, symmetrically located on both sides of the unshifted incident frequency. These were interpreted as Doppler-shifted scattering off moving sound waves. The sound waves are propagating in all directions, but because of phase matching conditions (conservation of momentum) given frequencies scatter in specific directions. The specific direction of the scattered light can be also described by Bragg’s law, where the scattering is pictured as a constructive interference from successive wave fronts of the sound waves. This will be described in more detail later in this chapter. The shifts are smaller than in the case of Raman scattering, and typically in the order of 1-50 GHz, comparable
In 1930 Brillouin scattering by liquids was reported by Gross [35]. He attempted to find rotational Raman lines in scattering by various organic liquids. Because of the low frequencies of the pure rotation spectrum, he expected the lines to be situated very close to the incident line. During the experiments, the Brillouin doublet or, as he liked to call it, ”a very interesting phenomenon” was observed.

Further studies on Brillouin scattering were performed by Landau and Placzek [36] in 1934, who found that the ratio of the integrated intensity of the central Rayleigh spectrum to that of the shifted spectra is given by the heat capacity ratio of the scattering medium. The first observation of Brillouin scattering from various gases dates back to the early 1960s, when Greytak and Benedek [37] used a narrow-band He-Ne laser ($\lambda = 632.8$ nm) and a Fabry-Perot interferometer to observe the spectrum. The scattering spectrum takes on different shapes in different scattering regimes, and this was investigated by various authors. The shape is determined by a dimensionless $y$ parameter which is proportional to the ratio between the scattering wavelength and the mean free path (more on this in § 2.4). Depending on this parameter, two major regimes can be defined: the hydrodynamic regime and kinetic regime. When the scattering wavelength is larger than the mean free path we are in the hydrodynamic regime. Ghaemmaghami et al. [38] investigated the Rayleigh-Brillouin scattering in both the kinetic and hydrodynamic regimes and introduced a definition for $y$ to characterize the gas spectrum.

The first coherent Rayleigh-Brillouin scattering was reported by She et al. [39, 40]. They relate the scattering spectrum to the imaginary part of the third-order susceptibility $\chi^{(3)}$ and also compared the gain spectra for spontaneous and stimulated scattering. In coherent Rayleigh-Brillouin scattering the perturbation is induced by dipole forces in the intersection of two laser beams and the generated perturbation is probed by a third laser. The probe laser is scattered from the induced grating, which results in beam-like scattered light. Due to this directionality the S/N ratio is higher and the signal suffers less from background noise as compared to spontaneous Rayleigh-Brillouin scattering. Coherent Rayleigh-Brillouin scattering measurements can also
be performed in the time domain. Here the delay between the probe laser and the pump lasers is changed stepwise and the scattered light is collected with sufficient temporal resolution. A theoretical and experimental study in the time domain was performed by Stampanoni et al. [41]. Using a density wave equation in the hydrodynamic regime, they verified the possibility of measuring acoustic quantities with their setup, employing two nearly co-propagating laser beams to create a relatively long-period grating. They also studied the coherence effect by varying the time delay between the pump beams and they showed that the intensity is reduced by a factor of $\tau_c/\tau_p$ compared to coherent excitation. Here $\tau_c$ is the coherence time and $\tau_p$ is the pulse width. The coherent Rayleigh scattering was verified experimentally by measuring the power spectrum of the scattered light by Grinstead and Barker [42]. They demonstrated gas-phase coherent Rayleigh-Brillouin scattering in the collisionless regime, and later on Pan et al. [43] showed it in the kinetic regime. The latter authors also developed a kinetic model to obtain an analytic solution of the line shape for monatomic gases, and good agreement with the experimental data was achieved. Later on the model was improved by taking into account the internal energy modes of the gas particles to extend the model to molecular gases [43].

2.2 Spontaneous Brillouin Scattering

To study the scattering signal we need to study the time dependent fluctuations in the optical properties of the medium. Light scattering arises because of fluctuations in the optical properties of a material medium; a completely homogeneous material will scatter light only in the forward direction.

The propagation of a pressure wave in a medium can leads to Stokes and anti-Stokes scattering. The scattering wave vectors and frequency shifts are represented by:

Stokes: $k' = k - q$ and $\omega' = \omega - \Omega$ \hspace{1cm} (2.2)

anti-Stokes: $k' = k + q$ and $\omega' = \omega + \Omega$ \hspace{1cm} (2.3)

Schematic diagrams of Stokes and anti-Stokes scattering are provided in figure 2.2.
2 Rayleigh Brillouin Scattering

Figure 2.2: Stokes (a) and anti-Stokes (b) scattering off a pressure wave; $k$ is the incident wave vector $k'$ is the scattered wave vector and $q$ is the scattering wave vector.

The (angular) frequency $\omega$ and wave vector $k$ of the incident optical field are related by $\omega = kc/n$. Similarly the frequency and wave vector of an acoustic wave are related by $\Omega = qv$. It follows from equations 2.2 and 2.3 and figure 2.2 that $q = 2k \sin(\theta/2)$. Then the acoustic frequency is related to $k$ by $\Omega = 2kv \sin(\theta/2) = 2n\omega_v \frac{v}{c} \sin(\theta/2)$. The scattered light gets a doppler shift upon reflection off the moving grating. It is easy to show that the frequency shift of the signal due to the Doppler shift is equal to the grating frequency $\Omega$. Following the Bragg condition the

Figure 2.3: The Bragg reflection from moving grating

path difference between two beams reflecting off two successive wave
2.3 Stimulated scattering

fronts of the sound wave, as it is shown in figure 2.3 is

\[ \lambda = 2 \frac{2\pi}{q} \sin \frac{\theta}{2}, \]

(2.4)

The Doppler shift of a light wave reflected off a moving object is given by:

\[ \Delta \omega = 2 \omega \frac{u}{c}, \]

(2.5)

where \( \omega \) is the angular frequency of the light wave, \( c \) is the speed of light and \( u \) is the speed of the moving object in the direction of the scattered wave and is given by \( u = v \sin \theta / 2 \). Replacing the \( \omega \) in eq. 2.5 by \( \frac{cq}{2 \sin \theta / 2} \) from eq. 2.4 we have:

\[ \Delta \omega = 2 \frac{cq}{2 \sin \theta / 2} \frac{v \sin \theta / 2}{c} = qv = \Omega. \]

(2.6)

In summary, light can be scattered due to temporal and spatial variations in the density of the medium. It can also explain a Doppler shift, due to the Bragg reflection off sound waves.

2.3 Stimulated scattering

In this section the basis of stimulated scattering is described. Stimulated scattering involves scattering off an induced grating that is produced by interference of two other light beams. In this method the scattered light beam is directional and this offers a background free measurement. The describing equations and measurement methods follow below.

Two identical light pulses (in practice originating from the same laser) crossing at an angle \( \theta \) produce an optical interference pattern in their intersection which, by various resonant and non-resonant mechanisms, can result in the formation of a wave-like periodic density perturbation \( \delta \rho \) in a medium. The induced perturbations appear as traveling acoustic waves (Brillouin scattering) and stationary isobaric density fluctuations (Rayleigh scattering) [42]. The generated waves move with the sound velocity in the medium and decay with rate \( \Gamma \), which is a function of various gas parameters, such as shear viscosity, specific heat and density.
Such laser-induced grating-like structures can be formed in various ways. One possibility is by tuning the laser wavelength to absorption lines of the medium, which deposits heat into the sample or alters the population distribution in the high-intensity regime of the grating [44]. Heat generation results in a temperature modulation and, consequently, a density modulation.

On the other hand, so-called electrostrictive gratings can be formed at any wavelength. In resonant laser-induced grating measurements the electrostrictive contribution appears as a background contribution to the signal, which does not depend on the wavelength of the excitation lasers.

Electrostriction can be studied from a microscopic but still largely classical point of view. If a molecule is subject to an electric field $E$ it develops a dipole moment $P = \epsilon_0 \alpha E$, where $\alpha$ is the molecular polarizability. In the presence of an electric field $E$, the energy stored in the polarization of the molecule is given by:

$$U = -\int_0^E P(E') \cdot dE' = -\frac{1}{2} \epsilon_0 \alpha E^2. \quad (2.7)$$

The polarized molecules experience a force towards the higher intensity regions which is proportional to the gradient in intensity [45]:

$$F = -\nabla U = \frac{1}{2} \epsilon_0 \alpha \nabla E^2. \quad (2.8)$$

To study the formed grating we consider two intersecting light beams having electric fields of $E_1(r, t) = E_0 \cos(k_1 \cdot r - \omega_1 t)$ and $E_2(r, t) = E_0 \cos(k_2 \cdot r - \omega_2 t)$ with frequencies of $\omega_1$ and $\omega_2$. The interference of these two produces several gratings which oscillate at the beat frequency of the pump waves, that is, $\Omega = \omega_1 - \omega_2$, with grating wave vector of $|q| = |k_1 - k_2| = 4\pi/(\lambda \sin(\theta/2))$, which we assume is in $z$ direction. The exerted force is in the $z$ direction which is perpendicular to the fringes and is given by [46]:

$$F = \alpha \frac{\partial}{\partial z} (E_1 + E_2)^2 = -\frac{\alpha q(E_0)^2}{2} \sin(qz - \Omega t) \quad (2.9)$$
2.3 Stimulated scattering

The generated force field is a sinusoidal wave which travels with a velocity of $\Omega/q$. As will follow in the next sections, those particles moving with velocity close to the phase velocity of the force field, $\Omega/q$, are trapped by the potential or force field wave and form the periodic density perturbation from which the probe beam scatters. In fact, the modulated density pattern serves as a moving Bragg reflector, and it can reflect the probe laser light efficiently in particular directions. Due to the phase matching condition, the signal beam travels exactly against the pump beam. This is a consequence of momentum conservation and $k_1 - k_2 = k_p - k_s$. This is illustrated in figure 2.4 where two pump beams with wave vectors of $k_1$ and $k_2$ make an interference pattern and the probe beam with wave vector of $k_p$ is scattered into a wave with wave vector as $k_s$. The signal’s polarization does not change with respect to the probe but its frequency is shifted by the frequency of the traveling density perturbation wave, as was described by equation 2.6. The power spectrum of the scattered electric field is proportional to the power spectrum of the density grating. Due to the coherent nature of scattering the intensity of the signal is higher than in spontaneous
Rayleigh-Brillouin scattering, and this allows an accurate and more reliable measurement.

2.4 Describing equations

In this section we will consider the theoretical basis, based on the work developed by Pan et al. [46] and the models developed to study light scattering off the gas molecules. Rayleigh-Brillouin scattering phenomena can be studied from two points of view. By considering the density $\rho$, velocity $v$ and temperature $T$ as variables of the medium the macroscopic equations can be utilized [45, 41]. On the other hand the more fundamental and general microscopic Boltzmann equation can be used to describe a wider class of problems where the macroscopic density equations can not predict the gas behavior [46]. Which of the approximations applies depends on the value of the $y$ parameter, which is the ratio between the scattering wavelength $2\pi/q$ and the mean free path between molecular collisions. For a single-component gas the $y$ parameter is defined as:

$$y = \frac{p}{qv_0 \eta} = \frac{n k_B T}{qv_0 \eta},$$

(2.10)

with $q$ the scattering wave vector, $n$ the number density, $T$ the temperature, $p$ the pressure, $v_0$ the thermal velocity, $v_0 = (2k_B T/M)^{1/2}$ in which $M$ is the molecular weight, and $\eta$ the (shear) viscosity. The shear viscosity emerges as a parametrization of the mean free path. When $y \gg 1$ the scattering wavelength is much larger than the molecular mean free path; this is the hydrodynamic regime. The gaseous medium can be considered as a continuous medium and density wave analysis can be applied here. A central Gaussian Rayleigh peak associated with non-propagating density fluctuations and two side bands associated with Brillouin scattering off propagating sound waves can be observed in this regime. When $y < 3$ we are in the kinetic regime and we should treat the gas as a collection of particles. The Boltzmann equation should be used to describe the gas particle dynamics in this regime. For $y > 3$ the line shape obtained by the Boltzmann equation analysis agrees with that obtained for the hydrodynamic regime. If $y = 0$ then there is no collective effect and the resulting spectrum is Gaussian corresponding to the Maxwellian velocity distribution of the gas particles [42]. This
is the so-called Knudsen regime. The spectrum of the scattered signal changes with the $y$ parameter. Figure 2.5 illustrates the gradual change of the scattered spectrum with $y$ parameter.

Figure 2.5: The Coherent Rayleigh Brillouin scattering line shape for different values of the $y$ parameter.

As $y$ increases the central peak becomes wider and for $y > 1$ the Brillouin peaks start to appear. These peaks are Doppler shifted away from the central peak, with a shift that corresponds to the speed of sound in the gas. With increasing $y$ the Brillouin peaks get more dominant. In the kinetic regime, the density fluctuations and thus the scattering spectrum can be found from the Boltzmann equation,

$$\frac{\partial f(v,r,t)}{\partial t} + v \cdot \nabla f + a \cdot \nabla_v f = - \left[ \frac{\delta f}{\delta t} \right]_{\text{coll}} \quad (2.11)$$

where $f(v,r,t)$ is defined as a distribution function; $f(v,r,t)dvdr$ is the probability of finding a particle at time $t$ in the position $r$ with range of $dr$ and with velocity of $v$ with range of $dv$. The right hand side is the term describing collisions, the so-called collision operator. It depends non-linearly on the distribution function $f(v,r,t)$. Since the deviation from the Maxwellian $f(v,r,t)$ is small, the collision operator can be lin-
earized. The linearized collision operator embodies kinematic effects as well as collisions changing the internal degrees of freedom of the collision partners, as is the case for the polyatomic gases. The linearized Boltzmann equation describes hydrodynamics, for example the number density follows from the distribution function as \( n(r, t) = \int_{-\infty}^{\infty} f(v, r, t) \, d^3v \).

In the hydrodynamic description, the transport coefficients: the viscosity \( \eta \), the heat conductivity \( \lambda \) and the bulk viscosity \( \eta_b \), are determined by the linearized collision operator. The bulk viscosity \( \eta_b \) is due to the relaxation of internal modes of a molecule. In order to compute the collision operator, detailed knowledge about collision cross sections is needed. This knowledge is currently not available. Instead, Wang Chang & Uhlenbeck \[47\] developed a model based on measured values of the transport coefficients. This model was further developed by Hasen and Morse \[48\], while Tenti and Boley \[49\] used it to derive a theory for the spectrum of Rayleigh scattering. Later on, Pan et al.\[46\] added a source term due to the optical dipole field in order to describe the spectrum of coherent Rayleigh Brillouin scattering.

### 2.5 Measurement methods

In the literature on laser-induced gratings, there are two approaches for measuring the grating efficiency, operating in the time domain and the spectral domain, respectively. Both will be briefly discussed below. These two methods are identical in a way that they measure the same parameters. But when using the time domain technique the angle between the pump beams is limited to small values and if we want to measure the gas parameter at higher frequencies (larger angles) the frequency domain is more appropriate.

#### 2.5.1 Time domain

The time evolution of the scattered signal, generated by diffraction of a probe beam off the grating, echoes the time evolution of the density variation. This can be easily performed by sending the scattered signal to a photomultiplier tube.

A variable delay generator changes the timing stepwise between pump pulses and the probe and the averaged signal over a large number of pulses (\( \sim 100 \)) is integrated to resolve a single point of decay. It is nec-
2.5 Measurement methods

necessary to have a probe pulse width smaller than the grating oscillation period to resolve the time evolution of the grating. For small intersection angles this is not an issue, and for $\theta = 2.9^\circ$ which corresponds to an oscillation period of $T_p = 16$ ns, a pulse duration of 8 ns available from standard commercial Nd:YAG lasers is sufficient. Hubschmid et al. [41] performed experiments to measure the time-resolved scattered signal. They showed damped oscillations of acoustic waves for different intersection angles of the pump laser beams, and they developed a theoretical framework based on the density wave equation for a viscous medium. Measurements of sound velocity and attenuation constant have been performed for Ar and N$_2$ [41]. A variable-delay, integrated-intensity-grating experiment was also performed to measure the coherence time of the probe beams. The decay function remained unchanged while they observed a drop in the integrated intensity with delay.

This method is not suitable to study the gratings which are formed with very large pump beam interference angles and in practice it is limited to the situations where the oscillation period of the grating is larger than the probe pulse width.

2.5.2 Frequency domain

In the frequency domain technique the idea is to resolve the spectrum of the scattered light, rather than the time evolution of the induced gratings. Both scanning Fabry-Perot [46] and Fizeau [50] spectrum analyzers have been employed to record the spectra. The probe pulse duration is not a limitation and it can be employed to probe the gratings formed with intersection angles up to $\theta = 178^\circ$. The corresponding oscillation period for this angle is $T_p = 400$ ps. This method will be discussed in more detail in the next chapter.
3 Spectral Narrowing in Coherent Rayleigh-Brillouin Scattering
3.1 Introduction

Optical coherence theory describes the correlation between optical fields, and it is concerned with the statistical properties of the fluctuations of light. The concept of coherence can be understood from interference experiments, in which the observed patterns are related to correlation between interfering light beams. In many optical experiments, the statistical properties of light determine the outcome of the experiments, and interference and correlation experiments are among the simplest that have been used to demonstrate the time and space correlations between light beams. Based on this, laser induced grating setups have been used to measure the coherence function of pulsed lasers using resonant [44, 51] and non-resonant [41] techniques. The efficient and coherent diffraction off these gratings makes them suitable for measurement of ultrashort pulse lengths and coherence times [44] in a pump and probe scheme, a time-resolved method developed to overcome the difficulties with slow detectors and electronics. The interference pattern is stored in the sample under investigation by electrostriction or absorption where they change the index of refraction or absorption coefficient. The diffraction of a probe laser beam from the induced grating is a direct measure of the visibility of the pattern which can be measured after a suitable delay [51], depending on the time needed for the formation of the grating in the sample under investigation. The diffraction is measured as a function of time delay of the pump beams producing the grating to extract the mutual coherence function of light pulses. This function provides information on frequency spectrum of light pulses and it can be used to estimate the degree of mode-locking by measuring the pulse length simultaneously [44].

3.2 Two-field interference

The superposition of two electric fields $E_1(t)$ and $E_2(t)$ of two pulses can be expressed by:

$$E(t) = E_1(t + \tau) + E_2(t)$$

(3.1)

where $\tau$ is the delay between pulses. The irradiance measured by a square-law detector over a finite time interval $T$ is: $I = \langle E(t)E^*(t) \rangle_T$
3 Spectral Narrowing in Coherent Rayleigh-Brillouin Scattering

where \( \langle ... \rangle_T \) denotes the time average, which, by assumption of ergodicity, can be replaced by an ensemble average. The total measured radiance due to the field of Eq.(3.1) can be expressed by:

\[
I \propto \langle E(t)E^*(t) \rangle = \langle E_1(t)E_1^*(t) \rangle_T + \langle E_2(t)E_2^*(t) \rangle_T + 2\text{Re}\langle E_1(t + \tau)E_2^*(t) \rangle_T
\]

The term \( \langle E_1(t + \tau)E_1^*(t + \tau) \rangle \) is replaced by \( \langle E_1(t)E_1^*(t) \rangle \) because of stationarity. The total intensity can be written in terms of the mutual coherence function \( \Gamma_{12}(\tau) = \langle E_1(t + \tau)E_2^*(t) \rangle_T \) and self coherence functions \( \Gamma_{11}(0) = \langle E_1(t)E_1^*(t) = I_1 \rangle_T \) and \( \Gamma_{22}(0) = \langle E_2(t)E_2^*(t) \rangle_T = I_2 \). We can now write the measured irradiance as:

\[
I = I_1 + I_2 + 2\text{Re}[\Gamma_{12}(\tau)]
\]

The highest intensity and also visibility is achieved for zero delay and it is when the pulses have maximum overlap. This can be explained by considering the light pulses as an extended spectrum which consists of many monochromatic components. Each monochromatic couple produces an interference pattern with a period which depends on its frequency. At zero delay the optical path length difference is same for all components and they produce a strong interference pattern with maximum visibility. As the delay increases, the superposition of different components becomes more destructive, due to the fact that the phase shifts of different monochromatic components which depend on its frequency, are different. At larger delays the superposition of monochromatic components generates a constant average intensity. This suggests the dependency of the temporal coherence function on the light spectrum: Monochromatic light can be considered as light with infinite coherence time.

3.3 Second and Fourth order coherence functions

What we discussed in the previous section, was the description for the classical theory of coherence. It is also referred to as second-order coherence theory. Before the invention of lasers, results of coherence measurements could be explained by the classic theory of coherence and the fluctuations of natural light could be represented by a Gaussian random
function. However, development of modern light sources revealed shortcomings of second order theory. The second order theory is an easy to understand concept and it provides an insight for most commonly occurring coherence phenomena. After development of second order theory some important experiments by Hanbury Brown and Twiss [52] led to the study of higher-order correlation properties in optical fields which is a more general approach to provide a complete statistical description of any optical field. It is possible to have the same mutual coherence functions for completely different wave fields which explains the necessity of higher order coherence functions. As mentioned before, the second-order coherence function for describing the interference experiments, is defined by:

\[ \Gamma(t_1, t_2) = \langle E(t_1)E^*(t_2) \rangle \]  \hspace{1cm} (3.4)

As a general function the higher order coherence function can be introduced by [53]:

\[ \Gamma^{(2n)}(t_1, ... t_{2n}) = \langle E(t_1)...E(t_n)E^*(t_{n+1})...E^*(t_{2n}) \rangle \]  \hspace{1cm} (3.5)

To understand the differences, the reflection efficiency of a laser induced grating by second order theory is expressed by [51]:

\[ \eta = K^2 \langle | \int_{-\tau_p/2}^{\tau_p/2} E_1(t)E_2^*(t)dt|^2 \rangle \]  \hspace{1cm} (3.6)

Where \( K \) is a proportionality constant and the integration is performed over the pulse duration \( \tau_p \). We can rewrite the equation as:

\[ \eta = K^2 \langle \int_{-\tau_p/2}^{\tau_p/2} \int_{-\tau_p/2}^{\tau_p/2} E_1(t_1)E_2^*(t_1)E_1^*(t_2)E_2(t_2)dt_1dt_2 \rangle \]  \hspace{1cm} (3.7)

Rewriting this equation in terms of dimensionless field amplitudes, \( u_i(t) \), which are defined as \( E_i(t) = E_iu_i(t) \), we have

\[ \eta = K^2 |E_1|^2|E_2|^2 \int_{-\tau_p/2}^{\tau_p/2} u_1(t_1)u_2^*(t_1)u_1^*(t_2)u_2(t_2)dt_1dt_2 \]  \hspace{1cm} (3.8)
3 Spectral Narrowing in Coherent Rayleigh-Brillouin Scattering

By normalizing to $K^2|E_1^2||E_2^2|\tau_p^2$, which is the diffraction efficiency for two equal intensity monochromatic beams, we have:

$$\eta = \frac{1}{\tau_p^2} \int_{-\tau_p/2}^{\tau_p/2} \langle u_1(t_1)u_2^*(t_1)u_1^*(t_2)u_2(t_2) \rangle dt_1 dt_2$$

(3.9)

If we have excitation pulses from same laser where one of the pulses is delayed by $\tau_d$ then we can write $u_2(t) = u_1(t + \tau_d)$. Then the integrand in Eq.3.9 becomes $\langle u_1(t_1)u_1(t_2+\tau_d)u_1^*(t_2)u_1^*(t_1+\tau_d) \rangle$ which according to Eq.3.5 is the fourth order coherence function. In the Gaussian approximation we can write the fourth order coherence function as a product of two second order functions [51].

$$\Gamma^{(4)}(t_1, t_2; t_3, t_4) = \Gamma^{(2)}(t_1 - t_3)\Gamma^{(2)}(t_2 - t_4) + \Gamma^{(2)}(t_1 - t_4)\Gamma^{(2)}(t_2 - t_3)$$

(3.10)

If we consider thermal radiation with a Lorentzian line shape the second order coherence function can be expressed by:

$$\Gamma^2(t) = \exp(-|t/\tau_c|)$$

(3.11)

The normalized diffraction efficiency is found by integrating the fourth order coherence function over the pulse length which is identical to equation 3.9 [51]:

$$\eta = \frac{1}{\tau_p^2} \int_{-\tau_p/2}^{\tau_p/2} \Gamma^{(4)}(t_1, t_2 + \tau_d; t_2, t_1 + \tau_d) dt_1 dt_2$$

(3.12)

Combining 3.11 and 3.10 and using 3.12 we have:

$$\eta = \frac{\tau_c}{\tau_p} + \exp(-2|\tau_d/\tau_c|) = \frac{\tau_c}{\tau_p} + |\Gamma^{(2)}(\tau_d)|^2$$

(3.13)

when the pulse length, $\tau_p$, approaches infinity the diffraction efficiency approaches the expected result from second order theory which is $\eta = |\Gamma^{(2)}(\tau_d)| = \exp(-2|\tau_d/\tau_c|)$. Interestingly, when the coherence time $\tau_d \gg \tau_c$ we have $\eta = \tau_c/\tau_p$. This explains the nonzero diffraction efficiency at larger delays which is the source for deviation from second order theory.
3.4 Coherence in CRBS

Figure 3.1: Experimental arrangement for measurement of the coherence function $\Gamma(\tau)$. The probing beam corresponds to $V(t + \tau)$

Figure 3.1. shows the setup that Eichler et al. used for measuring the coherence function of light pulses generated from a frequency-doubled Nd:YAG laser (532 nm). The probe beam is also derived from the same laser and the pump beams are focused in a solution of rhodamine 6G in methanol. Both Gaussian and Lorentzian functions were tried but the Gaussian function gives less agreement. Trebino et al. [51] studied the results recorded by Eichler et al. [44] by 4th order coherence theory which yielded a better fit. They derive a coherence time of $8.5 \pm 0.5$ ps from the width of the central spike which was larger than the experimental value measured by Eichler et al. of 2.7 ps.

3.4 Coherence in CRBS

One of the key parameters in CRBS measurement is the spectral bandwidth of the pump laser. As we have seen in chapter 2, molecules are trapped by dipole forces in a periodic interference pattern. In order to cover the whole velocity a distribution of particles, a measure for which is the Doppler line-width, the pump spectrum must be white with respect to the spectral extent of the response of the medium. To date all experiments have been performed using essentially independent pump beams derived from broad-band Nd:YAG lasers with nanosecond pulse duration [46, 42]. On the other hand, the coherence properties of the pump pulses also affect the dipolar forcing and ultimately it alters the recorded spectrum because the scattered spectrum is a product of the forcing spectrum and the response of the medium. To study the coher-
ence effect we investigate the dependence of the forcing spectrum on pump coherence. The forcing spectrum appears as a driving term in the Boltzmann equation which is proportional to the spatial variation of the intensity of the interference pattern,

\[ \mathbf{A} \propto \nabla (E_1 E_2^*) \]

Since the measured signal is proportional to \(|n(k, \omega)|^2\), and since the linear response \(n\) is proportional to \(\nabla (E_1 E_2^*)\), the signal spectrum depends linearly on \(|\mathbf{A}(\omega)|^2\). The scattered signal from this induced grating is integrated over many coherence times of the (broadband) pump laser. In the time domain, we write the fields as \(E(t) = a(t)u(t)\), in which \(a(t)\) is the (real, deterministic) field envelope, and \(u(t)\) contains the (complex, stochastic) time dependence. Assuming that one field is the time-delayed version of the other, we then have for the spectral distribution

\[ \langle |A(\omega)|^2 \rangle = \int \int dt \, dt' \, e^{-i\omega(t-t')} \langle a(t)u(t)a(t-\tau_d)u^*(t-\tau_d) \rangle \langle a(t')u^*(t')a(t'-\tau_d)u(t'-\tau_d) \rangle \]

Using the Gaussian approximation (eq. 3.10) we can write:

\[ \langle u(t) u^*(t-\tau_d) u^*(t') u(t'-\tau_d) \rangle = \langle u(t) u^*(t-\tau_d)\rangle \langle u(t') u^*(t') \rangle + \langle u(t) u^*(t') \rangle \langle u^*(t-\tau_d) u(t'-\tau_d) \rangle = \Gamma(\tau_d) \Gamma(-\tau_d) + \Gamma(t-t') \Gamma(t'-t) \]

We assume Gaussian correlations with correlation time \(\tau_c\) for the optical field so that the second-order correlation functions are given by [51],

\[ \Gamma(t) = e^{-t^2/2\tau^2_c} \]

For the pulse envelope with duration \(\tau_p\) we also assume a Gaussian,

\[ a^2(t) = P^2 e^{-t^2/\tau^2_p} \]

with \(P^2 = \frac{I_p}{\tau_p n^{1/2}}\)
3.4 Coherence in CRBS

which greatly facilitates further computation. The first term in the rhs of Eq. 3.15 represents the sharp coherent peak \( I_c \) at frequency 0 in the coherent Rayleigh-Brillouin scattering spectrum

\[
I_c = e^{-\tau_d^2/\tau_c^2} \int \int dt \, dt' \, e^{-i\omega(t-t')} a(t)a(t-\tau_d)a(t')a(t' - \tau_d)
\]

since \( a(t) \) is known, all integrations can be done, with the result

\[
I_c = I_p^2 e^{-\tau_d^2/\tau_c^2} e^{-\tau_d^2\omega^2/2 - \tau_d^2/2\tau_p^2}.
\]

(3.18)

The height of the peak is determined by the first factor which involves the ratio of the time delay \( \tau_d \) over the coherence time \( \tau_c \). The width of the peak is determined by the pulse duration \( \tau_p \), whereas the second term in the exponent controls the temporal overlap between the two pump pulses. A measurement of the height of the coherent peak as a function of the time delay \( \tau_d \) between the pump pulses reveals the coherence time \( \tau_c \) of the pump field.

We now turn to the broad–band part of the pump spectrum,

\[
I_b = \int \int dt \, dt' \, e^{-i\omega(t-t')} a(t)a(t-\tau_d)a(t')a(t' - \tau_d) \Gamma(t - t') \Gamma(t' - t)
\]

\[
= P^4 \int \int dt \, dt' \, e^{-i\omega(t-t')} e^{-\frac{t^2}{2\tau_p^2}} e^{-\frac{(t-\tau_d)^2}{2\tau_p^2}} e^{-\frac{(t'-\tau_d)^2}{2\tau_p^2}} e^{-\frac{(t-t')^2}{\tau_c^2}}
\]

\[
= P^4 e^{-\frac{\tau_d^2}{\tau_p^2}} \int \int dt \, dt' \, e^{-i\omega(t-t')} e^{-\frac{t^2}{\tau_p^2}} e^{-\frac{t^2 + \tau_d^2}{\tau_p^2}} e^{-\frac{t'^2 + \tau_d^2}{\tau_p^2}} e^{-\frac{t^2 + 2t't'-t'^2}{\tau_c^2}}
\]

with the result:

\[
\langle |A(\omega)|^2 \rangle = I_p^2 \exp(-\frac{\tau_d^2}{2\tau_p^2}) \times
\]

\[
\left[ \exp(-\frac{\tau_d^2}{\tau_c^2}) \exp(-\frac{1}{2}\omega^2\tau_p^2) + \gamma \exp(-\frac{1}{2}\gamma^2\omega^2\tau_p^2) \right]
\]

(3.19)

in which \( \gamma^2 = (1 + 2\tau_p^2/\tau_c^2)^{-1} \). The overall strength of the spectral forcing is determined by the temporal overlap of the two Gaussian pump pulses. Its spectral structure consists of two components, a coherent
and an incoherent one. The frequency bandwidth of the coherent component, $\Delta \nu_{\text{coh}}$, is determined by the pulse duration, and its amplitude vanishes if the delay between the pulses considerably exceeds the coherence time ($\tau_d \gg \tau_c$). The incoherent component is broader by a factor of $\gamma^{-1} > 1$, which involves the pulse coherence times, and which persists, irrespective of the delay time between the two pulses.

In the case of zero time delay, this pump spectrum takes on a particularly simple form. Since in the case of a broad-band Nd:YAG laser, the pump pulse duration far exceeds its coherence time, $\tau_p \gg \tau_c$, the incoherent component is both much broader, with a frequency bandwidth $\Delta \nu_{\text{inc}}$ determined by $\tau_c$, and much weaker, by a factor of $\tau_c/\sqrt{2}\tau_p \ll 1$, than the coherent component. Using representative values for broadband Nd:YAG lasers of $\tau_p = 5$ ns and $\tau_c = 25$ ps, we find (widths expressed as full width at half maximum, FWHM) $\Delta \nu_{\text{coh}} \approx 75$ MHz, $\Delta \nu_{\text{inc}} \approx 30$ GHz, and $\tau_c/\sqrt{2}\tau_p = 0.0035$. Evidently, in the case of CRBS experiments using broad-band Nd:YAG lasers for pumping [43, 54, 50], only the incoherent component has sufficient bandwidth to drive the full Rayleigh-Brillouin spectrum of the scattering medium, but under conditions of perfectly matched pump beam path lengths, that is, zero time delay, this component becomes swamped by the much stronger, but narrow-band coherent contribution. The latter, however, can be suppressed by introducing a delay time between the two pump pulses that is long relative to the coherence time, but short relative to the pulse duration. Thus, we conclude that, in spite of its name, all experiments to date on Coherent RBS have in fact been conducted in the incoherent regime.

### 3.5 Experimental setup and results

The (broad-band) pump laser beam (532 nm from an unseeded Nd:YAG laser) is split into two equal-intensity parts, which are focused by 500 mm lenses. The power of the pump beams are controlled by a half wave plate. The initial power of the laser is about 300 mJ but to avoid the perturbation the power is lowered to 16 mJ. The discussion on perturbation and power requirements will follow later. The beams cross at their foci under an angle of $178^\circ$, and form the grating (period of 266 nm). Since the pump beams are broad-band (estimated width about
3.5 Experimental setup and results

25 GHz), they produce a range of gratings of about the same spectral width. The density waves are probed by a narrow-band laser beam (532 nm, from a seeded Nd:YAG laser). Its polarization is perpendicular to that of the pump beams to avoid interference. The power and the polarization of the probe beam are controlled via a set of half wave plate and a polarizer as shown in figure 3.2. The probe beam is counter-propagating to pump beam $k_2$, so that the signal beam emerges counter-propagating to pump beam $k_1$; The signal beam is separated from the pump by means of a thin-film polarizer, and fed into a custom-built Fizeau spectrometer through a single-mode optical fiber. In order to induce an adjustable time delay $\tau_d$ between the two excitation pulses, a series of plan-parallel glass blocks can be inserted into the path of one of the pump laser beams. The total thickness of the blocks was varied in small steps such as to span a delay of 130 ps. The signal intensity is corrected for attenuation of the pump beam by the glass delay line (mainly reflection losses). Reported spectra are averages over 1000 laser shots. The result of the experiment is shown in Fig. 3.3. Figure 3.3a displays the recorded spectra as a function of delay time between arrival of the two laser pulses in their common focus; for clarity these spectra

![Figure 3.2: The experimental setup of CRBS.](image-url)
have been normalized (constant area). These spectra correspond to the product of the forcing spectrum and the Rayleigh-Brillouin response of the scattering medium [54].

Figure 3.3: (a) Coherent Rayleigh-Brillouin spectra $I(f)$ measured as a function of time delay $\tau_d$. For clarity the spectra have been intensity normalized, $\int I(f) \, df = 1$, this highlights the spectra at large $|\tau_d|$. (b) Full line, spectrum at $\tau_d = 0$, dashed line: Gaussian fit, $I(f) = b + a \exp(-f^2/\sigma^2)$, with $\sigma = 182$ MHz. (c) Dots: peak heights $I_m = a + b$, with $a, b$ from fits such as shown in (b), as a function of delay time $\tau_d$. Full line: Gaussian fit $I_m(\tau_d) = \alpha_m + \beta_m \exp(-\tau_d^2/\tau_c^2)$, with $\tau_c = 12$ ps and $\beta_m/\alpha_m = 73$. 
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Figure 3.4: Normalized amplitude of the forcing spectrum for zero delay as a function of pump laser pulse duration. The amplitude is plotted in a linear gray scale; pump pulse duration in units of the coherence time, $\tau_c = 12$ ps, logarithmic.

Under the conditions of the present experiment, air under ambient conditions, the Rayleigh-Brillouin response is close to Gaussian, as seen in the front-most spectrum of Fig. 3.3a. For large delay times $|\tau_d|$, the induced gratings span a broad spectrum and the true spectrum is registered. Around $\tau_d = 0$, however, the forcing spectrum is dominated by the sharp coherent peak, and so is the registered spectrum. In order to extract the coherent contribution to the pump spectrum, we subtract an average of the spectra recorded at large delay times from all spectra in Fig. 3.3a. The result $I(f)$, is then fitted to a Gaussian curve, $I(f) = a + b \exp(-f^2/\sigma^2)$, as illustrated for one of the spectra close to $\tau_d = 0$ in Fig. 3.3b (dashed line). We find that $\sigma = 180$ MHz (FWHM = 300 MHz), essentially independent of $\tau_d$. Finally, the height of the central peak (that is, coherent and incoherent contributions), $I_m$ is plotted as a function of delay time $\tau_d$, and again fitted to a Gaussian.
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function, \( I_m = \alpha_m + \beta_m \exp(-\tau_d^2/\tau_c^2) \). The result is shown in Fig. 3.3c; we find \( \tau_c = 12 \) ps and \( \beta_m/\alpha_m = \gamma^{-1} = 73 \). We take the location of the maximum of this fit to be the factual \( \tau_d = 0 \); the time axis of Fig. 3.3a has been adjusted accordingly.

We can compare these results to the Gaussian prediction of the grating spectrum, Eq. (3.19). First we realize that in our experiment \( \tau_p \gg (\tau_d, \tau_c) \), so that we can approximate \( \gamma \approx \tau_c/\sqrt{2} \tau_p \). Two limiting cases of Eq. (3.19) then become

\[
\langle |A(\omega| \tau_d=0)|^2 \rangle \propto e^{-\omega^2 \tau_p^2/2} + \frac{\tau_c}{\sqrt{2} \tau_p} e^{-\omega^2 \tau_c^2/4} \tag{3.20}
\]

\[
\langle |A(\tau_d| \omega=0)|^2 \rangle \propto e^{-\tau_d^2/\tau_c^2} + \frac{\tau_c}{\sqrt{2} \tau_p} \tag{3.21}
\]

The spectrum at zero delay is dominated by the first (coherent) term in Eq. (3.20), a narrow spike with frequency bandwidth \( \Delta \nu \propto \tau_p^{-1} \), and contains only a small incoherent broad-band contribution \( (\tau_c/\sqrt{2} \tau_p) \exp(-\omega^2 \tau_c^2/4) \). Figure 3.3b shows this spectrum, multiplied by the relatively broad Rayleigh-Brillouin response. Our result of 300 MHz for the central peak must be considered an upper limit of the actual width, because it is comparable to the estimated bandwidth of the probe laser. It corresponds to a (lower limit of the) pulse duration \( \tau_p = 1.2 \) ns.

At the central frequency, \( \omega = 0 \), the intensity of the grating spectrum should be described by Eq. (3.21). Our experimental result is shown in Fig. 3.3c, from which we compute (from a Gaussian fit) \( \tau_c = 12 \) ps, corresponding to a bandwidth of 31 GHz (FWHM) of the pump laser. This fit also provides an estimate for the ratio of the Gaussian peak height over the background, \( \beta_m/\alpha_m = 73 \). According to Eq. (3.21) this should correspond to the ratio \( \gamma^{-1} = \sqrt{2} \tau_p/\tau_c = 140 \), in which the numerical value is calculated from the experimentally determined lifetimes.

There is a factor of two difference between the estimates of \( \gamma^{-1} \), which seems reasonable, given the assumptions made. In deriving Eq. (3.19) we have assumed a Gaussian correlation function of the optical field, and a Gaussian pulse envelope. Also, the width of the coherent spike in the

50
3.5 Experimental setup and results

spectra of Fig. 3.3a is determined to a significant extent by the frequency resolution of our experiment (probe laser and Fizeau spectrometer), but this will affect both our estimate of $\tau_p$ (width) and that of $\beta_m$ (area) in about the same way. We conclude that our description of the forcing spectrum Eq. (3.19) is adequate, and allows us to predict how the coherent component of the forcing spectrum can be exploited.

Figure 3.4 shows the forcing spectrum for zero time delay, $\tau_d = 0$, as a function of pump laser pulse duration, as predicted by Eq. (3.19). The figure plots $\langle |A(\omega)|^2 \rangle / I_p^2$ in a linear grey scale against the (real) frequency and the logarithm of the pump pulse length in units of the pump pulse coherence time, fixed at the value found above, $\tau_c = 12$ ps. As discussed earlier, in the case of long pulse duration ($\tau_p \to 100\tau_c$), the spectrum is dominated by the narrow coherent component. If the pulse duration decreases, this coherent component broadens, and simultaneously the incoherent component becomes stronger. These two effects combine to result in a significant spectral broadening.

For the special case of Fourier-limited pulses, we must have temporal overlap within the coherence time, $\tau_d < \tau_c$. Setting $\tau_d = 0$ and $\tau_c = \tau_p$, the forcing spectrum Eq. (3.19) now is the sum of two broad-band contributions

$$\langle |A(\omega)|^2 \rangle = I_p^2 \left[ \exp \left( -\frac{1}{2} \omega^2 \tau_c^2 \right) + \frac{1}{\sqrt{3}} \exp \left( -\frac{1}{6} \omega^2 \tau_c^2 \right) \right].$$

(3.22)

As compared to the equally broad, but incoherent forcing using nanosecond pump pulses (second term in Eq. (3.21)), the use of Fourier-limited picosecond pulses provides more than a factor of 200 increase in signal strength (factor $(1 + 3^{-1/2}) \sqrt{2\tau_p/\tau_c}$ at $\omega = 0$).

Thus, we predict that Coherent Rayleigh-Brillouin Scattering performed with bandwidth-limited picosecond pump laser pulses will benefit from about two orders of magnitude gain in signal strength, as compared to the case of regular nanosecond pulses of the same energy. This should allow spectra to be recorded on the basis of single laser pulses. If we estimate the size of the induced perturbation of the molecular velocity distribution as the momentum gain in half a period of the sound wave or within the pump pulse length, whichever is shorter, these short pulses should still be considered as non-perturbative.
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3.5.1 Perturbation analysis

The fluctuating optical lattice in coherent Rayleigh-Brillouin scattering can be viewed as non-perturbative if the depth of the dipole potential well is smaller than the kinetic energy $k_B T$ of the molecules, or, equivalently, if the momentum gain during one period $\tau_s$ of the sound oscillation is small compared to $m(k_B T)^{1/2}$. For pump laser pulses lasting $\tau_c$ that are shorter than $\tau_s$, it is the time interval $\tau_c$ that matters. The scattering wavevector $q$ is the wavevector of the sound wave, and $\tau_s \approx 2\pi/(qv_0)$, where we have taken the velocity of sound approximately equal to the thermal velocity.

Let us first work the equivalence of the two statements. The dipole potential $U$ is

$$U(x, t) = \frac{2\alpha I c}{\epsilon_0} \cos^2(q x - \Omega t), \quad (3.23)$$

where the intensity $I$ is expressed in the intensity of the two crossing laser beams $I = (I_1 I_2)^{1/2}$, and $\alpha$ is the polarizibility. The electric force $F$ is the gradient of $U$,

$$F(x, t) = \frac{\alpha I q c}{\epsilon_0} \sin(2(q x - \Omega t)). \quad (3.24)$$

For the momentum gain argument we consider the ratio $\epsilon$ which is small in the non-perturbative regime

$$\epsilon = \frac{F \tau_s}{mv_0} = \frac{F^{2\pi} c}{mv_0} = \frac{\pi \alpha I c}{\epsilon_0 k_B T} = \frac{\pi U}{2 k_B T}. \quad (3.25)$$

For long pulses, therefore, the two arguments are the same (but refinements of the prefactor are possible). If the pulse duration of the pump laser is smaller than the period of sound, it is the momentum gain argument that matters, and not the depth of the potential well since the time is too short to explore the potential well.

Let us assume that indeed $\epsilon$ is small for our slow pulse non-coherent experiments. The pulse energy $I \sim E^2 \tau_{nc}$, where $\tau_{nc}$ is the pulse duration. Picosecond pulses have energies comparable to those of our current ns pump laser. Therefore, the electric field is much larger, and...
we have to worry.

First, going to the coherent regime by setting the relative time delay between the pulses to zero, enormously enhances the driving spectrum. However, this does not increase the perturbation level. The electric field magnitudes remain the same, but now they contribute coherently to the spectrum.

Let us further denote the current non–coherent situation with the subscript \( \text{nc} \) and the pico–second transform–limited pulses with the subscript \( c \), pulse duration \( \tau_c \). Then

\[
\frac{E_{\text{nc}}^2 \tau_s}{mv_0} = \epsilon,
\]

therefore

\[
\frac{E_c^2 \tau_c}{mv_0} = \frac{E_{\text{nc}}^2 \tau_c}{E_{\text{nc}}^2 \tau_s} = \frac{E_{\text{nc}}^2 \tau_{nc}}{E_{\text{nc}}^2 \tau_s} = \epsilon \frac{\tau_{nc}}{\tau_s}.
\]

The conclusion is that the small number \( \epsilon \) is compromised by the large fraction \( \frac{\tau_{nc}}{\tau_s} = O(10) \), which may dampen our euphoria.

### 3.6 Prospects

CRBS can be used to measure translational temperature in fluids and flames. This has been demonstrated by Pan et al.[55]. The temperature is estimated from the velocity distribution, which affects the shape of the scattered spectrum. Experiments on CRBS using nanosecond pulsed lasers in principle allow to measure spectra on a single laser pulse basis, if one stays away from the coherent limit. In practice, however, they suffer from the poor shot-to-shot reproducibility of Nd:YAG lasers, and averaging is required in order to obtain sufficient spectral quality. We predict a considerable improvement if bandwidth-limited pulses with a duration of several tens of picoseconds are used for pumping. This will benefit from a two-order-of-magnitude gain in signal strength, because the experiment can be performed in the coherent regime, and will provide shot-to-shot reproducibility. Figure 3.5 shows a simulation using the Tenti model. We have calculated the CRBS spectrum as a function of temperature ranging from 500\(^\circ\)K to 1500\(^\circ\)K in a gas pressure of 2 bar. The peaks separation is a direct measure of the sound velocity and finally the temperature. The widths of individual peaks are also
subject to change with temperature, due to the molecular velocity profile dependence on temperature. These features can provide a reliable means to measure the temperature with CRBS in a seedless scheme. In figure 3.6 we show the half width at half maximum of the spectra as a function of temperature. This shows a good sensitivity over the selected temperature range.

Figure 3.5: Simulated CRBS spectra as a function of temperature at a pressure of 2 bar.

Figure 3.6: Half width of CRBS spectrum as a function of temperature at a pressure of 2 bar.
4 Two lines atomic fluorescence in saturation
In this chapter we will investigate the performance of the two-lines atomic fluorescence (TLAF) technique in the saturation regime by numerical simulations. These simulations will be based on rate equations for the atomic level populations under the influence of a resonant laser beam. Since we will be interested especially in the response of the system under strong excitation, a first question to be answered is whether the use of rate equations, rather than a more comprehensive approach that takes coherence into account, like the optical Bloch equations (e.g. [56]), is still a valid approach. As a general rule, rate equations are valid when either the bandwidth of the excitation is large relative to the transition line-widths, or the collision- and Doppler-broadened line width is much larger than the natural line width [30]. In the present case, the former condition is not necessarily fulfilled, but the second one is, given that the natural width of both transitions of interest amounts to about 100 MHz. Thus, the rate equation approach is expected to be valid for the case of interest here.

\textbf{4.1 Introduction}

As it was mentioned in chapter 1.8, TLAF is based on sequentially pumping atoms out of two closely spaced ground states to a same upper state, and collecting the fluorescence signal on the alternate transition, respectively. We will here introduce the basic philosophy of the method, on the basis of Figure 4.1; a more quantitative analysis follows later. The figure illustrates the two steps of the process. In the first step,

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4_1.png}
\caption{Principle of two-lines atomic fluorescence. Atoms are excited twice, in quick succession, out of two closely spaced ground states (1 and 2), respectively, to a common excited state 3 (solid lines). Fluorescence (dashed lines) down to both ground states will occur, but only on the alternate transition is it detected.}
\end{figure}

atoms are excited out of level 1 to level 3. Fluorescence and collisional quenching will occur, causing the atoms to relax back to either ground state. In this step, only the fluorescence down to level 2 is detected. (Fluorescence into level 1 is to be rejected by proper spectral filtering.) This fluorescence is red-shifted relative to the excitation, so is called *Stokes fluorescence*. In the second step, to be executed some finite delay time $\Delta t$ after the first, atoms are excited out of level 2 to the same excited level 3, after which the fluorescence into level 1 only is recorded. This fluorescence is blue-shifted relative to the excitation, and is called *anti-Stokes fluorescence*. $\Delta t$ should (in the basic process described here) be sufficiently long to allow re-thermalization of the level populations, but sufficiently short so as to freeze the flow of interest. In that case, quenching (usually the big unknown in quantitative LIF measurements) can be taken to affect both steps in the same way, and in taking the fluorescence intensity ratio, its effect cancels out. The fluorescence intensity ratio then directly reflects the ground state population ratio of levels 1 and 2, that is, the Boltzmann factor, that is, the temperature. The strong point of this method is therefore that there is no need to know quenching rate constants. The strong point of using atoms (rather than molecules, in which level combinations like that of Figure 4.1 can also be found, of course) is that electronic transition strength is not diluted over many ro-vibrational transitions. The weak point is that atoms with suitably split ground states must be introduced into the flow of interest.

In the subsequent analysis the main goal will be to correlate the Stokes to anti-Stokes fluorescence yield ratio to flame temperature. This is accomplished by considering the fact that, at least in the basic process described above, the ratio of the measured fluorescence intensities reflects the population ratio of the two closely spaced atomic ground states, which is governed by Boltzmann statistics. Based on this assumption, temperatures can be estimated by measuring the fluorescence intensities and by using a single equation and proper calibration.

### 4.2 Pulse energy and rate equations

Pulse energy is the most important parameter which determines both the level kinetics and the model that we need in order to estimate
4.2 Pulse energy and rate equations

the temperature. There are various other parameters which determine the behavior of the system upon excitation, and we don’t have exact knowledge of all of them. These include spontaneous and stimulated transition rates, quenching rates and relaxation rates between the two ground states of the atoms\(^1\). In the linear regime the effect of quenching cancels out, and due to low excitation energy the deviation of ground state populations from equilibrium is negligible during and after excitation. As a result, the effect of thermalization can conveniently be ignored. This also removes the requirements for the exact knowledge of quenching rates and ground state relaxation rates. As shall we see in this chapter, in the non-linear regime, which we consider as an intermediate regime between the linear and saturation regimes, the quenching becomes important, it does not cancel out any more, and its influence on temperature estimation needs to be accounted for by an extra calibration.

In the saturation regime the excitation energy needs to be increased to a considerably higher level than for the linear regime, and this requires that we take into account all of the involved parameters properly. We will show in this chapter that the effects of quenching and the ground state relaxation can be taken into account by a single calibration parameter.

The process of excitation and relaxation of a three level system, which is here understood to be atomic Indium, as this is often used in practice, is illustrated in Figure 4.2. We label the ground states with 1 and 2 and the upper state with 3. The fluorescence yield is determined by the transient population of the upper state. The rate equation for the excited level population, if we pump either from level 1 or 2, is

\[
\frac{dn_3}{dt} = (B_{i3}E_{\nu i3})n_i - (B_{3i}E_{\nu i3} + Q_3 + A_{31} + A_{32})n_3
\]  

(4.1)

where \(i = 1, 2\), \(n_i\) is the atomic seed level population, \(E\) is the laser spectral energy density in J m\(^{-3}\) Hz\(^{-1}\), \(A_{ij}\) and \(B_{ij}\) are Einstein spontaneous and stimulated emission coefficients of transitions \(i \rightarrow j\) and \(Q_{3j}\) is the collisional quenching rate (with \(Q_3 = Q_{31} + Q_{32}\)). We distinguish

\(1\)We will call the latter process ground state relaxation in this chapter.
4 Two lines atomic fluorescence in saturation

Figure 4.2: Stokes and anti-Stokes LIF generation in an Indium atom. The half-integral numbers indicate the electronic angular momentum, \( J \), of each ground state.

three different regimes according to the excitation power:

a) Linear regime:

\[
B_{3i}E_{\nu i3} \ll Q_3 + A_{31} + A_{32} \quad (4.2)
\]

b) Non-linear regime:

\[
B_{3i}E_{\nu i3} \sim Q_3 + A_{31} + A_{32} \quad (4.3)
\]

c) Saturation regime:

\[
B_{3i}E_{\nu i3} \gg Q_3 + A_{31} + A_{32} \quad (4.4)
\]

4.2.1 Linear regime

In the linear regime and considering a steady state situation, the excited state population during laser excitation becomes:

\[
n_3 = \frac{B_{3i}E_{\nu i3}}{Q_3 + A_{31} + A_{32}} n_i \quad (4.5)
\]

Let us denote by \( F_{32} \) the power that falls on the detector due to fluorescence on the transition \( 3 \rightarrow 2 \), that is, the fluorescence we are interested
in upon laser excitation on the transition \(1 \rightarrow 3\). \((F_{31} \text{ is interpreted in a similar way.})\) The measured LIF signal on the two individual transitions is proportional to this fluorescence power, described by

\[
F_{32} = h \nu_{32} S L \frac{\Omega}{4\pi} A_{32} n_3^{(1)}
\]

\[
F_{31} = h \nu_{31} S L \frac{\Omega}{4\pi} A_{31} n_3^{(2)}
\]

in which \(h\) is Planck’s constant, \(\nu\) is the frequency of the fluorescence, \(S\) and \(L\) are interaction cross section and length and \(\Omega\) is the solid angle of the collecting optics. \(n_j^{(j)}\) is used to denote the steady-state population in level 3 (eq. 4.5) after excitation out of level \(j\). The laser spectral energy density is defined by

\[
E_{\nu_3} = \frac{\Phi_{i3}}{(SC\delta \nu_3)}
\]

where \(\Phi_{i3}\) is the laser power, \(c\) is the speed of light and \(\delta \nu_3\) is the spectral width of the laser radiation. Then, if we make a ratio of two fluorescence measurements (we will call this the fluorescence ratio henceforth),

\[
\frac{F_{31}}{F_{32}} = \frac{\eta \delta \nu_{13} \Phi_{23} A_{31} B_{23} \nu_{31} n_2}{\delta \nu_{23} \Phi_{13} A_{32} B_{13} \nu_{32} n_1},
\]

which is independent of quenching. It includes a relative detector efficiency \(\eta\), assumes equal probe volumes and measurement times for both wavelengths, and also assumes that both measurements are carried out quickly after one another, on a time scale short relative to possible variations in the quenching rate.

The Einstein coefficients are related to level degeneracy and transition frequency by

\[
\frac{A_{31} B_{23}}{A_{32} B_{13}} = \left(\frac{\nu_{31}}{\nu_{32}}\right)^3 \frac{g_1}{g_2}.
\]

The number density ratio of levels 1 and 2 can be obtained from the
Boltzmann ratio, which is temperature dependent:

\[
\frac{n_2}{n_1} = \frac{g_2}{g_1} \exp \left( -\frac{\Delta E}{k_B T} \right).
\]  

(4.11)

Here \( T \) is the gas temperature, \( \Delta E = E_2 - E_1 \) is the energy difference between the two ground state levels and \( k_B \) is the Boltzmann constant. By using all of the above we can evaluate the temperature as:

\[
T = \frac{\Delta E/k_B}{\ln F_{32}/F_{31} + \ln \Phi_{23}/\Phi_{13} + C_T},
\]  

(4.12)

in which the single calibration constant \( C_T \) takes into account all fixed parameters pertaining to the two transitions and the detector efficiencies. This TLAF equation is valid in the linear regime. Increasing the laser fluence causes a deviation from the linear response (eq. 4.5). The permissible energy fluence for the linear regime is found by measurement. Figure 4.3 illustrates the Indium fluorescence (Stokes) as a function of spectral intensity. Above a certain point the approximation resulting in eq. 4.12 is not applicable any more, and as the excitation intensity increases the signal gradually becomes less dependent on excitation intensity.

Figure 4.3: Illustration of typical LIF yield curves as a function of spectral irradiance by the excitation laser. In this case the linear regime extends up to about 2.5 kW/cm\(^2\)/cm\(^{-1}\). (Based on data published by Medwell at al. [4].)
In this particular case [4], the linear regime extends up to spectral irradiances of about 2.5 kW/cm$^2$/cm$^{-1}$.

### 4.2.2 Non-linear regime

Working beyond the linear regime offers some advantages. In this section we will briefly consider what we call the non-linear regime for TLAF, or NTLAF [4], understood to be the regime between linear response and full saturation. Due to lower sensitivity of the signal to laser pulse energy fluctuations, higher stability in signal can be achieved. Operating at higher intensities requires some modification of the TLAF equation and extra calibration effort [4]. Medwell et al. performed an experiment in the non-linear regime, and they achieved higher accuracy as compared to linear TLAF [4]. Increasing the irradiance from 2.5 kW/cm$^2$/cm$^{-1}$ to 250 kW/cm$^2$/cm$^{-1}$ results in an increase of the signal to noise ratio from 8:1 to 20:1.

According to Eq. 4.3, in the non-linear regime we can not ignore the stimulated emission rate, and the TLAF equation needs to be modified to take this term into account. The modification has been shown by Medwell et al. [4] to take the form

$$T = \frac{\Delta E/k}{\ln (F_{32} (1 + C_S/\Phi_{31})) - \ln (F_{31} (1 + C_A/\Phi_{32})) + C_T}.$$  \hspace{1cm} (4.13)

The additional constants $C_A$ and $C_S$ can be derived experimentally from a fluorescence versus irradiance plot; they take into account the unknown quenching terms. As before, $C_T$ is the global calibration constant, which is derived by measurement of the local temperature in a point in the flame by means of a thermocouple.

### 4.2.3 Saturation regime

In the treatment of the linear regime the relationship between excitation power and collected fluorescence is considered to be linear, and it is also assumed that the level populations reach steady state. The latter has been considered in many studies, including the NTLAF ones, undoubtedly because it simplifies the analysis of the data.

The extent to which this assumption is valid does not seem to have been studied before (or at least it is not reported in the literature).
Furthermore, our calculations based on the rate equations for decay kinetics of the level populations show that for a given temperature the fluorescence ratio does not obey the traditional formulation but shows a deviation from the expected value. There are two major reasons behind this. First of all it is always assumed that the excitation source is constant in time which enables us to assume steady state behavior for the simple level equation for the population ratio. Second, we assume an invariant population of the ground states during the excitation. In the saturation regime, the former assumption might remain valid, whereas the latter is obviously not even intended to be valid any more. By means of the simulations presented below we will investigate the time evolution of level populations for realistic excitation pulse shapes in various excitation regimes.

An immediate benefit of working in the saturation regime would be the higher fluorescence intensity which results in more signal, so hopefully in more accurate temperature estimation and perhaps even enable single shot measurements. This would be very interesting for turbulent combustion applications, where the temperature profile changes on a very short time scale. Another advantage is the reduced sensitivity for pulse to pulse fluctuations of the laser intensity. In the limit of full saturation, the generated fluorescence becomes completely independent of excitation laser intensity variations, and the TLAF method becomes immune to such intensity fluctuations. Thus, reaching the saturation level over the whole field of view means that there would be no requirement for spatial monitoring of the excitation laser profile and subsequent image corrections.

There is, of course, a caveat, or several. First of all, it is unlikely that saturation can be maintained over the whole excitation laser beam profile, and notably in the wings. By proper apertures it can be attempted to keep the contribution of the non-saturated wings negligible. Secondly, whereas in the linear regime the thickness of the excitation laser beam along the line of sight of the detection system doesn’t play a role for the detected signal (apart from depth-of-field issues), the signal scales linearly with the beam thickness (as far as it induces saturation) in the case of saturation. By keeping the geometry of the setup the same, however, this influence can be calibrated out.
4.2 Pulse energy and rate equations

The theoretical treatment of the TLAF problem over the full excitation strength range requires a solution of the pertinent rate equations. Although these equations are linear (see below), a manageable analytical solution exists only for square excitation, that is, a constant-intensity light pulse that switches on and off instantaneously (Zizak et al. [57]). For a practical laser pulse such a model is not very realistic, and moreover the analytical solution is still quite complicated, and does not yield much insight. This is compounded by the fact that we do not know all the relevant relaxation rates in the system. As we will shortly see in this chapter, these parameters are deterministic for the behavior of level populations, which in turn determines the developed model for data analysis.

Our calculations are based on the general rate equations for a three level system, as described in detail by Zizak et al. [57].

![Figure 4.4: The three level system and the transition rates involved.](image)

Briefly, we consider a three-level system with transitions, described by rate constants, between any level pair (Figure 4.5). The transitions can be due to anything, collisional or light-induced, and the associated rate constants $R_{ij}$, for a transition $i \rightarrow j$, may be time-dependent (for a contribution due to a laser pulse, for instance). We will describe the level populations in terms of fractional populations $n_i(t)$, for which the
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Rate equations take the form

\[
\frac{dn_1}{dt} = -(R_{13} + R_{12})n_1 + R_{31}n_3 + R_{21}n_2
\]
\[
\frac{dn_2}{dt} = -(R_{23} + R_{21})n_2 + R_{32}n_3 + R_{12}n_1 \tag{4.14}
\]
\[
\frac{dn_3}{dt} = -(R_{31} + R_{32})n_3 + R_{13}n_1 + R_{23}n_2
\]

We will take the thermal Boltzmann fractions as initial conditions, and assume the 3-level system to be closed, that is

\[n_1(t) + n_2(t) + n_3(t) = 1 \quad \forall t, \tag{4.15}\]

so that the set of rate equations can be reduced to, for instance,

\[
\frac{dn_2}{dt} = R_{12} - (R_{21} + R_{23} + R_{12})n_2 + (R_{32} - R_{12})n_3 \tag{4.16}
\]
\[
\frac{dn_3}{dt} = R_{13} + (R_{23} - R_{13})n_2 - (R_{31} + R_{32} + R_{13})n_3 \tag{4.17}
\]

For the particular case of TLAF, transitions between levels 1 and 2 are dipole-forbidden. We will assume them to be collision-induced, and relate the downward and upward rates through detailed balancing \[?\], that is,

\[
\frac{R_{12}}{R_{21}} = \frac{g_2}{g_1} \exp \left( -\frac{\Delta E}{k_BT} \right), \tag{4.18}
\]

in which the \(g_i\) are level degeneracies and \(\Delta E\) is their energy difference. Two separate fluorescence measurements need to be considered. For the Stokes fluorescence we excite \(3 \leftarrow 1\) and monitor \(3 \rightarrow 2\), whereas for the anti-Stokes fluorescence we excite \(3 \leftarrow 2\) and monitor \(3 \rightarrow 1\). The rate constants pertinent to both situations are listed in Table 4.1. They are expressed in terms of the Einstein \(A\) and \(B\) coefficients for spontaneous and induced radiative transitions, respectively, and the collision-induced quenching rate coefficients \(Q\). The spectral energy density of the incident radiation is denoted by \(E\), and subscripts indicate the individual transitions, as above.

A Gaussian laser pulse with pulse duration of 10 ns is assumed that
4.2 Pulse energy and rate equations

is,

\[ P(t) = \frac{E_0}{\sqrt{2\pi} \tau} \exp \left( -\frac{t^2}{2\tau^2} \right), \quad (4.19) \]

in which \( P(t) \) is the instantaneous laser power and \( E_0 \) is the total pulse energy. The spectral band width is assumed to be 3 GHz and the beam is formed into a light sheet with dimensions of \( 10 \times 3 \text{ mm}^2 \). The total number of generated photons after excitation is calculated by integrating by \( A_{31} n_3 \) or \( A_{32} n_3 \) over time for the anti-Stokes and Stokes transitions, respectively. Note that the level population densities are normalized to total density and the calculated number of photons is therefore also normalized. This is illustrated in figure 4.5 which shows the generated number of photons for anti-Stokes and Stokes transitions in atomic Indium as a function of spectral power density. Some of the relevant parameters for the Indium atom are summarized in Table 4.2. Closer examination of figure 4.5 reveals two facts. First of all, the generated number of Stokes photons upon 410 nm excitation is considerably higher than that of anti-Stokes photons upon 451 nm excitation, under otherwise similar conditions. This is mainly due to the higher population density in the lowest ground state. Moreover, the rate at which the generated number of photons reaches saturation is faster with 451 nm excitation in comparison to 410 nm. In saturation the deterministic parameter is the ratio of stimulated transition to spontaneous transitions. For 410 nm excitation this parameter amounts to \( B_{31}/(A_{32} + A_{31}) = 1.4 \times 10^{12} \text{ m}^3\text{J}^{-1}\text{s}^{-1} \) and for 450 nm it takes a higher value \( B_{32}/(A_{32} + A_{31}) = 3.5 \times 10^{12} \text{ m}^3\text{J}^{-1}\text{s}^{-1} \) [59]. As we will see later

<table>
<thead>
<tr>
<th>Stokes (3 ← 1 excitation)</th>
<th>anti-Stokes (3 ← 2 excitation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{13} = B_{13} E_{13} )</td>
<td>( R_{13} = 0 )</td>
</tr>
<tr>
<td>( R_{31} = B_{31} E_{13} + Q_{31} + A_{31} )</td>
<td>( R_{31} = Q_{31} + A_{31} )</td>
</tr>
<tr>
<td>( R_{23} = 0 )</td>
<td>( R_{23} = B_{23} E_{23} )</td>
</tr>
<tr>
<td>( R_{32} = Q_{32} + A_{32} )</td>
<td>( R_{32} = B_{32} E_{23} + Q_{32} + A_{32} )</td>
</tr>
</tbody>
</table>

Table 4.1: Rate constants for the two excitation processes in TLAF; see also Figure 4.4 and the text for explanation.
Two lines atomic fluorescence in saturation

Table 4.2: Properties of atomic indium and the levels we use for TLAF experiments. (Data from the NIST Atomic Spectra Database[58].)

<table>
<thead>
<tr>
<th>Air λ [nm]</th>
<th>( A_3 [MHz] )</th>
<th>( E'' [cm^{-1}] )</th>
<th>( E''' [cm^{-1}] )</th>
<th>Designation</th>
<th>( g'' )</th>
<th>( g''' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>410.176</td>
<td>56</td>
<td>0</td>
<td>24372.956</td>
<td>[Cd]5p–6s</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>451.131</td>
<td>102</td>
<td>2212.598</td>
<td>24372.956</td>
<td>[Cd]5p–6s</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

this will be confirmed by experiments. Figures 4.6 and 4.7 show typical results for the two different regimes, which includes the temporal behavior of all levels. In the linear regime (albeit with a laser pulse energy that is already a bit high; level populations change by about 10%), the upper level population follows the laser pulse, and so does the fluorescence yield. In this case the fluorescence ratio will directly reflect the population ratio of the lower states. The decay kinetics of the upper level determines the fluorescence signal intensity, and by increasing the excitation energy the transition from the linear regime to saturation becomes visible. This is confirmed by the fact that in saturation the transient population of the third level deviates from the Gaussian excitation profile and it levels out at high laser intensities. One interesting point is the coupling of the ground levels; they both experience a similar variation during excitation. This is due to the large thermal relaxation term, which tries to force the level populations to thermal equilibrium. For example, in figure 4.6 the first level is pumped to third level but the population of level 2 is also decreased. This term also helps the ground state populations to recover after excitation. In order to investigate the effect of the thermal ground state relaxation rate we repeat the calculations of figures 4.6 and 4.7 with ground state relaxation rate \( R_{21} \) reduced by two orders of magnitude, that is, \( R_{21} = 0.1A_{32} \). The results are shown in figures 4.8 and 4.9 for 410 nm and 451 nm excitations, respectively. As expected, the ground levels take longer time to reach equilibrium after excitation. The excited state population \( n_3 \) now shows an initial peak, followed by a gradual decline. The latter is due to population slowly being trapped in the level that is not pumped by the excitation laser.
4.2 Pulse energy and rate equations

Figure 4.5: a) The generated photon number as a function of pulse energy for 451 nm excitation (anti-Stokes fluorescence detection) and 410 nm excitation (Stokes fluorescence detection). The laser pulse profile is assumed to be a Gaussian profile with pulse duration of 10 ns and spectral band width of 3 GHz. b) Zoomed in to show the linear region. The beam is formed into a light sheet with dimensions of $10 \times 3$ mm$^2$. 
Figure 4.6: Calculated temporal behavior of level populations in atomic Indium after excitation at 410 nm (1 → 3) by a laser pulse with a 10 ns pulse width, for a) linear and b) saturation regime. We used following parameters in the calculations: $R_{21} = 10A_{32}$, $Q_{32} = A_{32}$, $Q_{31} = A_{31}$, $E_{\text{linear}} = 0.1 \, \text{mJ}$ and $E_{\text{saturation}} = 4 \, \text{mJ}$. Note the vertical scale differences between the various panels.
4.2 Pulse energy and rate equations

Figure 4.7: Calculated temporal behavior of level populations in atomic Indium after excitation at 451 nm (2 → 3) by a laser pulse with a 10 ns pulse width for a) linear and b) saturation regime. Other parameters as in Figure 4.6.
Two lines atomic fluorescence in saturation

Figure 4.8: As Fig. 4.6, but $R_{21} = 0.1 A_{32}$. 
4.2 Pulse energy and rate equations

Figure 4.9: As Fig. 4.7, but $R_{21} = 0.1A_{32}$.

Note that the speed of ground state relaxation (thermalization) is governed by $R_{21}$ and $R_{12}$, which are now considerably reduced relative
to the situation of Figures 4.6 and 4.7. We have tried to monitor the fluorescence time dependence experimentally. In this experiment we recorded the laser intensity (elastic scattering) and the fluorescence intensity as a function of time by changing the delay between the laser trigger and the ICCD gate in steps of 5 ns. The camera gate width was kept fixed at 50 ns. Although the exact time profile of the opening of the image intensifier gate is not known, we expect the opening edge to be steeper than the closing one. Thus, in this experiment, the fluorescence is sampled by something that resembles a square gate, that itself lasts much longer than the fluorescence, and is stepped in 5 ns steps over the fluorescence time profile. As shown in figure 4.10 the fluorescence intensity more or less follows the laser pulse. It does not ‘almost precede’ the laser pulse as simulated in figures 4.6(b) and 4.7(b), but neither does it show an initial maximum as in figures 4.8(b) and 4.9(b).

Figure 4.10: Normalized intensities of the excitation laser and the induced fluorescence as a function of time delay between laser pulse and camera gate. \( t = 0 \) is arbitrary.

The ground state relaxation rate is one of the parameters that we don’t have enough knowledge of, and with this simulation and the com-
4.2 Pulse energy and rate equations

Comparison to our experimental evidence, we conclude that $R_{21}$ is in the order of or larger than the spontaneous emission rates.

**Temperature estimation in the saturation regime**

Working in the saturation regime requires a model that describes the process and our final goal here is to find an equation to calculate the temperature from measured fluorescence signals. As indicated before there are a few parameters that become important in the transition from linear to non-linear and saturation regimes. We also investigate the sensitivity of the system to temperature variations in the saturation regime by plotting the fluorescence ratio $F_{31}/F_{32}$ for different excitation pulse energies and temperatures. Figure 4.11 shows the fluorescence ratio as a function of excitation pulse energy and temperature. Since the fluorescence ratio is plotted here, the saturation trend is more visible here than in the individual fluorescence yields of figure 4.5. The figure clearly shows the temperature sensitivity of the fluorescence ratio even at high energies; as high energy as required for saturation. This figure also clearly shows the deviation from linear behavior at larger energies.

![Figure 4.11: The fluorescence ratio $F_{31}/F_{32}$ as a function of temperature and laser pulse energy (the same for both lasers). We have used $R_{21} = 10A_{32}$ and $Q = 0.1A_{32}$](image)

Figure 4.11: The fluorescence ratio $F_{31}/F_{32}$ as a function of temperature and laser pulse energy (the same for both lasers). We have used $R_{21} = 10A_{32}$ and $Q = 0.1A_{32}$
Let us derive the equation that relates temperature to fluorescence ratio in the case of saturation. Based on Figures 4.6 and 4.7, we assume steady state during the whole pulse in the saturation regime, and solve the rate equations 4.16 and 4.17 for the upper level population under conditions of heavy saturation.

\[
\begin{align*}
\dot{n}_2 &= R_{12} - (R_{12} + R_{21} + R_{23})n_2 + (R_{32} - R_{12})n_3 \\
\dot{n}_3 &= R_{13} + (R_{23} - R_{13})n_2 - (R_{13} + R_{31} + R_{32})n_3
\end{align*}
\] (4.20)

We use the rate constants from Table 4.1 for the two excitation schemes. Taking degeneracies into account we have

\[B_{13} = B_{31}\text{ and } B_{32} = 2B_{23}.\]

For 410 nm excitation \((1 \rightarrow 3)\) the steady-state solution for \(n_3\) becomes

\[n_3^{(13)} = \frac{R_{21}}{Q_{32} + A_{32} + R_{12} + 2R_{21}} \] (4.22)

and the fluorescence yield \((3 \rightarrow 2)\) is (in this steady-state approximation) given by

\[F_{32} \propto A_{32} n_3^{(13)} \tau_{13} = \frac{A_{32} R_{21} \tau_{13}}{Q_{32} + A_{32} + R_{12} + 2R_{21}}, \] (4.23)

in which \(\tau_{13}\) is the pulse duration of the excitation laser.

Similarly, for 451 nm excitation \((2 \rightarrow 3)\) the steady-state solution for \(n_3\) becomes

\[n_3^{(23)} = \frac{R_{12}}{Q_{31} + A_{31} + 3R_{12} + 2R_{21}} \] (4.24)

and the fluorescence yield \((3 \rightarrow 1)\) follows as

\[F_{31} \propto A_{31} n_3^{(23)} \tau_{23} = \frac{A_{31} R_{12} \tau_{23}}{Q_{31} + A_{31} + 3R_{12} + 2R_{21}}, \] (4.25)

in which \(\tau_{23}\) is the pulse duration of the (other) excitation laser.

For the fluorescence ratio we then find a somewhat complicated expression,

\[
\frac{F_{31}}{F_{32}} = \frac{A_{31} \tau_{23}}{A_{32} \tau_{13}} \frac{Q_{32} + A_{32} + R_{12} + 2R_{21}}{Q_{31} + A_{31} + 3R_{12} + 2R_{21}} \frac{R_{12}}{R_{21}}. \] (4.26)
4.2 Pulse energy and rate equations

In the largest fraction, the rate constants occur as a sum. From the temporal shape of the fluorescence, it looks as if \( R, A \) and \( Q \) are of the same order of magnitude, so as a first approximation we take this fraction to be temperature-independent. Calling it \( D \), and using the detailed balancing relation 4.18 between \( R_{12} \) and \( R_{21} \), we find

\[
\frac{\Delta E}{k_B T} = \ln \frac{F_{31}}{F_{32}} + \ln \frac{A_{31}}{A_{32}} + \ln \frac{\tau_{23}}{\tau_{13}} + \ln 2D. \tag{4.27}
\]

Thus, we end up with a temperature equation that is quite similar to the one used in the linear regime, Eq. 4.12, but the calibration constant will now also possess some temperature dependence.

Interestingly, the temperature derived in the saturation regime is qualitatively different from the one measured in the linear regime. In order to explain this, let us revisit the rate equations. Temperature is here in two ways: via the initial level populations, and via the detailed balancing relation between the two ground state relaxation rate constants, eq. 4.18. In the linear regime, the fluorescence yield is directly proportional to the initial level populations, and the ground state relaxation rates are irrelevant. Thus, the fluorescence ratio is essentially the population ratio, and this is translated into a temperature (eq. 4.11). From figures like 4.6(b) and 4.7(b), however, it is clear that during most of the fluorescence lifetime the populations are heavily perturbed from their initial values. In fact, the population distribution during the excitation pulse is largely determined by the ground state relaxation process. The temperature involved here is a gas kinetic one, that determines the relative magnitude of the forward and backward relation rates between the two ground states. In thermal equilibrium these two temperatures are equal, but in non-equilibrium situations they need not. For combustion processes, it might be argued that the gas kinetic temperature measured by saturated TLAF is the more relevant one.

In order to investigate the validity of our assumption on invariant population over excitation and the derived equation for temperature, a simulation is performed for a given temperature and calculating the \( F_{32} \) and \( F_{31} \). We can estimate the temperature using equation 4.27. The simulation is repeated with different values of thermal relaxation...
rate $R_{21}$ and quenching rate $Q$. This is to investigate the effect of these parameters on temperature estimation and its sensitivity on variation of these parameters. The calibration constant is found by solving equation 4.27 for $D$ at a known temperature. Below we will illustrate the validity of this calibration constant over a temperature range of 500 K. The simulation is performed over a 500 K temperature range where the central temperature is set to 1500 K. The results are shown in figures 4.12 and 4.13. Figure 4.12 shows the relative error in temperature estimation as a function of temperature and thermal relaxation rate $R_{21}$ which is repeated for $Q = 10 \times A_{32}$, $Q = 1 \times A_{32}$ and $Q = 0.1 \times A_{32}$.

![Figure 4.12](image)

Figure 4.12: The relative error of temperature estimation as a function of thermal relaxation rate, for a) $Q = 10A_{32}$, b) $Q = 1A_{32}$ and c) $Q = 0.1A_{32}$.

By varying the temperature from 1250 K to 1750 K, the maximum relative error is found to be 2.5%. Moreover no obvious variation in relative error is observed by changing the quenching rate and the error is a function of temperature itself. This means that in a flame with
a maximum variation of temperature of 500 K the maximum relative error amounts to 2.5%. In figure 4.13 the relative error in temperature estimation is plotted as a function of quenching rate which is varied from $Q = 0.1A_{32}$ to $Q = 100A_{32}$. The results are repeated for different $R_{21}$ values varied from $R_{21} = 0.1A_{32}$ to $R_{21} = 10A_{32}$. By increasing the thermal relaxation rate $R_{21}$ the error converges to 2.5% at maximum and be decreasing the $R_{21}$ the relative error gets lower values. These simulations support the idea of working in the saturation regime. A maximum relative error of 2.5% is calculated over a temperature range of 500 K. In many practical applications the temperature variation will typically be less than that.

Figure 4.13: The relative error of temperature estimation as a function of quenching rate $Q$, for a) $R_{21} = 10A_{32}$, b) $R_{21} = 1A_{32}$ and c) $R_{21} = 0.1A_{32}$.
5 TLAF Experiments and results
In this chapter the experimental considerations and TLAF thermometry results in the saturation regime will follow. Several requirements needed to be fulfilled in order to perform TLAF experiments properly, and we will discuss them in detail.

5.1 Excitation

TLAF needs two laser pulses at two different wavelengths to excite the split ground state population to a common upper state. The employment of lamps [60] and continuous wave lasers [27] are reported for temperature measurement in laminar flames. For turbulent flames we will need the time resolution provided by pulsed lasers, and the delay between the pulses must not exceed the order of hundred ns to avoid variations of flame temperature and spatial profile due to turbulent fluctuations.

In the linear regime, a finite delay is nevertheless needed to assure the re-thermalization after the first laser pulse, and therefore it is limited by atomic relaxation times. This requirement is relaxed in the saturation regime, because then it is the laser which drives the populations. Moreover, fluorescence lifetimes and laser pulse widths also limit decreasing the time delay to a given extent. Due to the finite decay time of the excited state [59] the second pulse can not arrive immediately after the first pulse and the excited state needs to relax to the ground state to avoid cross talk. A 100 ns delay is often considered appropriate [28].

Dye lasers [28], Nd:YAG-pumped optical parametric oscillators [20] and diode lasers [59] have all been used for exciting the Indium transitions.

For Indium as a seed atom, one of the transitions is induced by a 410 nm laser pulse, and the resulting fluorescence is detected at 451 nm, while the 410 nm fluorescence is blocked by a filter. The reverse process is performed by exciting at 451 nm and collecting the emission at 410 nm while blocking the 451 nm emission. The filters are requisite to block the resonance fluorescence as well as the elastically scattered light from the excitation laser. Hult et al. [59] used both fluorescence lines and used only one detector. They corrected the TLAF equations by considering the fluorescence from both lines, and claimed that the method doesn’t suffer from elastic scattering because they measured the temperature in
a clean flame without soot particles. In our case, this approach would fail, because of the seeding system, as described below.

The pulse energies are very important parameters; they determine the fluorescence regime, as has been discussed in detail in chapter 4.

5.2 Seeding

Normally, in TLAF-related techniques, Indium atoms are seeded into the flame, but the use of naturally occurring species like OH [61] and NO [62], is also reported. Atoms are advantageous because of higher oscillator strengths and simple spectra. The large spin-orbit splitting of the ground state of many metal atoms makes them potentially suitable as seeding species in TLAF thermometry. The problem is to find a suitable atom for the desired temperature range. Depending on the ground state splitting the temperature sensitivity changes in different temperature ranges. As the splitting of the ground state increases, the sensitivity range shifts toward higher temperatures.

Indium is usually seeded in flames as InCl$_3$ salt, dissolved in distilled water, by using a nebulizer. The seeding concentration varies from $4.5 \times 10^{-4}$ to $1.0 \times 10^{-2}$ with a seeding rate of 2.5 ml/h [59]. Adding the water mist was found to decrease the flame temperature by 100-150 K, and to change the soot oxidation and production rates [63]. Recently, the effect of different solvents on signal intensity was investigated [64] and it was shown that aceton and methanol provide more signal compared to water. On the other hand, methanol behaves as an extra fuel source which increases the temperature of the flame. Besides nebulizers, laser ablation [65], has also been used to generate atomic Indium. This technique requires an extra laser (Nd:YAG @ 532 nm) and an extra chamber which complicates the setup considerably.

Due to the disturbing effects on flame temperature and burning velocity, related to fluid evaporation and, in some cases, combustion, the application of the TLAF method was previously restricted mainly to near-stoichiometric flames, which have the minimum sensitivity to these kind of disturbances. We will use a new seeding technique, in which Indium salt is deposited on the surface of micron-size metal-oxide particles (Al$_2$O$_3$) and fed into the flame with a modified PIV seeding system. This method provides fast salt decomposition at small particle seeding
5.3 Imaging

rates, making this methodology truly non-intrusive and allows obtaining strong TLAF signals without flame perturbation even for very lean flames.

In order to investigate the seeding effect on flame shape, two images of a flame with equivalence ratio of $\phi = 0.647$ and burning velocity of $u = 40 \text{ mL/h}$ are recorded with seeding and without seeding. The results are shown in figure 5.1. As the figure shows, the seeding hardly changes the flame shape. The luminosity, of course, is significantly altered, due to the seeding of small solid particles in the flame. Unfortunately, performing thermocouple measurements in the seeded flame proved impossible.

![Figure 5.1: Natural luminosity images of the central flame of the slot burner used in our experiments, a) without seeding and b) with seeding for equivalence ratio of $\phi = 0.647$.](image)

5.3 Imaging

A cylindrical telescope is used to make a light sheet, so as to excite the flame in 2D. In front of that, a combination of polarizer and half wave plate is used to control the input intensity. Two ICCD cameras are used for recording the TLAF signals. For steady flames it is possible to use only one camera, with exchangeable filters for recording Stokes and anti-Stokes signals. For turbulent flames, where the pulses arrive with a time delay in the order of 100 ns, it is not possible to change the filters and still record two successive images. For this reason two cameras equipped with their own proper filter are used to record the TLAF signals. They are synchronized with the lasers and are operated
sequentially. A difficulty related with this equipment is image alignment, since any pixel by pixel misalignment introduces errors into the results, especially in regions of steep temperature gradients.

5.4 Experimental setup

5.4.1 Optical setup

Our experimental setup (Figure 5.3) comprises two pulsed Nd:YAG lasers (QuantaRay, SpectraPro 150 & 170) with 10 Hz repetition rate. The frequency-tripled laser pulses are launched into two dye laser systems (Sirah) which are operated on Exalite 411 and Coumarine 2, respectively, to generate the desired wavelengths for the TLAF experiment. Exalite 411 and Coumarine 2 are used to generate 410 nm and 451 nm, with pulse energies set to 2.5 mJ and 2.2 mJ, respectively, to excite the Indium atoms in the saturation regime. These energies are evaluated by plotting the fluorescence intensity as a function of input energy, as will be discussed later in this chapter. A combination of a cylindrical \( f = -4 \text{ mm} \) and a spherical lens \( f = 120 \text{ mm} \) is employed to make a light sheet with approximate size of \( 2 \times 60\text{ mm}^2 \) to cover the full flame height. The laser beams arrived at the flame from opposite sides, and this removes the requirement for combining the lasers with a beam combiner, which simplifies the setup and the alignment.

The fluorescence emissions are captured by two ICCD cameras (PI-MAX 3) equipped with either one band pass (448/20) or one short pass (440 SP) filter (Semrock) to reject the elastically scattered light at wavelengths of 410 nm and 451 nm, respectively. The transmission curves for each filter are shown in figure 5.2. The cameras and lasers are synchronized by two delay generators (Stanford Research Systems DG535) to fire the lasers with a delay of 100 ns and open the intensifiers of the cameras accordingly. On this time scale the temperature field can be considered as frozen.

The ICCD cameras are used with a gate width of around 50 ns. This small width reduces collecting the background signal, yet it ensures collecting the fluorescence signal efficiently. A photodiode is used to determine the arrival time of the pulses at the burner and to adjust the required delay between firing of the lasers and opening of the camera.
5.4 Experimental setup

![Graph showing transmission curves for different wavelengths.]

Figure 5.2: Transmission curves (as specified by the manufacturer) of the spectral filters used in the TLAF setup.

gates. The fluorescence images were recorded by two separate PCs. A schematic diagram of the setup is shown in figure 5.3.

5.4.2 Image registration and analysis

The recorded images were analyzed with a homemade code developed in Matlab. Registration (alignment) of the two images recorded by the two ICCD cameras is also performed in Matlab, with the help of a calibration image: a metal plate with four holes close to its edges was illuminated uniformly from the back side and the image was recorded by the two ICCDs, respectively. The transformation matrix is determined and we used this matrix to transform the fluorescence image of 410 nm. This transformation includes affine and projective transformations, which correct the camera mismatch. The initial analysis, comprising background subtraction, Gaussian filtering and speckle removal, are performed in ImageJ [66].
5 TLAF Experiments and results

Figure 5.3: Schematic diagram of the TLAF setup. The vertical bars between the two cameras represent the burner, detailed in fig. 5.4.

5.4.3 Burner and seeding system

Figure 5.4 shows a schematic of the burner used in the experiments, with gas supply, seeding, and thermostating systems. The burner was designed to study flame cusps formed in flames of ultra-lean mixtures, in particular of hydrogen-methane-air mixtures. The cusps are represented by tips of 2-D Bunsen flames stabilized on the burner. The burner has seven slots with $4 \times 40 \text{ mm}^2$ cross-section, separated by 4 mm distance. The multi-slot configuration has been chosen for the burner because of two reasons. First, due to the mutual support of the flames, much leaner flames can be stabilized on such a burner than would be possible with a single-slot burner. Second, the three central flames stabilized on the burner are nearly identical, which allows simplifying numerical simulations of these flames (planned for the future, and not discussed here), by
5.4 Experimental setup

applying periodic boundary conditions. The mixture is supplied to the burner plenum chamber and then evenly distributed between slots and along each slot using a plate with double rows of uniformly spaced 0.5 mm diameter holes positioned along each slot entrance. A wire mesh roll surrounding the mixture inflow is installed in the plenum chamber to quench turbulence inside the chamber and thereby remove pressure pulsations, which otherwise would disturb the flames.

Figure 5.4: Schematic diagram of the slot burner and seeding system. (Design by Y. Shoshin.)

Flow straighteners are installed inside each slot before the exit to
5 TLAF Experiments and results

laminarize the flow after passing through small holes in the flow distribution plate, and to form near-uniform mixture velocity profiles at the burner exit. Flames formed above the two edge slots are anchored to the burner only at one, inner, side. If no special precautions are made, periodic vortices form above these flames and disturb these and all other flames. To render the flame stable, a duct made of fused silica plates is installed above the burner. Besides removing above-mentioned vortices, the duct protects the flames from occasional drafts and improves flame anchoring to the burner, thereby extending the range of mixture equivalence ratios at which flames can be stabilized. Two side plates of the duct are slightly inclined outward, as it was found empirically that inclining these plates was required for the central flames to be near-identical. The duct is covered with a metal grid which helps to remove instabilities related to natural convection. The burner surface is kept at constant temperature (45 °C) using a thermostated water flow, which is pumped though the channels drilled between neighboring slots and along the burner perimeter. High-purity cylinder gases (hydrogen, methane, and dry synthetic air) were used for preparing the tested fuel-air mixtures. Mixtures were prepared in-line with the help of three mass flow controllers installed in the air, hydrogen, and methane lines. After combining all three flows together, the mixture is split between two lines. One line is connected to the fluidized bed seeding system and another one is a bypass line. The fraction of the total flow traveling through the bypass line is controlled by two needle valves installed in both lines after the flow splitting, and monitored using a ball rotameter installed in the bypass line. By varying this fraction, the seeding density is varied. After combining bypass and seeded flows again, the mixture is directed to the burner plenum chamber. The fluidized bed vessel was mounted on a flexible support and shaken (not stirred) by a vibrating motor attached to the vessel, to prevent accumulation of seeding powder onto its walls. To keep the seeding powder dry, a ring-like container with perforated walls was filled with silica gel and installed inside the fluidized bed vessel in its upper part. A piece of wide (2 cm diameter) tube, installed horizontally after the fluidized bed, works as a gravity filter. The flow inside this tube is slow and laminar, allowing coarse particle agglomerates initially present in the seeded mixture to
settle inside the tube.

**5.4.4 Seeding atoms and levels**

For our purposes, with a desired sensitivity range of 1000–1500 K, both Indium and Gallium atoms would be suitable seed atoms [67]. Figure 5.5 shows the electronic level diagrams for Indium and Gallium. The transition wavelengths and relative intensities of spectral lines are also shown. An intensity of 1000 is arbitrarily assigned to the strongest line of each spectrum. The ground states are similar in both atoms and the spin orbit splittings are suitable for temperature measurements in the 1000 K range. We tried both atoms by seeding the InCl$_3$ and GaCl$_3$ dissolved in water using a nebulizer. We also tried generating atomic Indium by laser ablation of the pure metal and by vaporization in a high-temperature gas flow, but this didn’t result in any reasonable fluorescence signal.

![Figure 5.5: The electronic transitions in atomic Indium and Gallium in the accessible range. The wavelengths are shown in Ångstrom and relative intensities are shown for each transition [68].](image)

For Indium we used DCM for pumping the 325.6 nm and 303.93 nm
transitions, and for Gallium we used Pyrromethene 580 to excite 287.4 nm and 294.4 nm transitions. Both dye lasers were pumped by the second harmonic output of Nd:YAG laser and frequency-doubled. It would be desirable if a single laser could be used to excite both transitions in an atom, but the requirement for successive excitation of levels in turbulent applications with a finite delay time (∼100 ns) and low detected fluorescence intensities prohibited using these lines. On the other hand, atomic Gallium is toxic and it showed a lower fluorescence intensity in comparison to Indium. For our experiments we used Indium as a seed atom and the 410 nm and 451 nm transitions.

5.5 Results

5.5.1 Saturation curves

In order to estimate the required intensity to reach the saturation regime, fluorescence images of the flame excited by 410 nm and 450 nm, respectively, are recorded and analyzed for different excitation pulse energies. The result is depicted in Figure 5.6. As expected, both fluorescence curves show a linear behavior at lower energies, and they reach a plateau at higher excitation energies, which is the characteristic of the saturation regime. While the excitation on the 451 nm transition (Figure 5.6a) reaches saturation at about 0.4 mJ/pulse, the other transition starts to saturate only after 1.0 mJ/pulse. This behavior is explained by the larger stimulated transition rate of the former transition. \(B_{32} = 5.6 \times 10^{20} \text{ m}^3 \text{ J}^{-1} \text{ s}^{-2}, B_{31} = 2.3 \times 10^{20} \text{ m}^3 \text{ J}^{-1} \text{ s}^{-2}\). The intensity of fluorescence images at different excitation energies are integrated to provide the total fluorescence intensity. The background is calculated by binning a fluorescence-free region upstream of the flame, and subtracted from the whole image. The fluorescence intensity in saturation regime is expected to be independent of excitation energy. The fluctuation in fluorescence yield that are still present in Figure 5.6 after reaching saturation pulse energies can be explained by variations in seeding concentration. We have found that seeding quality benefits from using fine powder, and degrades with increasing ambient air humidity.
5.5 Results

Figure 5.6: Saturation curves for excitation of a) 410 nm and b) 451 nm. Note the different scales on the horizontal axes. Each data point corresponds to the integrated intensity of a background-corrected LIF image, averaged over 100 laser shots.

To ensure that we have reached saturation in all flame zones, we draw the saturation curves for 451 nm excitation for two different regions in the flame by making regions of interest and averaging the collected fluorescence. The results are shown in figure 5.7. This figure shows a fluorescence image of the flame obtained by 451 nm excitation, and the
5 TLAF Experiments and results

two selected regions of interest. The corresponding saturation graphs for both regions show good similarity, indicating that both regions have reached saturation after 0.4 mJ/pulse. To quantify the comparison the fluorescence intensity of one region is plotted against the fluorescence intensity from the other region. The intensities are linearly correlated with a slope of $0.972 \pm 0.068$, and $R^2 = 0.896$.

![Saturation curves for emission wavelength of 451 nm for two region of interests](image)

Figure 5.7: Saturation curves for emission wavelength of 451 nm for two region of interests (a). c) Fluorescence intensity of both regions plotted against each other for various excitation laser pulse energies. The fitted line and corresponding details are also shown.
5.5.2 Temperature calibration

In order to determine the calibration parameter for saturated TLAF (sTLAF) experiments, the temperatures in two regions of the flame are measured with an S-type thermocouple (bead size 150 µm), and the measured temperature is corrected for conduction and convection heat losses. One of the points is used for calibration and the other point is used for testing the validity of the TLAF experiment by comparing the temperature measured by the thermocouple to those from the TLAF experiment. In general, we expect the flame tip to show a lower temperature than the sides, in this type of flame.

5.5.3 Temperature images

Series of 100 single shot fluorescence images each of a variety of flames with different equivalence ratios are recorded and analyzed. The process of analysis is shown in figure 5.8. From panels a) and b) in this figure, it is clear that the seeding density is far from uniform. In-atoms are created in the flame front, and disappear fairly quickly further downstream. In this application we are interested in fuel-lean flames, so there is considerable oxygen left downstream of the flame front, and In is expected to quickly become oxidized, and thereby invisible for the LIF system. (Although InO does have spectral bands in the region between the two wavelengths used here [69], we have seen no evidence of spectral interference at the exact wavelengths used for In-atom excitation.) The scattering observed outside the flame front is probably fluorescence that is elastically scattered by seed particles. We determine the background from a small region upstream of the flame front, in the cold gas, and subtract this value from the whole image. Since, like any ratio method, TLAF is also susceptible to noise generated by the division of small numbers, we apply thresholding to evaluate the signals only in those locations where it is sufficiently strong. The resulting images are shown in panels e) and f). The fluorescence ratio image, finally, is shown in panel h). Panel g) shows the result if thresholding is omitted; the global flame structure can still be seen, but the noise produced by low signal areas is also very obvious. Some of the results on a few of the flames actually studied are shown below. Figure 5.9 shows temperature distributions in two different flames.
5 TLAF Experiments and results

Figure 5.8: Image processing steps for temperature estimation with sT-LAF. LIF images at a) 410 nm and b) 450 nm fluorescence wavelength. c) and d) are the background subtracted images, for which the background signal is calculated by averaging the pixels in the yellow rectangles in panels a) and b). e) and f) show the thresholded images. Temperature images g) without thresholding and h) with thresholding. The analysis clearly benefits from thresholding the original images, before pixel-by-pixel division.
5.5 Results

The flame with equivalence ratio $\phi = 0.711$ burns on only methane and air, but the flame with $\phi = 0.674$ includes methane, air and hydrogen (20% relative to methane, v/v). Laser energies are set to 2.5 mJ/pulse and 2.2 mJ/pulse for 410 nm and 451 nm excitation, respectively; sufficiently high to ensure that we perform the experiments in the saturation regime.

![Temperature images of two flames estimated by saturated TLAF](image)

Figure 5.9: Temperature images of two flames estimated by saturated TLAF for a) $\phi = 0.711$, $u = 40$ mL/h; b) $\phi = 0.674$, $u = 40$ mL/h. 4 single shot images are binned for better signal.

The temperature is measured for two regions, labeled in figure 5.9 with 1 and 2, with size of 10 × 10 pixels. The temperatures in these two regions are also measured with a thermocouple and region 2 is used to calibrate the measurements, as discussed above.

For comparison we also show the result from linear excitation in figure 5.10. The excitation energies are lowered to 0.08 mJ/pulse by means of a polarizer cube. The results are summarized in table 5.1. The estimated temperature from saturated TLAF and linear TLAF together with standard errors are shown. The signal to noise for linear TLAF is lower and the standard errors show higher values in comparison to saturated excitation.
5 TLAF Experiments and results

Table 5.1: Temperature results for the labeled regions in Fig. 5.9. Standard errors reflect pixel-to-pixel variation, rounded to above.

<table>
<thead>
<tr>
<th>Flame</th>
<th>$\phi = 0.711$ $u = 40$ mL/h</th>
<th>$\phi = 0.674$ $u = 40$ mL/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region 1 thermocouple T(°C)</td>
<td>1842</td>
<td>1775</td>
</tr>
<tr>
<td>Region 1 sTLAF T(°C)</td>
<td>1846</td>
<td>1772</td>
</tr>
<tr>
<td>Standard error</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>Region 1 TLAF T(°C)</td>
<td>1817</td>
<td>1781</td>
</tr>
<tr>
<td>Standard error</td>
<td>17</td>
<td>14</td>
</tr>
</tbody>
</table>

Figure 5.10: Temperature images of two flames estimated with linear TLAF for the same flames as in Figure 5.9. 4 single shot images are binned for better signal.

The results from linear TLAF compare well with results obtained in saturation, although the measurement in the linear regime shows a larger error, which is due to the lower number of collected photons. Imaging in the saturation regime provides higher signal and finally higher accuracy. The structure of the images, however, is the same in both cases.
5.5 Results

Table 5.2: Temperature results for different equivalence ratios and flow rates, obtained by TLAF in the saturation regime and from thermocouple data.

<table>
<thead>
<tr>
<th>Flame</th>
<th>$\phi = 0.647$</th>
<th>$\phi = 0.631$</th>
<th>$\phi = 0.619$</th>
<th>$\phi = 0.58$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region 1 T ($^\circ$C) thermocouple</td>
<td>1714</td>
<td>1696</td>
<td>1658</td>
<td>1565</td>
</tr>
<tr>
<td>Region 1 T ($^\circ$C) sTLAF</td>
<td>1718</td>
<td>1671</td>
<td>1642</td>
<td>n/a</td>
</tr>
<tr>
<td>Standard error ($^\circ$C)</td>
<td>9</td>
<td>10</td>
<td>10</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Figure 5.11: Temperature images four flames with cold gas flow velocity of $u = 40$ mL/h and equivalence ratios of a) $\phi = 0.647$, c) $\phi = 0.619$, e) $\phi = 0.631$ and g) $\phi = 0.58$. The corresponding fluorescence images of 451 nm are shown in panels b, d, f and h, correspondingly. The temperature information for $\phi = 0.58$ is missing in the flame tip due to very low signal.
5 TLAF Experiments and results

Fluorescence images of four flames with different flow rates were recorded in the saturation regime and analyzed. The results are collected in table 5.2. As before, region 2 is used for calibration and the temperature from region 1 is compared to the one from thermocouple measurements. The standard errors are also calculated. The intensity images for 450 nm transition and the temperature images are shown in figure 5.11 for various equivalence ratios. The temperature image of \( \phi = 0.580 \) is not complete due to very low signal in the flame tip. This flame contains 40% hydrogen. Figure 5.11 panels c) and e) show temperature images for flames with 20% hydrogen. The temperature cross section for temperature image of the flame with equivalence ratio of \( \phi = 0.647 \) is shown for two different region of interests. The temperature shows a gradient from inside to outside of the flame.

Figure 5.12: Temperature image of a flames with equivalence ratios of \( \phi = 0.647 \). The temperature cross section is shown for two different regions of interest shown on the temperature image.

5.6 Conclusion

We have developed a theoretical framework for TLAF measurement in saturation regime (sTLAF), and found that it compares well to independent thermocouple measurements. Seeding of In atoms into the flame was achieved by means of a modified PIV seeding system. The spatial extent of the In atom distribution in the fuel-lean flames stud-
ied here was found to be very limited, probably due to oxidation. The lower errors of saturation regime, provides a mean to single shot basis imaging. All the temperature estimations are performed using a single frame with acceptable errors and we detected temperature gradients as low as $60^\circ$C. This possibility can be very useful for turbulent combustion applications.
6 Conclusion and outlook
This thesis focuses on the further development of two laser-diagnostic techniques that have potential for accurate temperature measurement. Both techniques, Coherent Rayleigh-Brillouin Scattering (CRBS) and Two-Line Atomic Fluorescence (TLAF) are not new in themselves, but neither have their application ranges been exhaustively investigated. In this final section, the contribution of the work described in this thesis to the fundamental understanding of these techniques, as well as the potential drawbacks of both will be outlined.

We studied Coherent Rayleigh-Brillouin Scattering in gaseous media. We observed a very strong variation on the scattering signal as a function of delay between the two pump pulses, that has not been reported in literature. An intense, but monochromatic peak in scattered signal was observed at zero delay, and we attribute this high intensity pulse to the coherent interaction of the two pump beams in their focus. An essential point in our investigation was the role of the 4th order coherent function, which not only described the observed spectral narrowing but also the variation of total signal as a function of delay. This phenomenon can not not be predicted by second-order theory, and we argue that all CRBS measurements so far have been conducted in the incoherent regime. An important aspect of this discovery is the benefit of using Fourier-limited picoseconds pulses. Keeping the energy constant, by transition from nanosecond pulses to mode-locked picosecond pulses two order of magnitude gain in signal strength can be achieved. This promises the possibility of single shot measurement which can be very beneficial for the instantaneous measurement of several gas kinetic parameters, and especially temperature and flow velocity.

A second technique that has been studied in this thesis is known as Two-Lines Atomic Fluorescence (TLAF) in the saturation regime. Development and application of TLAF in the linear and non-linear regimes has been reported, but both are less suitable for single shot operation. The saturation regime, however, had not been studied, possibly because of the general understanding that the initial level populations are not decisive for the final result any more. Owing to the fact that they use low excitation powers, the collected fluorescence signal doesn’t provide enough accuracy for temperature estimation. One of the major unknowns is the collisional decay rate of the state that is populated by
the absorption of laser light, and this has been a major hurdle in the quantitative interpretation of laser-induced fluorescence data. Excitation energy is an important parameter, which determines the kinetics of the level after excitation; at lower energies the generated fluorescence signal is generally assumed to be a linear function of excitation energy. We investigated the three level system kinetic by simulating the temporal behavior of all levels upon excitation. By comparing the results from numerical calculations with experimental evidence, we obtain a clue on the order of magnitude of the thermal relaxation rate, which shows that it is in the order of the spontaneous decay rate of the excited state level. Assuming this, we predict a steady state behavior for fluorescence in the saturation regime. This allows us to arrive at a simple model for the calculation of temperature on the basis of the fluorescence signals. Our proposed technique, based on the saturation regime, provides higher fluorescence signal simply due to higher excitation energy. This opens a way for single shot temperature imaging. The method is also immune for laser intensity fluctuations. This means that we don’t need to take into account the intensity variation, and it removes the requirements for monitoring the excitation pulses during the experiments.

On the other hand the theoretical model involves some approximations. We assume a full saturation condition and also we consider the downward stimulated transitions as dominant process and we ignore the spontaneous decay rates. This introduces an error in the temperature estimation, that we have estimated at chapter 4. We also introduce a novel seeding system. After all, the TLAF method requires the presence of metal atoms, that would not normally be present in a flow. This is a PIV-based system where the InCl$_3$ salts are seeded as a fine powder into the flame. This allows faster decomposition of the salt in a non-intrusive way. It also provides a uniform distribution even for lean flames. Several liquid-solution-based techniques have been tried so far, but they are considered as intrusive methods, because of the interaction of the solvents with combustion procedure. Our new seeding technique shows an improvement over the conventional techniques but employment of this method in high pressures and temperatures is not trivial and still needs improvement.
Bibliography


Bibliography


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Bibliography


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Curriculum Vitae

Atieh Manteghi was born on the 19th of February of 1982 in Tehran, Iran. After finishing her High school she obtained her BSc degree in Physics at the faculty of Natural Sciences, University of Kharazmi. Next, she joined the Laser and Plasma research Institute of Shahid Beheshti University and started a master in Photonics. Her master project concerned the development of a setup for laser induced incandescence measurement in sooty flames. After her graduation in 2008, with a final mark of 19.5/20 for her thesis defence, on August 2009 she started her PhD under supervision of Dr. Dam in the Combustion technology group of Eindhoven University.