Laser scattering on low temperature plasmas
High resolution and stray light rejection

Marco van de Sande
Laser scattering on low temperature plasmas

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Chapter 1

General introduction
1.1 Introduction

Plasmas are complex mixtures of free electrons and various kinds of “heavy” particles, such as molecules, atoms, and ions (positive or negative), possibly in excited electronic, vibrational, or rotational states. In most cases the exact composition of plasmas cannot be described by the equilibrium laws of statistical mechanics. In addition, the range of conditions in which plasmas can be operated (chemical input, gas flow pattern, wall geometry, electromagnetic field structure, pressure, power) is tremendous. Therefore, the freedom in the composition and chemical properties of plasmas is virtually unlimited. Because of this freedom, plasma properties such as a high temperature, light emission, and the presence of various (energetic) particles can readily be exploited for various domestic and industrial applications [1]. For example, plasmas can be used as heat sources for cutting and welding [2], as light sources in gas discharge lamps [3–5], plasma display panels [6], and lasers [7], or as particle sources for thin film deposition and etching [8]. Furthermore, the momentum gain of particles in pressure gradients or electromagnetic fields can be exploited, as in plasma thrusters for rocket propulsion or laser wakefield accelerators.

Since all plasma applications are based on the extraction of particles, momentum, or energy from the plasma, power must be supplied in order to sustain it. Most artificial plasmas are driven by an externally applied electromagnetic field. This can be a static field, or an alternating field of almost any frequency. A number of examples, in order of increasing frequency, is given below.

DC fields, for which capacitive and inductive effects can be neglected, are applied in arcs [9], which can be used for plasma deposition [8, 10], and fluorescent lamps [3]. Radio Frequency (RF) waves (100 kHz – 1 GHz) can be coupled capacitively or inductively into a plasma. The parallel plate reactor [11] is an example of the former; inductive gas discharge lamps [5, 12] are of the latter type. Microwave plasmas (1–100 GHz) can be created in cavities [13], torches [14, 15], or wave launchers [16]. Finally, electromagnetic radiation in the visible range can be used, for instance in the case of laser-induced breakdown [17].

Generally, the spatial extent of a plasma can be divided into a creation zone and an application zone. In the creation zone, energy is supplied to the plasma. This leads to ionising behaviour: dissipated energy is used for the creation of free electron-ion pairs and excitation of heavy particles. Excitation and ionisation in the creation zone are predominantly caused by electron impact (Electron Excitation Kinetics, EEK). In the application zone, the particles, momentum, and energy gained in the creation zone are used for applications such as the ones mentioned above. The application zone is often governed by heavy-particle processes, such as charge or excitation transfer, Penning ionisation, molecule formation, and chemical reactions. Also excitation and ionisation can be the result of heavy-particle collisions (Heavy-particle Excitation Kinetics, HEK). One of the best examples of such a division is demonstrated by remote processing plasmas [8]. The plasma is created in a source where electrons play a dominant role, and subsequently applied for chemistry (heavy-particle processes) at a remote surface. Such a division, however, is also possible for other plasma sources. The work described in this thesis is focused primarily at the creation zone and the role of electrons in this zone.
General introduction

The importance of free electrons in plasmas

The main characteristic of a plasma is that its behaviour is significantly influenced by the presence of charged particles. Of all charged particles that can exist in plasmas, electrons play a special role. They are appreciably lighter than positive and negative ions, and therefore much more mobile. This simple fact has far-reaching implications:

- **Energy dissipation**
  Although the momentum that equally charged particles gain per unit of time in an electromagnetic field is identical, the velocity, and thus energy gained by lighter particles is much higher. Therefore, electrons are largely responsible for energy dissipation from external electromagnetic fields.

- **High electron temperature**
  In the creation zone of a plasma, the dissipation of energy by electrons results in an electron temperature that is much higher than that of other species in the plasma. For instance, the heavy-particle temperature in an ordinary fluorescent lamp is little above room temperature, whereas the electron temperature is around 10000 K.

- **Excitation and ionisation**
  The energy exchange between free and bound electrons is very efficient because of their equal masses. Therefore, (de)excitation and ionisation of heavy particles by collisions with free electrons is much more likely than by collisions with other heavy particles. Thus, collisions with electrons can contribute significantly to the total (de)excitation and ionisation rates, in spite of the relatively low electron density. The high electron temperature in the creation zone of the plasma usually causes EEK to be dominant over HEK.

Clearly, the balance between creation of charged particles via ionisation and losses (for instance via diffusion) is strongly coupled to the temperature and density of free electrons in the plasma. Therefore, these two electron gas parameters, commonly designated by $T_e$ and $n_e$ respectively, are important parameters for the characterisation of a plasma.

Determination of the electron gas properties

Many experimental studies are devoted to the determination of the properties of the electron gas, $n_e$ and $T_e$, in various plasmas and a wide range of experimental techniques is used for those studies [18–20].

One class of techniques to determine plasma properties is formed by electric and magnetic probes. The best known is the Langmuir probe. By inserting such a probe into the plasma and applying a voltage across the probe, charged particles are attracted or repelled. By varying the voltage and monitoring the probe current, the density and temperature of electrons as well as ions can be determined. Disadvantages of probe techniques are their perturbative character and difficult interpretation. Furthermore, probes cannot be applied
to reactive plasmas or plasmas with a high gas temperature. As an alternative to probes, spectroscopic techniques can be used.

Emission spectroscopy, i.e. the study of the emission spectrum of a plasma, is the most simple optical technique. Radiation of electrons in the plasma (e.g. cyclotron radiation and bremsstrahlung) or heavy particles (line emission) may be detected. In the latter case, the absolute intensity or shape of a spectral line is studied. Emission spectroscopy is relatively simple and inexpensive: a spectrograph and a detector are the only prerequisites. Absorption spectroscopy, that is the study of absorption of radiation by heavy particles, is in some cases a more sensitive technique than emission spectroscopy. Examples are Diode Laser Absorption (DLA) and Cavity Ring-Down Spectroscopy (CRDS). A disadvantage of both emission and absorption spectroscopy is that measurements are always integrated over a line of sight through the plasma so that tomoraphic techniques, such as Abel inversion, are required to obtain spatial resolution, thus reducing the accuracy of the measurement.

Aside from absorption and emission spectroscopy, laser diagnostic techniques such as Coherent Anti-Stokes Raman Spectroscopy (CARS) and Laser Induced Fluorescence (LIF) are available. All of these techniques are very powerful to determinate the density and temperature of heavy particles in particular excited states. However, relating these properties to those of the electron gas is often troublesome for plasmas that are not in Local Thermodynamic Equilibrium (LTE) [21].

Laser Thomson scattering, i.e. scattering of laser radiation by free electrons in the plasma, is a diagnostic technique that provides direct access to $n_e$ and $T_e$. Interpretation of scattering spectra is in most cases rather straightforward, and spatial resolution is obtained without Abel inversion. In addition, scattering by other species in the plasma, such as atoms (Rayleigh scattering) or molecules (Rayleigh or Raman scattering) can be done with the same experimental system and provide information on the heavy particles in the plasma. A drawback of laser scattering compared to emission spectroscopy is its experimental difficulty and costly instrumentation.

Another powerful method to obtain the electron density and temperature is plasma modelling. In many cases, a numerical model divides the plasma into a large number of control volumes, for each of which the particle, momentum, and energy balances are solved. In this way, modelling can provide very detailed information with spatial and temporal resolution. However, such models are usually highly complex and require detailed knowledge of the relevant processes and operational conditions of the plasma.

A simple plasma model may assume uniform values of plasma parameters throughout the computational domain (a zero-dimensional model), and thus effectively consist of only one control volume. Obviously, this is a very rough approximation, which is generally not suitable to obtain accurate, spatially resolved information. Nevertheless, such a model may provide a quick and simple estimate of average values of $n_e$ and $T_e$ based on the operational conditions of the plasma, such as its size and shape, power density, pressure, and composition. Usually, a superficial knowledge about various processes in the plasma is sufficient. As in more complex models, the key equations of a zero-dimensional model are formed by the various particle and energy balances.
1.2 Scope of this thesis

For a proper understanding of plasmas and possible optimisation for their applications, knowledge of parameters such as \( n_e \) and \( T_e \) is essential. In industrial environments, complicated experimental techniques are often not practical, and real-time modelling of the plasma is often not possible. Thus, the required information must be gained from simple spectroscopic techniques or models based on the semi-empirical relationship between plasma parameters and operational conditions of the plasma, which can be controlled or monitored easily. A method for this purpose was studied before by Jonkers et al. [22].

The primary objective of this thesis is to validate the method of estimating the plasma parameters \( n_e \) and \( T_e \) from operational conditions of the plasma in a number of cases, and to obtain knowledge of the relevant fundamental processes. Such a method is particularly valuable in two cases. The first case is plasmas that must be monitored continuously, such as the ones used for plasma-assisted fabrication processes and for spectrochemistry. The second case is plasmas that are less accessible to diagnostic methods, i.e. more or less enclosed plasmas such as the ones in gas discharge lamps. Validation of the method to estimate plasma parameters from operation conditions was done by comparing results of this method to those of detailed laser Thomson scattering experiments.

A second objective is to design a suitable laser scattering facility for this purpose. The plasmas studied in this work have their small size and proximity to surrounding walls in common. Walls can lead to a large amount of stray light, which adversely affects measurements. Hence, minimising the influence of this stray light is the main concern in the design. In addition, the experimental system must be suitable for plasmas with low electron temperatures (down to 3000 K) in order to study gas discharge lamps.

Much previous work at the plasma groups at Eindhoven University of Technology has been devoted to spectrochemical plasmas [23–28]. The close cooperation with Philips Lighting in Eindhoven and Aachen has also lead to many studies of gas discharge lamps in the past [5, 12, 29–31]. Thus, a wide experience in both experimental work and modelling of these plasmas has been built up over the years. Therefore, spectrochemical plasmas and lamps are logical candidates for this study. Next, we give a short overview of the plasma sources that are considered in this work.

The first plasma that was studied is the spectrochemical Inductively Coupled Plasma (ICP) [32], one of the most established plasma sources in spectrochemistry. The plasma is operated in an argon flow in the open air and is powered by an induction coil around the plasma at a frequency of 50 or 100 MHz with a typical power of 1 kW. The plasma was operated under various conditions of power and composition, and was also subjected to power interruptions in order to study electron production and transport processes.

The second plasma under study is a low-pressure, inductively coupled light source, the Philips QL lamp [5]. This gas discharge lamp is powered by an induction coil (2.65 MHz,

---

\(^1\) Spectrochemical analysis, also referred to as Atomic Emission Spectroscopy (AES) or plasma emission spectroscopy, is a technique to determine the atomic composition of a sample by studying the emission spectrum of a plasma in which it is injected.
85 W) and operates on an argon-mercury mixture at a typical pressure of 100 Pa. The absence of electrodes in this lamp enhances its lifetime, while the efficacy is comparable to that of a conventional fluorescent lamp. Because of complications induced by stray light and coupling a high power laser beam into the plasma, no Thomson scattering measurements on this lamp have been performed before.

Finally, a small spectrochemical helium RF discharge was considered. The plasma is capacitively powered at a frequency of around 110 kHz. The power to the plasma (∼35 W on the average) is strongly modulated in time. Due to the relatively low frequency and the high mobility of helium, this modulation is found in the electron temperature and density as well. This makes this plasma source very suitable for the study of transient effects.

### 1.3 Thesis outline

Chapter 2 reviews the laser scattering theory relevant for this work. This includes, among other things, the interpretation of Thomson, Rayleigh, and Raman spectra.

Chapter 3 presents the design and tests of the experimental arrangement for laser scattering that was used in this work. Discussions about the design are aimed at the plasma sources that were studied. As pointed out above, the main concern is stray light. In order to address this problem, we used a Triple Grating Spectrograph (TGS) instead of a conventional spectrograph (with a single grating). The system allows a high spatial, spectral, and temporal resolution, and can be used for plasmas with an electron temperature in the range 0.2 to 4 eV. The electron density detection limit was calculated from a detailed noise study and verified experimentally, and can be below $10^{16}$ m$^{-3}$.

In Chapter 4, the electron gas parameters $n_e$ and $T_e$, and the heavy-particle temperature $T_h$ of the ICP are estimated from the external operational conditions of the plasma. The estimates of $n_e$ and $T_e$ were verified by Thomson scattering experiments. This was done for various external conditions. The plasma was operated in steady-state.

Chapter 5 describes experiments in which the power to the ICP is interrupted for a short period. The resulting temporal behaviour of $n_e$ and $T_e$ is discussed on the basis of production and transport processes related to these parameters. It was found that molecular processes are relevant, and especially so at the edge of the plasma.

Chapter 6 deals with laser scattering measurements on the QL lamp. An experimental version of this lamp is described and experimental results are compared to calculations of $n_e$ and $T_e$ on the basis of previous experiments using diode laser absorption.

Chapter 7 is devoted to the spectrochemical helium RF discharge. The temporal behaviour of $n_e$ and $T_e$ was measured with Thomson scattering. In addition, $T_e$ was estimated from the measured absolute intensity of a spectral line, which was monitored in time. A large difference was observed between the electron temperatures calculated from the spectral line intensity and found by Thomson scattering. A simple model to calculate the time-dependent electron density based on these two temperatures is presented.

Chapters 4 to 7 have been or will be published.
References


Chapter 1


Chapter 2

Laser scattering on low temperature plasmas

Abstract

Laser scattering, being the generic term for among others Thomson scattering, Rayleigh scattering, and Raman scattering, is a very powerful diagnostic technique to determine fundamental plasma parameters such as the electron density $n_e$, the electron temperature $T_e$, and the gas (heavy-particle) temperature $T_h$. This chapter presents a brief overview of the physics of these scattering processes. In addition, a calibration method to measure densities in an absolute manner is described and the derivation of the Electron Energy Distribution Function (EEDF) from a measured Thomson spectrum is discussed. Finally, the effect of coherent Thomson scattering and the influence of the laser on plasma are discussed briefly.
2.1 Introduction

Laser scattering experiments on a plasma can provide a substantial amount of information about plasma parameters such as the electron density \( n_e \), the electron temperature \( T_e \), and the heavy-particle (gas) density \( n_h \) and temperature \( T_h \) [1–3]. In general, the method is relatively non-intrusive (compared to e.g. Langmuir probe measurements) and the interpretation of the measurement results is rather straightforward under the usual conditions in this work. Assumptions on the plasma parameters or equilibrium departure are in principle not necessary. This makes laser scattering very attractive as a diagnostic tool to measure the plasma parameters mentioned above and to verify results from other diagnostic techniques. Chapter 3 is concerned with the experimental details of laser light scattering; this chapter deals with the relevant physics.

2.1.1 Laser light scattering

Upon illumination of a plasma with a laser, the electrons in the plasma oscillate in the electric field produced by the laser. These accelerated electrons emit electromagnetic radiation themselves, which can be interpreted as scattering of the incident radiation. Scattering by free electrons in the plasma is called Thomson scattering. This is an elastic process. Elastic scattering by the electron clouds surrounding atoms, ions, and molecules is termed Rayleigh scattering. In addition, scattering by molecules can induce a rotational or vibrational transition. This inelastic scattering process is referred to as Raman scattering.

In general, if radiation passes a certain scattering volume, the scattered power \( P_s \) is

\[
P_s = P_i \cdot nL_{\text{det}}\sigma,
\]

where \( P_i \) is the incident power, \( n \) is the density of particles that scatter, \( L_{\text{det}} \) is the length of the detection volume along the incident light beam, and \( \sigma \) is the scattering cross section. The total number of scattering particles in the detection volume is \( N = nAL_{\text{det}} \). The scattering probability \( nL_{\text{det}}\sigma \) could be thought of as the fraction \( N\sigma/A \) of the laser beam cross section \( A \) that is “covered” with particles (see Fig. 2.1), although it must be noted that \( \sigma \) does not necessarily represent the physical size of the particles.

The frequency \( \omega_s \) of the scattered light may differ from the frequency \( \omega_i \) of the incident light because of two subsequent Doppler shifts by the scattering particle. If the particle moves at a velocity \( v \), it first “sees” a frequency \( \omega_p = \omega_i - k_i \cdot v \) because of its velocity component in the direction of the light source. Second, the observer measures a frequency \( \omega_s = \omega_p + k_s \cdot v \) because of the particle’s velocity component in the direction of the observer. Here \( k_i \) and \( k_s \) are the wave vectors of the incident and scattered light respectively. The two Doppler shifts may add or cancel, depending on the direction of the particle velocity \( v \) relative to the scattering vector \( k \), which is defined as

\[
k \equiv k_s - k_i.
\]
Laserscattering on low temperature plasmas

![Diagram](image)

**Fig. 2.1:** The scattering probability is proportional to the fraction $N\sigma/A$ of the laser beam cross section $A$ that is “covered” with particles.

The resulting frequency shift of the scattered waves may be written as

$$\Delta \omega \equiv \omega_s - \omega_i = \mathbf{k} \cdot \mathbf{v}. \quad (2.3)$$

This shift is thus proportional to the particle velocity component along the scattering vector $\mathbf{k}$ and the length of the scattering vector, which can be written as

$$k = |\mathbf{k}_s - \mathbf{k}_i| \approx 2k_i \sin(\theta/2) \quad (2.4)$$

since $k_s \approx k_i$ for particles with a velocity $v \ll c$. The scattering angle $\theta$ is the angle between the incident and scattered light. The Doppler shift can also be written in the form

$$\frac{\Delta \omega}{\omega_i} = 2\sin(\theta/2) \cdot \frac{v_k}{c}, \quad (2.5)$$

where $v_k = \mathbf{k} \cdot \mathbf{v}$ is the component of $\mathbf{v}$ along $\mathbf{k}$. This equation is similar to the well-known Doppler formula $\Delta \omega/\omega_i = v_k/c$, apart from the factor $2\sin(\theta/2)$, which arises from the fact that we are dealing with two subsequent Doppler shifts instead of one.

If scattered waves do not bear a certain phase relation, interference effects (coherent scattering, see Section 2.6) can be neglected. In that case, it is clear from Eq. 2.3 that the frequency distribution of waves scattered by different particles is directly related to the velocity distribution in the direction $\mathbf{k}$. This makes laser scattering suitable to measure the velocity and energy distributions of particles in a plasma, and parameters related to this distribution, such as the temperature of the scattering particles. If the energy distribution is Maxwellian, the scattering spectrum has a Gaussian shape and its width is proportional to the square root of the temperature, see Fig. 2.2.

The expression that is generally used to describe scattering processes is a refinement of Eq. 2.1,

$$\frac{dP_s}{d\omega_s}d\omega_s = P_i \cdot nL_{det} \frac{d\sigma}{d\Omega} \cdot \Delta \omega \cdot S_k(\Delta \omega)d\omega_s, \quad (2.6)$$

in which $\sigma$ is replaced by the differential cross section $d\sigma/d\Omega$ times the solid angle of detection $\Delta \Omega$ because the scattering cross section generally depends on the direction of scattering. In addition, the spectral distribution function $S_k(\Delta \omega)$ is introduced to describe...
the shape of the scattering spectrum. In the case of incoherent scattering the spectral distribution function is not important for the total scattered power since

$$\int_{-\infty}^{\infty} S_k(\Delta \omega) d\omega_s = 1.$$  \hspace{1cm} (2.7)

In order to calculate absolute particle densities and temperatures from a scattering spectrum, the scattering cross section and the relation between the spectral distribution function and the particle velocity distribution function must be known accurately. In Section 2.2 the scattering cross section of electrons (Thomson scattering) is derived, and the spectral distribution function for a Maxwellian Electron Energy Distribution Function (EEDF) is described. In Section 2.3 the scattering cross sections for Rayleigh and Raman scattering by atoms and simple molecules are discussed.

In addition, the sensitivity of the experimental setup must be calibrated. A common technique is to perform a Rayleigh scattering experiment on a gas sample with known composition and density. De Regt et al. [4] used an alternative calibration method with rotational Raman scattering. However, this calibration technique yielded electron densities that were about a factor of three higher than those found by conventional Rayleigh scattering calibration. At that time, this discrepancy was overcome by “calibrating” Raman scattering against Rayleigh scattering. In section 2.4 this problem is re-addressed and the calibration technique with rotational Raman scattering is derived correctly.

Several authors have calculated the EEDF from a measured Thomson spectrum [5–7]. However, if the EEDF is not Maxwellian, this calculation is not trivial. Section 2.5 presents a method to derive the EEDF in a simple way.

In plasmas with increasing electron density, the positions of electrons in the plasma, and hence the phases of scattered waves, become more correlated and interference effects become more pronounced. This is referred to as coherent (or collective) Thomson scattering. For the plasmas studied in this work, the effect of coherent Thomson scattering is rather limited, though sometimes present. Therefore section 2.6 gives a brief overview of weak coherent effects in Thomson scattering experiments.

Finally, the effect of heating or ionising the plasma by the laser beam is discussed shortly in Section 2.7.
Laserscattering on low temperature plasmas

Fig. 2.3: The definition of the position vectors $r_j$, $r$, and $R$, and the unit vector $e_s$ in the scattering direction.

2.2 Thomson scattering

As pointed out above, the scattering cross section and the relation between the scattering spectrum and the particle velocity distribution are relevant for the interpretation of the results of scattering experiments. In this section, the scattering cross section for Thomson scattering is derived, and the shape of the scattering spectrum for a Maxwellian Electron Energy Distribution Function (EEDF) is discussed.

The classical description of the scattering process is based on the calculation of the (scattered) electromagnetic field generated by an electron in an external electromagnetic field, which is produced by incident coherent radiation. Below, this electromagnetic approach is followed in order to calculate the power radiated by the electron. Subsequently, this power is used to calculate the scattered photon flux and scattering cross section (the particle point-of-view). This particle approach, which is much more convenient for experimental discussions, is used throughout the rest of this thesis. The same applies for Rayleigh and Raman scattering, which are discussed in Section 2.3.

2.2.1 A single electron

The electric field generated by an electron in an externally applied electric field can be derived from the electron’s equation of motion in the external field. The external electric field, which is produced by a laser, is a monochromatic, linearly polarised plane wave,

$$E_i(r, t) = E_{i0} \exp[j(k_i \cdot r - \omega_i t)].$$

An electron at position $r_j(t)$ and with velocity $v_j$ is accelerated by this field:

$$\dot{v}_j(t) = \frac{dV_j}{dt}(t) = -\frac{e}{m_e}E_i(r_j, t).$$

The electric field that is generated by the accelerated electron is given by (see [1, 8]):

$$E_s(r, t) = -\frac{e}{4\pi\epsilon_0 c^2} \left[ \frac{1}{R(t')} e_s \times \left( e_s \times \dot{v}_j(t') \right) \right].$$

Here $R = r - r_j = Re_s$, thus $R$ is the distance between the electron and the observation point $r$, and $e_s$ is the unity vector in the scattering direction, as shown in Fig. 2.3. The
Fig. 2.4: The scattering geometry and definition of the scattering angle $\theta$ and the angle $\varphi$ between the plane of scattering and the polarisation of the laser beam.

Quantities $\dot{v}_j$ and $R$ must be evaluated at an earlier time $t' = t - R(t')/c$ in order to account for the time needed for the electric field to travel towards the observation point $r$. Eq. 2.10 is based on a number of assumptions; these are summarised in Section 2.2.3.

With the classical electron radius

$$r_e = \frac{e^2}{4\pi\varepsilon_0 m_e c^2} = 2.818 \cdot 10^{-15} \text{ m} \quad (2.11)$$

and the approximation $R(t) \approx R(t')$, the scattered field can be written as

$$E_s(r, t) = r_e [e_s \times (e_s \times E_{i0})] \frac{1}{R(t)} \exp [j(k_i \cdot r_j(t') - \omega t')] . \quad (2.12)$$

The radiated power per unit of solid angle at a distance $R$ from the electron is then [8]:

$$\frac{dP_s}{d\Omega} = R^2(T) \cdot \frac{1}{2} \varepsilon_0 c |E_s(r, t)|^2 = \frac{1}{2} \varepsilon_0 c r_e^2 |e_s \times (e_s \times E_{i0})|^2 . \quad (2.13)$$

The angular dependence of the scattering process is represented by the factor in brackets. It is commonly described in terms of the scattering angle $\theta$ between the incident and scattered wave vectors $k_i$ and $k_s$ and the angle $\varphi$ between the plane of scattering and the incident electric field $E_{i0}$ (see Fig. 2.4). Eq. 2.13 can then be rewritten as

$$\frac{dP_s}{d\Omega} = \frac{1}{2} \varepsilon_0 c r_e^2 (1 - \sin^2 \theta \cos^2 \varphi) |E_{i0}|^2 . \quad (2.14)$$

The scattered radiation is thus distributed like that of a radiating dipole; the radiation field is rotationally symmetric around the dipole axis (i.e. $E_{i0}$), and most intense in directions perpendicular to this axis. No radiation is emitted along the dipole axis.

As already indicated in Section 2.1.1, the scattered power is related to the Thomson scattering cross section via

$$P_s = P_i \cdot N \frac{\sigma_T}{A} . \quad (2.15)$$
For scattering from one particle we have \( N = 1 \). Comparing this equation to Eq. 2.14, and using the incident irradiance \( P_i/A = \frac{1}{2} e_0 c |E_{i0}|^2 \), we can write the differential cross section for Thomson scattering as:

\[
\frac{d\sigma_T}{d\Omega} = r_r^2 (1 - \sin^2 \theta \cos^2 \varphi).
\] (2.16)

The Doppler shift of the scattered radiation, which is derived in Section 2.1, can also be found by evaluating the phase \( \Phi \) of the scattered waves. This phase is described by the argument of the exponential in Eq. 2.12:

\[
\Phi(\mathbf{r}, t) = \mathbf{k}_i \cdot \mathbf{r}_j(t') - \omega_i t',
\] (2.17)

where \( t' = t - R(t')/c \). Here the first term represents the Doppler shift in the frequency received by the electron, and the second term corresponds to the Doppler shift in the frequency recorded by the observer. With the origin chosen close to the scattering volume, \( r_j \ll R, R(t') \) can be approximated by \( r - \mathbf{e}_s \cdot \mathbf{r}_j(t') \). If the electron is moving at a constant velocity during the scattering process we have \( \mathbf{r}_j(t') = \mathbf{r}_j(0) + \mathbf{v}_j t' \). With these approximations the time \( t' \) can be written as

\[
t' = \left[ t - \frac{r - \mathbf{e}_s \cdot \mathbf{r}_j(0)}{c} \right] \cdot \left[ 1 - \frac{\mathbf{e}_s \cdot \mathbf{v}_j}{c} \right]^{-1}.
\] (2.18)

Then the phase \( \Phi \) can be written as

\[
\Phi = k_s r - \omega_s t - \mathbf{k} \cdot \mathbf{r}_j(0),
\] (2.19)

with

\[
\omega_s = \frac{\omega_i - \mathbf{k}_i \cdot \mathbf{v}_j}{1 - \mathbf{e}_s \cdot \mathbf{v}_j/c}
\] (2.20)

\[
k_s = k_s e_s = \frac{\omega_s}{c} \mathbf{e}_s
\] (2.21)

\[
\mathbf{k} = \mathbf{k}_s - \mathbf{k}_i.
\] (2.22)

Eq. 2.20 can be rearranged to

\[
\omega_i - \mathbf{k}_i \cdot \mathbf{v}_j = \omega_s \left( 1 - \frac{\mathbf{e}_s \cdot \mathbf{v}_j}{c} \right) = \omega_s - k_s \cdot \mathbf{v}_j.
\] (2.23)

As already shown in Section 2.1.1, the frequency shift \( \Delta \omega \) that scattered photons experience can then be written as

\[
\Delta \omega \equiv \omega_i - \omega_s = \mathbf{k} \cdot \mathbf{v}_j.
\] (2.24)
2.2.2 A plasma with a Maxwellian EEDF

The total electric field induced by Thomson scattering by a plasma rather than by a single electron is the vector sum of the field of each individual electron in the scattering volume. If the phases of these single electron fields are uncorrelated, i.e. the positions of the electrons are not correlated, the powers of these fields can simply be added (incoherent scattering). In this section, this is assumed to be the case; Section 2.6 examines this assumption more thoroughly.

In the incoherent limit, the Thomson scattered power per unit of frequency and within a solid angle $\Delta\Omega$ is (cf. Eq. 2.6):

$$\frac{dP_s}{d\omega_s} d\omega_s = P_i \cdot n_e L_{det} \cdot \frac{d\sigma_T}{d\Omega} \cdot \Delta\Omega \cdot S_k(\Delta\omega) d\omega_s. \quad (2.25)$$

$S_k(\Delta\omega)d\omega_s$ is the probability that the frequency shift of a scattered photon lies within a range $d\omega_s$ around $\Delta\omega$. This equals the probability that the electron that scatters has a velocity component along $k$ within a range $dv_k$ around the corresponding velocity $v_k = \Delta\omega/k$:

$$S_k(\Delta\omega)d\omega_s = F_k(v_k) dv_k = \frac{F_k(\Delta\omega/k)}{k} d\omega_s, \quad (2.26)$$

where $F_k(v_k)dv_k$ is the one-dimensional electron velocity distribution along $k$. In terms of wavelengths rather than frequencies, this can be rearranged to

$$S_k^*(\Delta\lambda)d\lambda_s = \frac{c}{2\lambda_s \sin(\theta/2)} \cdot F_k \left( \frac{c}{2 \sin(\theta/2)} \cdot \frac{\Delta\lambda}{\lambda_s} \right) d\lambda_s. \quad (2.27)$$

Thus, the spectral distribution function has exactly the same shape as this velocity distribution. In the case of a Maxwellian EEDF we have

$$F_k(v_k) = \frac{1}{\hat{v} \sqrt{\pi}} \cdot \exp \left[ - \left( \frac{v_k}{\hat{v}} \right)^2 \right], \quad (2.28)$$

where $\hat{v}$ is the most probable velocity\(^1\) of the electrons,

$$\hat{v} = \left( \frac{2k_BT_e}{m_e} \right)^{\frac{1}{2}}. \quad (2.29)$$

Now Eq. 2.25, converted into wavelength rather than frequency, becomes

$$\frac{dP_s}{d\lambda_s} d\lambda_s = P_i \cdot n_e L_{det} \cdot \frac{d\sigma_T}{d\Omega} \cdot \Delta\Omega \cdot \frac{1}{\Delta\lambda_{1/e} \sqrt{\pi}} \exp \left[ - \left( \frac{\Delta\lambda}{\Delta\lambda_{1/e}} \right)^2 \right] d\lambda_s, \quad (2.30)$$

\(^1\)Note that the most probable velocity is a factor of $\sqrt{3/2}$ lower than the velocity of an electron with the average electron energy of $\frac{3}{2} k_BT_e$. 

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with $\Delta \lambda_{1/e}$ being the half $1/e$ width of the scattering spectrum (see also Fig. 2.2),

$$
\Delta \lambda_{1/e} = \lambda_i \cdot 2 \sin(\theta/2) \cdot \frac{\hat{v}}{c}.
$$

The electron temperature $T_e$ is related to this width according to

$$
T_e = \frac{m_e c^2}{8 k_B \sin^2(\theta/2)} \cdot \left(\frac{\Delta \lambda_{1/e}}{\lambda_i}\right)^2.
$$

For the case of a perpendicular scattering geometry ($\theta = 90^\circ$) and a wavelength $\lambda_i = 532$ nm, which are used for the experiments described in this thesis, this becomes

$$
T_e = 5238 \cdot \left(\Delta \lambda_{1/e}\right)^2 \text{[K]},
$$

where $\Delta \lambda_{1/e}$ is given in nm.

### 2.2.3 Assumptions on the Thomson scattering experiment

In the theory described above, a number of assumptions was made. This section summarises these assumptions.

First of all, the incident radiation is assumed to be monochromatic and linearly polarised. Furthermore, scattering by positive or negative ions is not taken into account because of their much larger mass compared to electrons (cf. Eq. 2.9). In addition, the recoil of the electron by a photon (the Compton effect) is neglected, which is justified if the energy of an incident photon is much less than the electron rest energy, $h\nu_i \ll m_e c^2$. Relativistic effects are neglected as well, which can safely be done if the electron velocity is low compared to the speed of light, $v \ll c$. The magnetic field of the incident radiation is neglected in the electron’s equation of motion, which is permitted for the laser power we use. For extremely high laser powers ($\sim 10^{22}$ W m$^{-2}$), higher harmonic frequencies of the scattered radiation are generated. This was recently observed experimentally [9].

Scattered radiation is assumed to be detected in the far field. That means that $R$ must be much larger than the distance travelled by the electron during scattering, the wavelength $\lambda_i$ of the incident and scattered radiation, and the typical dimensions of the detection volume. It is also required that the electromagnetic wave of the laser be transmitted very well by the plasma. In order to achieve this, the frequency $\omega_i$ of the incident radiation must be much higher than the electron plasma frequency $\omega_{pe}$, the plasma must be optically thin for the incident radiation, and the scattering probability must be low. In that case, also multiple scattering can safely be neglected.

For the work described here, all of these assumptions are readily justified. Apart from these assumptions, which are made throughout this work, the theory described in Section 2.2.2 also assumes a Maxwellian EEDF and incoherent Thomson scattering. The latter point is discussed in some more detail in Section 2.6.

Finally, the strong laser beam is assumed not to perturb the plasma, i.e. influence $n_e$ or $T_e$. This is briefly discussed in Section 2.7.
Ro-vibrational Raman
$\Delta \nu = -1$

Rotational Raman
$\Delta J = -2$

Rotational Raman
$\Delta J = +2$

Ro-vibrational Raman
$\Delta \nu = +1$

Fig. 2.5: Sketch of a Raman spectrum of N$_2$ molecules at room temperature using incident radiation of wavelength $\lambda_i = 532$ nm. The peak intensities and widths are not to scale and cannot be intercompared.

2.3 Rayleigh and Raman scattering

Apart from scattering by free electrons, photons can also be scattered by the electron clouds around atoms, ions, and molecules. Like Thomson scattering, this process is often most conveniently discussed in terms of particles. Nevertheless, the classical calculation of the scattering intensities is usually done from the electromagnetic point-of-view. In this view, the movement of electron clouds in an electric field (polarisation of the atom or molecule) and the electric field generated by this movement are calculated. In a similar way as for Thomson scattering, this can be used to determine scattering cross sections. Not surprisingly, they are related very directly to the polarisability of the particles. Like this polarisability, the cross sections are strongly wavelength dependent, in contrast to that for Thomson scattering.

Elastic scattering of photons by heavy particles is called Rayleigh scattering. The particles do not gain or lose internal energy in this process. Inelastic scattering by molecules, which can undergo a rotational or vibrational transition, is referred to as Raman scattering. The internal (rotational or vibrational) energy of the molecules changes, resulting in specific wavelength shifts of the scattered photons.

Since heavy particles in the plasma are much slower than electrons, photons that are Rayleigh or Raman scattered do not undergo a significant Doppler shift. Therefore, a Rayleigh spectrum consists of one narrow line at $\lambda = \lambda_i$, and a Raman spectrum shows a large number of narrow lines at different wavelength shifts corresponding to different rovibrational transitions. This is schematically depicted in Fig. 2.5.

Rayleigh and Raman scattering are mainly determined by neutral species for gas or plasma of sufficiently low ionisation degree. Therefore, scattered radiation is in general incoherent; the length scale on which correlations in the neutral particle positions may occur (e.g. by acoustic waves) is under the conditions of this work much larger than that
for charged particles (e.g. by plasma waves). In addition, Raman scattered radiation has an arbitrary phase relation with the incident radiation, so that Raman scattering is always incoherent [10]. Hence, for scattering by heavy particles, the total scattered power is the sum of the scattered powers of individual particles.

Rayleigh and Raman scattering can be used to measure a number of plasma parameters. First of all, atomic and molecular densities in the plasma can be deduced from the scattering intensity. Furthermore, the temperature of the scattering particles can in principle be determined from the line width in the scattering spectrum, but the spectral resolution of the experimental setup is usually too low for accurate temperature measurements. However, when the pressure of the gas or plasma is known, the temperature can be derived from the measured density via the ideal gas law, \( p = n \kappa T \), where \( n \) and \( T \) are the heavy-particle (gas) density and temperature respectively. This may be more complicated if different species are present. The depolarisation ratio of Rayleigh scattered photons (see Section 2.3.4 and [11]) provides a way to distinguish between molecular and atomic species (e.g. H\(_2\) and H) and thus determine the dissociation degree of a molecular plasma. Finally, the so-called rotational and vibrational temperatures, \( T_{\text{rot}} \) and \( T_{\text{vib}} \), which are often indications of the heavy-particle temperature, can be determined from the relative intensities of rotational and vibrational Raman lines.

Apart from this, both Rayleigh and Raman scattering by a gas sample with known composition and density can be used to calibrate the experimental setup for absolute density measurements, as described in Section 2.4. Raman scattering was used for calibration in a previous work of De Regt et al. [4,12], but a difference of a factor of about three was found between calibrations using Rayleigh scattering and Raman scattering. For a correct calibration of the experimental arrangement, the Rayleigh and Raman scattering cross sections have to be known accurately. The remainder of this section deals with these cross sections.

### 2.3.1 Rayleigh scattering by atoms

The total Rayleigh scattered power can be expressed similar to Eq. 2.6:

\[
P_R = P_i \cdot n_h L_{\text{det}} \cdot \frac{d\sigma_R}{d\Omega} \cdot \Delta\Omega, \tag{2.34}
\]

where \( n_h \) is the heavy-particle density in the gas. The differential scattering cross section for Rayleigh scattering by an atomic gas is determined by the polarisability \( \alpha \) of the atoms [13]:

\[
\frac{d\sigma_R}{d\Omega} = \frac{\pi^2 \alpha^2}{\epsilon_0 \lambda_i^4} \cdot (1 - \sin^2 \theta \cos^2 \varphi). \tag{2.35}
\]

The (microscopic) polarisability \( \alpha \) can also be written in terms of the (macroscopic) refractive index \( \mu \) of the gas,

\[
\alpha = \frac{3 \epsilon_0}{n_\mu} \cdot \frac{\mu^2 - 1}{\mu^2 + 2}, \tag{2.36}
\]
Table 2.1: A few values of Rayleigh and typical rotational Raman scattering cross sections for atoms and molecules in the electronic and vibrational ground state for the experimental conditions used in this work ($\lambda_i = 532 \text{ nm}$ and $\theta = \varphi = 90^\circ$) [13–15].

<table>
<thead>
<tr>
<th>Particle</th>
<th>$d\sigma_R \left( 10^{-32} \text{ m}^2 \right)$</th>
<th>$d\sigma_{J \rightarrow J'} \left( 10^{-32} \text{ m}^2 \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>5.40</td>
<td></td>
</tr>
<tr>
<td>Ar$^+$</td>
<td>2.12</td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>0.087</td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>6.07</td>
<td>0.038</td>
</tr>
<tr>
<td>O$_2$</td>
<td>4.99</td>
<td>0.10</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>13.6</td>
<td>0.38</td>
</tr>
</tbody>
</table>

where $n_\mu$ is the gas density at which the refractive index $\mu$ is measured. For $\mu - 1 \ll 1$ this can be approximated by $\alpha \approx 2\epsilon_0(\mu - 1)/n_\mu$, so that

$$
\frac{d\sigma_R}{d\Omega} = 4\pi^2 \frac{(\mu - 1)^2}{\lambda_i^4} \cdot \left( 1 - \sin^2 \theta \cos^2 \varphi \right),
$$

(2.37)

The values of this cross section for Ar, Ar$^+$, and He at a wavelength of $\lambda_i = 532 \text{ nm}$ (i.e. the wavelength used in this work) are listed in Table 2.1. Apart from its normal wavelength dependence, the scattering cross section increases dramatically if the laser wavelength $\lambda_i$ approaches that of an atomic transition. The cross section of excited atoms is also much larger than that given in Table 2.1. For highly excited atoms, the outermost electron can be regarded as almost free and the Rayleigh scattering cross section approaches that of Thomson scattering.

2.3.2 The polarisability tensor

Molecules, which have a certain internal structure, generally have a different polarisability for different orientations with respect to the applied electric field [10]; the direction of the induced dipole moment can even differ from the direction of the electric field (see Fig. 2.6). Therefore, for an individual molecule the polarisability is not just described by a constant, but by a tensor $\bar{\alpha}$. This molecular polarisability tensor depends on the orientation of the molecule. Because in practice a great number of randomly oriented molecules is examined, a tensor that is averaged over all possible molecule orientations is used. This tensor is solely determined by the mean molecular polarisability $\alpha$ and the anisotropy $\gamma$ of the molecular polarisability tensor, which are the same for any molecule orientation [10]. Hence, scattering by molecules can be described in terms of $\alpha$ and $\gamma$. It turns out that the cross section for Rayleigh scattering by molecules is determined by both these parameters, but cross sections for rotational Raman scattering only depend on $\gamma$. 
2.3.3 Rotational Raman scattering by molecules

In this work only rotational Raman scattering by simple linear molecules\(^\text{2}\) is considered, and all molecules are assumed to be in the vibrational ground state, which is a good approximation at low temperatures (\(< 1000 \text{ K}\)).

For nitrogen, the energy of a state with rotational quantum number \(J\) is in approximation \(E_J = BJ(J + 1)\), with \(B = 2.48 \cdot 10^{-4} \text{ eV}\) [15]. Only transitions from \(J\) to \(J \pm 2\) (where \(J\) and \(J \pm 2\) are positive) are allowed, and the wavelengths of different peaks are given by

\[
\lambda_{J \rightarrow J+2} = \lambda_i + \frac{\lambda_i^2}{\hbar c} \cdot B(4J + 6)
\]

\[
\lambda_{J \rightarrow J-2} = \lambda_i - \frac{\lambda_i^2}{\hbar c} \cdot B(4J - 2),
\]

where \(\lambda_i\) is the wavelength of the incident radiation. The scattered power of a certain Raman peak \(J \rightarrow J'\) is given by (cf. Eq. 2.6):

\[
P_{J \rightarrow J'} = P_i \cdot n_J \cdot L_{\text{det}} \cdot \frac{d\sigma_{J \rightarrow J'}}{d\Omega} \cdot \Delta\Omega,
\]

where \(n_J\) is the density of the initial rotational state \(J\). In the case of perpendicular scattering, i.e. the angles \(\theta\) and \(\varphi\) equal 90°, the differential cross section for a Raman transition \(J \rightarrow J'\) can be written in terms of \(\gamma\) according to [15]:

\[
\frac{d\sigma_{J \rightarrow J', \perp}}{d\Omega} = \frac{64\pi^4}{45\epsilon_0^2} \cdot b_{J \rightarrow J'} \cdot \frac{\gamma^2}{\lambda_{J \rightarrow J'}^4},
\]

where \(b_{J \rightarrow J'}\) are the Placzek-Teller coefficients, given by

\[
b_{J \rightarrow J+2} = \frac{3(J + 1)(J + 2)}{2(2J + 1)(2J + 3)} \quad \text{and}
\]

\[
b_{J \rightarrow J-2} = \frac{3J(J - 1)}{2(2J + 1)(2J - 1)}.
\]

\(^2\) e.g. \(\text{N}_2\), and in approximation also \(\text{O}_2\) and \(\text{CO}_2\), see [15].
Table 2.2: Values of $\gamma^2$ according to [15] (interpolated for $\lambda_1 = 532$ nm).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\gamma^2$ ($10^{-82}$ $\text{F}^2\text{m}^4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2$</td>
<td>0.395 ± 8%</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>1.02 ± 10%</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>4.08 ± 13%</td>
</tr>
</tbody>
</table>

Fig. 2.7: Perpendicular Raman scattering cross sections of $\text{N}_2$ ($\lambda_1 = 532$ nm) as a function of the wavelength of the Raman line. Transitions $J \rightarrow J$, which do not induce a wavelength shift, are part of the Rayleigh scattering cross section, see Section 2.3.4.

Penney et al. [15] measured the polarisability anisotropy $\gamma$ of nitrogen, oxygen, and carbon dioxide for scattering of radiation with a wavelength of 633 nm and 488 nm. Interpolation for the wavelength $\lambda_1 = 532$ nm, which is applied in this work, yields the values listed in Table 2.2. The resulting perpendicular Raman scattering cross sections of $\text{N}_2$ are plotted in Fig. 2.7.

Raman scattered radiation is not entirely polarised; the cross section of Eq. 2.40 is only valid for photons polarised along the “natural” polarisation direction $\mathbf{e}_s \times (\mathbf{e}_s \times \mathbf{E}_{i0})$ from a dipole along $\mathbf{E}_{i0}$, as for Thomson scattering. For Raman scattering also some photons with a polarisation perpendicular to this direction can be detected. The polarisation direction that is accepted by the detector is usually expressed in an angle $\xi$ with respect to the natural polarisation direction, as shown in Fig. 2.8. A perpendicular scattering geometry refers to the situation that not only $\theta = \varphi = 90^\circ$, but also $\xi = 0^\circ$. For an arbitrary combination of $\theta$, $\varphi$, and $\xi$ the differential cross section can be written as [15]:

$$
\frac{d\sigma_{J \rightarrow J'}}{d\Omega} = \frac{d\sigma_{J \rightarrow J', \perp}}{d\Omega} \cdot \left[ (1 - \rho) \cos^2 \xi (1 - \sin^2 \theta \cos^2 \varphi) + \rho \right].
$$

Here $\rho$ is called the depolarisation ratio, the ratio between the depolarised ($\xi = 90^\circ$) and polarised ($\xi = 0^\circ$) part of scattered radiation, and it equals 3/4 for simple linear molecules.
Laserscatteringonlowtemperatureplasmas

![Diagram of polarization direction](image)

**Fig. 2.8:** The “natural” polarisation direction for radiation from a dipole along \( \mathbf{E}_i \) is given by \( \mathbf{e}_s \times (\mathbf{e}_s \times \mathbf{E}_i) \). \( \xi \) is the angle between the natural polarisation direction and the polarisation direction \( \mathbf{E}_s \) that is accepted by the detector. The scattering geometry is defined by the angles \( \theta \) and \( \varphi \).

### 2.3.4 Rayleigh scattering by molecules

Rayleigh scattering by molecules consists of two contributions: firstly the polarised contribution of the mean polarisability \( \alpha \), given by Eq. 2.37, and secondly the partly depolarised contribution \( (\rho = 3/4) \) of the polarisability anisotropy \( \gamma \). The latter contribution is the sum of all rotational “transitions” \( J \rightarrow J \). The total cross section is thus

\[
\frac{d\sigma}{d\Omega} = \frac{d\sigma_{R,\alpha}}{d\Omega} + \sum_J \frac{n_J}{n} \frac{d\sigma_{J \rightarrow J}}{d\Omega},
\]

(2.44)

where \( n_J/n \) is the fraction of molecules in rotational state \( J \); this cross section is thus temperature dependent. The cross section \( d\sigma_{J \rightarrow J}/d\Omega \) is similar to the Raman cross section given in Eq. 2.40 and 2.43, with

\[
b_{J \rightarrow J} = \frac{J(J+1)}{(2J-1)(2J+3)}.
\]

(2.45)

With the definition

\[
S \equiv \sum_J \frac{n_J}{n} b_{J \rightarrow J}
\]

(2.46)

the depolarisation ratio for perpendicular Rayleigh scattering is

\[
\rho_R = \frac{16\pi^2\gamma^2 S\rho}{45\epsilon_0^2 \left( \frac{\mu_0^{-1}}{N} \right)^2 + 16\pi^2\gamma^2 S}.
\]

(2.47)

For \( N_2 \) at \( T = 295 \) K we have \( S \approx 0.255 \) and at wavelength \( \lambda_i = 532 \) nm the depolarisation ratio equals \( \rho_R = 2.7 \cdot 10^{-3} \), thus practically all Rayleigh scattered radiation is polarised like Thomson scattered radiation. This value of the Rayleigh scattering depolarisation ratio agrees closely to the value that was measured by Meulenbroeks *et al.* [11].

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2.4 Absolute calibration of scattering intensities

Intensities of Rayleigh and Raman scattering by a gas sample with known composition, density, and temperature can be calculated from the absolute cross sections given in the previous section. These intensities can subsequently be used for absolute sensitivity calibration of the experimental setup, which is necessary for absolute particle density measurements.

Raman scattering offers some advantages over Rayleigh scattering. First of all, Rayleigh scattered radiation has the same wavelength as stray light, whereas Raman scattered radiation does not. To distinguish Rayleigh scattering from stray light, measurements on different gases or at different pressures would be required. Secondly, although the Rayleigh scattering cross section is much smaller than that for Thomson scattering, the Rayleigh scattering intensity is generally much higher than the Thomson scattering intensity for the experimental conditions in this work. Therefore, filters or a different detector gain setting must be employed for Rayleigh scattering, thus decreasing the accuracy of the calibration. Finally, since the experimental system is designed so as not to transmit the Rayleigh and stray light photons (see Chapter 3), it has to be adapted in order to detect Rayleigh scattering, possibly changing the system characteristics that are being calibrated. Therefore, in this work Raman scattering is used to calibrate the experimental system (see also [4,16,17]).

The calibration gas is nitrogen at room temperature and a perpendicular scattering geometry is used. The measured Raman line powers are then (cf. Eq. 2.39):

\[ P_{J \rightarrow J'} \propto n_J \frac{d\sigma_{J \rightarrow J'}}{d\Omega}. \]  (2.48)

The density \( n_J \) of the rotational state \( J \) is

\[ n_J = \frac{n}{Q} \cdot g_J (2J + 1) \exp(-E_J/kT), \]  (2.49)

where \( n \) is the nitrogen density, \( g_J = 6 \) or \( 3 \) for even or odd \( J \) respectively, and \( Q \) is partition sum, given by [15,18]

\[ Q = \sum J g_J (2J + 1) \exp(-E_J/k_BT) \approx \frac{9k_BT}{2B}. \]  (2.50)

\( T \) is the temperature that governs rotational (de)excitation processes; in this work it is taken \( T = 295 \) K. For nitrogen molecules, \( B = 2.48 \cdot 10^{-4} \) eV. The total power measured in a Thomson scattering experiment is (cf. Eq. 2.6 and 2.16):

\[ P_T \propto n_e \cdot r_e^2. \]  (2.51)

with the same proportionality constant as that in Eq. 2.48, provided that scattering is incoherent\(^3\). Hence, the electron density follows from \( P_T \) and \( P_R \) (often given in units of

\(^3\) For incoherent scattering \( \int S_k(\Delta\omega) d\omega \approx 1. \) For coherent scattering, the right hand sides of Eqs. 2.51 and 2.52 must be multiplied by a factor \( 1/(1 + \alpha^2) \) and \( (1 + \alpha^2) \) respectively (cf. Eq. 2.69).
Table 2.3: Calibration factors $\Gamma$ for perpendicular ($\theta = \varphi = 90^\circ$ and $\xi = 0^\circ$) Rayleigh (R) or rotational Raman (RM) scattering of $\lambda_i = 532$ nm radiation by nitrogen and argon. The Raman scattering calibration factors are calculated for room temperature (295 K).

<table>
<thead>
<tr>
<th>$J \to J'$</th>
<th>$\lambda_{J \to J'}$ (nm)</th>
<th>$\Gamma_{J \to J'}$</th>
<th>$J \to J'$</th>
<th>$\lambda_{J \to J'}$ (nm)</th>
<th>$\Gamma_{J \to J'}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-6</td>
<td>530.32</td>
<td>4.00$\cdot10^{-6}$</td>
<td>6-8</td>
<td>533.69</td>
<td>5.21$\cdot10^{-6}$</td>
</tr>
<tr>
<td>7-5</td>
<td>530.54</td>
<td>2.02$\cdot10^{-6}$</td>
<td>5-7</td>
<td>533.47</td>
<td>2.54$\cdot10^{-6}$</td>
</tr>
<tr>
<td>6-4</td>
<td>530.76</td>
<td>3.89$\cdot10^{-6}$</td>
<td>4-6</td>
<td>533.24</td>
<td>4.73$\cdot10^{-6}$</td>
</tr>
<tr>
<td>5-3</td>
<td>530.99</td>
<td>1.78$\cdot10^{-6}$</td>
<td>3-5</td>
<td>533.02</td>
<td>2.09$\cdot10^{-6}$</td>
</tr>
<tr>
<td>4-2</td>
<td>531.21</td>
<td>3.02$\cdot10^{-6}$</td>
<td>2-4</td>
<td>532.79</td>
<td>3.42$\cdot10^{-6}$</td>
</tr>
<tr>
<td>3-1</td>
<td>531.44</td>
<td>1.14$\cdot10^{-6}$</td>
<td>1-3</td>
<td>532.56</td>
<td>1.25$\cdot10^{-6}$</td>
</tr>
<tr>
<td>2-0</td>
<td>531.66</td>
<td>1.34$\cdot10^{-6}$</td>
<td>0-2</td>
<td>532.34</td>
<td>1.41$\cdot10^{-6}$</td>
</tr>
</tbody>
</table>

$\Gamma_{RM} = 8.15 \cdot 10^{-5}$
$\Gamma_{R,N_2} = 7.64 \cdot 10^{-3}$
$\Gamma_{R,Ar} = 6.80 \cdot 10^{-3}$

detector counts) according to

$$n_e = n \cdot \frac{P_T}{P_{J \to J'}} \cdot \left\{ \frac{d\sigma_{J \to J'}}{d\Omega} \cdot \frac{n_J}{n} \right\} \equiv n \cdot \frac{P_T}{P_{J \to J'}} \cdot \Gamma_{J \to J'}.$$ (2.52)

The calculated values of $\Gamma_{J \to J'}$ for various Raman lines are given in Table 2.3. Essentially, these are just the ratios of the Raman and Thomson scattering cross sections, taking into account the relative rotational level density. Alternatively, the total Raman scattering power or the power of Rayleigh scattering by nitrogen or argon can be used for calibration. The corresponding calibration factors $\Gamma_{RM}$, $\Gamma_{R,N_2}$, and $\Gamma_{R,Ar}$ are also listed in Table 2.3.

A similar calibration procedure was used in the work of De Regt [4]. In his work, the Raman scattering cross sections were derived from the Rayleigh scattering depolarisation ratio. Subsequently, the absolute intensities of various Raman lines were calculated from these cross sections and the densities of rotationally excited states. However, the result of this calculation was wrong by a factor of approximately three. De Regt noticed this problem by observing a difference between the measured and expected ratio of Raman and Rayleigh scattering intensities. In order to have correct Thomson scattering results, he “calibrated” Raman line intensities against the Rayleigh scattering intensity.

Nevertheless, a satisfactory explanation of the error of De Regt is desirable. This resulted in the study above. It turns out that the calculation of De Regt contains a number of flaws. The most important one is that he used the density of the final state rather than the initial state for the calculation of the intensity of a Raman line (cf. Eq. 2.48). Furthermore, the Placzek-Teller coefficients used by De Regt were incorrect. In addition, the polarisation dependence of the detection sensitivity, in the work of De Regt described by a factor $C_0$, was taken into account incorrectly. These errors amount to a total factor of approximately three, varying slightly for different rotational transitions.
2.5 Deriving the EEDF from a Thomson Spectrum

As pointed out in Section 2.2.2, the spectral distribution function $S_k(\Delta \omega) d\omega$ (or, equivalently, $S_k(\Delta \lambda) d\lambda$) of an incoherent Thomson spectrum directly reflects the one-dimensional electron velocity distribution function $F_k(v_k)$ (cf. Eqs. 2.26 and 2.27). If the velocity distribution is isotropic\(^4\), the Electron Energy Distribution Function (EEDF) in a plasma can be derived from $F_k(v_k)$ [19–21]. In Section 2.2.2 this was already done for a Maxwellian EEDF. For a non-Maxwellian EEDF, however, this is not so straightforward.

The three-dimensional electron velocity distribution, i.e. the density in velocity space or the probability that an electron has a velocity within a one unit of volume in velocity space, is denoted by $F_v(v)$. For an isotropic distribution, this is only a function of the magnitude of the velocity, not of its direction, so that we can use $F_v(v)$ instead of $F_v(v)$. The Electron Velocity Distribution Function (EVDF) $f_v(v)$ is the integration of $F_v(v)$ over a spherical shell with radius $v$:

$$f_v(v) = F_v(v) \cdot 4\pi v^2.$$  \hspace{1cm} (2.53)

The EEDF $f_E(E)$ follows from a transformation from velocity to energy via $E = \frac{1}{2} m_e v^2$:

$$f_E(E) = f_v(v) \cdot \frac{dv}{dE} = F_v(\sqrt{2E/m_e}) \cdot \frac{4\pi \sqrt{2E}}{m_e^{3/2}}.$$  \hspace{1cm} (2.54)

For a Maxwellian EEDF, the three-dimensional velocity distribution can be written as the product of three one-dimensional velocity distributions, each depending on only one velocity component $v_x$, $v_y$, or $v_z$:

$$F_v(v) = F_x(v_x) F_y(v_y) F_z(v_z),$$  \hspace{1cm} (2.55)

where $F_x(v_x)$ is the probability that an electron has a velocity with a component $v_x$ along the $x$-axis, and $F_x = F_y = F_z$ because the velocity distribution is isotropic. If we choose the $x$-axis parallel to the scattering vector $k$, the Thomson spectrum directly gives this probability. Since

$$F_x(v_x) = \frac{1}{\hat{v} \sqrt{\pi}} \exp \left[ -\frac{v_x^2}{\hat{v}^2} \right],$$  \hspace{1cm} (2.56)

we have

$$F_v(v) = \frac{1}{\hat{v}^3 \pi^{3/2}} \exp \left[ -\frac{v^2}{\hat{v}^2} \right],$$  \hspace{1cm} (2.57)

which leads to

$$f_E(E) = \frac{2}{k_B T_e \sqrt{\pi}} \cdot \sqrt{\frac{E}{k_B T_e}} \cdot \exp \left[ -\frac{E}{k_B T_e} \right].$$  \hspace{1cm} (2.58)

\(^4\) If the velocity distribution is not isotropic, e.g. in magnetised plasmas, $F_k(v_k)$ depends on the direction of $k$. Hence, the complete EEDF must be constructed from the one-dimensional velocity distributions $F_i(v_i)$ in multiple directions.
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\[ F_x(v_x) \]

\[ F_x(v_x, v_y, 0) \]

\[ F_x(v_x, 0, 0) \]

\[ F_x(v_x, -v_y, 0) \]

\[ F_x(v_x) \]

\[ \text{integration over } v_y \text{ and } v_z \]

**Fig. 2.9:** The relation between the three-dimensional velocity distribution \( F_\nu(v) \) and the one-dimensional velocity distribution \( F_x(v_x) \), which is measured with Thomson scattering, for a Maxwellian (left) and a non-Maxwellian EEDF (right).

Here \( \hat{v} = \sqrt{2k_B T_e/m_e} \). From Eqs. 2.56 and 2.57 it is clear that \( F_x(v_x) \) and \( F_\nu(v) \) have similar shapes. Consequently, not only \( F_\nu(v) \), but also \( F_x(v_x) \) is directly related to the EEDF. Hence, the Thomson scattering intensity at a certain frequency shift \( \Delta \omega \) can be interpreted as a direct measure for the value of the EEDF at the corresponding energy \( E = \frac{1}{2}m_e v^2 = m_e \Delta \omega^2 / 2k^2 \).

In contrast, for a non-Maxwellian EEDF \( F_\nu(v) \) cannot be split into its \( x \), \( y \), and \( z \) components. Generally, the one-dimensional and three-dimensional velocity distributions are related by

\[
F_x(v_x) = \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z F_\nu(v).
\] (2.59)

Now the one-dimensional velocity distribution is not a direct reflection of \( F_\nu(v) \), as shown in Fig. 2.9. Determining \( F_\nu(v) \) from a measured \( F_x(v_x) \) is basically a two-dimensional variant of Abel Inversion. The solution, however, is much simpler. The integration over the \( y-z \) plane in Eq. 2.59 can also be performed by integrating \( F_\nu(v) \) over rings in this plane:

\[
F_x(v_x) = 2 \int_{v_x}^{\infty} dv \frac{\partial v_y}{\partial v} \cdot 2\pi v_y F_\nu(v) = \int_{v_x}^{\infty} dv v \cdot 2\pi v_y F_\nu(v) = 2\pi \int_{v_x}^{\infty} v F_\nu(v) dv.
\] (2.60)

Differentiation of both sides of this equation gives

\[
F_\nu(v) = -\frac{F'_x(v)}{2\pi v}.
\] (2.61)
Combining Eq. 2.54 and 2.61 yields the EEDF,

\[ f_E(E) = -\frac{2}{m_e} F_x'(\sqrt{2E/m_e}). \]  

(2.62)

Thus, the three-dimensional velocity distribution and the EEDF are related to the derivative of the measured one-dimensional velocity distribution. This is the result of the fact that the presence of electrons with a certain velocity \( v \) contributes equally to the whole one-dimensional velocity distribution for velocities lower than \( v \). For example, a depleted high energy tail of the EEDF is expressed in the scattering spectrum by an overall decrease of the intensity, see Fig. 2.10.

It should be noted that derivatives of measured data are very sensitive to noise. Therefore, measuring deviations from a Maxwellian EEDF at an energy of several times \( k_B T_e \) requires a measurement with a large dynamic range and an extremely low noise level.

## 2.6 Coherent Thomson Scattering

The treatment of scattering spectra and scattering intensities above relies on scattered powers of individual particles being additive. This is only true if there is no phase relationship between the waves scattered by different particles. This section examines how a certain phase relationship can arise and how that may affect the scattering spectrum and intensity.

As stated before in Section 2.2.2, the total Thomson scattered electric field is the vector sum of the individual contributions of electrons in the detection volume,

\[ \mathbf{E}_s(r,t) = \sum_n \mathbf{E}_{s,n}(r,t). \]  

(2.63)

Each scattered field has the form \( \mathbf{E}_{s,n} \propto \mathbf{E}_{i0} \exp(j\phi_n) \), i.e. they are identical except for the phase \( \phi_n \). The total scattered power is proportional to the square of the modulus of the
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total electric field, \( \frac{dP_s}{d\Omega} \propto |E_s|^2 = \sum_n E_{s,n} \cdot \sum_m E_{s,m}^* \)
\( \propto \sum_n |E_{i0}|^2 + \sum_{n \neq m} |E_{i0}|^2 \cos(\phi_n - \phi_m) \)
\( = N \cdot |E_{i0}|^2 + N(N - 1) \langle \cos(\phi_n - \phi_m) \rangle \cdot |E_{i0}|^2 \). \(2.64\)

Here \( E_{s,m}^* \) is the complex conjugate of \( E_{s,m} \), \( N \) is the number of electrons in the detection volume, and \( \langle \cos(\phi_n - \phi_m) \rangle \) is an average value of \( \cos(\phi_n - \phi_m) \). The last term in this equation is zero if the electrons have random positions. In that case, the total scattered power is the sum of each electron’s contribution; this is termed incoherent scattering. If the electron positions in the plasma, and thus the phases of scattered waves, are correlated, the last term in Eq. 2.64 is important. The scattered power in a certain direction can be anything between zero and \( N^2 \) times the power scattered by a single electron. This is called coherent (or collective) scattering. Correlated electron positions may be caused by periodic density fluctuations (waves) in the plasma and give rise to grating-like behaviour of the plasma. Therefore, the spectral distribution function \( S_k(\Delta \omega) \) is affected, and even the normalisation given in Eq. 2.7 may not hold in the case of coherent scattering.

The phase of scattered waves contains a factor \( k \cdot r_j \), where \( r_j \) is the initial position of electron \( j \), cf. Eq. 2.19. Scattered waves thus have the same phase when the electrons involved are separated by a distance of \( 2\pi/k \) along \( k \), see Fig. 2.11 (a). If electron positions are random within this distance, the phases of scattered waves are also random and scattering is incoherent. On the other hand, if electron positions are correlated on the scale of \( 2\pi/k \), coherent effects are introduced. Therefore, the length scale \( 2\pi/k \) is a “sample length” over which coherent effects are probed. In general it can be stated that scattering takes place on electron density fluctuations of wavelength \( 2\pi/k \) \([1]\). If these fluctuations are random, scattering is incoherent.

The Debye shielding length
\[ \lambda_D = \left[ \frac{\epsilon_0 k_B T_e}{e^2 n_e} \right]^{\frac{1}{2}}, \]  \(2.65\)
is a length scale over which electron positions certainly show no correlations. Although the electrons within the Debye sphere strongly feel each others presence, their thermal motion causes them to be distributed randomly over the sphere. Thus, if \( 2\pi/k \) is much smaller than the Debye length, electron density fluctuations are random on this length scale and scattering is incoherent. In contrast, if \( 2\pi/k \) is much larger than \( \lambda_D \), electron density fluctuations can be correlated on this length scale, so that scattering can be coherent. In this case, all waves scattered by electrons within a Debye sphere have the same phase, see Fig. 2.11 \([3]\). Electron density fluctuations on a length scale larger than \( \lambda_D \) are related to the motion of both electrons and ions in the plasma. Therefore, a coherent scattering spectrum contains information about both the electron and ion energy distribution functions. A more
Fig. 2.11: (a) Waves that are scattered by electrons separated by a distance $2\pi/k$ along $k$ are in phase. (b) Incoherent scattering, $\alpha \ll 1$. (c) Coherent scattering, $\alpha \gg 1$ [3].

A complete description of the spectral distribution function under different circumstances is given by Sheffield [1].

Commonly, the influence of coherent effects is described by the scattering parameter,

$$\alpha \equiv \frac{1}{k\lambda_D} \approx \frac{1}{4\pi \sin(\theta/2)} \frac{\lambda_i}{\lambda_D}. \quad (2.66)$$

If $\alpha \ll 1$, scattering is incoherent. As $\alpha$ approaches unity or becomes even larger, coherent effects become important. Clearly, the scattering angle $\theta$ influences the scattering parameter. For very small scattering angles, Thomson scattering is coherent for any plasma condition, whereas at large angles coherent effects are smallest. For our standard scattering conditions $\theta = 90^\circ$ and $\lambda_i = 532$ nm and a plasma source with $n_e \approx 10^{20}$ m$^{-3}$ and $T_e \approx 1$ eV$\approx 11600$ K, the scattering parameter is $\alpha \approx 0.08$, so the treatment of Section 2.2.2 is sufficient. However, for higher electron densities or lower electron temperatures, i.e. for small Debye lengths, a correction to the spectral distribution function must be made.

The spectral distribution function can be written in terms of an even power series of $\alpha$. For fairly small scattering parameters ($\alpha < 0.3$) an approximation to order $\alpha^2$ suffices and assuming Maxwellian electron energy distributions we have [1]:

$$S_k(\Delta\omega) \approx \frac{F_k(\Delta\omega/k)}{k}(1 - 2\alpha^2 \Re w(\Delta\omega/k\hat{v})), \quad (2.67)$$

where $\Re w(\Delta\omega/k\hat{v})$ is the real part of the plasma dispersion function,

$$\Re w(x) = 1 - 2x \exp(-x^2) \int_0^x \exp(p^2)dp. \quad (2.68)$$

This function is shown at the left hand side of Fig. 2.12. The integrated area of $S_k(\Delta\omega)$ is approximately

$$\int_{-\infty}^{\infty} S_k(\Delta\omega)d\omega \approx \frac{1}{1 + \alpha^2}. \quad (2.69)$$

---

5 Here the typical dimensions of the detection volume are assumed much larger than $\lambda_i$ and $2\pi/k$. 

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Fig. 2.12: Left: the real part of the plasma dispersion function. Right: comparison of a weakly coherent Thomson spectrum ($\alpha = 0.3$) with an incoherent spectrum ($\alpha = 0$) for perpendicular scattering, $\lambda_i = 532$ nm and $T_e = 1$ eV.

The spectral distribution functions $S_k(\Delta \omega)$ for weakly coherent and incoherent scattering are compared at the right hand side of Fig. 2.12. A coherent spectrum is lower in the centre and has slightly broader wings than an incoherent (Gaussian) spectrum. Therefore, fitting a Gaussian to a coherent spectrum leads to an underestimation of the electron density (approximately 7%) and an overestimation of the electron temperature (approximately 21%). In this work, for weakly coherent Thomson scattering spectra, the electron temperature and density are derived from a fit of Eq. 2.25 and 2.67 to the recorded spectrum.

2.7 Perturbation of the plasma by the laser

Focusing a strong laser beam into a plasma can considerably influence the plasma’s electron temperature and density. This renders the measured values of these parameters useless. This section gives a brief overview of the influence of the laser beam on the plasma for typical laser and plasma conditions in this work.

2.7.1 Electron heating

The electric field of the intense laser beam can heat electrons in the plasma. This takes place via the process of inverse bremsstrahlung, which is the absorption of a photon by an electron near an ion, the latter serving to conserve momentum [22]. Kunze [23] estimated the relative change in electron temperature due to heating by the laser beam. The laser pulse length is assumed to be long enough to heat the electrons, but too short for the electrons to transfer this heat to the heavy particles: $t_{ee} < \tau < t_{ie}$, where $t_{ee}$ and $t_{ie}$ are the electron-electron and electron-ion collision times respectively, and $\tau$ is the laser pulse duration. Under this worst case assumption, the relative change of $T_e$ is approximately

$$\frac{\Delta T_e}{T_e} \approx 3.38 \cdot 10^{-39} \frac{n_i Z^2}{(k_B T_e)^{3/2}} \lambda_i^3 \left\{ 1 - \exp \left( - \frac{h \nu_i}{k_B T_e} \right) \right\} . Q_i,$$

(2.70)
where \( n_i \) is the ion density, \( Z \) the charge number of the ions, \( \nu_i \) the laser frequency, and \( Q_i \) the incident laser pulse power (J m\(^{-2}\)). This estimation assumes the laser beam not to affect the absorption coefficient of the plasma. This is true if the maximum kinetic energy that a free electron can gain in the radiation field is less than the photon energy [1]:

\[
\frac{e^2 F_i^2}{2m_e \omega_i^2} \ll \hbar \omega_i.
\] (2.71)

This condition is readily fulfilled for the laser conditions in this work.

The laser that is used in this work has a wavelength \( \lambda_i = 532 \) nm and a pulse power of 450 mJ in a focused spot of 0.2 mm diameter, yielding \( Q_i = 14.3 \) MJ m\(^{-2}\). In the plasmas discussed in Chapters 6 and 7 we have \( k_B T_e > 0.5 \) eV and \( n_e < 10^{20} \) m\(^{-3}\), and we can take \( Z = 1 \) so \( n_i = n_e \). The relative temperature increase is then \( \Delta T_e/T_e < 0.03 \). The accuracy of the measurements is generally worse, so that the effect of heating may be neglected for these plasmas. In the Inductively Coupled Plasma (ICP, Chapters 4 [24] and 5 [25]) the electron density and temperature are around \( n_e \approx 10^{21} \) m\(^{-3}\) and \( T_e \approx 0.7 \) eV. For these values, Eq. 2.70 yields \( \Delta T_e/T_e \approx 0.2 \). This is still not much above the measurement accuracy, but it cannot be ignored. However, measurements by Jonkers \textit{et al.} [26], performed at different laser powers, show that the effect of laser heating is negligible even for the ICP plasma.

### 2.7.2 Photo-ionisation effects

In addition to heating the plasma, the laser beam can increase the ionisation degree and thus the electron density \( n_e \) by direct photo-ionisation or multi-photon processes. Direct photo-ionisation is only possible for excited atomic states that are less than 2.33 eV below the continuum (for 532 nm laser light). For the plasmas considered in this work, the density of these states is small compared to the electron density, and the laser does not have the appropriate wavelength to populate these states from lower excited states. Therefore, direct photo-ionisation is expected to be small or negligible.

The cross sections of multi-photon processes are much smaller than that of direct photo-ionisation, but multi-photon processes may nevertheless become important at very high laser irradiances. Laser induced breakdown, which is initiated by multi-photon ionisation, has indeed been observed in an argon flow at room temperature [27]. In helium this was not observed, since the laser power required to produce breakdown is much higher for helium than it is for argon [28]. This can be attributed to a larger number of photons involved in multi-photon processes with helium, and hence a low probability of these processes.

The probability of multi-photon processes also depends on the density of the breakdown medium. Although the argon density in the ICP is, due to the higher temperature, much lower than that in an argon flow at room temperature, breakdown within the plasma was observed for very strong focusing. This limits the laser irradiance (power and focal diameter) that can be used for such plasmas.
Other effects that may play a role under certain circumstances are photo-detachment of electrons from negative ions and photo-dissociation of molecules. Since the plasmas studied in this work contain significant numbers of neither negative ions nor molecules, these effects are not discussed here.

References


Chapter 2


Chapter 3

The experimental system for laser scattering

Abstract

Because of the small scattering cross section, Thomson scattering experiments demand a high power light source and a sensitive, low noise detection device. In addition, stray light can be a severe problem, especially for plasmas with a low electron density and temperature close to surrounding walls, such as gas discharge lamps. This chapter deals with these experimental problems. First the basic system for Thomson scattering is presented. A two-dimensional intensified CCD camera facilitates simultaneous electron temperature and density measurements at different positions in the plasma. A triple grating spectrograph, the design of which is discussed, lowers the stray light redistribution to around $7 \cdot 10^{-9}$ nm$^{-1}$ at 0.5 nm from the laser wavelength. This allows for measurements in plasmas with electron temperatures down to 0.1 eV. A detailed noise calculation estimates the detection limit of the experimental system at around $n_{e,\text{det}} = 2 \cdot 10^{15}$ m$^{-3}$. The calculated characteristics of the system were verified by measurements.
Chapter 3

3.1 Introduction

Thomson Scattering as a method to measure the electron density and temperature in a plasma has a long history. It was predicted by Thomson already at the beginning of the 20th century [1]. However, due to the low scattering probability it was not observed until the late 1950s when in studies of the earth’s ionosphere, an anomalous reflection of radio waves was explained by scattering instead of reflection [2]. This lead to the development of the theory of coherent Thomson scattering [3, 4] and Thomson scattering started to be recognised as a promising plasma diagnostic technique. It was not until the development of the first high power ruby lasers that Thomson scattering was first applied to a laboratory plasma in the form of a tokamak [5]. A ruby laser can deliver an energy of up to tens of Joules in a single pulse (\(\sim 30\) ns). This is very suitable for pulse operated plasmas, such as a tokamak. For smaller and more stable plasmas, however, a high average output is preferable over a single pulse with a huge energy. The advent of high power lasers with higher pulse repetition rates (of the Nd:YAG type, nowadays still the most common lasers for this application [6]) in the 1980s started the breakthrough of Thomson scattering on small laboratory plasmas. Since then, both coherent and incoherent scattering measurements have been done on various plasma sources, and with all kinds of detectors and scattering angles (see for instance [7–14]).

The two main difficulties when studying plasmas with a low electron density and temperature are the weakness of the scattered radiation (the scattering probability is on the order of \(10^{-16}\) under our scattering conditions) and the small spectral width (\(\sim 2–5\) nm), leading to stray light problems. Numerous experimental setups have been built to deal with these difficulties, ranging from multi-pass systems [14] for extremely low detection limits, down to below \(10^{16}\) m\(^{-3}\) [11], and even at low laser power [15], to atomic notch filters and multiple spectrographs in the detection branch for efficient stray light reduction [16, 17].

This work is concerned with spectrochemical plasmas and gas discharge lamps that have electron densities ranging from \(10^{17}\) to \(10^{21}\) m\(^{-3}\) (see Chapter 1). Hence an extremely low detection limit is not required. Electron temperatures lie between 0.5 and 2 eV, and most of the studied plasmas are very close to surrounding objects or contained in glass. Therefore, stray light is our greatest concern.

This chapter describes the experimental system that was used in this work. It is based on a perpendicular scattering geometry and includes an intensified CCD camera and an image rotator to allow for spatial resolution. Section 3.2 discusses the basic experimental system and restrictions to the detection limit, these being stray light and noise. Section 3.3 describes the design of a triple grating spectrograph to reduce the effect of stray light. A detailed noise study determines the theoretical detection limit of the complete system in Section 3.4. Finally, Section 3.5 presents a number of measurements with the experimental system to verify the its calculated characteristics.
The experimental system for laser scattering

Fig. 3.1: The perpendicular scattering geometry that is used in this work. The scattering angle is $\theta = 90^\circ$ and the polarisation of the laser beam is perpendicular to the horizontal plane of scattering, $\varphi = 90^\circ$.

### 3.2 Basic Thomson scattering system

For laser scattering experiments, we used a pulsed, frequency doubled Nd:YAG laser (Quanta Ray GCR 3), with a wavelength of $\lambda_i = 532$ nm, pulse length of 7 ns, pulse repetition rate of 10 Hz, and maximum pulse energy of 0.45 J. The laser beam was guided by a pair of dichroic mirrors and focussed into the detection volume by a plano-convex lens with a focal length of one metre, as shown in Fig. 3.1. The cross section of the laser beam in the detection volume is approximately Gaussian with a $1/e$ width of about 200 $\mu$m.

The plane of scattering, formed by the laser beam and the scattering direction, is horizontal and the polarisation of the laser beam is chosen vertical. Thus, $\varphi = 90^\circ$ so that the scattering probability is at a maximum (cf. Eq. 2.16). Scattered photons are detected at a perpendicular scattering angle, $\theta = 90^\circ$. For this angle, stray light is expected to be minimised and it is the most convenient angle for sharp imaging of different points along the laser beam. A large scattering angle minimises coherent effects and maximises the width of the scattering spectrum (see Eqs. 2.66, 2.3, and 2.4). For $\theta = 90^\circ$, the scattering parameter and the width of the spectrum differ by only 30% of the most ideal value at $\theta = 180^\circ$, so a perpendicular scattering angle is convenient for most purposes.

A pair of achromatic doublet lenses (focal length $f = 600$ mm and diameter $\phi = 95$ mm) creates a 1:1 image of the detection volume onto the entrance slit of a spectrograph, which disperses scattered radiation for detection. The entrance slit is horizontal, i.e. parallel to the laser beam. Compared to a vertical slit, as used by De Regt et al. [10], this has the advantage that the detection length can be chosen longer and that spatial resolution over the length of the entrance slit can be obtained in a single measurement.

The incident radiation must be dispersed in a direction perpendicular to the entrance slit. For convenience, the dispersion direction and the optical axis of the spectrograph system are taken horizontal as well by placing a 90$^\circ$ image rotator behind the entrance slit. A notch filter inside the spectrograph system reduces the effect of stray light; below this is discussed in more detail. An intensified CCD camera (detector area $16.5 \times 11$ mm$^2$) records scattering spectra along its horizontal axis, and contains spatial information along its vertical axis. Fig. 3.2 shows a schematic overview of the experimental system.
Fig. 3.2: Schematic overview of the experimental system for laser scattering. The iCCD camera records scattering spectra at different positions along the laser beam. A viewing dump, baffles, and a notch filter inside the spectrograph reduce the problem of stray light.

3.2.1 The detection limit

Besides the Thomson spectrum, the recorded spectrum contains a continuous background, caused by continuum radiation from the plasma and dark current in the detector. In addition, the spectrum has a strong stray light contribution in the centre, which is caused by scattering on the surroundings of the plasma and heavy particles in the plasma (Rayleigh scattering). These contributions can be subtracted from the recorded spectrum, but their noise cannot. This noise can obscure the Thomson spectrum itself and therefore determines the detection limit of the experimental setup.

From Fig. 3.3, which schematically shows a recorded scattering spectrum, it is clear that the Thomson signal has to compete with the other sources. Noise mainly affects the low intensity wings of the Thomson spectrum, while stray light distorts the centre of the spectrum. The region in between must be large enough to determine $n_e$ and $T_e$ accurately from a fit to the measured spectrum. Since the Thomson signal intensity is proportional to $n_e$, an electron density detection limit $n_{e,\text{lim}}$ can be defined; above this limit, $n_e$ and $T_e$ can be determined with adequate accuracy, and below this limit they cannot.

Of course, the definition of the detection limit depends on the accuracy of the fit to the measured spectrum that is considered acceptable. Rather arbitrarily, we consider an error of about 30% in both $n_e$ and $T_e$ due to the fit to the scattering spectrum acceptable at the detection limit. The accuracy of the fit is, apart from noise, determined by the number of data points in the interesting part of the spectrum, and the number of data points in the centre of the spectrum that are unreliable due to stray light (and the effect of a stray light filter). A reasonable number of data points in a spectrum is a hundred, from which

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1 The total accuracy of the measurements is determined by both statistical errors (due to the fit to experimental data) and systematic errors (e.g. accuracy of the required scattering cross sections).
The experimental system for laser scattering

Fig. 3.3: Schematic image of a recorded scattering spectrum. Noise affects the low intensity wings of the Thomson spectrum and stray light governs the centre.

the central twenty may be affected by the stray light and filter. Then the following two criteria are sufficient for reliable detection:

1. The noise level must be less than half the Thomson scattering intensity at a wavelength $\Delta \lambda_{1/e}$ from the central wavelength $\lambda_i$ (the signal-to-noise ratio is two);

2. The stray light intensity must be less than the Thomson scattering intensity at a wavelength $\frac{1}{2} \Delta \lambda_{1/e}$ from the central wavelength $\lambda_i$.

Here $\Delta \lambda_{1/e}$ is the half width at $1/e$ height of the spectrum.

The problem of stray light is dealt with by a Triple Grating Spectrograph (TGS), the design of which is discussed in Section 3.3. Assuming that stray light is not the limiting factor, Section 3.4 presents a calculation of the detection limit of the designed system based on a noise study.

3.3 A Triple Grating Spectrograph (TGS) for stray light rejection

Stray light can distort a significant part in the centre of a Thomson spectrum. This is especially true for plasmas close to the plasma surroundings or contained in glass (high stray light level) in combination with a low electron density and temperature (weak and narrow Thomson spectrum). This is caused by non-idealities of the spectrograph in the setup, and can become such a problem that practical measurements are impossible. Below, this is examined in more detail. Subsequently a Double Grating Filter (DGF) for stray light rejection is introduced and the design of a Triple Grating Spectrograph (TGS) that uses such a filter is presented.
3.3.1 Stray light redistribution

A spectrograph has the task to assign a spatial position in its exit plane to a wavelength. To do this, it contains a narrow entrance slit, a dispersing element (commonly a grating), and two imaging elements (lenses or mirrors). The first of these imaging elements collimates the incident light for the grating, and the second focuses the light onto the exit plane. Due to non-idealities of the optics and the finite width of the entrance slit the relation between spatial position in the exit plane and wavelength is not sharp. For example, if perfectly monochromatic light illuminates the entrance slit of a spectrograph, the spectrum that is recorded in the exit plane has a certain width. The shape of this “redistributed” spectrum is called the instrumental profile of the spectrograph, and its full width at half maximum is termed the bandpass $\Delta \lambda_{bp}$, as shown in Fig. 3.4.

The narrow stray light peak in the centre of a scattering spectrum, which is virtually monochromatic compared to Thomson scattered radiation, is also redistributed by the spectrograph. If the stray light level is very high, the wings of this redistributed spectrum can completely outrange the Thomson spectrum. Therefore, it is useful to examine the instrumental profile more closely.

The instrumental profile $f(\lambda - \lambda_0)$, centred around $\lambda_0$, is normalised, i.e.

$$\int_{\lambda}^{\infty} f(\lambda - \lambda_0) d\lambda = 1.$$

(3.1)

The wavelength $\lambda_0$ is the wavelength that is assigned to the central position in the exit

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In some cases a concave holographic grating is used to combine the dispersive and imaging functions into a single optical element.
The experimental system for laser scattering

Fig. 3.5: Measured instrumental profile of a typical spectrograph at \( \lambda_0 = 532 \) nm. The bandpass is \( \Delta \lambda_{bp} \approx 0.1 \) nm.

plane, and \( \lambda \) is the wavelength that is actually detected\(^3\). For a given wavelength range \( d\lambda \) in the recorded spectrum, the measured spectral power \( P(\lambda) \) (in W nm\(^{-1}\)) is given by the instrumental profile \( f(\lambda - \lambda_0) \) and the spectrograph’s transmission \( T_s \):

\[
P(\lambda)d\lambda = P_0 \cdot T_s f(\lambda - \lambda_0)d\lambda, \tag{3.2}
\]

where \( P_0 \) (W) is the incident power of (monochromatic) light.

The instrumental profile is the result of a number of non-idealities in the spectrograph. Firstly, the width of the entrance slit gives rise to an uncertainty in the entrance position in the spectrograph, causing a similar uncertainty in the exit plane. This gives rise to a rectangular contribution to the instrumental profile. Secondly, the optical elements in the spectrograph introduce (monochromatic) image aberrations, which blur the image of the entrance slit. In fact, these aberrations cause the position in the exit plane to depend on the angle at which the spectrograph is entered. This contribution to the instrumental profile is more or less Gaussian. Thirdly, the diffraction pattern of the grating is not infinitely narrow, but leads to a \( \sin(x)/x^2 \) (approximately Lorentzian) behaviour of the instrumental profile. The total instrumental profile is the convolution of these three contributions.

A measured instrumental profile \( f(\lambda - \lambda_0) \) of a typical spectrograph is shown in Fig. 3.5. The central part of this profile, which determines the bandpass and spectral resolution, is caused by the entrance slit width and aberrations of the optics. The wings of this instrumental profile are caused by stray light that is produced in the spectrograph (e.g. dust or roughness of the optics), and by cross-over (‘signal diffusion’) effects in the iCCD detector that was used to record this spectrum; in fact the measured spectrum represents the instrumental profile of both the spectrograph and the detector. The wings of the instrumental profile are responsible for the problematic stray light redistribution in a Thomson scattering experiment.

\(^3\) More precisely, \( \lambda \) is the wavelength that is assigned to the position in the spectrograph’s exit plane where radiation is detected; of course, the wavelength of the incident radiation does not change.
The maximum tolerable redistribution level for a Thomson scattering measurement can be
determined from the relative intensities of Thomson scattering and stray light. For this
calculation the stray light intensity is expressed in terms of the gas density that would
lead to an equivalent amount of Rayleigh scattering (at a wavelength of \(\lambda_i = 532\) nm. As
an example, we take the stray light level encountered in experiments with the Philips QL
lamp, a low pressure gas discharge lamp that is the subject of Chapter 6 [18].

The stray light intensity produced by scattering of the laser on the glass of the QL
lamp is equivalent to Rayleigh scattering by argon with a density of approximately
\(n_{Ar} \approx 8 \cdot 10^{25} m^{-3}\). The spectral stray light power that is recorded at a wavelength \(\lambda\) is (cf. Eq. 3.2):

\[
P_{\text{stray}}(\lambda) \propto f(\lambda - \lambda_i) \cdot n_{Ar} \frac{d\sigma_R}{d\Omega}. \tag{3.3}
\]

Assuming the Thomson spectrum to be Gaussian, its spectral power is given by (cf. Eq. 2.30)

\[
P_T(\lambda) \propto \frac{1}{\Delta\lambda_{1/e} \sqrt{\pi}} \exp \left(- \frac{(\lambda - \lambda_i)^2}{\Delta\lambda_{1/e}^2}\right) \cdot n_e \frac{d\sigma_T}{d\Omega}, \tag{3.4}
\]

with the same proportionality constant as in Eq. 3.3 and \(\Delta\lambda_{1/e}\) is the half \(1/e\) width
of the Thomson spectrum\(^4\). Note that Thomson scattered photons detected at a certain
wavelength \(\lambda\) really have this wavelength, whereas stray light photons that are redistributed
to this position still have the wavelength \(\lambda_i\). For a plasma with an electron temperature
of 1 eV we have \(\Delta\lambda_{1/e} = 1.5\) nm (see Eq. 2.33). The ratio of the Thomson scattering and
stray light powers at \(\lambda - \lambda_i = \frac{1}{2}\Delta\lambda_{1/e} = 0.75\) nm is then

\[
\frac{P_T}{P_R} = \frac{0.3}{R} \cdot \frac{n_e}{n_{Ar}} \cdot \frac{d\sigma_T/d\Omega}{d\sigma_R/d\Omega}, \tag{3.5}
\]

where we define \(R \equiv f(0.75\) nm) as the redistribution level of the spectrograph system. To
have this ratio larger than unity for \(n_e = 10^{17} m^{-3}\), \(n_{Ar} \approx 8 \cdot 10^{25} m^{-3}\) and \(\sigma_T/\sigma_R = 147\),
the redistribution level must be less than \(R \approx 5 \cdot 10^{-8} nm^{-1}\).

The instrumental profile shown in Fig. 3.5 suggests a redistribution level of around \(10^{-2}\) nm\(^{-1}\);
for the moment we assume the influence of the detector to be negligible. A notch filter,
that blocks the stray light, can reduce the recorded stray light intensity and thus the ef-
fective redistribution level. For a sufficient decrease, the filter must reduce stray light by
around six orders of magnitude. In addition, the spectral width of the notch filter must
be much smaller than the Thomson spectrum itself, which is only around 3 to 4 nm wide
for electron temperatures of 1 to 2 eV. Commercially available filters cannot achieve this,
so another solution must be found.

One possibility is a resonant atomic filter, which was applied by Bakker et al. [17],
who reached an effective redistribution of about \(10^{-7}\) nm\(^{-1}\) with his setup. This value

\(^4\)Here the spectrograph redistribution is not taken into account since the scattering spectrum is broad
compared to the central part of the instrumental profile, so that a deconvolution is not needed.
The experimental system for laser scattering

Fig. 3.6: Two spectrographs in subtractive configuration as a notch filter. The first spectrograph disperses the light, a mask blocks part of the spectrum and the second spectrograph recombines the light again at the exit slit (so-called cross dispersion).

was limited by the Amplified Spontaneous Emission (ASE) of the dye-laser that had to be used to tune the laser wavelength to that of the atomic filter. This work follows a different approach, in which two spectrographs in subtractive configuration are used as a spectrally narrow notch filter.

3.3.2 The Double Grating Filter (DGF)

A Double Grating Filter (DGF) consists of two, usually identical spectrographs that are mirrored with respect to each other\(^5\) [16,19–22]. In this so-called subtractive configuration, the dispersion of the second spectrograph cancels that of the first. Part of the spectrum in between the two spectrographs can be blocked by a mask, thus decreasing the transmission function of DGF for a narrow spectral range. Fig. 3.6 sketches this principle.

The shape of the transmission function or filter profile \(F(\lambda)\) of the DGF is governed by the instrumental profiles \(f_{1,2}(\lambda - \lambda_0)\) of the constituent single spectrographs. The subscript denotes the first or second spectrograph; the two instrumental profiles may be slightly different since photons pass the second spectrograph in the opposite direction to the first. Positions in the exit plane of a spectrograph are referred to by the wavelength that is assigned to these positions by the corresponding spectrograph. In this way a distance in the exit plane is associated with a wavelength range via the dispersion of the spectrograph.

First we assume that no mask is placed between the two spectrographs. If a photon of wavelength \(\lambda\) enters the first spectrograph, the probability of finding the photon in its exit plane at a position assigned to wavelength \(\lambda'\) is (see Eq. 3.2)

\[
p_{1,\lambda}d\lambda' = T_s \cdot f_1(\lambda' - \lambda)d\lambda'.
\] (3.6)

Thus, this photon is redistributed to a position assigned to \(\lambda'\), which may differ from \(\lambda\).

\(^5\) The two spectrographs may differ, provided that the dispersions are matched to effectively yield zero dispersion.
Fig. 3.7: The probability that a photon of wavelength $\lambda$ passes the DGF via a position that is assigned to $\lambda'$. 

Note that $p_{1,\lambda}$, like $f_{1,2}(\lambda'-\lambda)$, is given per unit of wavelength, whereas transmissions such as $F(\lambda)$ are dimensionless. The second spectrograph is arranged in such a way that the photon is most likely to go through the spectrograph’s exit slit if the photon exits the first spectrograph at the correct position $\lambda$. On the other hand, if the photon is redistributed by the first spectrograph to a position $\lambda'$, it is most likely to fall next to the exit slit of the second spectrograph, so that it is blocked, see Fig. 3.7. However, the second spectrograph redistributes the photons as well. This second redistribution may cancel the first one, so that the photon does reach the exit slit of the second spectrograph. The probability that this happens is

$$p_2 = T_s \cdot \int_{\Delta \lambda_{\text{exit}}} f_2(\lambda'' - \lambda') d\lambda''$$

(3.7)

where $\Delta \lambda_{\text{exit}}$ is the spectral range that, via the dispersion of the second spectrograph, corresponds to the exit slit width. The probability that the photon passes the double spectrograph via the route $\lambda'$ is then $p_2 \cdot p_{1,\lambda} d\lambda'$. The total probability of the photon passing the double spectrograph is the sum of the probabilities of every possible route $\lambda'$:

$$\int_0^\infty p_{1,\lambda} p_2 d\lambda' = T_s^2 \int_0^\infty \left[ f_1(\lambda' - \lambda) \int_{\Delta \lambda_{\text{exit}}} f_2(\lambda'' - \lambda') d\lambda'' \right] d\lambda' \equiv T_d.$$  

(3.8)

This is the definition of the transmission $T_d$ of the double spectrograph without a mask. Apart from the square of the single spectrograph transmission it contains a factor due to
the redistributions by both spectrographs. For sharp instrumental profiles, which are not influenced by image aberrations in the spectrograph, this factor approaches unity.

A mask between the two spectrographs can block certain routes $\lambda'$ centred around $\lambda_i$, the wavelength of the laser light and hence the stray light. Via the dispersion of the first spectrograph, the mask width corresponds to a spectral range $\Delta \lambda_{\text{mask}}$. The probability of passing the double spectrograph equals $T_d$ minus the probability of hitting the mask:

$$F(\lambda) = T_d - T^2_s \int_{\lambda_i - \frac{1}{2} \Delta \lambda_{\text{mask}}}^{\lambda_i + \frac{1}{2} \Delta \lambda_{\text{mask}}} \left[ f_1(\lambda' - \lambda) \int_{\lambda - \frac{1}{2} \Delta \lambda_{\text{exit}}}^{\lambda + \frac{1}{2} \Delta \lambda_{\text{exit}}} f_2(\lambda'' - \lambda')d\lambda'' \right] d\lambda'.$$

(3.9)

$F(\lambda)$ is the transmission of the subtractive double spectrograph at wavelength $\lambda$. Dividing this filter profile by $T_d$ yields a profile that is normalised to unity outside the notch region.

Below, the DGF filter profile is calculated for four examples of single spectrograph instrumental profiles: an ideal instrumental profile, an instrumental profile that is determined by the entrance slit width, a profile governed by image aberrations, and a profile that is limited by the grating.

**Ideal spectrographs**

Ideal spectrographs, being comprised of an infinitely narrow entrance slit and a perfect grating do not exhibit image aberrations and have infinitely narrow instrumental profiles, described by the Dirac $\delta$-function:

$$f_{1,2}(\lambda' - \lambda) = \delta(\lambda' - \lambda).$$

(3.10)

In this case, the double spectrograph transmission is $T_d = T^2_s$ and the filter profile $F(\lambda)/T_d$ is zero within the notch range $\Delta \lambda_{\text{mask}}$ around $\lambda_i$, and unity outside the notch range, as shown in Fig. 3.8.

**Spectrographs with a finite entrance slit width**

Spectrographs with a finite entrance slit width, but free of image aberrations, have rectangular instrumental profiles,

$$f_1(\lambda' - \lambda) = \frac{\Delta \lambda_{\text{bp}}}{2} \text{ for } \lambda - \frac{1}{2} \Delta \lambda_{\text{bp}} < \lambda' < \lambda + \frac{1}{2} \Delta \lambda_{\text{bp}} = 0 \text{ otherwise.}$$

(3.11)

The bandpass $\Delta \lambda_{\text{bp}}$ equals the wavelength range that, via the dispersion of the first spectrograph, corresponds to the width of the image of the entrance slit. This instrumental profile is the result of the uncertainty in the position at which a photon enters the spectrograph. In contrast, the second spectrograph is entered at well-defined positions $\lambda'$. Therefore, the second instrumental profile can be taken a Dirac delta-function again.

When the widths of the entrance and exit slit are equal, we have $\Delta \lambda_{\text{bp}} = \Delta \lambda_{\text{exit}}$. The transmission of the double spectrograph is then $T_d = T^2_s$. If $\Delta \lambda_{\text{mask}} > \Delta \lambda_{\text{bp}}$, the transmission of the filter at wavelength $\lambda_i$ is zero. The resulting trapezoidal filter profile is shown in Fig. 3.9.
Fig. 3.8: The instrumental profiles \( f_{1,2}(\lambda' - \lambda) = \delta(\lambda' - \lambda) \) (left) of ideal single spectrographs and the resulting DGF filter profile \( F(\lambda)/T_d \) (right).

Fig. 3.9: The instrumental profile \( f_1(\lambda' - \lambda) \) (left) of an aberration-free single spectrograph and the resulting DGF filter profile \( F(\lambda)/T_d \) (right) with \( \Delta \lambda_{\text{mask}} > \Delta \lambda_{\text{bp}} \).

Fig. 3.10: The instrumental profiles \( f_{1,2}(\lambda' - \lambda) \) (left) of aberration-limited single spectrographs and the resulting DGF filter profile \( F(\lambda)/T_d \) (right). The mask width is such that \( F(\lambda_i)/T_d = 10^{-6} \).

Fig. 3.11: The instrumental profiles \( f_{1,2}(\lambda' - \lambda) \) (left) of diffraction-limited single spectrographs with \( \Delta \lambda_{\text{bp}} = 5 \) pm and the resulting DGF filter profile \( F(\lambda)/T_d \) (right). The mask width \( \Delta \lambda_{\text{mask}} = 1.0 \) nm is chosen such that \( F(\lambda_i)/T_d = 10^{-6} \).
Aberration-limited spectrographs

Spectrographs whose resolutions are limited by image aberrations have more or less Gaussian instrumental profiles,

\[ f_{1,2}(\lambda' - \lambda) = \frac{a}{\sqrt{2\pi}} \exp \left( -\frac{1}{2}a^2(\lambda' - \lambda)^2 \right), \]  

where \( a = \sqrt{\frac{\ln 2}{8\Delta\lambda_{bp}}} \). Since the instrumental profiles are aberration limited, \( \Delta\lambda_{bp} \gg \Delta\lambda_{\text{exit}} \) can be assumed and thus

\[ \int_{\lambda - \frac{1}{2}\Delta\lambda_{\text{exit}}}^{\lambda + \frac{1}{2}\Delta\lambda_{\text{exit}}} f_2(\lambda'' - \lambda') d\lambda'' \approx f_2(\lambda - \lambda') \cdot \Delta\lambda_{\text{exit}}. \]  

Then Eq. 3.8 reduces to

\[ T_d \approx T_s^2 \sqrt{\frac{2\ln 2}{\pi}} \cdot \frac{\Delta\lambda_{\text{exit}}}{\Delta\lambda_{\text{bp}}}. \]  

A narrower instrumental profile thus enhances the double spectrograph transmission, as long as the approximation of (3.13) is valid\(^6\). The resulting filter profile is

\[ \frac{F(\lambda)}{T_d} = 1 - \frac{1}{2} \left[ \text{erf}(ax) - \text{erf}(ay) \right], \]  

Here \( \text{erf}(x) \) is the error function and

\[ x = \lambda_i - \lambda + \frac{1}{2}\Delta\lambda_{\text{mask}} \]
\[ y = \lambda_i - \lambda - \frac{1}{2}\Delta\lambda_{\text{mask}}. \]  

Fig. 3.10 shows the filter profile \( F(\lambda)/T_d \) for a bandpass of 0.40 and 0.35 nm. The mask width, corresponding to a wavelength range of 1.2 and 1.0 nm respectively, is chosen so as to have \( F(\lambda_i)/T_d = 10^{-6} \). The relative transmission of the filter at \( \lambda = \lambda_i \pm 0.75 \text{ nm} \) is 90% and 99% respectively. Clearly the notch width of the filter decreases as the bandpass of the spectrographs becomes narrower.

The relative transmission at the centre of the spectrum, \( F(\lambda_i)/T_d \), decreases with decreasing a bandpass, thus improving the stray light suppression. Fig. 3.12 shows the transmission \( F(\lambda_i)/T_d \) that can be achieved for a given bandpass. The relative transmission of the filter at 0.75 nm from the centre of the spectrum is chosen 90% and 99% respectively by an appropriate mask width. A bandpass of 0.4 nm or better is required for a transmission \( F(\lambda_i)/T_d = 10^{-6} \), which is necessary for the experiments described later in this work (see also Section 3.3.1).

\(^6\) Note that the double spectrograph transmission is always very low if the instrumental profile is solely determined by aberrations.
Fig. 3.12: The transmission at wavelength λ_i of an aberration limited DGF as a function of the bandpass ∆λ_{bp}, requiring a transmission of 90% or 99% at λ = λ_i ± 0.75.

**Diffraction-limited spectrographs**

As a last example, we discuss spectrographs whose instrumental profiles are limited by diffraction on the grating. This is not likely in the centre of the instrumental profile, where other contributions play a significant role, but the wings of the instrumental profile may be determined by the grating. The grating gives rise to a \((\sin x/x)^2\) profile, which roughly equals a Lorentzian instrumental profile,

\[
F(\lambda') = \frac{2\Delta\lambda_{bp}/\pi}{4(\lambda' - \lambda)^2 + \Delta\lambda_{bp}^2}.
\]

(3.17)

The half width of the instrumental profile is determined by the resolving power of the grating, \(R = \lambda/\Delta\lambda = N\), where \(N\) is the number of illuminated grooves on the grating [23]. Generally, the width is only a few picometres. Nevertheless, the relatively broad wings of a Lorentz profile have a considerable effect on the rejection factor that can be achieved.

An analytical calculation of the filter profile resulting from a Lorentzian instrumental profile is not so straightforward. Therefore, it was calculated numerically. A typical spectrograph may have a 90 mm wide, 1200 grooves/mm grating, which results in a resolving power \(R \approx 10^5\). At a wavelength of \(\lambda_i = 532\) nm, the Lorentzian instrumental profile thus has a width of approximately 5 pm. The dispersion of a typical spectrograph is on the order of 1 mm/nm, and the exit slit is as wide as the entrance slit, say 250 \(\mu\)m, so that ∆λ_{exit} = 0.25 nm. The mask width is chosen to be ∆λ_{mask} = 1.0 nm so that the stray light rejection factor is \(10^6\). For these parameters, the double spectrograph transmission (cf. Eq. 3.8) is \(T_d = 98\%\). The resulting filter profile is shown in Fig. 3.11.

**Real spectrographs**

The true instrumental profile of a spectrograph is the convolution of all these simpler profiles, none of which can be eliminated completely. The bandpass induced by the entrance slit is limited by the width of this slit, which must have a width of approximately the width of (the image of) the laser beam, i.e. 250 \(\mu\)m in our case. The contribution of the grating
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Fig. 3.13: The focal length $f$ and size $\phi$ of the imaging optics, the length $a$ of the collimated beam, and the angles of incidence and diffraction $\alpha$ and $\beta$ (resulting in a deflection angle $\delta$) on the grating in a Triple Grating Spectrograph (TGS). In the second spectrograph, the roles of $\alpha$ and $\beta$ are reversed.

is limited by the size and groove density of the grating, which do not allow for much freedom either. This contribution can be decisive for the stray light rejection that can be achieved. The contribution of image aberrations determines the influence of the notch profile away from the central wavelength, i.e. the influence on the measured Thomson spectrum. Therefore, image aberrations must be kept to a minimum.

Apart from the instrumental profile, the stray light rejection properties of a spectrograph also depend on the amount of undesired scatter off optical elements within the spectrograph. Since this constitutes a fairly homogeneous background light level over the entire iCCD, this is discussed in some more detail in Section 3.4.2.

3.3.3 Design of the Triple Grating Spectrograph (TGS)

In order to combine the two spectrographs of the DGF with the primary spectrograph efficiently, a complete Triple Grating Spectrograph (TGS) consisting of three identical spectrographs was designed. Before discussing the design of the TGS, we first examine the design parameters and basic single spectrograph characteristics.

A spectrograph, consisting of a grating and two optical elements (lenses or mirrors), has a number of design parameters: the focal length $f$ and diameter $\phi$ of the optical elements, the length $a$ of the collimated beam, the grating constant $n$, and the deflection angle $\delta$ of the grating, which is the difference of the angles of incidence and diffraction $\alpha$ and $\beta$. These parameters are illustrated in Fig. 3.13. In this figure, Czerny-Turner spectrographs employing mirrors as optical elements are taken as an example; our design is based on lenses (see below). The choice of these parameters defines the characteristics of the single spectrographs, the most important being the bandpass $\Delta\lambda_{bp}$, the dispersive power $d$, and the solid angle of detection $\Delta\Omega$.

The relation between the design parameters of the spectrograph and the resulting char-
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**Fig. 3.14:** The dependence of the linear displacement $x$ of an image point in the focal plane of a lens on the angle $\beta$ of the collimated beam with the optical axis. The same relation applies for a concave mirror.

Characteristics follow from the grating equation,

$$\sin \alpha + \sin \beta = kn\lambda, \quad (3.18)$$

and the linear displacement of an image point in the focal plane of a lens or mirror as a function of the angle of the collimated beam with the optical axis (see Fig. 3.14),

$$\frac{x}{f} = \tan \beta \approx \beta. \quad (3.19)$$

In these equations, $f$ is the focal length of the optical elements, $\lambda$ is the wavelength of the diffracted radiation, and $k = 1$ since the grating is used in first order.

The linear dispersion $d$ of a spectrograph is

$$d = \frac{dx}{d\lambda} = \frac{dx}{d\beta} \cdot \frac{d\beta}{d\lambda} = \frac{knf}{\cos \beta}. \quad (3.20)$$

The contribution of the entrance slit width $s_{\text{ent}}$ to the instrumental profile is the spectral range corresponding to the width $s'_{\text{ent}}$ of the image of the entrance slit, which differs from $s_{\text{ent}}$, since the grating produces a horizontal magnification. This magnification is given by the derivative of the angle of diffraction to the angle of incidence on the grating, keeping $\lambda$ constant:

$$\left| \frac{d\beta}{d\alpha} \right| = \frac{\cos \alpha}{\cos \beta}. \quad (3.21)$$

The rectangular instrumental profile due to the entrance slit width thus covers a spectral range

$$\Delta \lambda_{\text{bp}} = \frac{s'_{\text{ent}}}{d} = s_{\text{ent}} \cdot \frac{\cos \alpha}{knf}. \quad (3.22)$$

Given the desired deflection angle $\delta = \beta - \alpha$, the required angle of incidence $\alpha$ on the grating follows from the goniometric relation $\sin \alpha + \sin \beta = 2 \sin \frac{1}{2} (\alpha + \beta) \cos \frac{1}{2} (\alpha - \beta)$ and the grating equation:

$$\alpha = \arcsin \left( \frac{kn\lambda}{2 \cos(\delta/2)} \right) - \frac{\delta}{2}. \quad (3.23)$$

The choices in the design of the spectrograph system are based on the desired performance, such as bandpass, dispersion, and opening angle.
As argued in the previous section, the bandpass $\Delta \lambda_{bp}$ must be narrower than 0.4 nm for an acceptable DGF performance if the spectrographs are limited by image aberrations. For a more ideal spectrograph this requirement is less stringent. Nevertheless, image aberrations must be kept as small as possible.

The dispersion must be such that a Thomson spectrum fits onto the CCD camera, which is 16.5 mm wide. A Thomson spectrum of a plasma with $T_e = 1$ eV has a half $1/e$-width of 1.5 nm. However, if hotter plasmas or the tail of the EEDF are studied, a spectral range of about 10 nm is more convenient. This spectral range allows for measurement of the “entire” Thomson spectrum for electron temperatures up to about 3 eV. Imaging only one half of the Thomson spectrum, electron energies of up to 45 eV are covered by this spectral range. Therefore, the dispersion $d$ must be between 1 and 2 mm/nm.

The solid angle of the spectrograph must be chosen as large as possible for efficient light collection; $\Delta \Omega = 0.01 \text{ sr} \ (f/9)$ or better is highly desirable.

For the optical elements, either lenses or concave mirrors can be used. Czerny-Turner spectrographs (cf. Fig. 3.13), which are common in most laboratories, employ mirrors since they do not exhibit chromatic aberration and can thus be used for a wide range of wavelengths. However, since mirrors are almost always used off-axis, they introduce astigmatism, i.e. the effect that the focal planes of optimal spatial resolution (sagittal focus) and optimal spectral resolution (tangential focus) do not coincide. For our application, spatial resolution is highly desirable, and spectral resolution is indispensable for efficient stray light reduction. Therefore, we chose to use lenses, which can be used (almost) on-axis and thus suffer less from astigmatism. Lenses have chromatic aberration, but the spectral range of interest is only a few nanometres wide. A more serious problem is spherical aberration. Using achromatic doublet lenses instead of ordinary plano-convex lenses reduces image aberrations.
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Fig. 3.16: Vignetting, i.e. the decrease in transmission of a lens system for off-axis objects, is least when $a = 2f$.

significantly, since they are not only optimised for chromatic aberration, but for spherical aberration, astigmatism, and coma as well. This is illustrated by the ray-trace simulation in Fig. 3.15. Therefore, the design discussed in this work uses achromatic doublet lenses.

Common grating constants are 1200 and 1800 grooves/mm. The latter is favourable since it results in the best dispersion (Eq. 3.20), yielding the best spectral resolution and narrowest instrumental profile. In addition, using larger grating constants the focal length of the lenses can be smaller for a comparable dispersion, which enhances the collection angle of the system.

The deflection angle of the grating was chosen to be $\delta = \pm 30^\circ$, being a convenient angle for a compact system. For $\lambda = 532$ nm, Eq. 3.23 yields $\alpha = 15^\circ$ and $\beta = 45^\circ$, or the reverse. The angle $\alpha = 45^\circ$ yields the narrowest bandpass, but the poorest dispersion, cf. Eqs. 3.22 and 3.20. A narrow bandpass is desirable, but with a larger dispersion the effect of image aberrations on the instrumental profile is smaller, as image aberrations affect the physical shape of the image irrespective of the wavelength range it represents. Furthermore, for $|\alpha| < |\beta|$ the reflected beam is narrower than the incident beam, which reduces vignetting in horizontal direction (see below). In addition, a small angle $\alpha$ is less demanding for the grating size. Therefore, at the expense of bandpass, $\alpha$ is chosen $15^\circ$.

The width of the entrance slit must be taken $s_{\text{ent}} = 250 \ \mu m$ to ensure that the whole width of the laser beam fits onto the entrance slit of the spectrograph. Since we use low-aberration achromatic lenses, the bandpass $\Delta \lambda_{\text{bp}}$ of the spectrograph is expected to be determined mainly by the entrance slit. For efficient stray light reduction $\Delta \lambda_{\text{bp}} \approx 0.3$ nm is needed. Eq. 3.22 then requires $f \approx 450$ mm. In our design we choose $f = 600$ mm to have some extra margin.

For optimal light gathering properties, the size of the lenses should be as large as possible. However, due to increasing image aberrations for increasing lens sizes, an opening angle of more than about $f/6$ (0.0218 sr) is not feasible. The present design uses lenses with a clear aperture of 95 mm, which thus have an opening angle of $f/6.3$ (0.0197 sr).

The length $a$ of the collimated beam influences vignetting by the system. Vignetting is the effect of a decreased transmission of the system for objects that are not on the optical axis, see Fig. 3.16. In a spectrograph, vignetting also occurs for on-axis objects that radiate with a different wavelength than that for which the spectrograph was optimised. The least vignetting occurs when $a = 2f$. For smaller values of $a$, the losses at the second lens caused by increasing $a$ are compensated further in the system. For objects at 5.5 mm (i.e. half the
The experimental system for laser scattering

Table 3.1: Chosen instrumental parameters and resulting single spectrograph characteristics.

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Single spectrograph characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>grating constant ( n = 1800 \text{ grooves/mm} )</td>
<td>Bandpass ( \Delta \lambda_{bp} = 0.22 \text{ nm} )</td>
</tr>
<tr>
<td>angle of incidence ( \alpha = 15^\circ )</td>
<td>Dispersion ( d = 1.52 \text{ mm/nm} )</td>
</tr>
<tr>
<td>angle of diffraction ( \beta = 45^\circ )</td>
<td>Solid angle ( \Delta \Omega = 0.0197 \text{ sr (} f/6.3 \text{)} )</td>
</tr>
<tr>
<td>focal length ( f = 600 \text{ mm} )</td>
<td></td>
</tr>
<tr>
<td>lens diameter ( \phi = 95 \text{ mm} )</td>
<td></td>
</tr>
<tr>
<td>collimated beam ( a = 600 \text{ mm} )</td>
<td></td>
</tr>
<tr>
<td>slit width ( s_{ent} = 250 \text{ \mu m} )</td>
<td></td>
</tr>
</tbody>
</table>

The values of the chosen instrumental parameters and the resulting single spectrograph characteristics are listed in Table 3.1. It should be noted that the bandpass and dispersion are slightly different for the second spectrograph because it is mirrored with respect to the first and third spectrograph, so the angles \( \alpha \) and \( \beta \) are interchanged.

With a bandpass of \( \Delta \lambda_{bp} = 0.22 \text{ nm} \), individual rotational Raman lines of nitrogen, which are 0.22 nm apart, can hardly be resolved. Therefore, the whole Raman spectrum is used for calibration of the setup (see Section 2.4). A dispersion of \( d = 1.52 \text{ mm/nm} \) leads to a visible spectral range on the (16.5 mm wide) CCD camera of 10.9 nm. The stray light reduction by the DGF can be estimated from the instrumental profile, see Section 3.3.2. Assuming a Gaussian instrumental profile with \( \Delta \lambda_{bp} = 0.22 \text{ nm} \), the resulting stray light transmission \( F(\lambda_i)/T_d \) of the filter is less than \( 10^{-8} \). For a completely aberration-free spectrograph, the transmission in the notch region would even be zero. However, taking into account the contribution of the grating, a transmission of around \( 10^{-6} \) is more realistic.

A TGS using the parameters discussed above is shown in Fig. 3.17. Each spectrograph contributes to stray light rejection in the wings of the recorded Thomson spectrum. The first spectrograph images most of the stray light onto the mask. The second spectrograph images most of the stray light remainder next to the exit slit of the second spectrograph (the intermediate slit). Finally, the third spectrograph images most of the remaining stray light in the centre of the spectrum rather than in the wings where the Thomson spectrum is to be detected.

The final design (see Fig. 3.18) also incorporates a 90° image rotator, consisting of three plane mirrors, to keep the dispersion direction and optical axis of the system horizontal (see Section 3.2). An additional plane mirror compacts the system and a polarising beam-
Fig. 3.17: The working principle of the designed TGS. Stray light that is redistributed by the first spectrograph and thus passes the mask is largely blocked by the exit slit of the second spectrograph (“intermediate slit”).

splitting cube is placed directly in front of the iCCD detector. This polariser transmits the polarisation direction of Thomson scattered photons, but reduces the (partly) unpolarised stray light and plasma emission. In addition, it blocks the depolarised part of Raman scattering, which is more convenient for calibration of the system (see Section 2.4).

The CCD camera can be placed either after three spectrographs, or after just one spectrograph (where the mask is placed normally). This latter option does not have the effective stray light reduction of a triple grating spectrograph, but the transmission of a single spectrograph is about a factor of two higher, leading to a lower detection limit if the wings of the stray light spectrum are not a problem. The stray light peak itself can be blocked by a mask directly in front of the iCCD camera in order to prevent saturation.

To prevent unwanted reflections, such as the zero order reflection on the gratings, from propagating through the system, a few metal plate obstructions were placed in the TGS.

### 3.3.4 Ray trace simulations

The maximum spatial and spectral resolution of the designed TGS is determined by image aberrations produced by the lenses. An analytical calculation of this resolution for a complete optical system is not straightforward. Therefore, the spatial and spectral resolutions were determined from ray-trace simulations. These simulations predict the image spots of point sources at the entrance slit that were produced by the spectrograph system at the position of the CCD camera. The spatial and spectral resolution of the system equal the sizes of these image spots in the respective direction.

Image aberrations, and hence the resolution of the system, depend on the position of the point source along the exit slit and the wavelength of the radiation emitted by
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\[ \text{The final TGS design. Obstructions (not shown in the figure) prevent unwanted reflections from propagating through the system. The horizontal entrance slit and image rotator enable simultaneous measurements at multiple positions in the plasma.} \]

the source. Therefore, two monochromatic point sources were simulated. The first point source is placed at the centre of the entrance slit (on the optical axis) and emits light of \( \lambda = 532 \text{ nm} \), for which the system is optimised. This point source thus represents the best possible case. The other point source is placed 5 mm off-axis along the entrance slit, and emits light of \( \lambda = 527 \text{ nm} \). The off-axis distance and wavelength are both at the edge of the ranges covered by the CCD camera (11 mm and 10.9 nm in spatial and spectral direction respectively). Therefore, this point source represents the worst case situation.

Ray-trace simulations are done for both a single spectrograph and the complete triple grating spectrograph. The mask between the first two spectrographs is omitted in the simulations. Fig. 3.19 gives the resulting image spots after a single and a triple grating spectrographs. Since a triple grating spectrograph contains three times more optical elements than a single spectrograph, it produces about three times larger spot sizes. The largest spot is around 100 \( \mu \text{m} \) wide and high.

The spatial resolution predicted by these ray-trace simulations ranges from 4 to 100 \( \mu \text{m} \). However, the spatial resolution obtained in a measurement cannot be better than the resolution of the image intensifier of the iCCD camera, which is about 85 \( \mu \text{m} \). Thus, the spatial resolution of the entire system (spectrograph and CCD camera) is better than 100 \( \mu \text{m} \) in all cases.

The spectral resolution of the spectrograph system, which follows from the horizontal size of the image spot and the dispersion \( d = 1.52 \text{ mm/nm} \), ranges from 2.6 to 66 pm. However, the resolution of the iCCD camera sets a limit of 56 pm to the spectral resolution. In addition, if the entrance slit of the system is wider than \( s_{\text{ent}} \approx 50 \mu \text{m} \), the spectral
resolution is limited by this width. For practical measurements, the entrance slit has a width of 250 $\mu$m, so that this is indeed the limitation; the spectral resolution of the system is then approximately 0.22 nm. With a narrower slit, a resolution of about 0.06 nm can be reached.

### 3.4 Noise and the detection limit

In this section, the Thomson scattering detection limit of the experimental system is calculated. As discussed in Section 3.2, the detection limit of the experimental system is determined by noise on the a continuous background superimposed on the spectrum and stray light. Due to the use of a stray light filter, as presented in the previous section, the latter is strongly reduced. Therefore, in the calculation below, only noise is taken into account. In Section 3.2 the detection limit is defined as the electron density for which the intensity at $1/e$ height of the Thomson spectrum is twice the noise on the detected spectrum (a signal-to-noise ratio of two). This definition is maintained here.

An important source of noise on recorded spectra is statistical noise on the number of photons detected by the iCCD detector. This noise source is discussed in Section 3.4.1. Subsequently, Section 3.4.2 examines other noise sources, such as dark current, and determines the detection limit of the system.
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Fig. 3.20: Working principle of an intensified CCD camera. Photons enter the photocathode of the intensifier on the top, where they generate a photo-electron. The MCP amplifies the electric current, and a fluorescent layer produces light again, which is subsequently detected in the CCD chip on the bottom. Voltages are an indication only.

3.4.1 Photon statistics

The statistical noise on the detected Thomson signal can be studied by following the propagation of Thomson scattered photons through the detection system, while ignoring other noise sources. Before determining the total statistical noise on the Thomson signal, each step in the series of statistical processes in the detection system is treated independently.

First, the laser emits a number of photons that is subjected to shot-to-shot power variations of about 10%. For \( n \) laser pulses, the relative standard deviation in the number of laser photons is \( 0.1/\sqrt{n} \).

Subsequently, a photon may be Thomson scattered, pass through the optics of the detection branch (with a transmission \( \eta \)), and generate a photo-electron in the photocathode of the iCCD camera (quantum efficiency \( \xi_1 \)). This chain of processes leads to a binomial distribution in the number of generated photo-electrons. Because of the low Thomson scattering probability, this can be approximated very well by a Poisson distribution. Thus, the relative noise on the number of photo-electrons is \( 1/\sqrt{N_T} \), where \( N_T \) is the number of photo-electrons as a result of Thomson scattering.

An electric field accelerates the photo-electrons from the photocathode to a Multi-Channel Plate (Fig. 3.20), which amplifies the electric current. For each photo-electron, the number of electrons produced by the MCP approximately follows a Poisson-like distribution, whose mean value is the gain factor \( g_i \). However, the standard deviation is mainly determined by the first amplification step [24]. This can be seen clearly in Fig. 3.21, which shows the single photon response of the iCCD camera in the highest gain setting. The Poisson fit in this figure suggests an average first amplification factor of approximately 1.35. This results in a relative standard deviation of 0.86. For \( N_T \) photo-electrons entering the MCP, the relative standard deviation is then approximately \( 0.86/\sqrt{N_T} \).

The electrons that are generated in the MCP are accelerated towards a fluorescent layer that converts the electrons (\( e^- \)) to photons (\( h\nu \)). A fibre-optic taper guides these photons to the smaller CCD chip where they are collected as electron-hole pairs. The quantum efficiency of this binomial process is \( \xi_2 \), and the number of electrons produced in the CCD
chip has a relative standard deviation of \( \left( \frac{1 - \xi_2}{N_T g_i \xi_2} \right)^{1/2} \).

The number of electrons in the CCD chip due to Thomson scattering is, on the average, 
\( S_T = N_T g_i \xi_2 \). In approximation, the relative standard deviations of the processes described above can be summed quadratically to yield the total standard deviation \( \varsigma_T \) on the Thomson signal:

\[
\left( \frac{\varsigma_T}{S_T} \right)^2 \approx \frac{0.01}{N_T} + \frac{1}{N_T} + \frac{0.74}{N_T} + \frac{1 - \xi_2}{N_T g_i \xi_2}.
\] (3.24)

For less than one Thomson photo-electron per CCD pixel per laser shot, which is always the case at the detection limit, \( N_T \ll n \), so that the first term (due to shot noise of the laser) is not significant. The gain factor of the intensifier of the iCCD camera is usually set to have \( g_i \xi_2 \gg 1 \), so that the last term, due to noise in the CCD chip, can be neglected as well. The total relative standard deviation on the Thomson signal detected by the CCD camera is then approximately

\[
\frac{\varsigma_T}{S_T} \approx \frac{1.3}{\sqrt{N_T}}.
\] (3.25)

Thus, the noise on the Thomson scattering intensity is only 30% higher than that predicted by Poisson statistics on the number of Thomson photo-electrons \( N_T \). This is a logical result since \( N_T \) is the smallest number of events in the chain of statistical processes. The intensifier behind the photocathode amplifies the number of electrons, but the noise on this number as well.

### 3.4.2 Detection limit

The total noise on the detected spectrum is not only determined by noise on the Thomson scattering intensity itself, but also by noise on the background superimposed on the Thomson spectrum. This background is the result of five contributions: plasma radiation, stray light, Equivalent Background Illumination (EBI), dark current, and readout noise.
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\[ \text{photon source} \rightarrow \text{optics} \rightarrow \text{photocathode} \rightarrow \text{MCP} \rightarrow \text{CCD} \rightarrow \text{ADC} \]

\[ \text{Thomson plasma light} \rightarrow \text{stray light} \rightarrow \eta \rightarrow \xi_1 \rightarrow EBI \rightarrow g_1 \rightarrow \xi_2 \rightarrow \text{digitisation} \rightarrow \text{counts} \rightarrow \text{signal} \]

**Fig. 3.22**: Propagation of the signal through the detection branch and the CCD camera.

EBI and dark current are the result of thermal generation of photo-electrons in the photocathode and electron-hole pairs in the CCD chip respectively. Dark current is strongly reduced by cooling the CCD chip to -40°C; the image intensifier is not cooled. EBI and plasma radiation are reduced by more than six orders of magnitude by gating the iCCD camera, i.e. using the intensifier as an ultra-fast shutter. With a laser pulse frequency of 10 Hz, the typical gating time of 20 ns leads to an intensifier duty-cycle of $2 \cdot 10^{-7}$, which is the fraction of the plasma light that is left in the recorded spectrum. The stray light contribution considered here consists of undesired scatter in the TGS. This stray light is blocked as much as possible by obstructions and baffles. In Fig. 3.22 these sources of signal and noise are shown schematically.

Below, the noise as a result of plasma radiation, EBI, dark current, and readout of the CCD is determined and compared to the statistical noise on the Thomson signal. This requires detailed knowledge of the performance of the equipment and experimental conditions that are used. Table 3.2 gives an overview of the relevant experimental parameters.

The first set of iCCD parameters in this table is specified for the camera used in this work. The amount of pixel binning (summing in the two directions) and the gate time can be chosen freely. For the experiments described later in this work, pixels are binned by a factor of four in each direction. This reduces statistical variations of the signal by a factor of four, while retaining the resolution of the measurement\(^7\). The gate time is taken 20 ns, which enough to cover the duration of a laser pulse (7 ns) and to allow for some time jitter.

The first set of detection branch parameters are the fixed specifications of the Nd:YAG laser and the TGS (cf. Section 3.3.3). The detection length $L_{\text{det}}$ can be chosen within the range of 28.6 µm (the size of one CCD pixel) to 11 mm (the size of the CCD chip in spatial direction). It equals the size of one binned pixel (superpixel) in spatial direction, i.e. 114 µm for $4 \times 4$ binning. The integration time of a measurement is taken 300 seconds (5 minutes), which is a trade-off between a good detection limit and stable experimental conditions. The electron temperature $T_e$ of the plasma that is studied is, of course, not a tunable parameter. Here we take it to be 1 eV, which is approximately the electron temperature of the plasmas studied in subsequent chapters of this thesis.

\(^7\) The resolution is limited by the resolution of the image intensifier in front of the CCD camera, which is on the order of four CCD pixels.
Table 3.2: Relevant parameters and settings of the iCCD camera and detection branch.

<table>
<thead>
<tr>
<th>iCCD camera</th>
<th>Detection branch</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi_1$</td>
<td>$P_1$ 4 W</td>
</tr>
<tr>
<td>$g_1\xi_2$</td>
<td>$\lambda_i$ 532 nm</td>
</tr>
<tr>
<td>EBI</td>
<td>laser pulse rate 10 Hz</td>
</tr>
<tr>
<td>dark current</td>
<td>$d$ 1.52 mm/nm</td>
</tr>
<tr>
<td>read noise</td>
<td>$\eta$ 0.12</td>
</tr>
<tr>
<td>pixel size</td>
<td>$\Delta\Omega$ 0.0197 sr</td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>pixel binning</td>
<td>$L_{\text{det}}$ 114 µm</td>
</tr>
<tr>
<td>gate time</td>
<td>integration time 300 s</td>
</tr>
<tr>
<td></td>
<td>$T_c$ 1 eV</td>
</tr>
</tbody>
</table>

The number of photo-electrons per superpixel that is generated as a result of background light (plasma radiation and stray light) is designated by $N_0$. The resulting number of electrons in a CCD pixel is $S_0 = N_0 g_1 \xi_2$. Its noise is, like for Thomson scattering, mainly determined by photon statistics, so the relative noise level on this signal is $\varsigma_0/S_0 \approx 1.3/\sqrt{N_0}$ (cf. Eq. 3.25). The plasmas studied in this work do not emit atomic or molecular lines around $\lambda_i = 532$ nm. Due to their small size and low density, and the small intensifier duty cycle, continuum radiation (e.g. Bremsstrahlung) is negligible. In contrast, stray light was found to be a significant source of noise\(^8\) during the experiments on a helium RF discharge in a quartz tube, which are described in Chapter 7 [25]. In these experiments, the measured background light level—mainly due to stray light—was found to be $I_0 \approx 1.6 \cdot 10^{-4}$ photo-electrons per (unbinned) pixel per second. Thus, for the experimental conditions listed in Table 3.2, this background light produced $N_0 \approx 0.75$ photo-electrons per superpixel.

The numbers of EBI photo-electrons and dark current electron-hole pairs are Poisson distributed, with a noise equal to the square root of the number of electrons. However, EBI and its noise are, during the gating period of the intensifier, also amplified by the MCP. Table 3.3 gives an overview of the intensities of plasma radiation, EBI and dark current and their noise. This table also lists the Thomson signal and its noise, based on seven Thomson scattering photo-electrons. This is the minimum number of photo-electrons per pixel that is needed for a signal-to-noise ratio of two (cf. Eq. 3.25).

The total noise on a measurement can be approximated by $\varsigma = (\sum j \varsigma_j^2)^{1/2}$. However, a recorded Thomson spectrum is always the difference of two measurements; one with the Thomson signal, and another to account for the background signal. Therefore, the noise on this background signal contributes twice to the final spectrum. Nevertheless, from Table 3.3 it is clear that the total noise level is dominated by the statistical noise on the Thomson signal, which cannot be prevented. Only for very long integration times or large binning factors, background light and dark current may become a problem.

\(^8\) This stray light turned out to be caused by the entrance slit of the TGS, and could later be eliminated largely. Nevertheless, it is taken into account in this discussion.
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Table 3.3: Background signal intensities and noise levels, given in electrons per binned CCD pixel. The integration time is 5 minutes. The Thomson scattering signal is based on seven photo-electrons per pixel.

<table>
<thead>
<tr>
<th>Source</th>
<th>Intensity (e⁻/pix)</th>
<th>Noise (e⁻/pix)</th>
</tr>
</thead>
<tbody>
<tr>
<td>background light</td>
<td>$S_0 = 2630$</td>
<td>$\varsigma_0 = 3940$</td>
</tr>
<tr>
<td>EBI</td>
<td>$S_e = 0.24$</td>
<td>$\varsigma_e = 37$</td>
</tr>
<tr>
<td>dark current</td>
<td>$S_d = 2064$</td>
<td>$\varsigma_d = 45$</td>
</tr>
<tr>
<td>readout noise</td>
<td></td>
<td>$\varsigma_r \approx 120$</td>
</tr>
<tr>
<td>Thomson scattering</td>
<td>$S_T = 2.45 \cdot 10^4$</td>
<td>$\varsigma_T = 1.20 \cdot 10^4$</td>
</tr>
</tbody>
</table>

The problem of dark current and readout noise can be eliminated by using a photon counting technique. Photon counting requires a high intensifier gain factor, so that single photons give rise to a signal that is larger than noise produced by the iCCD camera. Pulse height discrimination can then be applied to remove noise from the recorded spectrum. For this purpose, a high intensifier gain factor (much larger than the typical noise level of the iCCD camera) is required; for low intensifier gain factors, the efficiency of the photon counting algorithm can be significantly less than unity [15]. The photon counting algorithm that was used to determine the graph in Fig. 3.21 uses a discrimination threshold value of 160 electrons per pixel. All pixels adjacent to the pixel above threshold were deleted in order to prevent one photon from triggering multiple pixels.

Since it reduces noise, the use of such a photon counting technique is reported by several authors [15, 16]. Nevertheless, photon counting is not necessarily advantageous for given experimental conditions. Photon counting only eliminates noise produced inside the iCCD camera. As was shown above, the contributions of dark current and EBI to the total noise level are much smaller than noise on the Thomson and background light signal. In addition, the noise on the detected Thomson signal is only 30% larger than the noise expected on the basis of pure photon statistics on the number of photons incident on the iCCD camera (see Eq. 3.25). Therefore, photon counting would reduce the detection limit by only 30%. A drawback of the technique is that multiple photons at the same position are counted as single photons. In order to reduce the probability that this happens, only a few photons per CCD frame are allowed. This requires reading and processing many CCD frames per measurement, which makes the process more time consuming than simple integration. Therefore, photon counting is not applied in this work.

As indicated above, under the experimental conditions of Table 3.2, an intensity corresponding to approximately seven photo-electrons per pixel can just be distinguished from its own statistical noise. Due to the dispersion of the spectrograph, a binned pixel corresponds to a spectral region of 0.0753 nm. The minimum spectral intensity that can be measured is then seven photo-electrons in this wavelength range, or equivalently 90 photo-electrons per nanometre. The electron density detection limit is the electron density for which the spectral intensity at $1/e$ height of the spectrum is equal to this minimum of
90 photo-electrons/nm.

The number of Thomson scattering photo-electrons per unit of wavelength that is generated is (cf. Eq. 2.30)

$$\frac{dN_T}{d\lambda} = N_L \cdot n_e L_{det} \cdot \frac{d\sigma_T}{d\Omega} \cdot \Delta\Omega \cdot \eta \xi_1 \cdot \frac{1}{\Delta\lambda_{1/e}} \cdot \sqrt{\frac{\lambda - \lambda_i}{\Delta\lambda_{1/e}}} \cdot \exp\left(-\frac{(\lambda - \lambda_i)^2}{\Delta\lambda_{1/e}^2}\right), \quad (3.26)$$

where $N_L = P_i \cdot t \cdot \lambda_i / hc$ is the number of laser photons emitted during the integration time $t$. With the parameters given in Table 3.2, the spectral intensity at $1/e$-height of the spectrum ($\Delta\lambda = \Delta\lambda_{1/e}$) reaches its limiting value of 90 Thomson scattering photo-electrons per nanometre in five minutes at $n_{e, lim} = 9.3 \cdot 10^{17} \text{ m}^{-3}$. This detection limit can be improved by integrating over a longer period (e.g. 30 minutes), or by binning more pixels\(^9\) (e.g. $4 \times 32$ or $4 \times 385$, i.e. binning over the full length of the detection volume).

Clearly the detection limit depends on a large number of parameters, which cannot all be chosen freely when using a given experimental system. In general, if statistical noise is the restriction, the detection limit can be written as $n_{e, lim} = C/L_{det} \cdot t$. The constant $C$ follows from Eq. 3.26, and depends on the experimental system (e.g. laser power and solid angle of detection) and the electron temperature of the plasma under study. For the system described in this work, the detection limit (when restricted by statistical noise) is given by

$$n_{e, lim} = 2.97 \cdot 10^{14} \cdot \frac{\sqrt{T_e}}{t \cdot L_{det}}. \quad (3.27)$$

Here the electron temperature is limited to $0.1 \text{ eV} < T_e < 10 \text{ eV}$ by the spectral range of the DGF notch filter (as discussed in Section 3.5) and the size of the iCCD camera. $L_{det}$, which is determined by the spatial resolution of the system and the size of the camera may range from 0.1 to 11 mm. The integration time $t$ ranges from 0.1 s (one laser shot) to about one hour (for stability reasons).

A similar approach can be used to estimate the maximum electron energy $E_{e, lim}$ where the Electron Energy Distribution Function (EEDF) can be probed. Like the detection limit, this depends on the accuracy of the measurement that is considered acceptable. In order to have an error of less than 10% on the measured population of a certain velocity group, the signal-to-noise ratio of the spectrum at the corresponding energy must be at least 10. This criterion is used to define the maximum electron energy that can be measured.

The energy limit $E_{e, lim}$ also depends on the electron density $n_e$ and temperature $T_e$ of the plasma that is studied; for higher electron densities or temperatures, the measured Thomson spectrum is accurate up to higher electron energies. As an example, we take the plasma produced by the Torche à Injection Axiale (TIA) [26], which may have deviations of the high energy tail of the EEDF from a Maxwell distribution [27]. This plasma has

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\(^9\) Especially by binning in spatial direction, i.e. increasing the detection volume. Binning in spectral direction decreases the amount of data points in a spectrum, which gives rise to larger errors in the fitting procedure.
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Table 3.4: The detection limit in electron density \((n_e,\text{lim})\) and in electron energy \((E_e,\text{lim})\) that can be reached under various experimental conditions (the presence of background light, binning, and integration time \(t\)). This table assumes \(T_e = 1 \text{ eV}\) for the detection limit in electron density, and \(T_e = 2 \text{ eV}\) and \(n_e = 10^{21} \text{ m}^{-3}\) for that in electron energy (see text for further details).

<table>
<thead>
<tr>
<th>Binning</th>
<th>Without background light</th>
<th>With background light</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 × 4</td>
<td>(n_e,\text{lim} = 9.9 \cdot 10^{17} \text{ m}^{-3})</td>
<td>(n_e,\text{lim} = 1.2 \cdot 10^{18} \text{ m}^{-3})</td>
</tr>
<tr>
<td>(t = 5 \text{ min.})</td>
<td>(E_e,\text{lim} = 8.7 \text{ eV})</td>
<td>(E_e,\text{lim} = 8.7 \text{ eV})</td>
</tr>
<tr>
<td>4 × 32</td>
<td>(n_e,\text{lim} = 2.1 \cdot 10^{16} \text{ m}^{-3})</td>
<td>(n_e,\text{lim} = 7.9 \cdot 10^{16} \text{ m}^{-3})</td>
</tr>
<tr>
<td>(t = 30 \text{ min.})</td>
<td>(E_e,\text{lim} = 16.4 \text{ eV})</td>
<td>(E_e,\text{lim} = 15.9 \text{ eV})</td>
</tr>
<tr>
<td>4 × 385</td>
<td>(n_e,\text{lim} = 1.8 \cdot 10^{15} \text{ m}^{-3})</td>
<td>(n_e,\text{lim} = 2.0 \cdot 10^{16} \text{ m}^{-3})</td>
</tr>
<tr>
<td>(t = 30 \text{ min.})</td>
<td>(E_e,\text{lim} = 21.4 \text{ eV})</td>
<td>(E_e,\text{lim} = 19.3 \text{ eV})</td>
</tr>
</tbody>
</table>

A relatively high electron temperature and density \((T_e \approx 2 \text{ eV} \text{ and } n_e \approx 10^{21} \text{ m}^{-3} \text{ [12]}\) compared to plasmas that are studied in this work. Therefore, the EEDF can be probed up to relatively high energies\(^1\).

A signal-to-noise ratio in the measured Thomson spectrum is achieved for at a spectral intensity of 175 photo-electrons per pixel, corresponding to 2325 photo-electrons/nm. According to Eq. 3.26 this intensity is reached when \(\Delta \lambda = 4.4 \text{ nm}\), which corresponds to an electron energy of \(E_e,\text{lim} = 8.6 \text{ eV}\). Again, longer integration times or larger binning factors enhance this limit.

Table 3.4 gives an overview of the detection limit in electron density and electron energy that can be achieved with the experimental system under a number of experimental conditions. When applicable, the background light level was taken \(I_0 \approx 1.6 \cdot 10^{-4} \text{ photo-electrons per (unbinned) pixel per second}\). This is the background light level measured during experiments on a helium RF discharge in a quartz tube, as described in Chapter 7 \([25]\); this background was responsible for the relatively high detection limit in that study. The binning factor is chosen 4 in spectral direction, and ranging from 4 to 385 in spatial direction. It should be noted that the spatial binning factor determines the spatial resolution of the system. Therefore, a large spatial binning factor may not be useful for small plasmas.

The electron density detection limit \(n_e,\text{lim}\) is calculated for a plasma with an electron temperature of \(T_e \approx 1 \text{ eV}\), since this is approximately the temperature of the plasmas studied later in this work. In contrast, the electron energy limit \(E_e,\text{lim}\) is calculated for a plasma with \(T_e = 2 \text{ eV}\) and \(n_e = 10^{21} \text{ m}^{-3}\). These values are applicable to the TIA plasma (see above), which possibly has a non-Maxwellian EEDF.

Unfortunately, the detection limits given in Table 3.4 could not be reached with the present system, because of an unexpected low transmission of the TGS. This was found to

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\(^1\) This is necessary to see a deviation from a Maxwellian EEDF, since a deviation is only expected at energies above approximately 11 eV.
be caused by two of the three gratings in the system having an efficiency that is significantly lower than specified by the manufacturer (see also Section 3.5). This leads to an extra loss factor that increases the detection limit by approximately 40. This effect is not taken into account in Table 3.4. Nevertheless, the limits in this table should be achievable when the two inefficient gratings are replaced, which will be done in the near future.

3.5 Experimental characterisation of the system

In order to verify the calculations in the previous sections and to determine the characteristics of the spectrograph system, a number of Rayleigh, Raman, and Thomson scattering measurements were done. First only one spectrograph was used for measurement of, among other things, the instrumental profile. Subsequently, the TGS characteristics (e.g. the DGF filter profile) were determined. This section gives an overview of the measured performance of the experimental system.

3.5.1 A single spectrograph

Fig. 3.23 shows a CCD image of a spatially resolved Thomson scattering measurement on a microwave plasma torch (the Torche à Injection Axiale (TIA), see [26]). Spectral information is plotted along the horizontal axis, and spatial information is given along the vertical axis. The lines on the top and bottom of the CCD image are rotational Raman
scattering lines of air. The nozzle of the plasma torch is in the centre of the image; there are no molecules (and hence no Raman scattering) in the plasma volume. The plasma has a strongly hollow structure, which can be seen from the fact that there are two plasma filaments (where Thomson scattering is observed). A rectangular area in the centre of the CCD is darkened in order to block the relatively intense stray light and Rayleigh scattered radiation.

Fig. 3.24: The instrumental profile of a single spectrograph, measured with Rayleigh scattering on argon. The bandpass is $\Delta \lambda_{\text{bp}} = 0.22$ nm, as expected if image aberrations play only a modest role.

The instrumental profile of a single spectrograph is shown in Fig. 3.24. It consists roughly of three parts. The central part is mainly the result of the 250 $\mu$m entrance slit. This determines the bandpass $\Delta \lambda_{\text{bp}} = 0.22$ nm of the spectrograph. The wings just outside the central part are mainly caused by cross-over effects in the CCD camera\textsuperscript{11}. They limit the dynamic range of adjacent pixels. The much fainter wings on the outside of the spectrum are due to both the iCCD camera and redistribution by the spectrograph. The measured redistribution level at 0.75 nm from the centre is about $2 \cdot 10^{-2}$ nm$^{-1}$, of which about $1 \cdot 10^{-3}$ nm$^{-1}$ can be attributed to the spectrograph (see Section 3.5.2). The latter is the dominant factor for stray light rejection.

The transmission $T_s \approx 25 \pm 5\%$ of the single spectrograph was measured by Rayleigh scattering on argon. The transmission and efficiency specification of the optical elements in front of and inside the spectrograph\textsuperscript{12} suggest a transmission of about 41%. The factor of approximately 1.6 that is missing could not be explained with the present knowledge of experimental parameters; it could be caused by a lower iCCD quantum efficiency than specified, or a lower laser power than was measured by the power meter that was used. Other possibilities are a slight misalignment, or an inaccuracy of the specified transmissions.

\textsuperscript{11} These wings are strongly reduced by placing a mask in the centre of the spectrum, indicating that the wings are indeed produced by the CCD camera rather than the spectrograph.

\textsuperscript{12} Four lenses (98% each), four flat mirrors (90%), a grating (70% in first order), and a polariser (97%).
Fig. 3.25: Rotational Raman scattering spectrum of nitrogen using a 250 µm (left) and 50 µm entrance slit (right). With the latter, each Raman line can be resolved individually.

Fig. 3.26: A Thomson spectrum of the TIA plasma at 600 W using argon. The integration time is 10 seconds.

of the optics. The detection limit that is expected from this transmission (cf. Section 3.4) is approximately \( n_{\text{det}} \approx 3.7 \cdot 10^{17} \text{ m}^{-3} \).

The optimal spectral and spatial resolutions that can be obtained are about 85 µm and 0.06 nm respectively. They are limited by the resolution of the CCD camera (around 85 µm) rather than by image aberrations. Under normal experimental conditions, however, the spectral resolution is determined at 0.22 nm by the entrance slit.

Fig. 3.25 shows rotational Raman scattering spectra of nitrogen measured with 250 µm and 50 µm entrance slits. The spectra are corrected for the background of redistributed stray light and Rayleigh scattered radiation. The intensity of this spectrum corresponds to the intensity that is expected from the intensity of Rayleigh scattering and the cross sections given in Chapter 2. The dispersion of the spectrograph measured with these Raman spectra is 1.52 mm/nm, as was calculated in Section 3.3.3.

In Fig. 3.26 a Thomson spectrum of the TIA plasma is shown. The integration time is 10 seconds. The noise level on this spectrum is mainly determined by statistical noise, so
that it is given by Eq. 3.25. Hence, the noise level can be used to estimate the detection limit. The noise is around 50 counts, and the 1/e height of the spectrum is around 250 counts; the signal-to-noise ratio is 5. The electron density in the TIA plasma is about $n_e \approx 10^{21} \text{m}^{-3}$ [12]. Thus, the detection limit (where the signal-to-noise ratio is two) of this measurement is a factor of $(5/2)^2$ lower, i.e. about $1.7 \cdot 10^{20} \text{m}^{-3}$. Using $4 \times 4$ binning and an integration time of 300 seconds, the detection limit can be lowered to $n_{e,\text{det}} \approx 3.5 \cdot 10^{17} \text{m}^{-3}$. This is comparable to the value deduced above from the transmission of the spectrograph.

### 3.5.2 The Triple Grating Spectrograph (TGS)

The filter profile of the DGF can be measured by a tunable laser. However, a much more convenient method is by changing the mask position in the DGF; the position of the mask is related to a wavelength by the dispersion of the first spectrograph. Provided that vignetting effects in the spectral direction are negligible over the range of the notch profile, this method yields the same result as a direct measurement. The left hand side of Fig. 3.27 shows the measured DGF filter profile with 250 µm slits and a 1 mm mask.

The filter profile may be calculated from the single spectrograph instrumental profile according to Eq. 3.9. If this is done directly with the measured single spectrograph instrumental profile, this results in a notch depth that is much less than the measured one. The reason of this discrepancy is that the iCCD camera also influences (deteriorates) the measured instrumental profile. In order to get around this problem, the instrumental profile was simulated. This simulation is based on the convolution of a block profile (the entrance slit), a Gaussian profile (image aberrations), and a Lorentzian (the grating). The spectral half widths of these contributions are taken 0.20 nm, 0.05 nm, and 4 pm respectively. The latter follows from the resolving power of the grating, which is determined by the number of illuminated grooves. The right hand side of Fig. 3.27 compares the measured and simulated single spectrograph instrumental profiles. The difference between these profiles is attributed to the iCCD camera. Thus, the stray light redistribution level (see Section 3.3.1)
Fig. 3.28: Measured filter profiles of the DGF with 250 µm slits and different mask sizes (left), and the measured and simulated transmissions at λᵢ for various mask widths (right).

of the single spectrograph ranges from around $10^{-3}$ nm⁻¹ at $\Delta \lambda = 0.8$ nm from the laser wavelength to $10^{-2}$ nm⁻¹ at $\Delta \lambda = 0.3$ nm.

The DGF filter profile that follows from the simulated instrumental profile is also shown in this figure. The calculation of this profile is done with $\Delta \lambda_{\text{exit}} = 0.22$ nm and $\Delta \lambda_{\text{mask}} = 0.66$ nm, which follow from the exit slit and mask widths and the dispersions produced by both spectrographs of the DGF. The instrumental profile of the second spectrograph does not include a block profile, and the spectral width of the Gaussian is taken slightly broader to account for the difference in the horizontal magnification factors caused by both gratings. The measured transmission at the central wavelength, $F(\lambda_i)/T_d \approx 3 \cdot 10^{-6}$, is reproduced quite well by the simulation. However, the shape of the calculated profile in the centre of the notch is a bit different from the measured profile, which is slightly asymmetric. This difference may be caused by imperfections of the optics, alignment, or the model. Nevertheless, it is clear that the approach of Section 3.3.2 can predict the filter profile and rejection factor fairly accurately.

The wings of the filter profile determine the spectral range in the recorded spectrum that is affected significantly by the DGF. The half width of the filter profile is roughly the spectral width $\Delta \lambda_{\text{mask}}$ associated with the mask; the 98% width is approximately $\Delta \lambda_{\text{mask}} + \Delta \lambda_{\text{bp}}$, where $\Delta \lambda_{\text{bp}}$ is mainly determined by the entrance slit of the TGS. The distance from the laser wavelength at which the DGF does not significantly distort the Thomson scattering spectrum, given by the half 98% width $\Delta \lambda_{98}$, determines the minimum electron temperature that can be measured with the system. For a reliable fit to the measured spectrum, an electron energy of about $\frac{1}{2} k_B T_e$ must be detectable. This is the case when $\Delta \lambda^2_{1/e} = \frac{1}{2} \Delta \lambda^2_{98}$, so that, for the experimental conditions in this work, the lowest detectable electron temperature is approximately (cf. Eqs. 2.32 and 2.33):

$$T_{e, \text{min}} \approx 1.05 \cdot 10^4 \cdot \Delta \lambda^2_{98}, \quad (3.28)$$

where $\Delta \lambda_{98}$ is given in nm. For the filter profile shown in Fig. 3.27 we have $\Delta \lambda_{98} = 0.44$ nm, which results in $T_{e, \text{min}} \approx 2 \cdot 10^3$ K = 0.17 eV. The effective stray light redistribution at
The experimental system for laser scattering

Fig. 3.29: Left: measured filter profiles of the DGF with a 1 mm mask using different slit widths. Right: the filter profile for a 250 µm entrance slit and different exit slit widths.

$\Delta \lambda_{98}$ from the laser wavelength is $R_{\text{eff}} \approx 7 \cdot 10^{-9} \text{ nm}^{-1}$, which is the result of the final single spectrograph in the TGS ($3 \cdot 10^{-3} \text{ nm}^{-1}$), the DGF (a factor $3 \cdot 10^{-6}$), and the polariser in front of the iCCD detector (50–75%).

The filter profile, and hence $\Delta \lambda_{98}$, $R_{\text{eff}}(\Delta \lambda_{98})$, and $T_{\text{e,min}}$, depends on the size of the stray light mask used in the DGF. Fig. 3.28 shows the measured filter profile for a number of different mask widths. Clearly, a broader mask results in a wider but deeper notch profile. The right hand side of Fig. 3.28 compares calculated and measured stray light transmissions of the filter. The transmissions predicted by the model mentioned above are quite well in agreement with experimental values for narrow masks, but the model suggests a better rejection for wider masks. The reason that this is not observed may be that far from the central wavelength the instrumental profile is not determined by the Lorentzian shape induced by the grating, but by dust, scratches, and other imperfections of the optics.

Apart from the mask width, the width of the entrance and exit slits of the DGF is important for the filter profile. Usually, both slits are 250 µm wide. However, during measurements for which a long integration time is required, 500 µm slits are more convenient since they allow for a (small) drift of the position of the laser beam. The filter profile for both slit widths is shown on the left hand side of Fig. 3.29. For wider slits, the notch depth decreases slightly. The centre of the profile becomes narrower, but its wings extend to wavelengths further from $\lambda_i$.

The influence of the exit slit on the filter profile is shown on the right hand side of Fig. 3.29. When both the entrance and exit slits have the same width, the second grating in the DGF images stray light that passes the mask next to the exit slit. Therefore, it is logical that for a wider exit slit (or none at all) the stray light rejection deteriorates. The change in the shape of the profile is due to the increased influence of the Lorentzian contribution in the instrumental profile; this is reproduced by the model as well.

Table 3.5 summarises the half 98% widths $\Delta \lambda_{98}$ of the filter profile, the effective redistributions $R_{\text{eff}}(\Delta \lambda_{98})$ at $\Delta \lambda_{98}$ from the laser wavelength, and the lowest detectable electron temperature for various mask and slit widths in the TGS.
Table 3.5: TGS performance characteristics for various mask and slit widths.

<table>
<thead>
<tr>
<th>slit width</th>
<th>250 µm</th>
<th>500 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>mask width</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 mm</td>
<td>0.28</td>
<td>0.55</td>
</tr>
<tr>
<td>1.0 mm</td>
<td>0.44</td>
<td>0.27</td>
</tr>
<tr>
<td>2.0 mm</td>
<td>0.77</td>
<td>0.77</td>
</tr>
</tbody>
</table>

The optimal spatial and spectral resolutions of the TGS are approximately about 100 µm and 0.07 nm respectively. This is the result of both the resolution of the CCD camera and image aberrations (cf. the ray trace experiments in Section 3.3.4). During experiments the entrance slit limits the spectral resolution to about 0.22 nm.

Vignetting by the lenses inside and in front of the TGS causes the transmission of the system to decreases towards the edge of the field of view (cf. Fig. 3.16). Vignetting in spatial direction (i.e. for various positions along the detection volume) was measured by Rayleigh scattering on air, see Fig. 3.30. The efficiency of the system at the edge of field of view is only about 50% of that on the optical axis. As stated in Section 3.3.3, a decrease of about 22% can be attributed to the six lenses inside the TGS. Taking into account the two extra lenses in front of the spectrograph, which image the detection volume onto the entrance slit, the expected transmission at the edge of the field of view is 71%. The measured value (50%) is significantly lower, which might be caused by the other elements, such as the image rotator, in the optical path. Vignetting in spatial direction is accounted for in the measurements since it also occurs in calibration measurements.

Vignetting in spectral direction is much less pronounced, since firstly only three of the eight lenses contribute to this effect, and secondly the gratings produce a much narrower beam in the spectral direction than in the spatial direction. Therefore, vignetting in spectral direction is neglected in this work.

The absolute transmission of the TGS, which is measured with Rayleigh scattering on argon, is as low as approximately 0.25%. This is a factor of about 100 lower than that for a
The experimental system for laser scattering

single spectrograph. The use of two more gratings and four more lenses accounts for a factor of 2.2. An additional factor of 1.12 is due to the redistributions of both spectrographs in the DGF (cf. Eq. 3.8). The factor of about 40 that is missing in this calculation turned out to be caused by the two extra gratings that were used in the TGS. Each of those gratings had an efficiency of only 10-12% rather than the specified 70%. This severely affects the detection limits calculated in section 3.4: they all rise with a factor of 40. Measurements that were done in half an hour could have been done in less than a minute if the gratings did not show this problem. These gratings will be replaced in the near future.

References

Chapter 3


Chapter 4

The relation between internal and external parameters of a spectrochemical ICP

Abstract

The excitation kinetics in a spectrochemical plasma are governed by the electron density $n_e$, electron temperature $T_e$, and heavy-particle (gas) temperature $T_h$. Therefore, knowledge of these “internal” plasma parameters is important for an understanding of the relation between the sample concentration in the plasma and light emission. Because of the small size of the plasma, the internal plasma parameters are related rather directly to the “external” operational parameters of the plasma, such as the plasma dimensions, power density, and pressure. This relation is established by the various particle and energy balances, and can be used to estimate the internal plasma parameters and predict trends for a change in the operational parameters. In this chapter, this approach was applied to spectrochemical inductively coupled plasmas under various gas-flow, gas-composition, and plasma-power conditions, and validated by Thomson scattering experiments. The measured values and trends of the internal plasma parameters are in close agreement with those expected on the basis of the operational parameters of the plasma.

M.J. van de Sande, P. van Eck, A. Sola, and J.J.A.M. van der Mullen. Accepted for publication in Spectrochim. Acta B.
4.1 Introduction

Atomic Emission Spectroscopy (AES), or plasma emission spectroscopy, is a common technique to determine the atomic composition of a sample. The sample, which may be solid (powder), liquid (often a nebulised aqueous solution), or gaseous, is injected into a plasma. The plasma serves to vaporise, excite, and ionise sample atoms. These atoms subsequently start to radiate and allow the sample composition to be derived from the plasma radiation spectrum. A wide variety of plasmas is used for this purpose. Nevertheless, the most established plasma source in this area is undoubtedly the Inductively Coupled Plasma (ICP) [1].

Free electrons in such a plasma play an key role in Ohmic power dissipation, and can reach a high temperature in this way. Therefore, electron collisions are important for excitation and ionisation processes and heat transfer to heavy particles. The temperature of these heavy particles determines the ability to dissociate and vaporise samples. Hence, the excitation power and the relation between sample concentrations and light emission (the Concentration-Emission Relation, CER) of the plasma are strongly related to the “internal” plasma parameters, such as the electron density $n_e$, the electron temperature $T_e$, and the heavy-particle (gas) temperature $T_h$. The CER also depends on equilibrium departures, but these are reflected in $n_e$, $T_e$, and $T_h$ as well [2]. Obviously, knowledge of the internal plasma parameters is essential for plasma emission spectroscopy.

One of the most reliable and non-intrusive methods to measure $n_e$ and $T_e$ is laser Thomson scattering. Accurate methods to measure $T_h$ are Rayleigh scattering and diode laser absorption. These techniques were applied in previous studies of the spectrochemical ICP [3–9]. A major drawback of such techniques is their experimental difficulty and often costly instrumentation. Passive spectroscopic techniques, such as absolute line intensity measurements, are easier and less expensive, but interpretation of the results is not straightforward for plasmas that are not in Local Thermodynamic Equilibrium (LTE).

In industrial or processing environments, accurate plasma diagnostic techniques are often not available at all, and more global monitoring techniques are required. Because of the small size of the plasma, the surroundings have a large influence on the plasma. Therefore, the internal plasma parameters are related rather directly to the “external” operational parameters, such as the dimensions of the plasma, the power density $\varepsilon$, and the pressure $p$ [2,10]. This relation is established by the particle and energy balances of the heavy particles and free electrons in the plasma. Therefore, these balances can be used to estimate the internal plasma parameters and their trends from the operational parameters. Although this is not enough for a complete characterisation of the plasma and its spectrochemical properties, it can provide valuable information in the absence of better diagnostic techniques or for plasmas that are less accessible.

The aim of this study is to show that the internal plasma parameters can be estimated rather accurately from the external operational parameters, and to validate this method with Thomson scattering experiments on a spectrochemical ICP. Section 4.2 gives a short overview of the experimental arrangement we used. This arrangement employs an intensified CCD camera that facilitates measurements with simultaneous spatial and spectral
resolution, and hence strongly reduces the measurement time and positioning and stability problems. The various particle and energy balances, and the relation between internal and external parameters are investigated and applied to the ICP in Section 4.3. Section 4.4 presents measurements of \( n_e \) and \( T_e \) for various gas flows, gas compositions, and plasma powers, and shows how trends in these parameters can be predicted by the electron particle and energy balances. Conclusions are drawn in Section 4.5.

4.2 Experimental method

Thomson scattering is scattering of (laser) photons on free electrons in a plasma \([11–13]\). The relation between the scattering intensity \( I_T \) that is detected in an experiment and the electron density \( n_e \) is given by

\[
I_T \propto n_e \cdot \frac{1}{1 + \alpha^2}, \quad (4.1)
\]

where the scattering parameter \( \alpha \) represents the degree of coherence of scattered radiation. It is given by

\[
\alpha = \frac{1}{k\lambda_D} = \frac{1}{4\pi \sin(\theta/2)} \cdot \frac{\lambda}{\lambda_D}, \quad (4.2)
\]

where \( k = 4\pi \sin(\theta/2)/\lambda_i \) is the length of the scattering vector \( \mathbf{k} \), \( \theta \) the angle between incident and scattered radiation, \( \lambda_i \) the wavelength of incident radiation, and \( \lambda_D \) the Debye shielding length, given by \( \lambda_D = \sqrt{\frac{\epsilon_0 k_B T_e}{e^2 n_e}} \), in which \( \epsilon_0 \) is the electric constant, \( k_B \) the Boltzmann constant, and \( e \) the elementary charge.

The proportionality constant in Eq. 4.1 is determined by the laser power, the length of the detection volume, the solid angle of detection, and the sensitivity of the detection branch. The absolute electron density can be found by comparing the measured Thomson scattering intensity to the intensity \( I_R \) produced by Rayleigh scattering on argon with a known density \( n_{Ar} \). In terms of these intensities, the electron density \( n_e \) is

\[
n_e = n_{Ar} \cdot \frac{I_T}{I_R} \cdot \frac{1 + \alpha^2}{147}, \quad (4.3)
\]

where the factor 1/147 is the ratio of the cross sections of Rayleigh scattering on argon and Thomson scattering at a wavelength of \( \lambda_i = 532 \text{ nm} \) \([14]\).

The shape of the Thomson spectrum is determined by Doppler broadening by the electrons and by coherent effects. Therefore, this spectrum can be used to determine both \( T_e \) and \( \alpha \) \([11,13,15]\); the latter is required to determine \( n_e \) (cf. Eq. 4.3).

The experimental arrangement used for Thomson scattering is shown schematically in Fig. 4.1. The laser beam is produced by a frequency doubled, pulsed Nd:YAG laser \( (\lambda_i = 532 \text{ nm}) \) with a pulse energy of about 400 mJ and a pulse repetition rate of 10 Hz. The beam is focused into the detection volume by a lens of 1 m focal length. Two additional lenses \((f = 0.6 \text{ m})\) collect scattered radiation and image the detection volume onto the entrance
Fig. 4.1: Schematic overview (not to scale) of the Thomson scattering system that was used to determine the electron density and temperature in the ICP. A 90° image rotator consisting of three mirrors aligns the image of the horizontal laser beam with the vertical entrance slit of a spectrograph for spatially resolved measurements. The spectrograph employs a 1180 grooves/mm concave holographic grating that is corrected for astigmatism. An intensified CCD detector detects the scattered radiation.

slit of a spectrograph. The spectrograph, which disperses the scattered radiation, uses a concave holographic grating with 1180 grooves/mm. Its dispersion is about 1.8 mm/nm and the spectral resolution is around 0.15 nm. The solid angle of detection is $5.76 \times 10^{-3}$ sr ($f/11.6$). A two-dimensional intensified CCD camera records the Thomson spectra.

A 90° image rotator, consisting of three plane mirrors, is placed in front of the spectrograph to align the image of the horizontal laser beam to the vertical entrance slit of the spectrograph. In this way, each point along the laser beam corresponds to a point on the entrance slit of the spectrograph, and spatial resolution can be obtained in a single measurement.

The image of the ICP is demagnified by a factor of 1.3 in order to match the diameter of the image of the ICP to the height of the CCD chip. In this way, a lateral electron density and temperature profile is obtained in a single measurement (typically a few minutes), which strongly reduces the measurement time and problems with the stability and positioning of the plasma.

The height of the detection volume ($z$ direction in Fig. 4.2) is determined by the diameter of the laser beam (0.2 mm), since the entrance slit (0.25 mm) is wider than the laser beam. The “depth” of the detection volume in the direction of the detection branch is also determined by the laser beam. There are no significant gradients in that direction, since the laser beam is directed through the centre of the plasma in radial direction. The length of the detection volume along the laser beam, and hence the resolution in radial direction
Fig. 4.2: Typical iCCD image from which the electron density and temperature at various positions in the plasma can be determined. The horizontal and vertical axes correspond to the wavelength and the position along the laser beam respectively. The centre of the iCCD camera is darkened to block the intense Rayleigh and stray light peak. This picture clearly shows the hollow electron density structure of the ICP; in the centre of the plasma (at \( r \approx 0 \) mm) the scattering spectrum is less intense than in the active zones (\( r \approx \pm 5 \) mm).

The ICP plasma we use in the major part of the present study is powered by a 100 MHz Radio Frequency (RF) generator that consumes up to 2.1 kW from its power supply. Due to the limited generator efficiency, only about 50\% of this power is converted into RF power and dissipated by the plasma. Standard operational conditions are a plasma power
Table 4.1: Standard ICP operating conditions.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torch inner diameter</td>
<td>18 mm</td>
</tr>
<tr>
<td>Load coil</td>
<td>two turns</td>
</tr>
<tr>
<td>RF frequency</td>
<td>100 MHz</td>
</tr>
<tr>
<td>RF power</td>
<td>0.6 kW</td>
</tr>
<tr>
<td>Measurement position</td>
<td>7 mm ALC</td>
</tr>
<tr>
<td>Gas composition</td>
<td>Ar</td>
</tr>
<tr>
<td>Pressure</td>
<td>$10^5$ Pa</td>
</tr>
<tr>
<td>Outer gas flow</td>
<td>12 slm</td>
</tr>
<tr>
<td>Intermediate gas flow</td>
<td>0.3 slm</td>
</tr>
<tr>
<td>Central gas flow</td>
<td>0.6 slm</td>
</tr>
</tbody>
</table>

of 0.6 kW, atmospheric pressure, and argon flow rates of 12 standard litres per minute (slm) for the outer flow channel, 0.3 slm for the intermediate flow, and 0.6 slm for the central flow, see Fig. 4.2. All measurements are performed at 7 mm Above the Load Coil (ALC). These and other relevant standard conditions are listed in Table 4.1. For measurements at different RF powers, an additional ICP operating at 50 MHz was used. This ICP can operate at a higher RF power than the 100 MHz ICP.

4.3 Internal and external plasma parameters

As indicated in Section 4.1, the internal plasma parameters $n_e$, $T_e$, and $T_h$ are important for the excitation power and CER of the plasma. For small plasmas, these parameters are closely related to the external (operational) parameters, such as the plasma’s dimensions, power density $\varepsilon$, and pressure $p$. This relation is dictated by the steady-state particle and energy balances of the heavy particles and free electrons in the plasma [2,10]. In this section the relevant balances under typical ICP conditions (cf. Section 4.2) are discussed, and the internal plasma parameters are estimated on the basis of the operational conditions. In the following we confine ourselves to the region in the plasma where it is *ionising* and diffusion is the main electron loss channel, i.e. where large density gradients occur (see below). This region is designated as the “active” zone.

4.3.1 The steady-state electron particle balance

The steady-state electron particle balance is the balance between ionisation and recombination on one hand and convection and ambipolar diffusion on the other hand:

$$n_1 n_1 S_{\text{ion}} - n_e n_+ \alpha_{\text{rec}} = \nabla \cdot (n_e \mathbf{w}_p) - \nabla \cdot (D_a \nabla n_e),$$

(4.4)

where $n_1$ and $n_+$ are the argon atom and ion ground state densities. $S_{\text{ion}}$ and $\alpha_{\text{rec}}$ are the effective rate coefficients for ionisation and recombination respectively, $D_a$ is the coefficient for ambipolar diffusion, and $\mathbf{w}_p$ the plasma flow velocity.

The diffusion term is commonly written in terms of the gradient length $\Lambda_{n_e}$ of the electron density [2,10,17], which is defined by

$$|\nabla \cdot (D_a \nabla n_e)| \equiv n_e \frac{D_a}{\Lambda_{n_e}^2}.$$  (4.5)
This gradient length can be regarded as the typical length scale over which the electron density varies. In case of an exponential density profile it equals the 1/e length; in the centre of a Gaussian profile it equals $\Delta x_{1/e}/2\sqrt{2}$, where $\Delta x_{1/e}$ is the 1/e width of the profile. The gradient length is strictly spoken not directly an operational parameter, but it is determined by various external circumstances, such as the quartz torch dimensions, gas flow pattern, and electromagnetic field configuration. It can be estimated from the plasma geometry (as shown below) or from, for instance, a spectral line intensity profile. The ambipolar diffusion coefficient, which depends on $T_e$ and $T_h$, was calculated on the basis of the ion-atom collision integral by Devoto et al. [18, 19]. In the range $5400 < T_e < 13800$ K and $2000 < T_h < 7000$ K, these calculations are reproduced within 10% by the fit

$$D_a \approx 1.81 \cdot 10^{-11} \cdot (5864 + T_e) \cdot T_h \text{ [m}^2\text{s}^{-1}],$$

(4.6)

where $T_e$ and $T_h$ are given in K. For typical ICP parameters, $T_h \approx 4000$ K and $T_e \approx 8000$ K (see below), we have $D_a \approx 1 \cdot 10^{-3}$ m$^2$s$^{-1}$.

Convection is the result of the flow velocity of the plasma. In the same way as the diffusion term, a characteristic length $h_p$ over which this flow velocity varies can be defined. In terms of this length, the convection term can be written as

$$|\nabla \cdot (n_e w_p)| \equiv n_e \frac{w_p}{h_p};$$

(4.7)

where $w_p$ is the flow velocity of the plasma. As shown below, in the active zone of the ICP convection usually plays only a modest role compared to diffusion. In order to keep the discussion simple, this term is neglected in further calculations.

The ionisation term is governed by the effective ionisation rate coefficient $S_{\text{ion}}$. Because the thermal electron energy $k_B T_e$ in the ICP plasma is small compared to the ionisation energy of argon (15.76 eV), stepwise ionisation is much more important than direct ionisation. In addition, due to a sufficiently high electron density, the probability of further excitation of excited states is much larger than that of radiative decay. Therefore, $S_{\text{ion}}$ approximately equals the rate coefficient $K_{1,2}$ for excitation from the ground state to the first excited state [2, 10, 17]. This rate coefficient can be determined from a Collisional Radiative Model (CRM) of argon [2, 20] and can be cast in an Arrhenius form,

$$S_{\text{ion}}(T_e) \approx K_{1,2} \approx 6.81 \cdot 10^{-17} \sqrt{T_e} \exp \left( -\frac{E_{1,2}^*}{k_B T_e} \right) \text{ [m}^3\text{s}^{-1}],$$

(4.8)

where $E_{1,2}^* = 12.06$ eV is the effective excitation energy of the first excited state.

The recombination term, with the rate coefficient $\alpha_{\text{rec}}$, can be calculated with the same CRM. It can also be estimated from the overpopulation of the ground state with respect to Saha equilibrium. For plasmas with a sufficiently high electron density, such as the ICP, radiation losses are small. Therefore, in Saha equilibrium the recombination and ionisation rates are approximately equal, $n_e n^S_{\text{ion}} \approx n_e n_p^{1} \alpha_{\text{rec}}$, where $n^S_1$ is the ground state density in Saha equilibrium, which depends on $n_e$ and $T_e$. When the plasma is not in
Saha equilibrium, the ratio of the ionisation and recombination rates can be approximated by

\[
\frac{n_e n_1 S_{\text{ion}}}{n_e n + \alpha_{\text{rec}}} \approx \frac{n_1}{n_1^3} \equiv b_1,
\]

where \(b_1\) is the ground state overpopulation with respect to Saha equilibrium. The \(b_1\) parameter can be calculated from \(n_e, T_e,\) and \(T_h.\) Since we confine ourselves to the ionising part of the plasma, \(b_1 \gg 1,\) and recombination is negligible compared to ionisation.

Neglecting convection and recombination, we can state that ionisation is balanced by the diffusive efflux of charged particles, and the electron particle balance simplifies to

\[
n_1 S_{\text{ion}}(T_e) = \frac{D_a}{\Lambda_{n_e}^2}.
\]

Thus, the electron particle balance relates the electron temperature \(T_e\) to the size (gradient length \(\Lambda_{n_e}\)) of the plasma; a short gradient length results in a large diffusive flux, and to sustain the plasma the ionisation rate must be high, which requires a high electron temperature.

With Eqs. 4.6 and 4.8, and \(n_1 \approx p_0/(k_B T_h),\) where \(p_0 = 10^5\) Pa is the pressure, Eq. 4.10 can be written as

\[
\exp\left(\frac{E_{12}^*}{k_B T_e}\right) = 2.76 \times 10^{22} \cdot \frac{\Lambda_{n_e}^2}{T_h^5} \cdot \frac{\sqrt{T_e}}{5864 + T_e}.
\]

In the range \(3000 < T_e < 13000\) K, the right hand side of Eq. 4.11 is only weakly dependent on \(T_e;\) the last factor varies less than 5% around \(6.3 \times 10^{-3}.\) Thus, for various ICP conditions, the electron temperature can be related to the gradient length and heavy-particle temperature via

\[
\frac{k_B T_e}{E_{12}^*} = \frac{1}{46.6 + 2 \ln \Lambda_{n_e} - 2 \ln T_h}.
\]

### 4.3.2 The steady-state electron energy balance

The steady-state electron energy balance is the balance between electrons dissipating energy from the RF field and losing energy by inelastic and elastic collisions with other particles. In a simplified form it reads

\[
\frac{P}{V} \equiv \varepsilon = n_e n_1 S_{\text{ion}} I + n_e n_1 S_{\text{heat}} \cdot \frac{m_e}{M} \cdot 3 k_B (T_e - T_h),
\]

where \(P\) is the power dissipated in the plasma, \(V\) the plasma volume, \(I = 15.76\) eV the ionisation energy of a ground state argon atom, \(m_e/M\) the mass ratio of an electron and an argon atom, and \(S_{\text{heat}}\) an effective rate coefficient for heat transfer. Other terms that may be included in Eq. 4.13 are recombination and radiative losses. These terms can be neglected as long as we confine ourselves to the ionising plasma region. An additional loss term due to inelastic collisions with molecules can be seen as an enhancement of the elastic collision term (see Section 4.4.3).
The inelastic collision term is represented by the first term at the right hand side of Eq. 4.13. If radiative energy losses and heating of the produced electrons can be neglected, it equals the effective ionisation rate times the ionisation energy. Clearly, this term is strongly related to the electron particle balance.

The elastic collision term, represented by the second term at the right hand side of Eq. 4.13, describes cooling of the electrons by the colder atoms and ions. Here

\[ S_{\text{heat}} = \left( k_{\text{ea}} + \frac{n_+}{n_1} k_{\text{ei}}^m \right) \approx 1.9 \cdot 10^{-14} \text{ m}^3 \text{ s}^{-1}, \]

with \( k_{\text{ea}} \) and \( k_{\text{ei}}^m \) the rate coefficients for momentum transfer from electrons to neutral atoms and ions respectively. For simplicity we take \( S_{\text{heat}} \) constant since it is only weakly dependent on the plasma parameters \( n_e, T_e \), and \( T_h \) (via \( n_1 \)). According to the rate coefficients \( k_{\text{ea}} \) and \( k_{\text{ei}}^m \) obtained from experimental data of collision cross sections for momentum transfer (averaged over a Maxwellian EEDF) \([21,22]\), it varies less than 10% for \( 3000 < T_h < 5000 \text{ K} \) and \( 7000 < T_e < 10000 \text{ K} \), and less than 35% for \( 10^{19} < n_e < 10^{21} \text{ m}^{-3} \).

Thus, the electron energy balance relates the electron density \( n_e \) to the power density \( \varepsilon \) of the plasma, given \( T_e \) and \( T_h \) conditions; generally, a high \( \varepsilon \) can account for the large energy losses associated with a high \( n_e \).

From Eq. 4.13 it is clear that \( \varepsilon \) and \( n_e \) are roughly proportional (provided that the elastic and inelastic collision rate coefficients do not change considerably); maintaining more electron-ion pairs in the plasma requires more energy. As shown in Section 4.4.4, this was found to be the case in the ICP. For microwave discharges, this proportionality is expressed in a quantity \( \theta \), the power lost per electron in collisions of all kinds \([23]\). For given external conditions, this quantity is found to be rather constant within a plasma \([24]\), but it is strongly dependent on, for instance, the gas composition and pressure.

### 4.3.3 The steady-state heavy-particle energy balance

The steady state heavy-particle energy balance is the balance between heavy-particle heating by elastic electron collisions and convective heat loss. The elastic collision (heat transfer) terms in the heavy-particle and electron energy balances (cf. Eq. 4.13) are equal, although they represent respectively a source and loss term in these balances. In the electron energy balance, this term is dominant over the ionisation term for a wide range of electron and heavy-particle temperatures \( T_e < 11000 \text{ K}, T_h < 8000 \text{ K}, \) and \( T_h < T_e \). Therefore, it can be assumed that all dissipated RF power is converted into heat. In that case, the heavy-particle energy balance simplifies to

\[ \langle T_h \rangle \approx T_0 + \frac{P}{\Phi \rho c_p}, \]

where \( \langle T_h \rangle \) is the average heavy-particle temperature, \( P \) the dissipated power, \( c_p \approx 520 \text{ J kg}^{-1} \text{ K}^{-1} \) the heat capacity of argon, \( \rho \approx 1.79 \text{ kg m}^{-3} \) the mass density at room
temperature, and $\Phi$ the total argon flow at room temperature. $T_0$ is the temperature of the gas before entering the plasma, which we can take $T_0 \approx 300$ K. It should be noted that the temperature in the active zones of the plasma may be somewhat higher than this average temperature.

4.3.4 Application to the ICP

The theory presented above is a method to estimate the internal plasma parameters from the external operational parameters. In this section this is applied to the ICP under standard conditions. We confine ourselves to the active zone of the plasma, where the electron particle balance applies in the simple form of Eq. 4.10.

For typical ICP parameters at 7 mm above the load coil and off the plasma axis the plasma is ionising since $b_1 \approx 10 - 20$ [2]; this follows from the measurements presented below and results of previous studies [4,6]. In addition, as argued below, diffusion is more important than convection in the electron particle balance. Therefore, this position in the plasma is within the active zone.

The average heavy-particle temperature follows from Eq. 4.15 and the RF power dissipated by the plasma. A power of $P = 0.6$ kW and total argon flow of $\Phi \approx 13$ slm yield $\langle T_h \rangle \approx 3.3 \cdot 10^3$ K. The temperature in the active zones of the plasma is expected to be somewhat higher. This is confirmed by measurements in previous studies [4,7], which report temperatures of approximately 20% higher compared to the temperatures predicted by Eq. 4.15 for various plasma powers. For further calculations we have taken $T_h = 4.0 \cdot 10^3$ K.

In order to apply the electron particle and energy balance balances to the ICP, estimates of the power density $\varepsilon$ and the gradient length $\Lambda_{ne}$ are required.

The power dissipated by the plasma is approximately $P \approx 0.6$ kW, and the volume in which this power is dissipated is $V \approx 10^{-5}$ m$^3$. This results in a power density of $\varepsilon \approx 6 \cdot 10^7$ W m$^{-3}$.

The gradient length $\Lambda_{ne}$ in the active zone can be estimated from the hollow shape and the size of the plasma. As diffusion takes place mainly in radial direction, the $n_e$ profile in radial direction must be considered. In the centre of the active zone, this profile may be approximated by a Gaussian whose $1/e$ width is approximately $\Delta r_{1/e} \approx R/2$, where $R \approx 8$ mm is the plasma radius. This results in a gradient length $\Lambda_{ne} = \Delta r_{1/e}/2\sqrt{2} \approx 1.4$ mm. The $n_e$ profiles shown in Section 4.4 suggest that this is a reasonable value.

In the active zone, convection mainly takes place in axial direction. Therefore, the characteristic length $h_p$ over which the flow velocity varies is approximately the height of the plasma, $h_p \approx 6$ cm. The (axial) flow velocity in the active zone of the plasma is approximately $w_p \approx 10 - 12$ m s$^{-1}$. The relative importance of convection compared to diffusion can be determined from $h_p$, $w_p$, $\Lambda_{ne}$, and $D_a$, which follows from $T_e$ and $T_h$ according to Eq. 4.6. For $4000$ K $\approx T_h < T_e$, the convection term in Eq. 4.4 is smaller (typically a factor three to four) than the diffusion term. Therefore it plays only modest
role, and Eq. 4.10 is a reasonable approximation\(^1\).

With the values of \(\varepsilon, T_h,\) and \(\Lambda_n\) estimated above, the electron particle and energy balances (Eqs. 4.12 and 4.13) predict \(n_e \approx 7.6 \cdot 10^{20} \text{ m}^{-3}\) and \(T_e = 8.3 \cdot 10^3 \text{ K}\). These values agree closely to those reported in earlier studies [4,6] and in the following section.

### 4.4 Results and discussion

Apart from estimates of the internal plasma parameters, the theory presented in the previous section can be applied to understand trends of these parameters for varying plasma conditions or positions in the plasma. In this section, this is shown for the electron temperature and density on the basis of the results of Thomson scattering experiments on the spectrochemical ICP. The ICP was subjected to various operational conditions, e.g. by changing the central flow of the plasma, by introducing a molecular load, or by varying the plasma power.

#### 4.4.1 Comparison with previous results

The electron density and temperature of a spectrochemical ICP were studied elaborately before by, among others, Huang \textit{et al.} [4] and De Regt \textit{et al.} [6]. Fig. 4.3 shows the measured electron temperature and density at 7 mm ALC, and compares them to the results of De Regt, which were done with the same ICP source at 7 mm ALC.

The measured electron density profile agrees fairly well with the results of De Regt, although it is less asymmetric and a bit less hollow. This suggests that our measurements were performed on a slightly higher position ALC. Moreover, day-to-day reproducibility of the flow rates, power, and position of the quartz torch with respect to the load coil may not be perfect.

\(^1\) A more detailed approximation would introduce a dependence of flow velocity into Eq. (4.10).
Fig. 4.4: A rotational Raman spectrum of $N_2$ at room temperature measured by De Regt [6] (left) and in this study (right). Apart from the light detector, the relevant experimental conditions were identical. The weaker background in our spectrum (right) is due to the absence of Rayleigh light scattering off the mask.

The measured electron temperature profile shows a remarkable difference with that measured by De Regt et al. In contrast to their findings we measured that $T_e$ rises towards the plasma edge. In addition, the temperature we measured at other positions in the plasma is about 15% higher.

A possible explanation of the difference in observed electron temperature at the plasma edge in this study and previous work is the strong background spectrum in the work of De Regt [6]. In both previous and present work the Rayleigh background was not corrected for in recorded Thomson spectra. The background in the spectra obtained by De Regt was caused primarily by Rayleigh light scattering off the mask. By reflection on a quartz window in front of the mask, this light could reach the detector area next to the mask. The absence of such a quartz window in the present work results in a much weaker background close to the mask. Fig. 4.4 illustrates this difference by comparing rotational Raman spectra of nitrogen measured in this study and reported in [6]. The large Rayleigh residue increased the intensity of the recorded spectrum mainly in the centre, resulting in a narrower spectral profile. This may, erroneously, be explained as a lower electron temperature. This effect is most pronounced at positions in the plasma where the Thomson spectrum is weak (low electron density) and the Rayleigh scattering intensity is high (low gas temperature, so high gas density), i.e. at the edge of the plasma and, to a lesser degree, in the centre.

Moreover, the electron temperature profiles measured in this work were obtained from a single measurement, so that plasma instabilities and positioning problems are strongly reduced.

A rising electron temperature towards the edge is supported by the electron particle balance. The electron density gradient length decreases towards the plasma edge, leading to a large diffusive efflux of electrons. In addition, as suggested before [2], molecular processes at the edge of the ICP may provide for an efficient additional electron loss channel. These
loss channels in the electron particle balance must be compensated by an increase in $S_{\text{ion}}$ and hence $T_e$ must rise slightly.

More detailed plasma modelling studies of a closed ICP [25] has shown an increase of $T_e$ towards the plasma edge as well. Such an ICP has a similar size, field geometry, operation pressure, and $n_e$ and $T_e$ as the flowing ICP [26]. Therefore, even though the power used in the flowing ICP is much higher since it has a large flow of gas that must be heated, comparing trends in both plasmas seems reasonable.

The electron density profile can be clarified by the electron energy balance. Close to the plasma edge $T_h$ decreases (see [7]), so that $n_1$ increases. At a given power density Eq. 4.13 then predicts a decrease in the electron density. In addition, since electrons are the species that dissipate the RF power from the load coil, the lower electron density at the edge of the plasma implies a (locally) lower power density and hence, again, a lower electron density. In the centre of the ICP the central argon gas flow cools the plasma locally, which leads to a lower electron density in a similar way.

### 4.4.2 Central gas flow

As an example of a different external plasma condition we switched off the central argon flow of the ICP. Fig. 4.5 compares the measured $n_e$ and $T_e$ profiles of the ICP with and without a central argon flow, while all other operational conditions were similar. Clearly, the introduction of a central flow causes a strong decrease of the electron density in the centre of the ICP, and a slight increase in the active zones. A central flow does not affect the electron temperature beyond the experimental error.

The difference in the electron density profile for a plasma with and without central flow can be deduced from the electron energy balance in a similar way as above. Introducing cold argon atoms through the central flow channel gives rise to a decrease of $T_h$ and an increase of $n_1$ in the centre of the plasma. This results in a lower electron density (cf. Eq. 4.13). As the dissipated power density depends on the electron density, a decrease in electron density in the centre causes a redistribution of the power dissipation in the plasma;
the total plasma power is effectively deposited in a smaller volume. As a consequence, the power density in the active zones increases, resulting in a higher electron density in these zones.

The slightly smaller gradient length of the plasma with central flow results in a larger diffusive efflux of electrons. According to the electron particle balance this would lead to a slightly higher electron temperature. However, this is not observed experimentally, which indicates that the increase in diffusive losses is not dramatic if only argon is used in the central channel.

4.4.3 Introduction of a molecular load

During normal operation of a spectrochemical ICP a nebulised aqueous solution is injected into the plasma. As already shown before [4, 27], this strongly affects the electron density in the centre of the plasma. Thomson scattering experiments with a “wet” ICP cannot be performed with a simple nebuliser because of the possibility of hitting a water droplet with the laser beam, which results in an enormous increase in the background signal. The experiments in Reference [4] are done with a central argon flow that is (almost) saturated with water vapour. In the present work the effect of a molecular load on the plasma is studied by introducing a small flow of nitrogen. The energy required to dissociate a nitrogen molecule (9.8 eV) does not differ much from the energy needed to evaporate and dissociate a water molecule (10.1 eV) [28]. Moreover, the ICP can endure similar numbers of nitrogen and water molecules before getting noticeably perturbed. [29]. This suggests that the effect of nitrogen and water molecules on the plasma are comparable. A water load of 2 ml/hour, a typical load in spectrochemistry, corresponds to a gaseous nitrogen load of 20.7 ml/min to the plasma. In the experiments discussed below a nitrogen flow between 0 and 20 ml/min was added to the central argon flow of 600 ml/min.

Fig. 4.6 shows the electron density and temperature of the ICP for various nitrogen flows. Clearly, the electron density in the centre of the plasma drops dramatically upon the introduction of nitrogen into the plasma. The electron temperature rises a bit towards the edge of the plasma, but remains constant in the centre. For high nitrogen flow rates the plasma is confined to the outermost regions of the torch, and finally extinguishes at about 25 ml/min.

The strong decrease of $n_e$ in the centre of the plasma when nitrogen is injected can be attributed to increased losses in the electron energy balance. One mechanism for this is (ro)vibrational excitation of molecules. This is a very efficient process since the excitation rates involved do not carry the unfavourable mass ratio of electrons and heavy particles that is present in elastic collision rates [30]. The excited molecules can subsequently lose their energy to other heavy particles in the form of kinetic energy. Another mechanism that enhances losses in the electron energy balance is dissociation of the nitrogen molecules. Since molecular nitrogen has an ionisation energy close to that of argon (15.76 and 15.6 eV
respectively), Charge Transfer (CT) from argon ions to nitrogen molecules,
\[ \text{Ar}^+ + \text{N}_2 \xrightarrow{\text{CT}} \text{Ar} + \text{N}_2^+ , \]  
(4.16)
is an efficient process. The molecular ions formed in this way are subsequently destroyed by Dissociative Recombination (DR),
\[ \text{N}_2^+ + e \xrightarrow{\text{DR}} \text{N} + \text{N}^* . \]  
(4.17)
In this latter reaction a few eV of energy, depending on the state \( \text{N}^* \), is released in the form of heat [2]. The CT/DR mechanism thus provides an additional channel for energy transfer from the electrons to the heavy particles. Thus, the CT/DR and rovibrational excitation mechanisms may be interpreted as an enhancement of \( S_{\text{heat}} \) in Eq. 4.13, which leads to a decrease in \( n_e \).

The rising electron temperature in the active zones when nitrogen molecules are injected is due to the loss channel in the electron particle balance represented by these molecules. Firstly, the strongly decreased electron density in the centre of the plasma results in a much smaller gradient length, which enhances the diffusive efflux of electrons. Secondly, the DR reaction (Eq. 4.17) directly destroys free electrons. These particle loss channels require a higher ionisation rate and hence a higher electron temperature in the active zones of the plasma. Within the measurement accuracy, the temperature in the centre of the plasma is not affected. This is most likely caused by the high electron heat conductivity in the plasma.

In principle, the increased ionisation rate also leads to a larger loss in the electron energy balance. However, for the argon ICP the ionisation term in the energy balance is small compared to the heat transfer term [2], so that this effect does not play a significant role.

The CT/DR loss channel in the electron energy balance partly owes its efficiency to the CT reaction between argon and nitrogen being quasi resonant. This is not the case for water,
which has an ionisation energy of 12.5 eV, so that the energy losses in a “wet” plasma are presumably a bit slower. In addition, nebulised water droplets have to evaporate first, which also takes time. Hence, close to the load coil the effect of molecules described above might be less pronounced if water rather than nitrogen is injected into the ICP’s central flow channel, but the trend is expected to be the same.

### 4.4.4 Dissipated power

As a final example of the influence of operational parameters on the ICP we varied the RF power to the plasma. Fig. 4.7 shows the behaviour of \( n_e \) and \( T_e \) for various dissipated powers. All measurements were performed at 7 mm ALC and at radial position of 4.5 mm, i.e. in the active zone of the plasma. Two different ICP sources were used for this experiment: the 100 MHz ICP that was used in all other measurements, and a 50 MHz ICP that can operate at a higher power. In the case of the 50 MHz ICP, the forward RF power can be controlled directly. In contrast, for the 100 MHz ICP only the power to the RF generator is known. For this ICP we assume that about 50% of this power is converted into RF power and dissipated by the plasma; this assumption introduces a small error in the data points obtained with this ICP. The plasma geometry and flow conditions are similar for both ICPs. The frequency difference is found not to have a large influence on \( n_e \) and \( T_e \) at the position of the measurement. This is contrary to the findings of Huang et al. [5], but that may be explained by the different RF frequencies and higher plasma power they used and the uncertainty in the power dissipated by one of our ICPs.

Fig. 4.7 shows that the electron density scales approximately linearly with the dissipated power, whereas the electron temperature only increases slowly with increasing power. The electron energy balance makes clear that the electron density is directly proportional to the dissipated power provided that the plasma volume and other terms in Eq. 4.13 do not change significantly. The electron particle balance can explain the (small) rise in electron temperature for higher dissipated power. A higher power results in a higher \( T_h \) (see Eq. 4.15 and Reference [7]). In the particle balance (Eq. 4.10) this leads to a lower \( n_1 \) and higher
Therefore, a higher ionisation rate $S_{\text{ion}}$ and hence higher $T_e$ is required to sustain the plasma (see also Eq. 4.12).

### 4.5 Conclusions

This study describes the use of particle and energy balances for global plasma characterisation and estimations of values and trends of the internal plasma parameters $n_e$, $T_e$, and $T_h$ on the basis of the external operational parameters of the plasma. This approach is validated by Thomson scattering experiments on a spectrochemical ICP.

For measurements of $n_e$ and $T_e$ in the ICP under various plasma conditions, an experimental system for Thomson scattering was built. This setup employs a 2-dimensional intensified CCD camera, which facilitates simultaneous spatial (0.1 mm) and spectral (0.15 nm) resolution. Straylight is blocked efficiently by a mask in front of the detector.

The particle balance of the electrons and energy balances of electrons and heavy particles are used to relate the internal plasma parameters $n_e$, $T_e$, and $T_h$ to the external operational parameters of the plasma, such as the plasma dimensions (electron density gradient length $\Lambda_{n_e}$), power density $\varepsilon$, and operational pressure $p$. In this way, the internal parameters in the active zone of the spectrochemical ICP under standard conditions are estimated at $n_e \approx 7.6 \cdot 10^{20}$ m$^{-3}$, $T_e \approx 8.3 \cdot 10^3$ K, and $T_h \approx 4.0 \cdot 10^3$ K. These values are in close agreement with values reported in previous studies and measured in this work. In addition, trends of $n_e$ and $T_e$ for the different experimental conditions that were studied can be explained by the electron particle and energy balances.

Under standard conditions, the electron temperature of the ICP is found to rise towards the edge of the plasma, contrary to findings of previous work [6]. This may be caused by the rather large stray light residue that was present in the scattering spectra described in Reference [6]. The present detection system was improved on this point, so that it can achieve a higher accuracy at the edge of the ICP (where the electron density is low). In addition, a rising electron temperature towards the edge is supported by the electron energy balance and by more detailed plasma simulations of a comparable closed ICP [25]. Without a central gas flow in the ICP, the plasma becomes less hollow, but the temperature remains the same. A molecular nitrogen load in the central channel of the ICP results in a dramatic decrease in electron density (up to a factor of 20) in the centre of the ICP. At a nitrogen flow of about 25 ml/min, the plasma even extinguishes. The electron temperature increases slightly (less than 15%) when nitrogen is added. An increase in the power dissipated by the ICP results in a proportional rise of the electron density and a small increase ($< 20\%$) of the electron temperature.

With the theory demonstrated in this study, the behaviour of the internal plasma parameters can be estimated on the basis of operational conditions of the plasma. Nevertheless, such a global method will always involve additional estimations or simple spectroscopic methods as well, for instance to determine the relevant length scale $\Lambda_{n_e}$ and the volume $V$ of the active (ionising) plasma zone.
References


Internal and external parameters of a spectrochemical ICP


Chapter 5

The response of electron density and temperature to power interruption of an inductively coupled plasma

Abstract

Elementary production and destruction mechanisms in a plasma can be studied by monitoring plasma behaviour during and after a short interruption of the plasma power. In this work, this technique was applied to a spectrochemical argon Inductively Coupled Plasma (ICP). The electron density $n_e$ and temperature $T_e$ were measured with laser Thomson scattering. Furthermore, the density of entrained air and the heavy-particle temperature at the edge of the plasma were measured by rotational Raman scattering. In the centre of the plasma, the measured temporal development of $n_e$ and $T_e$ can be attributed to ambipolar diffusion, three-particle recombination, and ionisation. In contrast, at the edge of the plasma an additional electron loss process must be involved. In addition, the high electron temperature during power interruption indicates the presence of electron heating mechanisms. The energy gain by recombination processes is shown to be insufficient to explain this electron heating. These discrepancies are most likely due to the formation and destruction processes of molecular argon ions and excimers, which can be present in significant quantities. Because of the low air density in the plasma, air entrainment is not likely to play a significant role.

M.J. van de Sande, P. van Eck, A. Gamero, and J.J.A.M. van der Mullen. To be submitted for publication in Spectrochim. Acta B.
5.1 Introduction

In many cases plasmas can be divided into two zones: a creation (ionising) zone and an application (mostly recombining) zone. In the creation zone the electron temperature $T_e$ is relatively high, so that Electron Excitation Kinetics (EEK) prevail over other excitation mechanisms. In the application zone, Heavy-particle Excitation Kinetics (HEK) become important as well. Such a two-fold structure can also be found in a spectrochemical argon Inductively Coupled Plasma (ICP) [1]. The creation (“active”) zone is the annular area close to the load coil. The application zone, where the created plasma is used for the atomisation, excitation, and ionisation of injected samples (analytes), is located in the centre of the plasma and further downstream in the tail flame. The application zone is influenced by HEK processes, such as Penning ionisation, charge transfer, excitation transfer, and formation and destruction of molecular ions.

As various chemical and physical processes act on different time scales, relaxation techniques are a powerful tool to study these processes. The field of chemical relaxation studies has lead to valuable insights into reaction kinetics. In 1967, this resulted in Manfred Eigen being awarded with the Nobel prize for his work in this field. In plasma science, relaxation can be used to study the various (excitation) mechanisms that play a role in the creation and application zones of the plasma. In addition, this can be a first step in the understanding of transient plasmas.

Plasma relaxation techniques are commonly based on a short Power Interruption (PI) of the plasma. Under normal operation, the power balance of the ICP can be schematised by

$$\text{EM field} \longrightarrow \{e\} \longrightarrow \{h\} \longrightarrow \text{surroundings}. \quad (5.1)$$

The electrons $\{e\}$ in the plasma are heated by the ElectroMagnetic (EM) RF field. This energy is transferred to the heavy particles $\{h\}$ by elastic and inelastic collisions. Further downstream in the ICP, the heavy particles in turn lose their energy to the surroundings. Power interruption implies an interruption of the first step of Eq. 5.1 for a short time (on the order of $50 - 200 \, \mu s$). The response of the plasma to the sudden absence of power input and subsequent re-ignition is based on processes such as cooling, recombination, ionisation, (de-)excitation, and transport, which each have their own temporal development. This response manifests itself in, for instance, light emission by the plasma, which can thus be used to obtain insight in these processes.

Such a plasma relaxation technique was already proposed in the early 1960s by Gurevich et al. [2]. They applied this technique to the positive column of an arc discharge, as did others around 1980 [3, 4]. In the late 1980s, Parisi et al. [5] and Olesik et al. [6] modulated the RF power of a spectrochemical ICP by a sinusoidal and rectangular wave. Farnsworth et al. [7, 8] were able to apply a power modulation of 100% for a short period ($\sim 200 \, \mu s$). The main focus of these studies was to improve the ICP’s detection limits. In addition, these studies primarily dealt with the response of the intensities of spectral lines of the plasma on a ms time scale, i.e. the “delayed” response. The work of Bydder and Miller [9, 10] specifically addressed to the “instantaneous” response of the plasma to power interruption
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(µs time scale). They derived the ratio of the temperatures $T_e$ and $T_e^*$ before and directly after the start of the power interruption from the measured spectral line intensities. It was assumed that the absence of the EM field would cause the temperatures of the electrons and heavy particles to equilibrate, so that $T_e^* = T_h$. In this way, the steady state electron temperature was found to be higher than the heavy-particle temperature, $T_e > T_h$. This is, of course, the result of the power balance given in Eq. 5.1. In the work of Fey et al. [11], the instantaneous and delayed responses were elaborated further. It was found that the delayed response is mainly due to convective transport in the plasma. Hence, this provides a way to determine the velocity field of the ICP [11]. The instantaneous response was found to be due to cooling and recombination effects. These processes can clearly be distinguished because of their different time scales (typically 1 and 150 µs respectively). The power interruption technique was applied to the TIA microwave torch [12] by Timmermans et al. [13]. He found that cooling and recombination both take place on a comparable (short) time scale and cannot be distinguished any more.

The studies mentioned here were all based on the reaction of spectral line intensities to power interruption. However, the reaction of these line intensities is in fact induced by the response of the electron density $n_e$ and temperature $T_e$ to the power interruption. Therefore, monitoring $n_e$ and $T_e$ themselves is a much more direct way to study the instantaneous response of the plasma. In this way, also insight into various electron production and loss processes, such as diffusion, ionisation, and recombination, can be obtained.

The combination of laser Thomson scattering and power interruption for this purpose has already been applied by De Regt [14]. One of the surprising results was that the electron temperature $T_e^*$ during power interruption is significantly higher than the heavy-particle temperature $T_h$. In addition, the decay of the electron density was found to be much faster than can be explained by diffusion and three-particle recombination alone. As the plasma operates at atmospheric pressure in the open air, it was suggested that the mixing of molecules from the surrounding air might provide an additional loss channel for electrons and thus play a role in the short decay time.

In this work, the behaviour of $n_e$ and $T_e$ during power interruption is studied in more detail. In addition, these parameters are followed after re-ignition of the plasma as well. As in the work of De Regt [14], $n_e$ and $T_e$ were measured by Thomson scattering. Because of to the development of a more sensitive detection system with simultaneous spatial and spectral resolution [15], the electron density and temperature along the entire diameter of the ICP can be determined in a single measurement. In addition, by placing only one half of the ICP in the detection volume, scattering by the surrounding air can be measured also. Analysis of the rotational Raman spectra of air measured in the vicinity of the plasma can provide information about $T_h$ and entrainment of air in the plasma.

In Section 5.2, the experimental arrangement used for Thomson and Raman scattering is described briefly. The interpretation of scattering spectra to determinate of $n_e$, $T_e$, $T_h$, and the air density $n_{air}$ is explained. The results of power interruption and air entrainment measurements are presented in Section 5.3 and discussed in Section 5.4. Conclusions are drawn in Section 5.5.
5.2 Experimental method

5.2.1 Thomson scattering and rotational Raman scattering

Scattering of laser light by electrons, atoms, or molecules in a plasma can be used to determine the density and temperature of the various species that are present [16]. In this study scattering by electrons (Thomson Scattering) is used to measure the electron density \( n_e \) and temperature \( T_e \). The density is calibrated absolutely against scattering by argon atoms (Rayleigh scattering). Scattering by nitrogen molecules, accompanied by a transition of the rotational state of the molecule (rotational Raman scattering) is used to determine the air density \( n_{\text{air}} \) in the plasma and the heavy-particle temperature \( T_h \). In this section, a brief outline of the experimental system used in this study is given, and the interpretation of scattering spectra is discussed.

The experimental arrangement used for the laser scattering experiments in this study is shown schematically in Fig. 5.1. The laser beam is produced by a frequency-doubled Nd:YAG laser (wavelength \( \lambda_i = 532 \) nm, pulse energy 400 mJ, repetition rate 10 Hz) and focused into the ICP by a plano-convex lens (\( f = 1 \) m). Scattered radiation is imaged onto the (500 \( \mu \)m wide) entrance slit of a spectrograph that disperses the radiation. The scattering spectrum is recorded by an intensified CCD (iCCD) camera. A 90° image rotator, consisting of three plane mirrors, aligns the image of the horizontal laser beam with the (vertical) entrance slit of a spectrograph, spatial resolution is obtained in a single measurement. For the power interruption measurements, the ICP source and laser are triggered by an external pulse source.
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Fig. 5.2: Typical iCCD images obtained in this study (7 mm ALC). The horizontal and vertical axes represent wavelength ($\lambda$) and radial position ($r$) in the ICP respectively. Thus, a horizontal cross section of the image gives the scattering spectrum at a certain position. The vertical area in the centre of the image is darkened by a mask in order to block Rayleigh scattered light and stray light, which are both located at the laser wavelength. Left: the complete width of the ICP is imaged onto the camera. The hollow structure of the plasma is expressed in the weaker intensity around $r = 0$. Right: The plasma was shifted in order to measure Raman scattering in the surrounding air as well.

with the vertical entrance slit of the spectrograph. In this way, scattering spectra at different positions in the plasma can be obtained simultaneously. The spatial resolution is about 0.1 mm within a range of 11 mm. For Thomson and Raman scattering, only wavelengths off the laser wavelength are of interest. As Thomson and Raman scattering are very weak compared to Rayleigh scattering and stray light (at the laser wavelength), a mask is placed directly in front of the iCCD camera to block light within a range of about 0.7 nm around the laser wavelength. For more details about the experimental system, we refer to Chapter 4 [15].

Typical iCCD images that were obtained in this study are shown in Fig. 5.2. The horizontal axis represents the wavelength $\lambda$, and the vertical axis corresponds to the radial position $r$ in the ICP. Thus, a horizontal cross section of these images gives the scattering spectrum at a certain position $r$. The vertical bar in the centre of the iCCD images is the result of the mask in front of the camera. All measurements are performed at a height of 7 mm Above the Load Coil (ALC).

Fig. 5.3 shows two typical scattering spectra, resulting from horizontal cross sections of the iCCD images. The Thomson spectrum on the left hand side of this figure, which is obtained from a horizontal cross section of the iCCD image at $r = 5$ mm, is fitted with a modified Gaussian function (cf. [15–18]). The electron density $n_e$ and temperature $T_e$ were determined from the area and width of this function respectively. Absolute calibration of the measured scattering intensities is done by comparing them to the measured intensity of Rayleigh scattering by argon.

The rotational Raman spectrum of air at the right hand side of Fig. 5.3 is obtained from
Fig. 5.3: Left: a typical Thomson scattering spectrum, from which \( n_e \) and \( T_e \) in the plasma were determined. Right: a rotational Raman scattering spectra of air. The marked spectral lines, corresponding to the rotational transitions \( J = 4 \rightarrow 6 \) (533.3 nm) and \( J = 14 \rightarrow 16 \) (535.5 nm) of nitrogen, were used to determine \( T_h \) and \( n_{air} \).

A horizontal cross section of the iCCD image at \( r = 11 \) mm. It can be used to determine the air density \( n_{air} \) and heavy-particle temperature \( T_h \) around the plasma boundary. For this purpose, two relatively isolated lines with a reasonable wavelength difference must be identified. Since air is a mixture of mainly nitrogen (78%) and oxygen (21%), the rotational Raman spectrum of air contains lines of both gases. Here we only discuss the long wavelength (Stokes) part of the rotational Raman spectrum. The lines in this part of the spectrum correspond to transitions from a rotational state \( J \) to \( J + 2 \). The energy of a rotational state \( J \) is given by

\[
E_J = BJ(J + 1),
\]

(5.2)

where \( B = 2.48 \cdot 10^{-4} \) eV for \( \text{N}_2 \), and \( B = 1.78 \cdot 10^{-4} \) eV for \( \text{O}_2 \). The energy difference between the rotational states \( J \) and \( J + 2 \) is thus \( \Delta E = E_{J+2} - E_J = B(4J + 6) \). Since this energy difference is much smaller than the energy of a laser photon, the wavelength of the scattered photons may be approximated by

\[
\lambda_{J \rightarrow J+2} \approx \lambda_i + \frac{\lambda_i^2}{hc} \cdot \Delta E = \lambda_i + \frac{\lambda_i^2}{hc} \cdot B(4J + 6).
\]

(5.3)

For nitrogen all possible \( J \) states are allowed, but for oxygen only states with even \( J \) are populated. The wavelengths of rotational Raman lines of nitrogen and oxygen are shown at the left hand side of Fig. 5.4. This graph also gives the approximate (relative) intensities of the lines, calculated according to [19] for \( T_h = 300 \) K. The right hand side of Fig. 5.4 compares measured rotational Raman spectra of air and pure nitrogen, obtained by flushing part of the detection volume by nitrogen. For this measurement the entrance slit of the spectrograph was narrowed to 250 \( \mu \)m in order to reach a better spectral resolution. As follows from Fig. 5.4, the nitrogen lines corresponding to the rotational transitions \( 4 \rightarrow 6 \) (at 533.3 nm) and \( 14 \rightarrow 16 \) (at 535.5 nm) can clearly be distinguished from other lines. Therefore these lines are suitable for the measurement of \( n_{air} \) and \( T_h \).
The heavy-particle (gas) temperature $T_h$ is reflected in the distribution of nitrogen molecules over their rotational states since population and depopulation processes of these states are governed by heavy-particle collisions. Hence, the density of nitrogen molecules in rotational state $J$ can be related to the heavy-particle temperature via [16,19]

$$n_J = \frac{n_{N_2}}{Q} g_J (2J + 1) \exp \left( - \frac{E_J}{k_B T_h} \right), \quad \text{(5.4)}$$

where $n_{N_2}$ is the nitrogen density, $g_J$ the statistical weight, which equals 3 or 6 for odd and even $J$ respectively, $k_B$ the Boltzmann constant, and $E_J$ the energy of rotational state $J$ (cf. Eq. 5.2). The partition sum $Q$ results from the normalisation $\sum n_J = n_{N_2}$. For sufficiently high $T_h$ or small $B$, it can be approximated by [20] $Q \approx 9k_B T_h / 2B$; for nitrogen at room temperature this approximation is accurate within 0.3%. The Raman scattering intensity corresponding to a rotational transition $J \rightarrow J + 2$ is given by

$$I_{J\rightarrow J+2} \propto n_J \frac{d\sigma_{J\rightarrow J+2}}{d\Omega}, \quad \text{(5.5)}$$

with $d\sigma_{J\rightarrow J+2}/d\Omega$ the differential cross section of the scattering process. With the use of Eqs. 5.4 and 5.5, the ratio of the scattering intensities of the lines $J = 4 \rightarrow 6$ and $J = 14 \rightarrow 16$ can be written as

$$\xi \equiv \frac{I_{4\rightarrow 6}}{I_{14\rightarrow 16}} = \frac{9}{29} \cdot 1.15 \cdot \exp \left( \frac{E_{14} - E_4}{k_B T_h} \right) = 0.357 \cdot \exp \left( \frac{546}{T_h} \right). \quad \text{(5.6)}$$

The factor 1.15 is the ratio of the Raman scattering cross sections of the rotational transitions $4 \rightarrow 6$ and $14 \rightarrow 16$ [19]. In order to calculate $T_h$ from the measured ratio of the two

**Fig. 5.4:** Left: simulation of the wavelengths and intensities of rotational Raman scattering lines of nitrogen and oxygen molecules. The nitrogen lines indicated by arrows ($J = 4 \rightarrow 6$ at 533.3 nm and $J = 14 \rightarrow 16$ at 535.5 nm) are relatively isolated, so that their intensities can be measured accurately. Right: a comparison between rotational Raman scattering spectra of air (top) and nitrogen (bottom).
rotational lines, this equation can be rearranged to

\[ T_h = \frac{546}{\ln(\xi) - 1.03}. \]  

(5.7)

The air density \( n_{air} \) can be determined from the absolute intensity of a certain Raman line. According to Eqs. 5.4 and 5.5, \( n_{air} \) is proportional to the intensity of a line corresponding to a certain rotational transition \( J \rightarrow J + 2 \) and an exponential that depends on \( T_h \) and represents the relative occupation degree of state \( J \):

\[ n_{air} = C \cdot I_{J \rightarrow J+2} \cdot \exp \left( \frac{E_J}{k_B T_h} \right). \]  

(5.8)

The gas temperature is known from Eq. 5.7. The constant \( C \) is determined by the sensitivity of the experimental system and the fraction of nitrogen in air. It can be found by a measurement far from the plasma source, where \( T_h = 300 \) K and \( n_{air} = p_0 / k_B T_h = 2.5 \cdot 10^{25} \) m\(^{-3}\); \( p_0 = 10^5 \) Pa is the standard (atmospheric) pressure.

The argon density \( n_{Ar} \) follows from the heavy-particle temperature and the density of air (cf. Eqs. 5.7 and 5.8) and the ideal gas law:

\[ n_{Ar} = \frac{p_0}{k_B T_h} - n_{air}. \]  

(5.9)

In conclusion, the heavy-particle temperature \( T_h \) of the gas on the edge of the plasma can be determined from the ratio of the intensities of the Raman lines corresponding to the rotational transitions \( 4 \rightarrow 6 \) and \( 14 \rightarrow 16 \) of nitrogen. The spatial profile of the air density \( n_{air} \) follows from \( T_h \) and a spatial intensity profile of the \( 4 \rightarrow 6 \) or \( 14 \rightarrow 16 \) line. The argon density \( n_{Ar} \) equals the difference between the total gas density at the temperature \( T_h \) and the air density \( n_{air} \).

5.2.2 Power interruption

As stated in Section 5.1, the power interruption technique can yield valuable insights in excitation, production, and loss processes in the plasma. In this work, the electron density and temperature at various moments during power interruption were measured by Thomson scattering. In addition, measurements were done after re-ignition of the plasma, so that processes restoring the steady-state situation in the ICP can be studied. The laser was triggered by the same pulse source as the one triggering the power interruption; a variable delay (see Fig. 5.1) facilitates the measurement of a temporal profile. The trigger repetition rate is 10 Hz. The uncertainty in time of the actual begin and end of the power interruption with respect to the trigger signal is approximately 2 \( \mu s \). Hence, this is also the temporal resolution that can be achieved. The fall and rise time of the power delivered by the generator is in the order of 0.5 \( \mu s \) (50 RF cycles). During power interruption, the field generated by the RF coil is less than 2% of that during normal operation. Each measurement at a certain moment in the interruption cycle is an integration of several thousand subsequent power interruptions.
Fig. 5.5: Electron density and temperature at 7 mm ALC during a power interruption of 50 µs (starting at $t = 0$). The measurement at $t = -5$ µs represents the steady-state situation.

Fig. 5.6: Electron density and temperature at 7 mm ALC after a power interruption of 50 µs (starting at $t = 0$).

The ICP source used in this study operates at an RF frequency of 100 MHz, and is similar to one of the ICPs used in Chapter 4 [15]. The total argon flow is 13 l/min, and the quartz torch has an inner diameter of about 18 mm. The RF power that is dissipated in the plasma is about 600 W, and is applied by a two-winding coil. Measurements are done at a height of 7 mm Above the Load Coil (ALC). This height is approximately 5 mm above the quartz ICP torch. For further details about the ICP source we refer to [15].

5.3 Results

5.3.1 Response to short power interruptions

The measured radial profiles of the electron density $n_e$ and temperature $T_e$ in the ICP during a power interruption of 50 µs (starting at $t = 0$) are shown in Fig. 5.5. Clearly, the temperature drops to a lower level ($T_e^* \approx 7000$ K) “immediately” when the power is
switched off, so that the plasma becomes (weakly) recombining. Compared to \( T_e \), the electron density decays much slower; the decay time constant is roughly 0.1 – 1 ms, depending on the position in the plasma.

Radial profiles of \( n_e \) and \( T_e \) after re-ignition of the plasma are shown in Fig. 5.6. The electron temperature is observed to jump to a higher value than that in steady state. This is necessary to produce the required ionisation to return to the steady-state electron density. After this initial jump, \( T_e \) decreases to its steady-state value with a time constant of around 200 \( \mu s \). After the power interruption, the electron density increases because of the high electron temperature and the associated high ionisation rate. The electron density returns to steady-state at around \( t = 500 \mu s \).

The temporal development of both \( n_e \) and \( T_e \) before, during, and after the power interruption is shown in Fig. 5.7. As pointed out above, the time dependence of spectral lines is strongly related to that of \( n_e \) and \( T_e \). Spectral lines emitted by low energy excited states, such as the ones of metals and alkalis, are approximately in Boltzmann equilibrium with the ground state. Therefore, the spectral line intensities corresponding to these states show a time dependence similar to that of \( T_e \). In the work of Fey et al. [11], such Boltzmann-like responses were observed for various spectral lines. Higher excited states, mostly of argon, are more or less in Saha-equilibrium with the ionic ground state. Therefore, the densities of these states (and hence the intensities of spectral lines emitted by these states) increase when \( T_e \) decreases at the start of the interruption. Similarly, the densities decrease when the plasma is re-ignited. Fey reported such Saha-like responses for various argon lines as well [11].

### 5.3.2 Entrainment of ambient air

The density of air that is entrained into the plasma and the heavy-particle temperature are determined from the rotational Raman spectra obtained around the edge of the plasma, as described in Section 5.2. The results are shown in Fig. 5.8. The (extrapolated) quartz ICP
torch is located between the radial positions $r = 9$ mm and $r = 10$ mm. The measurements are performed at 7 mm ALC, which is about 5 mm above the quartz torch.

The air density decreases rapidly when approaching the plasma. A density of $n_{\text{air}} \approx 10^{24} \text{ m}^{-3}$ is reached at $r \approx 8.7$ mm, i.e. just inside the (extrapolated) torch. For lower densities, the Raman spectrum becomes too weak to determine $n_{\text{air}}$ and $T_h$ accurately. At $r = 9$ mm, the gas temperature is still rather low; it only starts to increase strongly for smaller radial positions $r$, where not much air could be detected.

A region where both electrons and air molecules are present in detectable amounts ($10^{24} \text{ m}^{-3}$ for air and $10^{19} \text{ m}^{-3}$ for electrons) could not be found. As shown at the right hand side of Fig. 5.2, the plasma region is confined to $r < 8$ mm, whereas nitrogen could be detected only for $r > 8.5$ mm. This suggests that the plasma is surrounded by a sheet of (mainly) argon gas, which strongly obstructs mixing of the plasma with the surrounding air.

In previous work by De Regt et al. [21] the entrainment of air in the plasma was discussed as well. De Regt used a combination of Rayleigh and vibrational Raman scattering to determine $n_{\text{air}}$ and $T_h$. In his work, the sharp decrease of $n_{\text{air}}$ was reported to be slightly ($\sim 0.5$ mm) closer to the plasma. In addition, close to the plasma, the decrease of $n_{\text{air}}$ was slightly more gradual. From the experiments it was concluded that a nitrogen density of approximately 1% of the heavy-particle density could be present at $r = 6$ mm.

However, Fig. 5.8 suggests that already at $r = 8.5$ mm the air density has decreased to a few percent of that of argon. Therefore, in light of the present results, a nitrogen (or air) concentration of 1% of the total heavy-particle density ($n_h \approx 2 \cdot 10^{24} \text{ m}^{-3}$) at $r = 6$ mm is very unlikely.
Chapter 5

5.4 Discussion

5.4.1 Electron production and loss processes

The decay of the electron density when the plasma power is switched off can be attributed to ambipolar diffusion and recombination processes. Hence, this decay can be described by a simplified particle balance of electrons,

\[
\frac{\partial n_e}{\partial t} \approx \nabla \cdot (D_a \nabla n_e) - n_e n_i \alpha_{\text{rec}} \equiv n_e (\nu_{\text{diff}} + \nu_{\text{rec}}),
\]

(5.10)

where \(D_a\) is the ambipolar diffusion coefficient, \(\alpha_{\text{rec}}\) the recombination rate coefficient, and \(n_i \approx n_e\) the ion density. At the right hand side of Eq. 5.10, diffusion and recombination are described in terms of the frequencies per electron of diffusion (\(\nu_{\text{diff}}\)) and recombination (\(\nu_{\text{rec}}\)) events. These frequencies both depend on the radial position \(r\) in the plasma. In addition, they slightly change in time. Here only the decay relatively short after the beginning of the power interruption is considered, so that the time dependence of \(\nu_{\text{diff}}\) and \(\nu_{\text{rec}}\) can be neglected.

As diffusion takes place mainly in radial direction, the diffusion term \(n_e \nu_{\text{diff}}\) can be written as

\[
n_e \nu_{\text{diff}} = D_a \left( \frac{1}{r} \frac{\partial n_e}{\partial r} + \frac{\partial^2 n_e}{\partial r^2} \right).
\]

(5.11)

Under typical ICP conditions, \(D_a \approx 1 \cdot 10^{-3} \text{ m}^2 \text{ s}^{-1}\) [15,22]. The diffusion frequency can be derived from the measured electron density profile. It is negative (i.e. diffusion is a loss term) in the most active zones (highest \(n_e\)), and positive (i.e. diffusion is a source term) in the centre of the plasma. For the calculations below we assume that, during the short power interruption, the electron density profile does not change significantly so that the diffusion frequency is constant in time. The \(n_e\) profiles in Fig. 5.5 show that this assumption is reasonable at relatively short times after the beginning of the power interruption.

Taking into account only three-particle recombination,

\[
\text{Ar}^+ + e^- + e^- \rightarrow \text{Ar}^{(s)} + e^-,
\]

(5.12)

where the argon atom may be left in an excited state, the recombination frequency is given by

\[
n_e \nu_{\text{rec}} = n_e \nu_{3p-\text{rec}} = -n_e^3 K_{3p-\text{rec}}.
\]

(5.13)

As recombination always represents a loss term, the frequency \(\nu_{\text{rec}}\) is negative. The rate coefficient for three-particle recombination, \(K_{3p-\text{rec}}\), depends strongly on the electron temperature. This dependence is assumed to be similar to that given by Thomson for a hydrogenic system [23,24],

\[
K_{3p-\text{rec}} \approx C_0 \cdot T_e^{-9/2}.
\]

(5.14)

For hydrogen, the constant \(C_0\) equals \(C_0 = 5 \cdot 10^{-21} \text{ K}^{9/2} \text{ m}^6 \text{ s}^{-1}\). For argon, the value of \(C_0\) is not known accurately; in this work it is used as a fit parameter.
In the graph at the left hand side of Fig. 5.9, the measured frequencies describing the electron losses at different radial positions in the plasma \((r > 0)\) are compared to the calculated frequencies. A good fit is obtained for \(K_{3p-rec} \approx 3.5 \cdot 10^{-39} \text{ m}^6 \text{s}^{-1}\). Since \(T_e \approx 7000 \text{ K}\), the constant \(C_0\) in Eq. 5.14 must be taken \(C_0 = 7 \cdot 10^{-22} \text{ K}^{9/2} \text{ m}^6 \text{s}^{-1}\).

In the central region of the plasma \((r < 4 \text{ mm})\), the model corresponds closely to experimental results. As shown at the right hand side of Fig. 5.9, in the centre of the plasma diffusion gives rise to a positive frequency, which means that diffusion is a source term at this position. The particle gain by diffusion is roughly cancelled by recombination. At larger radial positions, diffusion becomes a loss term and recombination gains more importance because of the higher electron density. This leads to a faster electron density decays.

However, at large radial distances \((r > 4 \text{ mm})\), our simple model is not accurate. At the edge of the plasma the plasma decays much faster than can be explained by only diffusion and three-particle recombination. As shown at the right hand side of Fig. 5.9, due to the low electron density, recombination becomes less important at the edge of the plasma. Although the radial \(n_e\) profile of the plasma (cf. Fig. 5.5 and 5.6) suggests larger diffusion losses towards the edge of the plasma, the gas temperature of the plasma is lower at large radial positions [25], which obstructs diffusion. Therefore, diffusion is too slow to explain the fast decay observed in the outer regions of the plasma, and an additional loss process must play a role. A possible loss process is provided by the influence of molecules in the plasma. This is discussed further in Section 5.4.3.

The temporal development of the electron density after re-ignition of the plasma at \(t = 50 \mu\text{s}\) can be described by ionisation and diffusion processes (cf. Eq. 5.10):

\[
\frac{\partial n_e}{\partial t} = n_e(\nu_{\text{diff}} + \nu_{\text{ion}}).
\]  

Due to the relatively high electron temperature, three-particle recombination may be neglected compared to ionisation. The diffusion frequency \(\nu_{\text{diff}}\) is given by Eq. 5.11. The
effective ionisation rate is
\[ n_e \nu_{\text{ion}} = n_e n_1 S_{\text{ion}}, \] (5.16)
where \( n_1 \approx n_{\text{Ar}} \) is the argon ground state density. This density follows from the heavy-particle temperature in the plasma, \( T_h \approx 4500 \text{ K} \) [25, 26], and the ideal gas law, \( n_1 \approx p_0/k_B T_h \approx 1.6 \cdot 10^{24} \text{ m}^{-3} \). The effective rate coefficient for ionisation, \( S_{\text{ion}} \), can be derived from a Collisional Radiative Model (CRM). Under typical ICP conditions, it can be approximated by [15, 27, 28]:
\[ S_{\text{ion}}(T_e) \approx 6.81 \cdot 10^{-17} \sqrt{T_e} \exp \left( -\frac{E_{1,2}^*}{k_B T_e} \right) \text{ [m}^3 \text{s}^{-1}], \] (5.17)
where \( E_{1,2}^* = 12.06 \text{ eV} \). Ionisation takes place mainly stepwise and radiation is relatively unimportant. Therefore, \( E_{1,2}^* \) is approximately equal to the excitation energy of the first excited state (11.5 eV), and \( S_{\text{ion}} \) is (almost) independent of \( n_e \).

The graph at the left hand side of Fig. 5.10 shows the measured and calculated frequencies describing the electron production process at different radial positions in the plasma. At the right hand side of Fig. 5.10, the calculated frequency is split into the ionisation and diffusion components. Diffusion represents a relatively low frequency compared to ionisation.

Close to the centre of the ICP (1 < \( r < 4 \text{ mm} \)), the observed production frequency is somewhat higher than that calculated on the basis of the ionisation rate given in Eq. 5.17. On the other hand, at the edge of the ICP the observed frequency is lower than that expected from the high electron temperature directly after re-ignition. This suggests the presence of an additional loss process at the edge. Presumably, this is the same mechanism as that responsible for the fast decay of the electron density during power interruption. Here, molecular processes may play a role as well, especially at the edge of the ICP. This is discussed in more detail in Section 5.4.3.
5.4.2 Electron temperature during power interruption

When the plasma power is interrupted, the electron temperature quickly drops and decreases only very slowly during the rest of the interruption period (cf. Fig. 5.7). During power interruption, electrons are not heated by the external electromagnetic field of the RF generator. In the absence of other heating mechanisms, it can be expected that elastic collisions cause the temperatures of electrons and heavy particles to equilibrate, i.e. $T^*_e = T_h$. However, from previous experimental studies at a similar RF power it is known that $T_h \approx 4500$ K in the active zones of the ICP [25,26]; this temperature is not influenced significantly by the power interruption. Thus, the value of $T^*_e \approx 7000$ K measured in this study requires the presence of an electron heating mechanism.

The power density required to sustain a temperature difference $\Delta T$ between heavy particles and electrons should at least be equal to the power transferred from electrons to heavy particles by elastic collisions [14]:

$$Q_{\text{heat}} = n_e n_1 S_{\text{heat}} \cdot \frac{m_e}{M} \cdot 3k_B \Delta T,$$

(5.18)

where $m_e/M$ is the mass ratio of electrons and argon atoms. The ground state argon density is approximately $n_1 \approx 1.6 \cdot 10^{24}$ m$^{-3}$. The factor $S_{\text{heat}}$, the effective rate coefficient for momentum transfer from electrons to heavy particles, can be expressed in terms of the rate coefficients for momentum transfer from electrons to atoms ($k_{\text{ea}}^m$) and ions ($k_{\text{ei}}^m$):

$$S_{\text{heat}} = \left( k_{\text{ea}}^m + \frac{n_+}{n_1} k_{\text{ei}}^m \right) \approx 1.9 \cdot 10^{-14} \text{ m}^3 \text{s}^{-1},$$

(5.19)

were $n_+$ is the ion density. The rate coefficients $k_{\text{ea}}^m$ and $k_{\text{ei}}^m$ were derived from experimental data of collision cross sections for momentum transfer, averaged over a Maxwellian Electron Energy Distribution Function (EEDF) [29,30]. It is found that $S_{\text{heat}}$ varies less than 10% in the range $3000 < T_h < 6000$ K and $5000 < T_e < 10000$ K, and less than 35% for $10^{19} < n_e < 10^{20}$ m$^{-3}$, and is therefore taken constant in this study. With $n_e \approx 6 \cdot 10^{20}$ m$^{-3}$ as an average value of the electron density, the power density required to sustain a temperature difference of $\Delta T \approx 2500$ K is $Q_{\text{heat}} \approx 2.6 \cdot 10^7$ W m$^{-3}$.

Recombination processes represent a heat source for electrons. The energy gained by three-particle recombination can be written as

$$Q_{3\text{p-rec}} \approx n_e \nu_{3\text{p-rec}} \cdot \Delta E_{3\text{p-rec}},$$

(5.20)

where $\Delta E_{3\text{p-rec}}$ is the effective energy gain per three-particle recombination event. This is smaller than the ionisation energy of argon (15.76 eV), since the recombined argon atom is usually left in an excited state so that part of the released energy may be emitted as radiation. Therefore, we take $\Delta E_{3\text{p-rec}} \approx 5$ eV. With $n_e \approx 6 \cdot 10^{20}$ m$^{-3}$ and the theoretical value of $\nu_{3\text{p-rec}}$ as given in Eq. 5.13 this leads to a power density of $Q_{3\text{p-rec}} \approx 6 \cdot 10^5$ W m$^{-3}$, which is by far not enough to explain the high $T^*_e$.  

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As discussed in Section 5.4.1, the electron losses are observed to be much larger than can be expected from diffusion and three-particle recombination. However, even if we take the observed loss frequency $|\nu_{\text{rec}}| \approx 10^4 \text{ s}^{-1}$ and $\Delta E \approx 5 \text{ eV}$, the energy gain by this recombination process is on the order of $4 \cdot 10^6 \text{ W m}^{-3}$. Obviously, this is much more than the energy gained by three-particle recombination, but still a factor of six below the power density needed to explain the high $T_{e*}$. Thus, an additional electron heat source must be present.

5.4.3 Molecular processes

The comparison of the experimental results with models based on atomic processes shows two important discrepancies. Firstly, the electron loss rate observed at the edge of the ICP is much higher than can be explained by diffusion and three-particle recombination. Secondly, the electron temperature during power interruption requires a much higher power density for electron heating than can be provided by recombination processes. These facts cannot be accounted for by atomic processes alone, so that the effect of molecular formation and destruction processes must be investigated.

Due to the high heavy-particle density in atmospheric pressure plasmas, formation of molecular ions ($\text{Ar}_2^+$) via heavy-particle interactions can become an important process, so that a significant amount of ions may be molecular instead of atomic. As suggested by Jonkers [27], the formation and destruction processes of molecular ions may affect the electron particle and energy balances considerably. Such processes were not taken into account in the simple forms of the electron particle and energy balances of Eqs. 5.10, 5.15, and 5.18, and may therefore explain the differences between observed and calculated quantities. As shown in Section 5.3.2, the density of air entrained into the plasma is very low, and is not likely to affect the observed part of the plasma. Therefore, the influence of air entrainment is not discussed further.

In Fig. 5.11 a schematic picture of the energy diagram of atomic and molecular argon is given. Several production and destruction processes of molecular ions ($\text{Ar}_2^+$) and excimers ($\text{Ar}_2^*$) are indicated in this figure. Collisions with heavy particles are an important mechanism for production (Atom Assisted Association, AAA) and destruction (Dissociation by Atom Impact, DAI) of molecular ions. Being each other’s inverse process, they form the balance

\[
\text{Ar}^+ + \text{Ar} + \text{Ar} \xleftrightarrow{\text{AAA}} \text{Ar}_2^+ + \text{Ar} \xleftrightarrow{\text{DAI}}. \tag{5.21}
\]

Collisions with electrons can lead to production (Electron Assisted Association, EAA) and destruction (Dissociation by Electron Impact, DEI) of molecular ions as well:

\[
\text{Ar}^+ + \text{Ar} + e^- \xleftrightarrow{\text{EAA}} \text{Ar}_2^+ + e^- \xleftrightarrow{\text{DEI}}. \tag{5.22}
\]
For the ranges of $n_e$, $T_e$, and $T_h$ in the ICP, production of molecular ions by AAA is typically a factor 10–20 faster than by EAA [27]. Destruction of molecular ions by DAI is slightly more important than by DEI. Other mechanism for the formation and destruction of molecular ions are Associative Ionisation (AI) and Dissociative Recombination (DR),

$$\text{Ar} + \text{Ar}^* \xrightarrow{\text{AI}} \text{Ar}_2^+ + e^- \xleftarrow{\text{DR}} (5.23)$$

These processes are slow compared to those in Eq. 5.21 and 5.22, and therefore do not contribute significantly to the density of molecular ions [27]. However, these processes provide efficient ionisation and recombination channels, and therefore may have a considerable effect on the electron particle balance.

The approximate rate coefficients of the processes given above can be found in literature [20,31–34] and by detailed balancing of inverse processes [27]. These rate coefficients and their temperature dependencies are summarised by Jonkers [27]. The density of molecular argon ions can be calculated from the particle balance of these ions,

$$n_1 n_+ k_{\text{AAA}} + n_e n_1 n_+ k_{\text{EAA}} = n_1 n_{\text{Ar}_2^+} k_{\text{DAI}} + n_e n_{\text{Ar}_2^+} k_{\text{DEI}} + n_e n_{\text{Ar}_2^+} k_{\text{DR}}, (5.24)$$

where the various $k$ coefficients represent the rate coefficients for the various processes. Associative ionisation has not been taken into account in this equation, since rates for this process are not accurately known and, as pointed out by Jonkers [27], it does not significantly influence the particle balance of molecular ions. The density of atomic ions is $n_+$, so that charge neutrality demands

$$n_e = n_+ + n_{\text{Ar}_2^+}. (5.25)$$
Combining this with Eq. 5.24 yields the molecular ion density

\[
n_{\text{Ar}^+_{2}} = \frac{n_{e}^2 k_{\text{AAA}} + n_{e} n_{e}^2 k_{\text{EAA}} + n_{e}^2 k_{\text{DAI}} + n_{e} k_{\text{DEI}} + n_{e} k_{\text{DR}}}{n_{e}^2 k_{\text{AAA}} + n_{e} n_{e} k_{\text{EAA}} + n_{e} k_{\text{DAI}} + n_{e} k_{\text{DEI}} + n_{e} k_{\text{DR}}}.
\]  

(5.26)

The density of molecular ions as a function of the heavy-particle temperature is shown in Fig. 5.12 for two values of the electron density. As stated above, AAA and DAI are usually the most important processes for formation and destruction of molecular ions.

Since these processes are each others reverse, the corresponding proper balance of Eq. 5.21 (almost) equilibrates, so that \(n_{\text{Ar}^+_{2}}\) can roughly be described by a Guldberg-Waage equation [23, 28]. This also explains the large dependence of \(n_{\text{Ar}^+_{2}}\) on the heavy-particle temperature \(T_h\). At high temperatures (\(T_h > 4000\) K, as found in the central plasma region), the molecular ion density is generally below 0.1% of the electron density. However, at temperatures below 2000 K, as found near the edge of the plasma, the molecular ion density can be 10% of the electron density or even more. Although EAA, DEI, AI, and DR depend on \(T_e\) as well, their influence on \(n_{\text{Ar}^+_{2}}\) is limited, so that the dependence of \(n_{\text{Ar}^+_{2}}\) on \(T_e\) is very weak. For high electron densities, destruction processes via DEI and DR become more important, which lowers \(n_{\text{Ar}^+_{2}}\).

Thus, it can be concluded that ions are mainly atomic in the centre of the plasma, and partly molecular at the edge of the plasma. Therefore, the discrepancies between experimental results and expectations on the basis of atomic processes are likely to be related to molecular ions in the plasma.

**Electron loss rate**

As shown in Section 5.4.1, the measured behaviour of \(n_e\) at the edge of the plasma is different from the calculated behaviour during and after a power interruption. During PI the decay of the electron density at the edge of the plasma is much faster than can be explained by three-particle recombination and diffusion (cf. Fig. 5.9). Directly after reignition of the plasmas, the electron density increases more slowly than expected given the ionisation rate associated with the electron temperature at that position (cf. Fig. 5.10). In
both cases, the difference between the model and measurements suggests the presence of an additional loss process with a frequency per electron of $|\nu| \approx 10^4$ s$^{-1}$. The fact that this frequency remains more or less constant before and after re-ignition of the plasma indicates that the electron temperature dependence of this electron loss mechanism is much weaker than that of three-particle recombination (cf. Eq. 5.14).

Dissociative recombination is a much more efficient process than three-particle recombination. Therefore, its contribution to electron losses may be much more important even though $n_{\text{Ar}_2^+} / n_e \ll n_e$. The rate coefficient for DR may be approximated by [27,33]:

$$k_{\text{DR}} \approx 3.89 \cdot 10^{-11} T_e^{-0.67} \approx 1 \cdot 10^{-13} \text{ m}^3 \text{s}^{-1}. \quad (5.27)$$

Over the range $6000 < T_e < 10000$ K, it changes less than 15% around the value given at the right-hand side of this equation. This weak electron temperature dependence makes DR a more likely candidate for electron loss than three-particle recombination, which depends strongly on $T_e$. Similar to the losses by three-particle recombination (cf. Eq. 5.13), electron losses by DR can be described by a frequency $\nu_{\text{DR}}$ given by

$$n_e \nu_{\text{DR}} = -n_e n_{\text{Ar}_2^+} k_{\text{DR}}. \quad (5.28)$$

Like $\nu_{\text{3p-rec}}$, this frequency is negative since it represents an electron loss channel. Due to the decreasing heavy-particle temperature towards the edge of the ICP [25,26], the ratio $n_{\text{Ar}_2^+} / n_e$ increases. This causes electron losses by DR to be more efficient towards the edge of the plasma. At $r = 8$ mm we have $n_e \approx 2 \cdot 10^{20}$ m$^{-3}$ and $T_h \approx 2500$ K [25,26]. For these values, $n_{\text{Ar}_2^+} \approx 10^{-2} \cdot n_e$ (cf. Fig. 5.12). With the molecular argon density and rate coefficient for DR given in Eqs. 5.26 and 5.27, this leads to $\nu_{\text{DR}} \approx -2 \cdot 10^5$ s$^{-1}$. Thus, DR can easily explain higher recombination frequencies than the ones calculated on the basis of atomic processes alone. In fact, losses by DR are roughly a factor of 20 larger than those observed. This suggests that most of the DR processes are balanced by its reverse process, AI (cf. Eq. 5.23). In conclusion, DR of molecular argon ions, partly obstructed by AI, is likely to be responsible for the large electron losses at the edge of the plasma.

**Electron heating**

As shown in Section 5.4.2, the high electron temperature during power interruption suggests the presence of electron heating mechanisms in the plasma. It was shown that three-particle recombination is insufficient. Even if the large observed electron loss rate ($|\nu_{\text{rec}}| \approx 10^4$ s$^{-1}$) at the edge of the plasma is attributed entirely to other recombination processes, such as DR, the corresponding electron heating is too small by a factor of six to explain the high $T_e^*$. Thus, the electron heating mechanism during power interruption is not related to recombination, and another mechanism is likely to play a role. Possible candidates are the formation of molecular ions or excimers (Ar$_2^*$, see Fig. 5.11) via electron collisions.

Another possibility is a cyclic process as schematically represented by Fig. 5.13. Molecular ions that are destructed by DR may yield an atom in an excited state, which is re-ionised by collisions with electrons $\{e\}$. This atomic ion may approach a neutral atom
via the repulsive branch, as shown in Fig. 5.13. This occurs at the expense of thermal energy of heavy particles \{h\}. Subsequently, a collision of the closely spaced atom-ion pair with an electron may lead to the formation of a molecular ion. The energy that is released is taken up by the electron. Thus, this cyclic process can heat electrons without effective recombination.

Unfortunately, the data offered by studies of molecular processes such as the ones sketched in this section is, as far as we know, not sufficient to yield a deeper understanding of the processes that are relevant in the ICP and other atmospheric plasmas. Therefore, it must be concluded that further elementary studies on this area are indispensable.

### 5.5 Conclusions

In this work, the behaviour of the electron density \(n_e\) and temperature \(T_e\) of a spectrochemical ICP during and after a short interruption of the plasma power is studied. Electron densities and temperatures are measured with spatial and temporal resolution by laser Thomson scattering. In addition, the influence of air entrainment in the plasma is studied. The air density and heavy-particle temperature of the plasma around the plasma boundary are determined from two nitrogen lines in rotational Raman scattering spectra of air.

The electron density \(n_e\) is found to react relatively slowly to a power interruption (typical time constant \(0.1 - 1\) ms). In contrast, \(T_e\) “instantaneously” falls to a lower value \(T_e^*\) after power interruption, and remains more or less constant during the rest of the power interruption. Directly after re-ignition of the plasma, \(T_e\) jumps to a value higher than that at steady state; the resulting high ionisation rate is required to return to the steady-state electron density. The observed behaviour of \(n_e\) and \(T_e\) is in accordance with that expected from spectral line intensities measured in previous work of Fey [11].

The behaviour of \(n_e\) during and after power interruption in the outer regions of the plasma (radial position \(r > 5\) mm) cannot be explained by simple particle balances that are confined to ambipolar diffusion, three-particle recombination, and ionisation. Measurements suggest an additional electron loss mechanism with a frequency per electron on the order of \(|\nu| \sim 10^4\) s\(^{-1}\). In addition, the electron temperature during power interruption, \(T_e^* \approx 7000\), is found to be much higher than the heavy-particle temperature reported in previous studies [25, 26]. This suggests the presence of a heating mechanism for electrons.
Due to the measured low air density above the wall of the quartz ICP torch, air entrainment is not likely to affect the electron density and temperature of the plasma significantly, possibly with an exception at the outermost plasma boundary. However, due to the low heavy-particle temperature at the edge of the plasma, formation of molecular ions ($\text{Ar}_2^+$) may become important. It is shown that the rate of Dissociative Recombination (DR) of $\text{Ar}_2^+$ is more than sufficient to explain the observed electron losses. The Associative Ionisation (AI), the reverse process of DR, may compensate part of the DR and thus account for the observed loss rate. Nevertheless, the observed recombination rate cannot explain the high electron temperature during power interruption. Other heating mechanisms, which do not lead to recombination, are likely to play a role. Possible mechanisms are the formation of molecular ions or excimers via electron collisions, or a cyclic mechanism that leads to energy transfer from heavy particles to electrons. However, more detailed studies on these elementary processes need to be done for a complete understanding of the relevant processes in the ICP and other atmospheric low-temperature plasmas.

References


Chapter 6

Thomson scattering on a low-pressure, inductively coupled gas discharge lamp

Abstract

Excitation and light production processes in gas discharge lamps are the result of inelastic collisions between atoms and free electrons in the plasma. Therefore, knowledge of the electron density $n_e$ and temperature $T_e$ is essential for a proper understanding of such plasmas. In this chapter, an experimental system for laser Thomson scattering on a low-pressure, inductively coupled gas discharge lamp and measurements of $n_e$ and $T_e$ in this lamp are presented. The experimental system is suitable for low electron temperatures (down to below 0.2 eV) and employs a triple grating spectrograph for a high stray light rejection, or equivalently a low stray light redistribution ($R_{\text{eff}} \approx 7 \cdot 10^{-9}$ nm$^{-1}$ at 0.5 nm from the laser wavelength). The electron density detection limit of the measurements presented here is $n_e = 4 \cdot 10^{17}$ m$^{-3}$. The modifications to the lamp that were necessary for the measurements are described, and results of the measurements are presented and compared to previous work. The electron density and temperature are about $n_e \approx 10^{19}$ m$^{-3}$ and $T_e \approx 1$ eV in the most active part of the plasma; the exact values depend on the argon filling pressure, mercury pressure, and position in the lamp. Trends of $n_e$ and $T_e$ can be explained qualitatively by the electron particle and energy balances.

M.J. van de Sande and J.J.A.M. van der Mullen. Accepted for publication in J. Phys. D.


6.1 Introduction

For a proper understanding of the plasmas inside gas discharge lamps, it is important to measure, apart from more global parameters such as impedance and efficacy, as many plasma parameters as possible [1,2]. Especially the electron gas properties (temperature $T_e$ and density $n_e$) are important, as electron-atom collisions are responsible for excitation and ionisation processes, and hence light production. Moreover, the electrons are important for the coupling of energy into the discharge.

Our laboratory is equipped for various plasma diagnostic tools, such as Diode Laser Absorption (DLA) and Absolute Line Intensity (ALI) measurements, which were applied to lamps previously [2–4]. However, these techniques do not provide accurate data on the electron temperature and density. These parameters can be derived from ALI or DLA measurements [3], but that involves assumptions on the plasma kinetics and equilibrium departures as described by so-called Collisional Radiative Models (CRM). It is the aim of this study to measure $n_e$ and $T_e$ in a more direct way, and to compare results with the values obtained by alternative methods. The lamp that is studied in this work is the QL lamp, a low-pressure, inductively powered (electrode-less) gas discharge lamp put on the market by Philips in 1992 [2].

The experimental technique that is applied in this work is laser Thomson scattering. As photons are scattered by the electrons in the plasma, this yields very direct access to $n_e$ and $T_e$. The main problem of this technique, connected to the low scattering intensity and low electron temperature in the plasma, is the presence of relatively intense stray light. Stray light can be reduced by a narrowband notch filter. Recently, Bakker et al. [5] presented an atomic filter for this purpose. The present study follows a different approach and solves the problem of stray light by using a Triple Grating Spectrograph (TGS). The first two gratings, placed in subtractive configuration, serve as a stray light filter. Such a TGS system was already applied for this purpose in the 1970s [6–8]. Recently, a comparable system has been built by Kono et al. [9]. These systems are all applied for measurement on plasmas with electron temperatures above 1 eV. The spectrograph described in this work is designed for lower electron temperatures (down to below 0.2 eV) for application to gas discharge lamps.

In Section 6.2 the experimental system designed for and applied in this work is described. Section 6.3 summarises the modifications of the QL lamp required in order to focus the high power laser beam into the plasma and detect Thomson scattering. Results of the experiments are presented in Section 6.4. In Section 6.5 the measurements are discussed qualitatively on the basis of the electron particle and energy balances, and compared to results that were previously obtained in our laboratory by DLA measurements [2,3]. Conclusions are drawn in Section 6.6.
6.2 Experimental arrangement for Thomson scattering

6.2.1 Thomson scattering

Thomson scattering is scattering of radiation by free electrons in the plasma, and hence provides a very direct method to measure properties of the free electron gas [10–12]. For relatively low electron density plasmas, such as the QL discharge, scattering is incoherent. In that case, the Thomson scattered intensity is directly proportional to the electron density $n_e$, and the shape of the scattering spectrum is determined by the Doppler shift caused by the electron motion.

The absolute electron density can be determined from the Thomson scattering intensity $I_T$ by comparison with, for instance, the intensity $I_{Rm}$ of rotational Raman scattering by $N_2$ with a known density $n_{N_2}$ [5,13,14]:

$$n_e = n_{N_2} \cdot \frac{I_T}{I_{Rm}} \cdot \left( \frac{1}{d\sigma_T/d\Omega} \sum_{J,J'} \frac{n_J}{n_{N_2}} \frac{d\sigma_{J\rightarrow J'}}{d\Omega} \right) \equiv n_{N_2} \cdot \frac{I_T}{I_{Rm}} \cdot \Gamma_{Rm}.$$ (6.1)

Here $d\sigma_T/d\Omega$ is the differential cross section for Thomson scattering, $d\sigma_{J\rightarrow J'}/d\Omega$ that for Raman scattering accompanied by a transition from rotational state $J$ to $J'$, and $n_J/n_{N_2}$ the fraction of nitrogen molecules in state $J$. The factor $\Gamma_{Rm}$ represents the ratio of the total Raman scattering cross section and the Thomson scattering cross section [5,13,15], taking into account relative occupations of the different rotational states $J$. As discussed below, the experimental system used in this work employs a perpendicular scattering geometry and a laser wavelength of $\lambda_i = 532$ nm. For these conditions, and at a nitrogen temperature of 300 K, $\Gamma_{Rm} \approx 8.15 \cdot 10^{-5}$ [13,15].

If the Electron Energy Distribution Function (EEDF) of the plasma is Maxwellian, the scattering spectrum is a Gaussian with a half $1/e$ width $\Delta\lambda_{1/e}$ that is related to the electron temperature $T_e$ according to

$$T_e = \left[ \frac{m_e c^2}{8k_B \lambda_i^2 \sin^2(\theta/2)} \right] \cdot \Delta\lambda_{1/e}^2,$$ (6.2)

where $\theta$ is the angle of scattering, $m_e$ the electron rest mass, $c$ the speed of light, and $k_B$ the Boltzmann constant. For the conditions used in this work, $\theta = 90^\circ$ and $\lambda_i = 532$ nm, the factor between brackets equals 5238 K nm$^{-2}$.

6.2.2 Basic system

The experimental system that was used in this study is shown schematically in Fig. 6.1. A frequency-doubled Nd:YAG laser produces 400 mJ, 7 ns laser pulses at a wavelength of $\lambda_i = 532$ nm. A plano-convex lens ($f = 1$ m) focuses the laser beam to a diameter of approximately 200 µm in the plasma, where electrons scatter the laser radiation. The
Fig. 6.1: The experimental system for Thomson scattering that was used in this study. Light from a frequency doubled Nd:YAG laser is scattered by electrons in the plasma. Scattered light is collected and dispersed by a Triple Grating Spectrograph (TGS). The first two gratings and the mask between them serve as a stray light filter. An intensified CCD camera records scattering spectra with spatial resolution.

detection volume is imaged onto the entrance slit of a Triple Grating Spectrograph (TGS), which rejects stray light and disperses the scattered light. An intensified CCD camera records the scattering spectrum.

The entrance slit of the system is horizontal, i.e. parallel to the laser beam. Together with a 90° image rotator inside the spectrograph system and the 2-dimensional iCCD camera this provides a spatial resolution of about 0.1 mm over a range of 11 mm in a single measurement. However, when less spatial information is required, or when the electron density is low, multiple pixel arrays can be binned, thus extending the effective length of the detection volume (integration length). Since the QL discharge is relatively large (110 mm diameter), the integration length was chosen 5.5 mm in this study, so that only two spatial positions were measured simultaneously. With a demagnification, the whole discharge might have been imaged onto the entrance slit, but this leads to a significantly smaller solid angle of detection and therefore does not save measurement time.

The setup employs a perpendicular scattering geometry, which implies that the scattering angle is $\theta = 90^\circ$, the laser beam is polarised perpendicular to the plane of scattering (i.e. vertical in this case), and only scattered radiation with the same (vertical) polarisation direction is detected. The latter has the advantage that stray light and plasma emission, which are (partly) unpolarised, are reduced.

6.2.3 The Triple Grating Spectrograph

Stray light is a persisting problem for Thomson scattering on gas discharges close to glass walls. It originates from scattering of part of the laser light on the static environment of the
plasma, and is usually much more intense than Thomson scattering. In contrast to Thomson scattering, stray light is virtually monochromatic. Therefore, it mainly contributes in the centre of the scattering spectrum. However, the finite width of the instrumental profile of a spectrograph causes a fraction of the stray light to be redistributed to other parts of the spectrum (typically around $10^{-3} \text{--} 10^{-2}$ nm$^{-1}$ at 0.5 nm from the laser wavelength). Thus, a high stray light intensity severely affects the accuracy of the measurement. The problem of stray light can be reduced by a narrowband notch filter in front of the (final) spectrograph.

Two gratings in subtractive configuration can be used as a narrowband notch filter [6–9,16]. The first grating disperses incident light (see Fig. 6.2). Subsequently, a mask blocks the central part of the spectrum that is formed, and the second grating recombines (“cross disperses”) the light again at the exit slit. Such a Double Grating Filter (DGF) essentially consists of two simple spectrographs. Combining it with a third spectrograph, which disperses the Thomson scattered radiation for detection, results in a Triple Grating Spectrograph (TGS). The intermediate slit in Fig. 6.1 is the exit slit of the DGF and the entrance slit of the third spectrograph. Below, the design of the TGS used in this study (cf. Figs. 6.1 and 6.2 and Table 6.1) is discussed on the basis of the requirements for the measurements on the QL lamp. In this discussion we follow the path of incident photons.

The entrance slit of the system must be wider than the laser beam (200 µm), and is taken 250 µm. The length of the entrance slit (11 mm) equals that of the iCCD detector. A 90° image rotator, consisting of three plane mirrors, is placed directly behind the entrance slit (see Fig. 6.1) to facilitate spatially resolved measurements, as discussed above.

The first achromatic doublet lens in the system produces a collimated beam for the
first grating. Since lenses can be used on-axis, they produce much less astigmatism than mirrors. Therefore, unlike for mirror-based spectrographs, a high spectral resolution can be combined with a high spatial resolution. In addition, achromatic lenses exhibit much less spherical aberration than single-element lenses, which is essential for multi-lens systems. Chromatic aberrations are not significant due to the limited wavelength range (a few nm) of the Thomson spectra. The clear aperture of all lenses in the TGS is \( \phi = 95 \text{ mm} \), and the focal length is \( f = 600 \text{ mm} \); this is a trade-off between a large dispersion and a large solid angle of detection.

The holographic grating has a groove density of \( n = 1800 \text{ mm}^{-1} \). This is sufficient to reach a dispersion of 1 to 2 mm/nm, which is required for a high spectral resolution and to image the entire spectral range of interest (\( \sim 10 \text{ nm} \)) onto the iCCD camera (16.5 mm wide). The angles of incidence \( \alpha \) and reflection \( \beta \) on the grating (see Fig. 6.2) are related to the groove density \( n \) and wavelength \( \lambda_i \) via the grating equation,

\[
\sin \alpha + \sin \beta = k n \lambda_i,
\]

where \( k \) is the order of dispersion, which is taken unity in the present design. We chose \( |\beta - \alpha| = 30^\circ \). In that case, and with \( \lambda_i = 532 \text{ nm} \), the angles of incidence and reflection can be \( \alpha = 15^\circ \) and \( \beta = 45^\circ \), or the reverse. This choice influences the width of the instrumental profile and the dispersion of the system [16,17]. A small angle \( \alpha \) leads to a broader instrumental profile, but also to a larger dispersion, which reduces the influence of image aberrations on the instrumental profile. In addition, for small \( \alpha \) the reflected beam is narrower than the incident beam, so that no signal is lost and vignetting in spectral direction (see below) is minimised. Therefore, we took \( \alpha = 15^\circ \) and \( \beta = 45^\circ \). For these parameters, the linear dispersion is \( d = k n f / \cos \beta = 1.52 \text{ mm/nm} \).

Vignetting is the decreased transmission of an optical system for off-axis objects (see for instance [18]). In a spectrograph, vignetting may occur for objects at different spatial positions and for different wavelengths. The total length \( a \) of the collimated beam (see Fig. 6.2) influences the amount of vignetting produced by the system. Vignetting in spatial direction by the complete system (i.e. the TGS and the lenses in front of it, which image the laser beam onto the TGS entrance slit) is at a minimum when \( a = 2f \) [16]. For smaller values of \( a \), the losses at the second lens caused by increasing \( a \) are compensated further in the system. For this value of \( a = 2f \), the (relative) transmission of the system at the edge of the field of view (5.5 mm off-axis) would be about 85%. However, in our spectrograph we chose \( a = f \) since a much larger value would result in an inconveniently large system. For this value, the transmission at the edge of the field of view is expected to be approximately 71% of that in the centre. In practice, it is found to be around 50%, which might be the result of other elements, such as the image rotator, in the optical path. This vignetting effect is taken into account by the calibration measurement, in which the same problem is encountered. Vignetting in spectral direction is negligible because firstly only three of the eight lenses contribute to it, and secondly the dispersed beam is narrower than the beam incident on the first grating, as described above.

The mask width \( m \) determines the width and depth of DGF filter (transmission) profile; a broader mask results in a deeper, but wider profile. The width must be at least the width
Table 6.1: Chosen instrumental parameters and the resulting performance characteristics.

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Performance characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>grating constant $n$</td>
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</tr>
<tr>
<td>angle of incidence $\alpha$</td>
<td>$15^\circ$</td>
</tr>
<tr>
<td>angle of reflection $\beta$</td>
<td>$45^\circ$</td>
</tr>
<tr>
<td>focal length $f$</td>
<td>$600$ mm</td>
</tr>
<tr>
<td>lens diameter $\phi$</td>
<td>$95$ mm</td>
</tr>
<tr>
<td>collimated beam $a$</td>
<td>$600$ mm</td>
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<tr>
<td>dispersion $d$</td>
<td>$1.52$ mm/nm</td>
</tr>
<tr>
<td>solid angle $\Delta \Omega$</td>
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<td>bandpass $\Delta \lambda_{bp}$</td>
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<tr>
<td>spatial res. $\Delta x$</td>
<td>$0.1$ mm</td>
</tr>
<tr>
<td>efficiency $\eta$</td>
<td>$0.25%$</td>
</tr>
<tr>
<td>half 98% width $\Delta \lambda_{98}$</td>
<td>$0.45$ nm</td>
</tr>
<tr>
<td>lowest temp. $T_{e,\min}$</td>
<td>$0.16$ eV</td>
</tr>
<tr>
<td>det. lim. $n_{e,\lim}$</td>
<td>$4 \cdot 10^{17}$ m$^{-3}$</td>
</tr>
</tbody>
</table>

$^a$ In the second spectrograph these angles are reversed.

of the image of the entrance slit. This is larger than the width of the entrance slit (250 $\mu$m) by a factor 1.4 because of the horizontal magnification produced by the grating. Unlike a mirror, a grating produces a change $d\beta \neq d\alpha$ of the angle of reflection $\beta$ for a change in the angle of incidence $\alpha$. This follows directly from the grating equation (Eq. 6.3), and results in a magnification factor $\left| \frac{d\beta}{d\alpha} \right| = \left| \frac{\cos \alpha}{\cos \beta} \right|$ of the image in horizontal (spectral) direction. In this work we take $m = 1.0$ mm.

The second grating in the DGF is mirrored with respect to the first. In this way, the dispersions of both gratings cancel, and the image curvature produced by the first grating is compensated by the second. The intermediate slit has the same width (250 $\mu$m) as the entrance slit. The third spectrograph in the TGS is identical to the first.

Table 6.1 summarises the chosen design parameters and the resulting TGS performance.

The spectral resolution of the system (the bandpass $\Delta \lambda_{bp} \approx 0.23$ nm) equals the spectral range corresponding to the width of image of the entrance slit.

The efficiency $\eta$ of the system (0.25%) is much lower than expected. This turned out to be caused by two of the three gratings delivered by the manufacturer each having an efficiency that is about 6 times below the specified 70%. This leads to a decrease of the overall transmission of the system by a factor of about 40, which is the cause of the relatively high electron density detection limit (see below).

The half 98% width $\Delta \lambda_{98}$ is the distance from the laser wavelength $\lambda_i$ at which the transmission of the filter is approximately 98%; the Thomson spectrum is not distorted significantly further than $\Delta \lambda_{98}$ away from $\lambda_i$. This determines the lowest electron temperature $T_{e,\min}$ that can be measured with the system. A reasonable accuracy (better than $\sim 30\%$) is possible when an electron energy of $\frac{1}{2}k_B T_e$ can be measured. For $\Delta \lambda_{98} = 0.45$ nm, this results in $T_{e,\min} = 0.16$ eV.

The effective redistribution $R_{\text{eff}}$ in Table 6.1 is the fraction of the incident stray light that is detected per spectral range at a distance of $\Delta \lambda_{98} = 0.45$ nm from $\lambda_i$. As described below, the redistribution of a single spectrograph is $3 \cdot 10^{-3}$ nm$^{-1}$ at this position. This is effectively decreased to $R_{\text{eff}} \approx 7 \cdot 10^{-5}$ nm$^{-1}$ by the DGF, which has a (normalised)
The DGF filter profile $F(\lambda)$ can be calculated from the instrumental profiles $f_{1,2}(\lambda' - \lambda)$ of the two single spectrographs that constitute the filter [16]. For simplicity, we take the single spectrograph transmission unity. First we assume that no mask is placed between the two spectrographs, and we follow the path of a photon at the laser wavelength $\lambda_i$. The probability $p_{1,\lambda_i}$ that this photon passes the first spectrograph’s focal plane at a position assigned to a wavelength $\lambda'$ is given by the instrumental profile $f_1(\lambda' - \lambda_i)$ of this spectrograph:

$$p_{1,\lambda_i}d\lambda' = f_1(\lambda' - \lambda_i)d\lambda'. \quad (6.4)$$

The upper graph in Fig. 6.3 schematically illustrates this redistribution of photons by the first spectrograph. If the photon $\lambda_i$ is redistributed to a position associated with a different wavelength $\lambda'$ ($\lambda' \neq \lambda_i$), this photon is most likely to be imaged next to the exit slit by the second spectrograph; this is expressed by the lower graph in Fig. 6.3. Nevertheless, there is a probability $p_2$ that it is redistributed again and passes the exit slit of the filter. This probability is given by the instrumental profile $f_2(\lambda'' - \lambda')$ of the second spectrograph integrated over the width of the exit slit:

$$p_2 = \int_{\text{exit}} f_2(\lambda'' - \lambda')d\lambda''. \quad (6.5)$$

**Fig. 6.3:** Calculation of the probability that a photon of wavelength $\lambda$ passes the DGF via a position that is assigned to $\lambda'$ (see text for an explanation).
Thus, the probability that a photon $\lambda$ passes through the DGF via the route $\lambda'$ is given by the product $p_{1,\lambda} \cdot p_{2}$. The integral of this probability over every possible route $\lambda'$ yields the transmission $T_0$ of the DGF without a mask:

$$T_0 \equiv \int p_{1,\lambda}p_2 d\lambda' = \int \left[ f_1(\lambda' - \lambda_i) \int_{\text{exit}} f_2(\lambda'' - \lambda') d\lambda'' \right] d\lambda'.$$

(6.6)

This transmission factor is due to the redistributions by both spectrographs. For sharp instrumental profiles, such as Dirac or block functions, it approaches unity.

A mask between the two spectrographs can block certain routes $\lambda'$ around $\lambda_i$, so that only photons that follow a path that deviates from the “proper” one ($\lambda'' = \lambda' = \lambda_i$) can reach the exit slit. Thus, the transmission $F(\lambda_i)$ of the DGF at the laser wavelength equals $T_0$ minus the probability of hitting the mask:

$$F(\lambda_i) = T_0 - \int_{\text{mask}} \left[ f_1(\lambda' - \lambda_i) \int_{\text{exit}} f_2(\lambda'' - \lambda') d\lambda'' \right] d\lambda'.$$

(6.7)

With a similar approach for other wavelengths than $\lambda_i$, the complete filter profile $F(\lambda)$ can be calculated. Dividing this by $T_0$ yields the filter profile normalised to unity outside the notch region.

The instrumental profiles $f_1$ and $f_2$ can be estimated from the design parameters of the system. The instrumental profile of the first spectrograph is the convolution of the contributions of the entrance slit, image aberrations, and the grating. The contribution of the entrance slit is a block function of 0.23 nm wide, this being the spectral range associated with the entrance slit width via the dispersion of the spectrograph and the horizontal magnification produced by the grating. The contribution of the image aberrations is more or less Gaussian with a spectral width of 0.05 nm, which follows from the estimated resolution of the lenses ($\sim 75 \mu m$). The contribution of the grating is a $(\sin x/x)^2$ function, which is approximately Lorentzian. Its half width, 4 pm, follows from the resolving power of the grating, $\lambda/\Delta \lambda = N$, where $N$ is the number of illuminated grooves on the grating [17]. The instrumental profile of the second spectrograph is similar to that of the first spectrograph except for the contribution of the entrance slit, which is absent in the former.

The left hand side of Fig. 6.4 shows the calculated and measured instrumental profile of the first spectrograph. According to the calculated profile, the redistribution produced by a single spectrograph at 0.5 nm from the laser wavelength is $R \approx 3 \cdot 10^{-3} \text{ nm}^{-1}$. The measured instrumental profile is, apart from the spectrograph, influenced by cross-over effects in the iCCD camera as well. This is the cause of the wings of the measured instrumental profile being much more intense than the true instrumental profile of the spectrograph. The right hand side of Fig. 6.4 shows the measured and calculated filter profile. The mask width is 1 mm, and the entrance and exit slits are 250 $\mu m$ wide. The measured filter profile matches closely to the calculated profile, which indicates that the approximations above are reasonable. The minor differences between the measured and calculated filter profile may be caused by imperfections of the optics, alignment, or the model.
**Fig. 6.4:** The measured and simulated instrumental profile of the first spectrograph of the DGF (left) and the measured and simulated DGF filter profile (right) with 250 µm slits and a 1 mm mask. The mask is positioned to block light of wavelength $\lambda_i$.

**Fig. 6.5:** The normalised DGF profiles with various mask widths (left) and slit widths (right).

The DGF filter profile depends on the width of the mask and slits that are used. A narrower mask results in a narrower filter profile, so that lower electron temperatures can be studied. This, however, increases the stray light transmission, so that the effective stray light redistribution of the TGS is deteriorated. The left hand side of Fig. 6.5 illustrates this for a number of mask widths. The effect of the slit width on the filter profile is shown in the right hand side of Fig. 6.5. Wider slits both increase the width of (the wings of) the filter profile and the stray light transmission. Each combination of mask and slit widths can be advantageous for particular experimental circumstances, such as the stray light level, the temperature of the plasma under study, and the stability of the position of the laser beam.

Table 6.2 shows the half widths at 98% $\Delta \lambda_{98}$ of the filter profile, the effective TGS redistribution at a distance $\Delta \lambda_{98}$ from the laser wavelength, and the lowest measurable electron temperature $T_{e,\text{min}}$ for the mask and slit widths of Fig. 6.5.

The experimental system described above shows similarities with that of Greenwald *et al.* [8] and those used in recent studies by Kono *et al.* [9] and Noguchi *et al.* [19].
Table 6.2: TGS performance characteristics for various mask and slit widths.

<table>
<thead>
<tr>
<th>slit width</th>
<th>250 µm</th>
<th>500 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>mask width</td>
<td>0.5 mm</td>
<td>1.0 mm</td>
</tr>
<tr>
<td>Δλ₉₈ [nm]</td>
<td>0.28</td>
<td>0.44</td>
</tr>
<tr>
<td>Tₑ,min [eV]</td>
<td>0.07</td>
<td>0.17</td>
</tr>
<tr>
<td>Rₑff(Δλ₉₈) [nm⁻¹]</td>
<td>6 · 10⁻⁸</td>
<td>7 · 10⁻⁹</td>
</tr>
</tbody>
</table>

A difference between our TGS system and that described by Greenwald et al. is that the latter is of the near-Littrow type (α ≈ β), so that only three lenses are needed. However, near-Littrow type spectrographs are known to produce a relatively large amount of stray light because of the proximity of the light beams incident on and reflected by the grating, and both beams sharing the same lens. In addition, a near-Littrow design involves off-axis use of the lenses, which introduces some astigmatism, thus deteriorating either spatial or spectral resolution. Another difference with the system of Greenwald et al. is the absence of additional field lenses to control vignetting in our case. Field lenses only have a positive effect for short lengths a of the collimated beam, which is possible only for near-Littrow spectrographs. In our design, the use of field lenses would improve the transmission at the edge of the field of view by only about 15%, while they would deteriorate the resolution and produce additional stray light. A third distinction is the symmetric arrangement of the first two gratings in our case, so that the image curvatures introduced by both gratings cancel. Finally, the system of Greenwald et al. is designed to image just one half of the Thomson spectrum.

However, the main difference between our setup and those described in previous work is that our setup is designed for measurements on plasmas with a lower electron temperature (Tₑ < 1 eV). This is expressed in the choice for a larger focal length f of the lenses and grating constant n, and different angles α and β. This results in a larger dispersion of the system and a narrower instrumental profile. Therefore, the width of the notch filter profile is much narrower; 90% relative transmission of the system is achieved at only 0.45 nm from the central wavelength. This makes the setup presented here especially suitable for low electron temperature plasmas, such as the ones in gas discharge lamps.

### 6.2.4 Detection limit

The detection limit nₑ,lim is the electron density for which nₑ and Tₑ can be determined from the scattering spectrum with a “reasonable” accuracy, say 30%. It is determined by properties of the experimental system, such as the transmission of the TGS, and by experimental conditions, such as the integration time (30 minutes in this work), the length of the detection volume (5.5 mm), and the width of the scattering spectrum (determined by Tₑ ~ 1 eV). The detection limit of the present system under these conditions is [16]

\[ nₑ,lim \approx 4 \cdot 10^{17} \text{ m}^{-3}. \]  

(6.8)
This is supported by both the measurements and a detailed calculation of the various noise sources, such as dark current of the iCCD camera, readout noise, residual stray light, and statistical noise on the Thomson scattering experiment itself.

The relatively high detection limit is the result of the two inefficient gratings in the TGS; replacing them would reduce $n_{\text{c, lim}}$ by a factor of approximately 40. This is also the reason for the long integration time required for the measurements. In addition, the laser beam was found to move slightly (0.1–0.2 mm) during lengthy measurement sessions. In order to allow for this small drift, the width of the slits in the TGS is taken 500 µm during the measurements described in this study, although this reduces the stray light rejection (cf. Fig. 6.5 and Table 6.2).

Measurements are performed by simply integrating the iCCD signal. A 2-dimensional photon counting technique, as described by Kono et al. [9], was not applied. A calculation of the relative importance of the noise sources in the experiment shows that in our case the most important noise source is by far the statistical noise on the Thomson scattering experiment, which cannot be eliminated by photon counting [16]. Experiments with and without photon counting confirm this presumption.

### 6.3 Experimental version of the QL lamp

The Philips QL lamp is a low-pressure, inductively powered (electrode-less) gas discharge lamp. The RF frequency of the lamp is 2.65 MHz, and the power delivered by the RF coil is 85 W [2,3,20]. Due to the absence of electrodes, this lamp combines a high efficacy with a long lifetime. The lamps studied in this work are filled with 66 and 133 Pa argon buffer gas. Mercury is supplied by an amalgam (Bi/In/Hg in a mass ratio of 68/29/3).

A number of modifications were made to the commercially available lamps in order to perform Thomson scattering experiments. First of all, the fluorescent coating is absent in the experimental QL bulb in order to have optical access to the discharge. Secondly, the amalgam is thermostated so that the mercury pressure in the lamp can be controlled. Finally, in order to allow the high intensity laser beam to enter the discharge, extension tubes with quartz laser windows were mounted onto the lamp (see Fig. 6.6).

The quartz laser windows are required since the glass of the QL bulb is too rough and weak for a high intensity laser beam. In addition, the windows must be placed far from the focal volume to withstand the high laser intensity close to the focal point inside the lamp. This also reduces the effect of stray light produced by these windows. Therefore, 60 cm extension tubes with quartz windows were mounted on either side of the lamp. The windows are placed at Brewster angle to minimise reflections of the laser beam.

Possible complications introduced by the large extension tubes are mercury condensation in the relatively cold tubes and a drop of the operational pressure of the lamp. Mercury condensation was prevented by heating the extension tubes to 50°C by a flat water hose wrapped around the tubes. Copper pipes were placed over the ends of the extension tubes...
Thomson scattering on the Philips QL lamp

Fig. 6.6: The experimental version of the Philips QL lamp that was used for the measurements. The extension tubes and Brewster angle laser windows are heated to 50°C by water hoses to prevent mercury condensation; copper pipes heat the air in front of the Brewster windows as well. The amalgam is thermostrated to control the mercury pressure in the lamp. The position of the detection volume is expressed in the coordinates $r$ (radial distance) and $h$ (height) with respect to the centre of the RF coil. The coil can be moved in vertical direction.

The drop of the operational pressure arises from the large temperature difference between the gas in the lamp and the extension tubes. Since the volume of the tubes is not negligible compared to that of the lamp (175 versus 740 ml), a significant fraction of the gas will escape to the extension tubes when the lamp is switched on, thus decreasing the operational pressure of the lamp. In order to compensate for this effect, the experimental lamps were filled at slightly higher pressures (80 instead of 66 Pa, and 160 instead of 133 Pa). The filling pressure correction factor is calculated from the volume ratio of the lamp and the extension tubes, the temperature of the extension tubes, and the operational pressure in an unmodified lamp (∼270 Pa for the 133 Pa lamp). The latter follows from the gas temperature distribution in the lamp. This distribution is not known for the entire lamp, but can be estimated roughly with the help of the radial gas temperature profile at the central height in the plasma, which was measured by Jonkers et al. [2].

The lamp was moved along the laser beam in order to measure at different radial positions $r$ in the plasma. The minimum radial position $r_{\text{min}}$ and height $h$ of the detection volume with respect to the centre of the RF coil are determined by the positions of the extension tubes on the QL bulb. In the 66 Pa lamp, $r_{\text{min}} \approx 23$ mm and $h \approx 18$ mm; in the 133 Pa lamp, $r_{\text{min}} \approx 28$ mm and $h \approx 34$ mm. In order to measure closer to the centre of the discharge, the RF coil was raised by approximately 21 mm in a second series of measurements, so that $h$ decreases. The shape of the plasma with respect to the RF coil is assumed not to change significantly if the position of the coil inside the QL bulb is varied.
As discussed in Section 6.2.1, the experimental system is calibrated with rotational Raman scattering on N$_2$. For this purpose, the lamp is removed and the detection volume is flushed by a gentle flow of nitrogen at atmospheric pressure and room temperature. However, placing the lamp in the detection area causes the laser beam to be displaced ($\sim 1$ mm) by refraction in the Brewster angle laser windows. Therefore, the system must be adjusted slightly so that the image of the laser beam coincides with (the centre of) the TGS entrance slit. If the image of the laser beam is on the edge of the entrance slit, the spectrum is shifted with respect to the stray light mask, which introduces a slight asymmetry of the recorded spectrum. The lenses in front of the TGS were moved slightly in vertical direction until the spectrum is symmetric and the scattering intensity is at a maximum.

For a correct measurement of the electron density, the transmission of Thomson scattered light by the QL bulb must be taken into account. The reflection coefficient of glass is approximately 8% at normal incidence. In addition, the QL bulb is coated to prevent mercury absorption by the glass, which lowers the transmission about 15%. Therefore, the measured electron densities are underestimated by approximately 20%. The measurements presented in Section 6.4 are corrected for this effect.

### 6.4 Results

Fig. 6.7 shows a rotational Raman spectrum used for calibration of the experimental system. The peaks in the spectrum correspond to the even rotational transitions. The weaker odd transitions, located between them, could not be resolved individually (cf. [21]). The dispersion of the system, which can be derived from this spectrum, is $d = 1.52$ mm/nm, corresponding to the dispersion calculated in Section 6.2.

Fig. 6.8 shows two typical Thomson scattering spectra that were measured with the 133 Pa lamp with a mercury pressure of $p_{\text{Hg}} = 0.95$ Pa. These spectra are taken at the same radial position $r$, but at different heights $h$ and on different sides of the glass core of
Thomson scattering on the Philips QL lamp

Fig. 6.8: Typical Thomson scattering spectra obtained with the 133 Pa lamp ($p^{\text{Hg}} = 0.95$ Pa) at $r = 29$ mm and height $h = 34$ mm (left) and $h = 13$ mm (right). The spectrum on the left hand side shows a relatively strong stray light residue in the centre.

The QL bulb. The spectrum on the left hand side was obtained at the side from which the laser beam entered the lamp. At this position, reflection of laser light on the glass core strongly increases the stray light intensity, as expressed by the residual stray light peak in the centre of the spectrum. From this figure it is clear that the electron density is higher at positions closer to the RF coil. The electron temperatures are comparable, seeing the uncertainty of approximately 10–15% in $T_e$, as discussed below.

The relative uncertainty in the measured electron temperatures ranges from about 7% at high electron densities ($10^{19}$ m$^{-3}$) to 30% at the electron density detection limit. This uncertainty is mainly determined by the accuracy of the Gaussian fit to the measured spectrum, which deteriorates rapidly for decreasing electron densities.

The relative uncertainty in the measured electron densities, ranging from about 15% to 30%, is primarily determined by the sensitivity calibration of the system. Firstly, the Raman scattering cross section used for calibration has an accuracy of approximately 8% [15]. Secondly, the transmission of the glass of the QL bulb is not known precisely. Thirdly, the alignment of the image of the laser beam onto the entrance slit may introduce an extra uncertainty. Note that part of the error in $n_e$ is systematic. Therefore, the measured values with respect to each other generally correspond better than suggested by the estimated error.

Fig. 6.9 shows radial profiles of the electron density in the 66 and 133 Pa lamps. Note that this argon filling pressure $p^{\text{Ar}}$ refers to the pressure when the lamp is off (cold); the operational pressure is about a factor of two higher. The amalgam temperature was 100°C during these measurements, so that the mercury pressure is $p^{\text{Hg}} = 0.95$ Pa. Measurements are done at the standard height above the centre of the RF coil (18 and 34 mm for the 66 and 133 Pa lamps respectively) and with the raised RF coil, i.e. 21 mm lower with respect to the coil. The plasma walls are located at $r = 9$ mm and 55 mm.

From this figure it is clear that the electron density decreases further from the RF coil
The highest measured electron density is in all cases located at the closest position to the coil that could be measured with the present experimental lamps. Therefore, no accurate statement can be made about the position of the maximum electron density in the lamp. The electron density in the 133 Pa lamp is higher by a factor of about 1.5–2 compared to the 66 Pa lamp, as can be seen by comparing the profiles at $h = 18$ mm in the 66 Pa lamp and $h = 13$ mm in the 133 Pa lamp.

In Fig. 6.10 radial profiles of the electron temperature are shown for the same experimental conditions. The electron temperature does not show a significant dependence on the height above the RF coil. The measurements suggest a small increase of $T_e$ towards the edge of the discharge. $T_e$ is slightly lower in the 133 Pa lamp than in the 66 Pa lamp.

Fig. 6.11 shows the electron density $n_e$ as function of the mercury pressure $p_{\text{Hg}}$ in the lamp. The electron density shows only a weak dependence on $p_{\text{Hg}}$, although it seems to go through a minimum at $p_{\text{Hg}} \approx 0.5$ Pa. The electron density in the 133 Pa lamp is again approximately 1.5–2 times higher than that in the 66 Pa lamp, and is higher for smaller heights $h$ above the RF coil.
Finally, Fig. 6.12 gives the electron temperature $T_e$ for different mercury pressures. Clearly, $T_e$ decreases for increasing mercury pressure, especially between 0.5 and 1 Pa. The electron temperature in the 133 Pa lamp is somewhat lower than that in the 66 Pa lamp, and slightly higher closer to the RF coil (smaller $h$).

### 6.5 Discussion

The electron density and temperature in (quasi) steady state plasmas of small dimensions can often be related to external control parameters of the plasma, such as size (expressed in an electron density gradient length $\Lambda_{n_e}$), power density $\varepsilon$, and pressure $p$. This relation is expressed by simplified versions of the electron particle and energy balances. In this section, these balances are treated briefly; for more information on this subject we refer to [3,21,22]. Subsequently, the values of $n_e$ and $T_e$ predicted by these balances and the results of calculations on the basis of DLA measurements, as described by Jonkers et al. [3], are compared to the measurements in the present study. Finally, the electron particle and energy balances are applied to explain observed trends of the electron density and temperature qualitatively.
6.5.1 Electron particle and energy balances

The measured values of $n_e$ and $T_e$ suggest a large overpopulation of the mercury ground state density with respect to that given by the Saha equation in the entire part of the plasma that is studied in this work. Therefore, recombination is relatively unimportant [21, 22], and can be neglected in the electron particle and energy balances.

A simplified version of the steady-state electron particle balance,

$$n_e n_{1}^{Hg} S_{ion} \approx n_e \frac{D_a}{\Lambda_{n_e}^2}, \quad (6.9)$$

equates electron production by ionisation (left hand side) to electron loss by ambipolar diffusion (right hand side).

The ionisation rate is mainly determined by mercury because of its relatively low ionisation energy (10.43 versus 15.76 eV for argon). Therefore, the ionisation rate is the product of the ground state mercury density $n_{1}^{Hg}$ and an effective ionisation rate coefficient $S_{ion}^{Hg}$ of mercury, which can be determined from a Collisional Radiative Model (CRM). Van Dijk et al. [20] have shown that, around $n_e \approx 10^{19} \text{m}^{-3}$ and $T_e \approx 1 \text{eV}$, roughly

$$S_{ion}^{Hg} \propto n_e^{0.4} \sqrt{T_e} \exp \left(\frac{-E^*}{k_B T_e}\right), \quad (6.10)$$

where $E^* \approx 7.5 \text{ eV}$. This indicates that direct and stepwise ionisation processes are of comparable importance. $S_{ion}^{Hg}$ increases if radiative trapping of resonant radiation becomes more important (i.e. if the so-called escape-factor $\Lambda_{esc}$ for resonant radiation decreases).

The diffusion rate depends on the electron density gradient length $\Lambda_{n_e}$ and the coefficient for ambipolar diffusion $D_a$,

$$D_a \approx \mu_{Ar}^{Hg} \cdot \frac{k_B T_e}{e} \propto \frac{T_e}{n_{Ar}^{Ar}}, \quad (6.11)$$

where $\mu_{Ar}^{Hg}$ is the mobility of mercury ions in argon and $n_{Ar}^{Ar}$ the argon density. This approximation is justified since the heavy-particle temperature $T_h$ is much smaller than the electron temperature $T_e$, and argon is the most important elastic collision partner of Hg$^+$. As the electron particle balance strongly depends on $T_e$, it may be applied to understand trends of this parameter for varying plasma conditions.

The simplified steady-state electron energy balance,

$$\varepsilon_{RF} \approx \varepsilon_{rad} + n_e n_{1}^{Hg} S_{ion}^{Hg} \cdot \left( I_{Hg} + \frac{3}{2} k_B T_e \right) + n_e n_{1}^{Ar} \cdot Q_{heat} \cdot \frac{3}{2} k_B (T_e - T_h), \quad (6.12)$$

states that the energy $\varepsilon_{RF}$ delivered to the electrons by the RF coil is converted into radiation, leads to ionisation of mercury, and heats the argon gas.

The radiative term may be approximated by

$$\varepsilon_{rad} \approx n_{1}^{Hg} \exp \left( \frac{-E_{1,2}}{k_B T_e} \right) \cdot A_{1,2} \Lambda_{esc} \cdot E_{1,2}. \quad (6.13)$$
Here $E_{1,2} = 4.89$ eV is the excitation energy of the $6^3P_1$ state, which radiates at 253.6 nm with a transition probability $A_{1,2} = 8 \cdot 10^6$ s$^{-1}$. Radiation from other excited states is much weaker because of their lower density. Eq. 6.13 assumes the $6^3P_1$ state to be populated according to the Boltzmann distribution, which is reasonable around $n_e \approx 10^{19}$ m$^{-3}$ since it has a relatively low excitation energy [20]. With $n_1^{Hg} \approx 3 \cdot 10^{19}$ m$^{-3}$ [3], $T_e \approx 1$ eV, $\Lambda_{esc} \approx 0.1$ [20], and a plasma volume of $V \approx 400$ ml, Eq. 6.13 yields $P_{rad} = V \varepsilon_{rad} \approx 57$ W, which is a reasonable value for a 85 W lamp.

The ionisation term is the product of the ionisation rate $n_e n_1^{Hg} \sigma_{ion}^{Hg}$ (cf. Eq. 6.9) and the energy required to ionise a mercury atom ($I_{Hg}$) and to heat the electron to $T_e$.

The argon buffer gas is mainly heated by elastic collisions of electrons with argon atoms. Therefore, this term is proportional to the electron density $n_e$ and the argon (ground state) density $n_1^{Ar}$. The constant $Q_{heat}$ represents the effective rate coefficient for momentum transfer from electrons to heavy particles. Furthermore, the heating term is proportional to the difference in the temperatures of electrons ($T_e$) and heavy particles ($T_h$).

The electron energy balance establishes a relation between the electron density $n_e$ on one hand, and the dissipated RF power $\varepsilon_{RF}$ and electron temperature $T_e$ on the other hand.

Jonkers et al. [2] measured the heavy-particle temperature $T_h$ and the argon metastable density by Diode Laser Absorption (DLA), and used these results to estimate $n_e$ and $T_e$ on the basis of the heavy-particle energy balance and an argon CRM [3]. In addition, they applied the electron particle and energy balances given above to estimate $n_e$ and $T_e$ [3]. Both methods in the work of Jonkers yield $n_e \approx 1 \cdot 10^{19}$ m$^{-3}$ and $T_e \approx 1.5$ eV in the 66 Pa lamp, and $n_e \approx 2 \cdot 10^{19}$ m$^{-3}$ and $T_e \approx 1.2$ eV in the 133 Pa lamp. These values apply in the most active region of the plasma, i.e. where $n_e$ is at a maximum. Unfortunately, the maximum of $n_e$ is located at a smaller radial position $r$ than could be used for the measurements in the present study.

The highest electron densities measured in the present study agree fairly well with the results of Jonkers. Note that the highest electron density in the 133 Pa lamp is measured at approximately 13 mm above the RF coil (see the right hand side of Fig. 6.9). Therefore, the maximum value of $n_e$ value is expected to be slightly higher.

The measured electron temperatures are systematically lower than those calculated by Jonkers. This may be attributed to the different conditions used in the present work. Firstly, Jonkers only gives values of $n_e$ and $T_e$ at smaller radial positions. The electron density gradient length $\Lambda_{n_e}$ used by Jonkers is based on the steep density gradient that is present near the centre of the lamp. The large electron losses associated with this gradient length require a high ionisation rate, and hence a high electron temperature. However, at larger radial positions, where the measurements in this study are performed, the electron density gradient length increases considerably, so that $T_e$ is lower. Secondly, the amalgam in the lamp was not heated and thermostrated during the experiments of Jonkers. Therefore, the mercury pressure $p_{Hg}$ in the lamp was not known precisely. As the lamp was oriented with the amalgam at the bottom, like in Fig. 6.6, the amalgam might have been at a lower temperature than in our experiments, which substantially lowers $p_{Hg}$. This results in severe depletion of mercury ground state atoms in the active part of the lamp. As shown

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Thomson scattering on the Philips QL lamp
by Eq. 6.9, a low $n_{iHg}^{\text{Hg}}$ requires a high ionisation rate in order to compensate for the diffusive efflux of charged particles, so that $T_e$ must have been higher in the case of Jonkers.

Although the electron temperatures $T_e$ measured in this study differ from those reported by Jonkers, similar trends of both $n_e$ and $T_e$, such as the effect of the argon filling pressure, were observed in this study. Below, the electron particle and energy balances are used to explain these trends qualitatively.

### 6.5.2 Radial $n_e$ and $T_e$ profiles

The electron density in the QL lamp shows a clear dependence on the distance to the RF coil; it is lower at positions further from the coil (either radially or axially). This is related to the lower power density $\varepsilon_{\text{RF}}$ and larger radiative losses $\varepsilon_{\text{rad}}$ (larger escape factor $\Lambda_{\text{esc}}$) further from the coil. According to Eq. 6.12, this leads to a lower electron density $n_e$.

The electron temperature profile is rather flat in the part of the QL lamp that was studied. However, the measurements suggest a slight increase of $T_e$ towards the edge of the lamp. A similar trend was found by simulations of an alternative inductively coupled plasma for lighting purposes [23], and observed in an atmospheric spectrochemical Inductively Coupled Plasma [21]. This increase can be attributed to the larger gradients of the charged particle density towards the edge of the plasma. This leads to large diffusion losses, which must be compensated by a higher ionisation rate (cf. Eq. 6.9), and hence a higher electron temperature. The same effect is present near the glass wall around the RF coil. Therefore, it is likely that the electron temperature also rises towards the centre of the plasma. This, however, could not be observed with the present experimental QL lamps, since the minimum radial position at which measurements could be done is $r = 23$ mm, i.e. 14 mm from the glass wall in the centre.

The electron temperature is slightly lower in the 133 Pa lamp compared to the 66 Pa lamp. This can be attributed to the longer diffusion life time of charged particles in the discharge. Due to the higher argon density in the 133 Pa lamp, the diffusion coefficient is smaller (cf. Eq. 6.11). Therefore, the ionisation rate and hence the electron temperature can be lower to sustain the discharge. Note that the heavy-particle temperature, which was measured by Jonkers et al [2], is also higher in the 133 Pa lamp. This results in an enhanced thermal depletion of argon in the centre of the plasma. Hence, the argon density at the wall rises even further, which leads to a further decrease of the total diffusive losses in the lamp.

The electron density in the 133 Pa lamp is clearly higher (a factor of $1.5 - 2$) than that in the 66 Pa lamp. This is indirectly caused by the lower diffusion rate as well. Firstly, as argued above, the ionisation rate is lower in the 133 Pa lamp. Secondly, the radiation losses $\varepsilon_{\text{rad}}$ are lower because of the lower electron temperature (cf. Eq. 6.13). Finally, at higher pressures the plasma is located closer to the RF coil [2]. This enhances the coupling between the coil and the plasma, so that $\varepsilon_{\text{RF}}$ increases. For each of these effects, Eq. 6.12 yields a higher electron density.
6.5.3 Values of $n_e$ and $T_e$ as function of mercury pressure

The dependence of the electron density on the mercury pressure is not very strong. Nevertheless, the measurements suggest that $n_e$ goes through a minimum between $p_{\text{Hg}} \approx 0.5$ and 1 Pa. The dependence of the electron temperature on $p_{\text{Hg}}$ is more pronounced. It slightly decreases with increasing $p_{\text{Hg}}$, and shows a sharper transition between 0.5 and 1 Pa. This may be understood from the electron particle and energy balances as follows.

For low mercury pressures, the plasma is optically open for resonant mercury radiation ($\Lambda_{\text{esc}} \rightarrow 1$). The loss of electron-ion pairs due to diffusion does not change significantly for varying mercury pressures, so that $n_{1}^{\text{Hg}} S_{\text{ion}}^{\text{Hg}}$ can be approximately constant. Hence, an increasing $p_{\text{Hg}}$, or equivalently $n_{\text{Hg}}$, allows for a lower ionisation rate coefficient $S_{\text{ion}}^{\text{Hg}}$, so that $T_e$ may decrease slightly (cf. Eq. 6.10). In spite of this (small) decrease of $T_e$, the radiative losses $\varepsilon_{\text{rad}}$ increase for increasing $p_{\text{Hg}}$. This is due to the weaker temperature dependence of $\varepsilon_{\text{rad}}$ compared to $S_{\text{ion}}^{\text{Hg}}$ (cf. Eqs. 6.10 and 6.13; $E_{1,2} < E^*$). According to the energy balance (Eq. 6.12), an increase of $\varepsilon_{\text{rad}}$ in turn leads to a decrease of $n_e$.

At a certain mercury pressure ($p_{\text{Hg}} \approx 0.5$ Pa), radiative trapping of resonant radiation becomes more important ($\Lambda_{\text{esc}} \rightarrow 0$). This leads to more efficient ionisation, so that the electron temperature drops more steeply around $p_{\text{Hg}} \approx 0.5$ Pa. In addition, a decreasing escape factor $\Lambda_{\text{esc}}$ leads to a decrease of the radiative losses, and hence an increase of $n_e$.

Obviously, for a lamp radiative “losses” must be as large as possible. A low mercury density $n_{1}^{\text{Hg}}$ (at low mercury pressures) or a small escape factor $\Lambda_{\text{esc}}$ (at high mercury pressures) are undesirable. Therefore, the optimum mercury pressure for light output is around $p_{\text{Hg}} \approx 0.5$ Pa, which is known to be a reasonable value for most low pressure gas discharge lamps [1].

6.6 Conclusions

In this work, the electron density and temperature in the Philips QL lamp were measured with laser Thomson scattering. For this purpose, a low stray light Triple Grating Spectrograph (TGS) was built. Measured trends of the electron gas properties were explained by the electron particle and energy balances.

The technique of Thomson scattering provides direct access to the electron gas parameters, but is not easily applicable on low electron density plasmas contained in glass. The main problem for such a measurement is stray light. By using a TGS instead of a single spectrograph, the effective redistribution $R_{\text{eff}}$ (the fraction of stray light detected per spectral range) at 0.5 nm from the laser wavelength was lowered from about $3 \cdot 10^{-3}$ nm$^{-1}$ to around $7 \cdot 10^{-9}$ nm$^{-1}$. The Thomson spectrum was not distorted significantly further than 0.5 nm from the laser wavelength, so that electron temperatures of $\sim 0.2$ eV can readily be measured. The detection limit of the measurements was approximately $n_{e,\text{lim}} \approx 4 \cdot 10^{17}$ m$^{-3}$, and can be lowered by a factor of 40 by replacing the two inefficient gratings in the setup.

For the measurements described in this work, a number of modifications were made to the commercially available lamps. First of all, the experimental version of the QL lamp does
Chapter 6

not have a fluorescent coating in the lamp, in order to have optical access to the discharge. Secondly, quartz laser windows at Brewster angle and far from the detection volume were mounted onto the lamp to allow a high power laser beam to enter the discharge. Thirdly, mercury condensation on cold spots, especially the Brewster windows, was prevented by additional heating. Finally, a small correction was made to the argon filling pressure of the lamp to compensate for the increased lamp volume.

The high stray light rejection of the detection system and the modifications to the lamp are sufficient for reliable Thomson scattering measurements on gas discharge lamps.

The electron density and temperature in the QL lamp are approximately $n_e \approx 10^{19} \text{ m}^{-3}$ and $T_e \approx 1.0 \text{ eV}$, and depend slightly on the operational conditions, such as the argon pressure $p_{Ar}$ and mercury pressure $p_{Hg}$.

The measured electron densities are in agreement with those reported in the work of Jonkers et al. [3]. However, the measured electron temperatures are systematically lower by approximately 0.3-0.4 eV. This is mainly caused by the fact that our measurements are done outside the region with the highest electron temperature, which is situated closer to the centre of the lamp than could be measured with the present experimental lamps. Observed trends of $n_e$ and $T_e$ for varying $p_{Ar}$ and $p_{Hg}$ and different positions in the lamp were explained by the electron particle and energy balances. A higher argon pressure reduces the diffusion coefficient. This results in a lower $T_e$ and higher $n_e$. A higher mercury pressure leads to a lower $T_e$ because of more efficient ionisation and a higher $n_e$ due to enhanced radiative trapping.

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References


Thomson scattering on the Philips QL lamp


Chapter 7

Time resolved electron density and temperature measurements on a capacitively coupled helium RF discharge

Abstract

Small capacitively coupled RF plasma sources operated with helium are popular as excitation sources for element detection, especially in combination with a gas chromatograph. The high mobility of helium and the use of relatively low RF frequencies lead to strong time dependencies of the electron density and temperature, and hence excitation efficiency. In this study, the electron gas parameters of such a plasma were measured with temporal resolution. This was done by Thomson scattering using a triple grating spectrograph for stray light rejection and by absolute spectral line intensity measurements. A model to explain the electron density behaviour on the basis of the measured electron temperatures is presented. The model reproduces experimental results reasonably well. The electron energy distribution function is shown to deviate in various ways from a Maxwellian equilibrium shape during the course of an RF cycle. The electron production temperature varies with the RF signal between 1.2 and 2.0 eV, whereas the electron bulk temperature shows much stronger time dependencies (ranging from 0.5 to 3.8 eV). The electron density varies within a factor of two around $1.4 \cdot 10^{19}$ m$^{-3}$.

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To be submitted for publication in Plasma Sources Sci. Technol.
7.1 Introduction

Atomic Emission Spectroscopy (AES) has since long been recognised as one of the most selective and sensitive methods for element detection. This resulted in the development of many different plasma excitation sources for this purpose, among others the Inductively Coupled Plasma (ICP) [1], various Microwave Induced Plasmas (MIP) [2–5], and many smaller, capacitively coupled RF plasmas, such as the one used for Furnace Atomisation Plasma Emission Spectroscopy (FAPES) [6]. This latter class is especially popular in combination with a Gas Chromatograph (GC) or Mass Spectrograph (MS), as these plasma sources operate at low power with a very small gas flow [7]. Therefore, these plasmas are flexible and have low operational costs. In addition, they show a large stability with respect to gas flow and sample injection [8]. Nevertheless, detection limits are comparable with those of the more traditional plasma sources, such as the ICP [1,9].

The RF plasmas used in combination with GC often operate on helium. As helium has a high ionisation energy, the electron temperature in such plasmas is rather high, which facilitates detection of fluorine, chlorine, bromine, and iodine in halogenated organic compounds. Because of its small mass, helium is very mobile. This, together with the small plasma size, leads to large diffusive fluxes out of the plasma. In combination with a relatively low driving frequency of the plasma, parameters as the electron temperature $T_e$ and density $n_e$ may become strongly time dependent. This, of course, influences the plasma’s excitation efficiency for spectroscopic applications.

This study is dedicated to the time dependence of the electron density and temperature of a capacitively coupled RF (112 kHz) plasma, operated with helium at atmospheric pressure [8]. These electron gas parameters are measured with temporal resolution by means of laser Thomson Scattering (TS) and Absolute spectral Line Intensity (ALI) measurements. Section 7.2 briefly describes the plasma setup and the diagnostic techniques that were used. Measurements of the plasma power and results of TS and ALI experiments are presented in Section 7.3 and discussed in Section 7.4. A model of the time dependence of the electron density on the basis of the measured electron temperatures and the electron particle and energy balances is developed. Conclusions are drawn in Section 7.5.

7.2 Experimental arrangement

7.2.1 The helium RF discharge

The helium RF discharge studied in this work is similar to the one described by Lepkojus et al. [8], see Fig. 7.1. The plasma is powered by an RF generator delivering about 35 W at a frequency of 112 kHz. The RF signal passes through a high voltage transformer (winding ratio 20:600) and powers the plasma by two Swagelok gas connections serving as electrodes. The quartz discharge tube, mounted between the electrodes, has an inner diameter (i.d.) of 4 mm and a length of 60 mm. A helium flow of 350 ml/min is sustained through the tube. The tube is open at one side, so that the plasma operates at atmospheric pressure.
When used for analytical purposes, the helium flow is mixed with another (small) helium flow containing the gaseous analyte to be studied, and emission from the plasma is detected head-on at the open end of the discharge tube. However, for the experiments described in this work a pure helium plasma (without analyte) is used. Plasma emission and Thomson scattered radiation are detected perpendicular to the plasma axis, through the discharge tube wall. For the Thomson scattering experiments, a laser beam is directed along the axis of the tube. The beam enters the tube at the gas inlet side through a quartz window at Brewster angle to minimise reflections. The window is placed far from the focal volume in order to withstand the high laser power.

7.2.2 Thomson Scattering (TS)

Thomson scattering, i.e. scattering of (laser) radiation by free electrons in a plasma, can be applied to measure the electron gas properties, such as density, temperature, and energy distribution [10–13]. For relatively low electron densities, scattering is incoherent. In that case, the scattering intensity is directly proportional to the electron density \( n_e \), and can be determined absolutely by calibrating the experimental system with, for instance, rotational Raman scattering on nitrogen [13–16]. The shape of the measured scattering spectrum is represented by the (normalised) spectral distribution function \( S(\Delta \lambda) \). If the Electron Velocity Distribution Function (EVDF) is isotropic, \( S(\Delta \lambda) \) directly reflects the one-dimensional EVDF \( F_x(v_x) \):

\[
F_x(v_x) = \frac{2\lambda_i \sin(\theta/2)}{c} \cdot S \left( -v_x \cdot \frac{2\lambda_i \sin(\theta/2)}{c} \right),
\]  

(7.1)
Fig. 7.2: The experimental system for Thomson scattering that was used in this study [16]. Light from a frequency doubled Nd:YAG laser is scattered by electrons in the plasma. Scattered light is collected and dispersed by a triple grating spectrograph. The first two gratings and the mask between them serve as a stray light filter. An intensified CCD camera records the scattering spectrum.

where $\theta$ is the scattering angle, which is taken $90^\circ$ in our experimental system. The Electron Energy Distribution Function (EEDF) is related to $F_x(v_x)$ via [13, 15, 17, 18]

$$f_E(E) = -\frac{2}{m_e} \cdot \frac{dF_x}{dv_x} \left( \sqrt{2E/m_e} \right).$$  \hspace{1cm} (7.2)

In the case of a Maxwellian EEDF, $S(\Delta \lambda)$ is a Gaussian, and the electron temperature $T_e$ can be derived directly from the half $1/e$ width $\Delta \lambda_{1/e}$ of this Gaussian:

$$T_e = \frac{m_e c^2}{8k_B \lambda_i^2 \sin^2(\theta/2)} \cdot \Delta \lambda_{1/e}. \hspace{1cm} (7.3)$$

Here $m_e$ is the electron rest mass, $c$ the light speed, and $k_B$ the Boltzmann constant. For $\theta = 90^\circ$ and $\lambda_i = 532$ nm, as used in the present work, the factor between brackets equals 5238 K nm$^{-2}$.

The experimental arrangement used in this work is similar to that described in Chapter 6 [16]. It is shown schematically in Fig. 7.2. A frequency doubled Nd:YAG laser (532 nm) produces 7 ns laser pulses of 400 mJ. A plano-convex lens ($f = 1$ m) focuses these light pulses into the plasma, where scattering takes place. Scattered photons are collected by a set of achromatic doublet lenses and imaged onto the entrance slit of a Triple Grating Spectrograph (TGS), which disperses the scattered radiation while rejecting stray light at the laser wavelength. An intensified CCD camera records the (horizontal) scattering spectrum. In principle, the vertical direction on the iCCD represents the spatial position in
the plasma. However, since the laser beam is parallel to the axis of the (roughly) cylindrical plasma, no spatial resolution is required. Therefore, recorded spectra are averaged over the entire detection volume (11 mm). The arrangement employs a perpendicular scattering geometry, i.e. the scattering angle is $\theta = 90^\circ$, the laser beam is polarised perpendicular to the plane of scattering, and only scattered radiation with the same polarisation direction is detected, so that the (partly) unpolarised plasma emission and stray light are reduced.

Together with the spatial filter between them, the first two gratings in the TGS serve as a stray light filter; a detailed description is given in [16]. The fraction of stray light detected in the scattering spectrum at 0.5 nm from the laser wavelength is on the order of $10^{-8}$ nm$^{-1}$. The Thomson spectrum is not distorted significantly further than 0.5 nm from the laser wavelength, and the spectral range of the system extends to 5 nm from the laser wavelength, so that the measurement is, in principle, reliable for electron energies in the range $0.2 \text{ eV} < E < 11 \text{ eV}$. However, as described below, for low $n_e$ and $T_e$, the upper energy limit is much lower ($\sim 4 \text{ eV}$).

In order to achieve temporal resolution, the Q-switch of the laser system and the iCCD gate are triggered by the RF signal that is picked up by a Rogowski coil around one of the cables of the high voltage transformer, as shown in Fig. 7.1. In this way, a time resolution better than 20 ns is achieved.

### 7.2.3 Absolute Line Intensity (ALI) measurements

The absolute intensity of a spectral line emitted by the plasma can be used to determine the density of the emitting excited particle. This density can subsequently be used in the Boltzmann equation to estimate the electron temperature. Because the plasma is ionising, the density of excited states is underpopulated with respect to the Boltzmann density; this was corrected for by a factor that follows from a Collisional Radiative Model (CRM) [19,20]. In this work only the spectral line at 587.6 nm ($3d \to 2p$ transition) is studied since this is the most intense line.

The experimental arrangement for ALI measurements is similar to the one for Thomson scattering (Fig. 7.2). As there is no stray light to reject, using a single spectrograph suffices. Therefore, the iCCD camera is placed at the mask position. The iCCD gate is triggered by the RF signal from the Rogowski coil (at a reduced frequency of 14 kHz), and the iCCD gate time, and hence temporal resolution, is 50 ns.

Intensity measurements are calibrated against the irradiance of a tungsten ribbon calibration lamp. The measured irradiance of a spectral line of the plasma (given in Wm$^{-2}$sr$^{-1}$) is the result of plasma emission integrated along a line of sight. Therefore, the measured irradiance must be divided by the length of the discharge along the line of sight to yield the average emission coefficient $j$ (in W m$^{-3}$ sr$^{-1}$) of the spectral line that is studied.

The emission coefficient $j_{pq}$ of the optical transition from excited state $p$ to $q$ is proportional to the density $n_p$ of the upper state,

$$ j_{pq} = \frac{1}{4\pi} A_{pq} n_p h \nu_{pq}, $$

(7.4)
Table 7.1: Properties of the $3d \rightarrow 2p$ optical transition of helium [20, 22].

<table>
<thead>
<tr>
<th>$E_p$</th>
<th>23.07 eV</th>
<th>$\lambda_{pq}$</th>
<th>587.6 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_p$</td>
<td>15</td>
<td>$h\nu_{pq}$</td>
<td>2.11 eV</td>
</tr>
<tr>
<td>$r_{pq}^1$</td>
<td>8 $\cdot$ 10$^{-7}$</td>
<td>$A_{pq}$</td>
<td>7.06 $\cdot$ 10$^7$ s$^{-1}$</td>
</tr>
</tbody>
</table>

where $A_{pq}$ is the transition probability (s$^{-1}$) and $h\nu_{pq}$ the energy of the emitted photons. The density $n_p$ can be written as the sum of contributions of population from the ground state and from the ion state [21]:

$$n_p = r_{pq}^1 n_p^B + r_{pq}^+ n_p^S,$$

where $n_p^B$ and $n_p^S$ are the Boltzmann and Saha densities of state $p$ respectively, which depend on $n_e$, $T_e$, and the ground state density $n_1$. In an ionising plasma, state $p$ is mainly populated by excitation from lower states, so that the second term at the right hand side of Eq. 7.5 is negligible compared to the first. In that case, Eq. 7.5 may be approximated by

$$n_p \approx r_{pq}^1 n_p^B = r_{pq}^1 n_1^B \frac{g_p}{g_1} \exp \left(-\frac{E_p}{k_B T_e}\right),$$

where $g_1$ and $g_p$ are the statistical weights of the ground state and state $p$ respectively, $E_p$ is the excitation energy of the state $p$, and $r_{pq}^1$ the underpopulation coefficient with respect to Boltzmann equilibrium. The coefficient $r_{pq}^1$ depends weakly on the electron temperature and density and can be found from a Collisional Radiative Model (CRM) of helium [19, 20]. The exponential in Eq. 7.6 leads to strong variations of $n_p$ (more than three orders of magnitude, see below) during an RF cycle. Compared to these variations, the small changes of $r_{pq}^1$ with $n_e$ and $T_e$ can be neglected; $r_{pq}^1$ is taken constant in this study.

The statistical weight factor of the ground state $g_1$ equals unity, and the ground state density $n_1$ follows from the pressure and heavy-particle temperature via the ideal gas law. The relevant properties of the transition $3d \rightarrow 2p$ emitting at 587.6 nm are listed in Table 7.1. It should be noted that a Maxwellian EEDF is assumed in the CRM from which $r_{pq}^1$ is calculated. Furthermore, this method is only suitable for ionising plasmas, i.e. where the ionisation rate is much larger than the recombination rate, so that the term $r_{pq}^+ n_p^S$ in Eq. 7.5 may be neglected. As discussed below, this is the case during most of the time.

7.3 Results

7.3.1 Power dissipation of the plasma

The power dissipated by the plasma was measured by monitoring the voltage and current on the primary side of the high voltage transformer in front of the plasma, see Fig. 7.1. The measured voltage and current are shown in Fig. 7.3, as well as the dissipated power, $P = V \cdot I$. The block-shaped voltage that is delivered by the RF generator has a duty cycle
that is not exactly one half. This may be the reason for the slight asymmetry between the two power peaks per RF cycle of 8.9 µs.

The current lagging slightly behind the voltage suggests inductive behaviour, probably caused by the transformer. A negative power means that the transformer converts magnetic field energy back into electric energy at the primary side. The average dissipated power is 35.2 W.

The power measurement was done on the primary side of the transformer because of the high voltage on the secondary side. Therefore, the measured power is not directly representative for the power dissipated by the plasma. Especially the exact time dependence is doubtful, but since the transformer did not heat significantly we may assume that the average power dissipated by the plasma approximately equals the average power delivered by the generator.

### 7.3.2 Time resolved absolute line intensity measurements

As discussed in Section 7.2.3, the length of the discharge along the line of sight of the intensity measurement must be known in order to determine absolutely the excited state density in the plasma. The plasma is assumed to have a cylinder symmetry, so that this length can be determined from a lateral line intensity profile. The measured lateral profile at a time \( t = 2.0 \) µs is shown in Fig. 7.4. At other times, a similar profile (with a different intensity) was observed. The profile is approximately Gaussian with a full 1/e width of 1.2 mm. The radial line intensity profile is approximately equal to the measured lateral profile since Gaussian profiles are not changed by Abel inversion. For the interpretation of the absolute line intensity measurements, we used integration length of 1 mm.

The importance of electron loss by ambipolar diffusion (cf. Section 7.4) can be estimated from this lateral line intensity profile as well. Diffusion losses are commonly described in terms of a so-called electron density gradient length \( \Lambda_{ne} \), i.e. the typical distance over which the gradient of the electron density changes [23, 24]. In the centre of a two-dimensional
Fig. 7.4: Lateral profile of the 587.6 nm spectral line at $t = 2.0 \, \mu s$.

Fig. 7.5: The measured density $n_{3d}$ of the 3d state in the centre of the plasma (left) and the derived electron temperature $T_e$ (right). The solid line in the graph on the right hand side indicates where Eq. 7.6 is a good approximation.

Gaussian profile, the gradient length is given by $\Lambda_{n_e} = \Delta x_{1/e}/4$, where $\Delta x_{1/e}$ is the full 1/e width of the profile. Thus, under the assumption that $n_e$ follows a similar profile as the measured line intensity profile, this measurement suggests a gradient length $\Lambda_{n_e} \approx 0.3 \, \text{mm}$.

The density of the 3d excited state in the centre of the discharge was determined from the absolute intensity of the 587.6 nm spectral line, cf. Eq. 7.4. This density was subsequently used to estimate the electron temperature of the plasma according to Eq. 7.6. Fig. 7.5 shows the measured 3d density $n_{3d}$ and the derived temperature $T_e$. As discussed above, this calculation is only meaningful when the plasma is ionising. Whether or not this is the case may be estimated from the density corresponding to a Thermodynamic Equilibrium (TE) situation. The temperature $T_{\text{TE}}$ of a TE plasma with given electron density $n_e$ and ground state density $n_1$ can be derived from the Saha equation applied to the ground state:

$$n_1 = \frac{g_1}{2g_+} n_e n_i \left( \frac{h}{\sqrt{2\pi m_e k_B T_{\text{TE}}}} \right)^3 \exp \left( \frac{I_1}{k_B T_{\text{TE}}} \right).$$

(7.7)

The ground state density is approximately $n_1 \approx p/k_B T_h \approx 7.5 \cdot 10^{24} \, \text{m}^{-3}$, where $p = 10^5 \, \text{Pa}$.
TimereolvedmeasurementsonahelelirRFdischarge

Fig. 7.6: Thomson spectra at three different times (left) and the electron density and temperature behaviour during one RF cycle (8.9 µs) of the plasma (right). The electron density detection limit of the experiments is \( n_{e, \text{det}} \approx 2 \cdot 10^{18} \text{ m}^{-3} \).

is the pressure and \( T_b \approx 1000 \text{ K} \) is estimated on the basis of a rough measurement with a thermocouple. As described below, the electron density in the RF plasma is always below \( 3 \cdot 10^{19} \text{ m}^{-3} \), so that \( T_{\text{TE}} \) never exceeds 0.8 eV. For this temperature and under TE conditions, \( n_{3d} \approx 10^{13} \text{ m}^{-3} \). Hence, for densities above this value, the plasma is ionising and the temperature derived from the density \( n_{3d} \) equals \( T_e \) if the EEDF is Maxwellian.

Note that the highest peaks of the \( 3d \) density and electron temperature profiles correspond to the higher of the two peaks in the power measurement (Fig. 7.3). Apparently, the asymmetry of the dissipated power between the two halves of the RF cycle also propagates into the plasma.

7.3.3 Time resolved Thomson scattering measurements

The electron temperature and density behaviour during an RF cycle of the plasma was studied by laser Thomson scattering also. Since the discharge channel only has a diameter of approximately 1 mm, proper alignment of the laser beam in the plasma is critical. For this purpose, a lens was placed on the laser beam axis behind the plasma, creating a head-on image of both the plasma and laser beam, which was strongly attenuated for this occasion.

Fig. 7.6 shows a few scattering spectra that were recorded as well as the measured electron temperature and density behaviour during one RF cycle of 8.9 µs. Each data point represents a measurement with an integration time of 20 minutes (12 000 laser shots). The electron density detection limit of the experiments was found to be on the order of \( 2 \cdot 10^{18} \text{ m}^{-3} \). This is rather high because of the low transmission of the present TGS system [16] and background light caused by a stray light leak of the system\(^1\). This background, and the stray light residue in the centre of the scattering spectrum are subtracted from the spectra in Fig. 7.6.

\(^1\) The stray light leak has been found and eliminated, and the efficiency of the TGS will be improved in the near future, lowering the detection limit to below \( 10^{16} \text{ m}^{-3} \).
Fig. 7.7: The measured Thomson spectrum at $t = 3.7$ $\mu$s, a single Gaussian fit of the bulk of the spectrum, and a double Gaussian fitted to the whole spectrum. Note that the data points in the centre of the spectrum ($\Delta \lambda^2 < 0.3$ nm$^2$) are not part of the scattering spectrum, as they are affected by the stray light filter.

Like most of the measured scattering spectra, those shown in Fig. 7.6 are Gaussian. This means that the EEDF is Maxwellian within the electron energy range of this measurement (approximately 0.2 to 4 eV). The electron temperatures and densities were derived from Gaussian fits to the measured scattering spectra. The central part of the scattering spectra, which is affected by the stray light filter, was not taken into account in the fits.

However, for the measurements at 3.5, 3.7, and 4.1 $\mu$s (during the decay phase of the plasma; low $T_e$ and decreasing $n_e$), a fit with a single Gaussian was found to be inaccurate. This is illustrated in Fig. 7.7, which shows the measured scattering spectrum at $t = 3.7$ $\mu$s and fitted profiles on a linear scale (left) and on a logarithmic vertical and quadratic horizontal scale (right). The Gaussian profile that fits the low-energy ($< 1$ eV) part of the measured spectrum is clearly not representative for the wings. However, a double Gaussian (the sum of two Gaussians) could reproduce all data satisfactorily.

The fact that a double Gaussian function was needed to fit the scattering spectra during the decay phase of the plasma indicates that during that period the EEDF of the plasma is not Maxwellian, even at low electron energies. The electron density was determined from the area of the double Gaussian fit. However, the electron temperature was deduced from the Gaussian fit to the low-energy part of the spectrum; hence it is not representative for all electron energy ranges.

### 7.4 Discussion

The measurements presented in the previous section show that both the electron density and temperature of the RF discharge are strongly modulated. The sharp rise of the electron density at $t \approx 2$ $\mu$s can be attributed to a high ionisation rate. The subsequent decrease of $n_e$ is due to ambipolar diffusion of electrons out of the discharge and possible other loss mechanisms. Although the values of the electron temperatures measured by ALI and by
TS are very different, both techniques indicate that the electron temperature shows two
peaks per RF cycle, the highest corresponding to the highest power delivered by the RF
generator (cf. Fig. 7.3). In contrast, the electron density shows only one clear peak per RF
cycle. In addition, this peak lags slightly behind the highest peak in the temperature.

In this section, the approximate ionisation and diffusion rates required to explain the
measured electron density profile are discussed. Subsequently, the difference between the
temperatures measured by ALI and TS is explained, and a model for the behaviour of the
electron density is presented.

7.4.1 Electron production and loss rates

The electron production (ionisation) rate during the ionising phase of the plasma ($t \approx 1−2 \mu s$) may be estimated from the increase in $n_e$ during that phase. The electron density rises with a time constant of approximately $\tau_i \approx 0.8 \mu s$. Due to the strongly ionising character of the plasma, electron loss processes such as diffusion and recombination may be neglected, so that the time constant $\tau_i$ can be related to the ionisation rate by

$$\frac{1}{\tau_i} = n_1 S_{\text{ion}}, \quad (7.8)$$

where $S_{\text{ion}}$ is the ionisation rate coefficient. As discussed above, the ground state density is $n_1 \approx 7.5 \cdot 10^{24} \text{ m}^{-3}$. Therefore, the ionisation rate must be on the order of $S_{\text{ion}} \approx 1.7 \cdot 10^{-19} \text{ m}^3 \text{ s}^{-1}$.

The ionisation rate coefficient is strongly dependent on the electron temperature. The relation between $S_{\text{ion}}$ and $T_e$ follows from a Collisional Radiative Model (CRM). At high electron densities, radiative de-excitation is slow compared to that by electron collisions. In that case, $S_{\text{ion}}$ is independent of $n_e$, and both the model of Drawin and Emard [25] and that of Goto and Fujimoto [26,27] can be approached within 10% by the fit

$$S_{\text{ion}} \approx 2.92 \cdot 10^{-17} \sqrt{T_e} \exp \left(-\frac{E^*}{k_B T_e}\right) \quad \left[\text{m}^3 \text{ s}^{-1}\right], \quad (7.9)$$

with $E^* = 19.38 \text{ eV}$. This energy can be interpreted as the effective energy for excitation of the first excited state, as this is the limiting step for ionisation in most low electron temperature plasmas [23]. According to Eq. 7.9, the ionisation rate required to explain the sharp increase of $n_e$ in the ionising phase of the plasma corresponds to an electron temperature of $T_e \approx 1.9 \text{ eV}$ (see Fig. 7.8).

The electron temperature found by Thomson scattering (cf. Fig. 7.6) is about 3.8 eV. This is much higher than the temperature estimated on the basis of the electron density rise time, and would lead to a huge production of electron-ion pairs with a time constant of about 4 ns. In contrast, the electron temperature measured by ALI (cf. Fig. 7.5) is close to that estimated on the basis of the electron density rise time.

The electron loss rate during the decay phase of the plasma (3 to 4.5 $\mu$s) can be estimated from the time constant $\tau_d \approx 2 \mu s$ of the decreasing electron density. For the moment, we
assume ambipolar diffusion to be the main electron loss mechanism. Ambipolar diffusion losses can be expressed in terms of the electron density gradient length $\Lambda_{n_e}$. With this gradient length, the time constant $\tau_d$ can be written as
\[
\frac{1}{\tau_d} \approx \frac{D_a}{\Lambda_{n_e}^2}.
\]
(7.10)

The ambipolar diffusion coefficient $D_a$ is a function of the electron and heavy-particle temperatures and is approximately [28]
\[
D_a \approx 1.06 \cdot 10^{-25} \frac{T_h^2}{\Omega(T_h)} \left(1 + \frac{T_e}{T_h}\right) \text{[m}^2\text{s}^{-1}],
\]
(7.11)

where the atom-ion collision integral $\Omega(T_h)$ is approached by
\[
\Omega(T_h) \approx (3.43 + 1.65 \cdot 10^{-3} T_h - 1.02 \cdot 10^{-7} T_h^2) \cdot 10^{-16} \text{[m}^3\text{s}^{-1}].
\]
(7.12)

This equation follows from a fit of the cross section for momentum transfer to data tabulated by Barnett et al. [29, 30]. The accuracy around $T_h = 1000$ K is limited by that of the tabulated cross sections (20%). For $T_h = 1000$ K and $T_e = 1.5$ eV, the ambipolar diffusion coefficient is $D_a \approx 4 \cdot 10^{-3}$ m$^2$ s$^{-1}$. Thus, the gradient length of the plasma required to explain the decay of the electron density on the basis of ambipolar diffusion is $\Lambda_{n_e} \approx 0.1$ mm.

The electron density gradient length $\Lambda_{n_e}$ estimated here is smaller than the value suggested by the lateral line intensity profile in Fig. 7.4. However, this profile is determined by the electron temperature profile as well, which may explain the small difference.

### 7.4.2 Electron bulk and production temperatures

The large difference between the electron temperatures found by Thomson scattering and by Absolute Line Intensity measurements suggests that the EEDF cannot be described entirely with a single temperature; it is not completely Maxwellian. For plasmas with
a high ionisation rate it is known that the high energy part of the EEDF may become depleted compared to what would be expected from the low energy part. The EEDF of such a plasma can often be described by multiple temperatures, each applying in a different part of the EEDF [31–33].

If two temperatures are used to describe the EEDF (a two-electron group model), the part with energies below the energy $E_{12}$ of the first excited state is referred to as the “bulk” with a temperature $T_{e,\text{bulk}}$. The EEDF at energies above $E_{12}$ is called the “tail”, and has a temperature $T_{e,\text{tail}}$. A depleted tail corresponds to $T_{e,\text{tail}} < T_{e,\text{bulk}}$. The effective electron temperature involved in the production of new electron-ion pairs (i.e. the temperature that must be used in Eq. 7.9) is termed the “production” temperature $T_{e,\text{prod}}$; it is a combination of $T_{e,\text{bulk}}$ and $T_{e,\text{tail}}$.

With Thomson scattering, only the low energy electrons can be probed, since the number of high energy electrons is too small to be detected accurately. Therefore, the temperature measured by Thomson scattering is $T_{e,\text{bulk}}$.

In contrast, the temperature found by absolute line intensity measurements is expected to be close to $T_{e,\text{prod}}$. At high electron densities, stepwise ionisation is dominant over direct ionisation [23]; this is approximately true for the RF discharge in this study as well. In that case, the ionisation rate approximately equals the rate of excitation to the first excited state. Therefore, the density of the first excited state is governed by the temperature $T_{e,\text{prod}}$. Due to the smaller energy gaps between higher excited states, (de)excitation processes between these states are related to $T_{e,\text{bulk}}$. Nevertheless, their density is strongly related to that of the first excited state, and hence the production temperature $T_{e,\text{prod}}$ in the plasma. As shown in Section 7.4.1, the temperature derived from $n_{3d}$ is indeed close to the production temperature required for the increase of $n_e$ in the ionising phase of the plasma.

Fig. 7.9 shows the electron temperatures that were measured by ALI and TS. In the periods $t = 0.5 - 3 \mu s$ and $t = 5 - 7 \mu s$, $T_{e,\text{prod}} < T_{e,\text{bulk}}$. As argued above in Section 7.3.2, the plasma is ionising during these periods. Outside these time intervals the plasma may be
recombining, so that the temperature deduced from ALI measurements is not meaningful.

As shown by Fig. 7.6 and discussed in Section 7.4.1, the electron density rises strongly
during the first ionising phase. However, during the second ionising phase, $n_e$ hardly
increases. This can be attributed to the lower production temperature (cf. Fig. 7.5), which
is probably due to the lower dissipated power. In the following section, a more detailed
model for the behaviour of $n_e$ is described.

### 7.4.3 Time dependent electron density

The time dependence of the electron density can be related to the measured electron
temperature by (a simplified form of) the time dependent electron particle balance,

$$\frac{\partial n_e}{\partial t} \approx \left( n_1 S_{\text{ion}}(t) - \frac{D_a(t)}{\Lambda^2_{n_e}} \right) n_e(t).$$  \hfill (7.13)

Here the first term between brackets on the right hand side represents ionisation processes,
and the second term describes ambipolar diffusive electron loss. Convection as a loss
channel may be neglected because of the low flow velocity (on the order of 1 m s$^{-1}$) of
the plasma. During the plasma decay phase, recombination may become important with
respect to ionisation, but it is assumed negligible compared to ambipolar diffusion.

Both the ionisation rate (Eq. 7.9) and the ambipolar diffusion coefficient (Eq. 7.11) depend
on the electron temperature, and are therefore time dependent. We take the gradient length
$\Lambda_{n_e}$ constant, as the shape of the radial line intensity profile does not change much in time
(cf. Section 7.3.2). Separation of variables and integration of Eq. 7.13 yields

$$\ln n_e(t) = n_1 \int S_{\text{ion}} dt - \frac{1}{\Lambda^2_{n_e}} \int D_a dt + c,$$  \hfill (7.14)

where $c$ is an integration constant that determines the absolute electron density. Below,
this constant is shown to follow from the electron energy balance.

The number of loss processes, described by the gradient length $\Lambda_{n_e}$, must be such that
$n_e$ is periodic: $n_e(t) = n_e(t + \tau)$, where $\tau$ is the period. This leads to

$$\Lambda^2_{n_e} = \int_t^{t+\tau} D_a dt \cdot \left[ n_1 \int_t^{t+\tau} S_{\text{ion}} dt \right]^{-1}.$$  \hfill (7.15)

This is in fact the time dependent version of the statement that the gradient length is such
that ambipolar diffusion and ionisation equilibrate in a quasi steady-state plasma [23, 24].

The electron particle balance describes the time dependence of $n_e(t)$, but not its absolute
value. This manifests itself in the constant $c$ in Eq. 7.14. However, the electron energy
balance, integrated over one RF period, can be applied to determine the value of $c$. 

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Since $n_e$ and $T_e$ are periodic, integration of the electron energy balance over one RF period $\tau$ yields

$$\langle \varepsilon \rangle \cdot \tau = \frac{\langle P \rangle}{V} \cdot \tau = \int_{t}^{t+\tau} n_e(t) \left[ Q_{\text{ion}}(t) + Q_{\text{heat}}(t) \right] dt,$$

(7.16)

where $\langle \varepsilon \rangle = \langle P \rangle / V$ is the average power density (power per volume) of the plasma, $Q_{\text{ion}}$ represents energy loss of the electrons to heavy particles by ionisation, and $Q_{\text{heat}}$ describes energy loss due to heating. The ionisation term equals the product of the ionisation rate $n_e n_1 S_{\text{ion}}$ and the energy lost per ionisation event:

$$n_e Q_{\text{ion}} = n_e n_1 S_{\text{ion}} (I + \frac{3}{2} k_B T_e),$$

(7.17)

with $I = 24.59$ eV the ionisation energy of helium and $\frac{3}{2} k_B T_e$ the energy required to heat the created electron to the temperature $T_e$. The heating term is approximately

$$n_e Q_{\text{heat}} \approx n_e \left\{ n_1 k_{\text{ea}}^m + n_e k_{\text{ei}}^m \right\} \cdot \frac{m_e}{M} 3k_B (T_e - T_h),$$

(7.18)

where $m_e/M$ is the mass ratio of an electron and a helium atom, and $k_{\text{ea}}^m$ and $k_{\text{ei}}^m$ are the collision rate coefficients for momentum transfer from electrons to atoms and from electrons to ions respectively. The values of these rate coefficients were obtained from experimental data of collision cross sections (averaged over a Maxwellian EEDF) [30,34,35]. The term between braces varies less than 25% for $5 \cdot 10^{18} < n_e < 5 \cdot 10^{19}$ m$^{-3}$, $1 < T_e < 4$ eV and $600 < T_h < 1400$ K. Therefore, for further calculations we take this term constant at $4.1 \cdot 10^{11}$ m$^{-3}$ s$^{-1}$.

We can write $n_e(t) = C \cdot f(t)$. The function $f(t)$ is the time dependent electron density found by taking $c = 0$ in Eq. 7.14, and $C$ is a constant given by $C = \exp(c)$ . Then Eq. 7.16 yields

$$C = \langle \varepsilon \rangle \cdot \tau \cdot \left[ \int_{t}^{t+\tau} f(t) \{ Q_{\text{ion}}(t) + Q_{\text{heat}}(t) \} dt \right]^{-1}.$$

(7.19)

Thus, setting $c = \ln C$ in Eq. 7.14 determines the time dependent electron density absolutely.

The model described in this section produces the time dependent electron density from the measured electron temperature profile. However, as discussed above, multiple temperatures are required to describe the EEDF. The ionisation rate $S_{\text{ion}}$ must be calculated from the production temperature $T_{e,\text{prod}}$ as found by ALI. As stated in Section 7.4.2, this is not useful during the recombining phase of the plasma, but during that period ionisation can be neglected compared to recombination. Diffusional losses and heat transfer ($D_a$ and $Q_{\text{heat}}$) should be evaluated with the bulk temperature $T_{e,\text{bulk}}$ since the majority of the electrons rather than the few energetic ones contributes to these processes. An exception to this was made for the plasma decay phase (3 to 4.5 $\mu$s). During this period, the bulk temperature is lower than the temperature determined by ALI. As described below in Section 7.4.4,
Fig. 7.10: Comparison of the electron density during one RF cycle of the plasma found by Thomson Scattering (TS) on one hand, and by using the numerical model on the other hand. The numerical model uses the production (ALI) temperature for $S_{\text{ion}}$ and the bulk (Thomson) temperature for $D_a$ and $Q_{\text{heat}}$. The heavy particle temperature was taken $T_h = 960$ K since that produced the best fit.

even the bulk of the EEDF is not Maxwellian, and the low temperature found by Thomson scattering is not representative for the majority of the electrons. Therefore, during that period the production temperature is used in the description of $D_a$ and $Q_{\text{heat}}$ as well.

The time dependent electron density that follows from the model above is compared to experimental data in Fig. 7.10. The model assumes $T_h = 960$ K, and a plasma diameter of $r = 0.90$ mm. The length of the plasma is 60 mm, so that the plasma volume is $V = 3.8 \cdot 10^{-8}$ m$^3$. With the average plasma power $\langle P \rangle = 35.2$ W, this results in a power density of $\langle \varepsilon \rangle = 9.3 \cdot 10^8$ W m$^{-3}$. The exact values of $T_h$ and $r$ taken in the model produce the best fit of the model to the measured electron densities. Fig. 7.4 shows that 0.90 mm is a reasonable value for the diameter.

Clearly, the simple model presented above can already explain the behaviour of $n_e$ rather precisely. Nevertheless, the gradient length that must be used to yield a periodical electron density profile is $\Lambda_{n_e} = 0.15$ mm. This is approximately a factor of 1.5 larger than the one estimated in Section 7.4.1. Thus, diffusive losses are on the average about a factor of two smaller. In addition, the low electron temperature during the decay phase of the plasma leads to a low diffusion coefficient during that period (cf. Eq. 7.11). This results in the fact that the model does not accurately reproduce the observed decrease of $n_e$ during the decay phase of the plasma. This suggests the presence of an additional electron loss process to play a role in Eq. 7.13, especially when the electron temperature is low.

Recombination of He$^+$ is a relatively slow process. The recombination rate coefficient following the same CRMs as those used in Eq. 7.9 is approximately $\alpha_{\text{rec}} \approx 1 \cdot 10^{-18}$ m$^3$s$^{-1}$, and is only weakly dependent on $n_e$ and $T_e$. Therefore, the recombination rate is on the order of $n_e \alpha_{\text{rec}} \sim 20$ s$^{-1}$. Thus, the electron density decay time $\tau_{d_{\text{rec}}} \approx 50$ ms associated with this recombination rate is much too slow to explain the decay of $n_e$.

A more likely candidate for an electron loss process is the influence of molecules in the
plasma. As suggested by Jonkers [30], due to the low gas temperature of the plasma, a substantial number of the ions in the plasma may be molecular helium (He\textsubscript{2}\textsuperscript{+}). The rate coefficient of Dissociative Recombination (DR) of He\textsubscript{2}\textsuperscript{+} given by Collins and Lee [36] may be approximated by

\[ k_{\text{DR}} \approx 5.4 \times 10^{-13} T_e^{-0.5} \text{ m}^3 \text{s}^{-1}. \]  

(7.20)

Thus, dissociative recombination becomes more important for low electron temperatures, i.e. during the plasma decay phase. Taking \( T_e \approx 1 \text{ eV} \) and assuming all ions to be molecular yields \( k_{\text{DR}} \approx 5 \times 10^{-15} \text{ m}^3 \text{s}^{-1} \). With \( n_e \approx 2 \times 10^{19} \text{ m}^{-3} \), this results in a decay time constant of \( \tau_{d,\text{DR}} \approx 10 \mu\text{s} \). Together with the time constant corresponding to the diffusion rate during the decay phase predicted by the model (\( \tau_{d,\text{diff}} \approx 5 \mu\text{s} \), cf. Fig. 7.10), this results in a decay time constant of \( \tau_d \approx 3 \mu\text{s} \). In light of possible uncertainties in the rate coefficient of Eq. 7.20, and possibly a smaller plasma (larger diffusive fluxes) during the decay phase, this may finally explain the observed behaviour of \( n_e \). It should be noted that molecular processes also affect, for instance, the ionisation rate. Therefore, a careful analysis of these processes and detailed knowledge of the rate coefficients associated with them are necessary to form a complete understanding of this type of discharge.

### 7.4.4 Non-Maxwellian EEDFs

During the plasma decay phase, a non-Maxwellian EEDF was observed by Thomson scattering, even though only the lower four eV of the EEDF of the plasma could be studied with this technique. For higher energies, the signal was too weak to draw reliable conclusions. Since the EEDF is calculated with the derivative of the Thomson spectrum (see Eq. 7.2), it is very sensitive to noise [13]. Therefore, the double Gaussian fits to the measured Thomson spectra were used for this calculation, rather than the experimental data itself.
Fig. 7.12: The densities and temperatures of the two ("hot" and "cold") groups of electrons.

Table 7.2: The densities and temperatures of the two ("hot" and "cold") groups of electrons.

<table>
<thead>
<tr>
<th>$t$ ($\mu$s)</th>
<th>$n_e$ (m$^{-3}$)</th>
<th>$T_e$ (eV)</th>
<th>$n_e$ (m$^{-3}$)</th>
<th>$T_e$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>$1.8 \times 10^{19}$</td>
<td>1.3</td>
<td>$0.3 \times 10^{19}$</td>
<td>4.1</td>
</tr>
<tr>
<td>3.3</td>
<td>$1.7 \times 10^{19}$</td>
<td>1.1</td>
<td>$2.0 \times 10^{19}$</td>
<td>3.4</td>
</tr>
<tr>
<td>3.5</td>
<td>$0.9 \times 10^{19}$</td>
<td>0.4</td>
<td>$0.8 \times 10^{19}$</td>
<td>2.0</td>
</tr>
<tr>
<td>3.7</td>
<td>$0.7 \times 10^{19}$</td>
<td>0.3</td>
<td>$0.8 \times 10^{19}$</td>
<td>1.7</td>
</tr>
<tr>
<td>4.1</td>
<td>$0.6 \times 10^{19}$</td>
<td>0.5</td>
<td>$0.9 \times 10^{19}$</td>
<td>1.6</td>
</tr>
<tr>
<td>4.5</td>
<td>$1.2 \times 10^{19}$</td>
<td>1.5</td>
<td>$0.1 \times 10^{19}$</td>
<td>3.4</td>
</tr>
</tbody>
</table>

The left hand side of Fig. 7.11 compares the EEDF of the plasma at $t = 3.7$ $\mu$s with a (scaled) Maxwellian EEDF at $T_e = 4500$ K. Clearly, the low energy part of the measured EEDF can be described satisfactorily with this Maxwellian function, but for energies above 1 eV, the EEDF is overpopulated with respect to this function. The right hand side of Fig. 7.11 shows linearised EEDFs (i.e. divided by $\sqrt{E}$ so that a Maxwellian EEDF yields a straight line) during the decay phase of the plasma. During most of this period, even the bulk of the EEDF is clearly not Maxwellian. As the Thomson spectra were fitted by the sum of two Gaussians, the total EEDF can be represented by the sum of two Maxwellian EEDFs. In fact, this implies the existence of two groups of electrons. Table 7.2 and Fig. 7.12 give an overview of the densities and temperatures of these two ("hot" and "cold") groups. Between $t = 3.3$ and 4.1 $\mu$s, the densities of both groups are comparable. The presence of relatively energetic electrons may be caused by superelastic collisions due to recombination, de-excitation, or molecular processes during the decay phase of the plasma.

7.5 Conclusions

In this work the time dependence of the electron density and temperature in a capacitively coupled helium RF plasma is studied. The electron gas parameters are measured by means
of laser Thomson scattering and absolute line intensity measurements. The temporal resolutions of the measurements with these techniques were 20 and 50 ns respectively.

The average power dissipated in the plasma is 35.2 W. The power shows two peaks per RF cycle, one being slightly higher than the other.

Absolute line intensity measurements were used to determine the electron production temperature $T_{e,\text{prod}}$, which is responsible for the generation of electron-ion pairs. This production temperature ranges from 1.2 to 2 eV and shows two peaks during RF cycle, the one coinciding with the highest power peak being highest.

The electron bulk temperature $T_{e,\text{bulk}}$ was measured with Thomson scattering, and varies over a much wider range (0.5 to 3.8 eV), and shows a comparable asymmetry in the two peaks observed during an RF cycle.

The electron density was measured by Thomson scattering as well. It shows only one clear peak per RF cycle, and it lags slightly behind the highest peak in the electron bulk and production temperatures. A simple model to describe the time dependence of the electron density, based on the measured electron temperatures and the electron particle and energy balances, was developed. Experimental results are reproduced fairly well by this model. In addition to ambipolar diffusion, dissociative recombination of He$^+_2$ ions may represent a significant loss of electrons during the decay phase of the plasma.

The EEDF of the plasma is not Maxwellian. Most of the time, the plasma is ionising and the high energy tail of the EEDF is depleted. This explains the bulk temperature $T_{e,\text{bulk}}$ being much higher than production temperature $T_{e,\text{prod}}$. In a short period during the plasma decay phase the plasma becomes recombining. During that period the bulk of the EEDF is not Maxwellian; this may be caused by superelastic collisions due to recombination, de-excitation, and molecular processes.

The measurements in this work give an insight into the temporal behaviour of low frequency helium RF discharges. A simple model, based on ionisation and diffusion is proposed to explain the observed behaviour. This model could explain the observed behaviour rather well. Nevertheless, more detailed knowledge of the shape of the EEDF, excitation and ionisation rate coefficients for non-Maxwellian EEDFs, and molecular processes occurring in the plasma is required for a complete understanding of this type of discharges.

References


Chapter 7


Time resolved measurements on a helium RF discharge


Chapter 7


Chapter 8

General conclusions
The primary goal of this research project was to validate a method to estimate relevant plasma parameters, such as the electron density $n_e$ and temperature $T_e$, from the operational conditions of a plasma in a number of cases. This was done by comparing these estimates with experimental results of laser scattering measurements. In general, a good agreement was found for the plasma sources studied in this work. This study also provided insight into various processes dependent on $n_e$ and $T_e$, such as excitation and transport mechanisms. With this knowledge, the method of estimating plasma parameters can be extrapolated to other, less accessible plasma sources or plasmas in industrial environments.

A second goal was to develop an advanced diagnostic facility for laser scattering experiments on small-scale plasmas in a high stray light environment, such as the ones in gas discharge lamps and other more or less enclosed plasmas. A Triple Grating Spectrograph (TGS) was designed to combine a high stray light rejection with low detection limits and a high spatial, spectral, and temporal resolution. Even in the presence of a relatively high stray light level, unambiguous Thomson scattering experiments to determine $n_e$ and $T_e$ can be done on plasmas with an electron temperature $T_e$ in the range $0.1 – 4$ eV and with an electron density $n_e$ down to below $10^{16}$ m$^{-3}$. Furthermore, the system can be used for rotational Raman scattering and Rayleigh scattering experiments and for (time resolved) spectral line intensity measurements. The experimental arrangement that was designed and built for this project was applied to an Inductively Coupled Plasma (ICP) and a capacitively coupled helium RF discharge, both of which are used in spectrochemistry, and the Philips QL lamp, an inductively coupled light source.

This chapter gives an overview of the main conclusions of this study.

- Small-scale plasmas are strongly influenced by external operational conditions, such as the size, shape, composition, energy density, and pressure. Therefore, fundamental plasma parameters such as the electron density $n_e$, electron temperature $T_e$, and heavy-particle temperature $T_h$ are related rather directly to these external settings. This relation is established via the electron particle and energy balances and the heavy-particle energy balance. Hence, these balances can be used to estimate $n_e$, $T_e$, and $T_h$ from the control parameters of the plasma. Such a method finds its application in the absence of advanced experimental techniques and for plasmas that are less accessible to diagnostic methods. (Chapter 4)

- The experimental system designed for this project facilitates simultaneous measurement of scattering spectra at various positions in the plasma. In this way, measurements on both electrons and molecules by Thomson and (rotational) Raman scattering can be combined. This is possible by aligning the entrance slit of the spectrograph that is used to disperse the scattered radiation with the image of the laser beam and by using a two-dimensional intensified CCD camera as a detector. (Chapters 3 and 5)
Power interruption in combination with spatially resolved Thomson scattering measurements can be used to study the relative importance of various production and loss processes of charged particles in a plasma. By applying this technique to a spectrochemical ICP, the electron loss frequency at the outer plasma regions was found to be much higher than can be explained by ambipolar diffusion and three-particle recombination. This is most likely due to the presence of molecular argon ions (Ar$_2^+$). With a possible exception at the outermost plasma boundary the influence of mixing with molecules from the surrounding air is negligible.

(Chapter 5)

The use of a Triple Grating Spectrograph (TGS) instead of a conventional (single grating) spectrograph significantly reduces stray light in measured scattering spectra. Stray light that is detected in scattering spectra at positions off the laser wavelength is the result of the stray light redistribution arising from the spectrograph’s imperfections. A conventional spectrograph produces a stray light redistribution of around $10^{-3}$ nm$^{-1}$ at 0.75 nm off the laser wavelength. This precludes the applicability of Thomson scattering to plasmas with a low electron density and temperature in combination with a high stray light level, such as the ones in gas discharge lamps. In a Triple Grating Spectrograph, the first two gratings and a spatial mask between them form a Double Grating notch Filter (DGF) that rejects stray light. The stray light transmission of the DGF designed in this project depends on the mask and entrance slit that are used and can be slightly below $10^{-6}$. Hence, the effective redistribution of the TGS is lowered to around $10^{-9}$ nm$^{-1}$. Such a notch filter is more practical than for instance an atomic notch filter, which rejects light of an atomic transition. This requires the use of a tunable laser system, which generally has a much lower spectral purity and reliability than a Nd:YAG laser.

(Chapter 3)

The transmission function of the DGF can be derived from the properties of the gratings, the entrance slit, the optical elements, and the mask. Measurements of this transmission function show a good agreement with calculations. For narrow masks, the limiting factor for stray light rejection is the diffraction pattern produced by the grating. For wider masks, scattering on the optics in the spectrograph is the limitation.

(Chapter 3)

Thomson scattering can be applied to gas discharge lamps by using a TGS for efficient stray light rejection and by modifying the lamp slightly, e.g. using quartz laser windows at Brewster angle and far from the discharge. Measurements on the inductively coupled QL lamp show that the electron density is on the order of $n_e \approx 1 \cdot 10^{19}$ m$^{-3}$ and the temperature is about $T_e \approx 1$ eV. Both depend on the partial argon and mercury pressures in the discharge.

(Chapter 6)
• The combination of Absolute Line Intensity measurements (ALI) with a Collisional Radiative Model (CRM) can provide insight into the excitation kinetics of a plasma. If the Electron Energy Distribution Function (EEDF) has a Maxwellian equilibrium shape, this method can be applied to measure the electron temperature $T_e$. If the EEDF is not Maxwellian, the temperature derived from ALI measurements may differ substantially from that found in Thomson scattering experiments. The temperature found by Thomson scattering is the temperature that governs the bulk of the EEDF, i.e. at low and moderate electron energies. This bulk is usually (more or less) Maxwellian. However, in strongly ionising plasmas the high energy tail of the EEDF can become depleted with respect to the Maxwellian function describing the bulk. In that case, the high energy tail may be described by a lower electron temperature than the bulk. The temperature found by ALI is a combination of the temperatures of the bulk and the high energy tail of the EEDF. It is closely related to the temperature that governs plasma production (ionisation) processes and therefore is called the “production temperature”. 

(Chapter 7)

• Small spectrochemical RF helium discharges operated at low RF frequencies ($\sim 100$ kHz) are alternately ionising and recombining within an RF cycle. Furthermore, the EEDF of such a plasma is not (entirely) Maxwellian. More specifically, the bulk and production temperatures can be very different. Both temperatures show large fluctuations in time. Due to the high mobility of helium, also the excited state densities and the electron density are strongly modulated. This time dependence must be taken into account in quantitative studies of spectral line intensities and their interpretation for plasma diagnostic or analytic purposes.

(Chapter 7)

In this work, a method to estimate plasma parameters from operational conditions of the plasma has been shown to be reasonably accurate in a number of cases. Furthermore, the applicability of Thomson scattering has been extended to small, enclosed plasmas. Insight into excitation and transport processes in the studied plasmas has been obtained by detailed laser scattering experiments.

The method of estimating plasma parameters from operational conditions, as investigated in previous work of Jonkers [1] and further explored in this thesis, must be refined in future studies. The knowledge gained in this way will contribute to the ability of continuous monitoring of plasmas in industrial environments and help to form an understanding of less accessible plasmas.

References

Summary

Free electrons play a special role in plasmas. Firstly, they are largely responsible for Ohmic power dissipation from external electromagnetic fields. Hence, in the plasma region where energy is dissipated from an external field the electron temperature is generally much higher than that of the heavy particles. Secondly, the high electron temperature causes excitation and ionisation by electron impact (electron excitation kinetics) to be dominant over other excitation mechanisms. Clearly, the electron density \( n_e \) and temperature \( T_e \) are important parameters to characterise a plasma.

One of the most accurate experimental techniques to determine these electron gas parameters is Thomson scattering: scattering of (laser) light by electrons in the plasma. This technique provides direct access to the electrons, which allows straightforward interpretation of experimental results. However, due to the experimental difficulty and stability demands the use of Thomson scattering is often limited to academic studies.

In industry more simple techniques must generally be relied on. In addition, plasma parameters often have to be monitored continuously, which makes Thomson scattering unsuitable. However, detailed information about the operational conditions of the plasma such as chemical input, pressure, size, shape, and power is usually available or can be obtained easily. This study shows that in some cases the relevant plasma parameters can be estimated from these operational settings if the most important processes in the plasma are known. This is possible by relating the plasma parameters to production and loss processes of particles and energy, which are affected by the operational conditions of the plasma.

This study is focused to two objectives. The first is to validate, by Thomson scattering experiments, the method of deriving plasma parameters from the operational conditions in a number of cases. This leads to insight in the dominant processes in the plasma, such as production and transport of electron-ion pairs. With this knowledge also plasmas in industrial environments or plasmas that are less accessible to diagnostic methods can be characterised.

The second aim of this work is to extend the applicability of Thomson scattering to plasma regions with a low electron temperature (< 3000 K) and close to a material wall. The proximity of a wall leads to a large amount of stray light, i.e. laser light that is scattered by the plasma’s surroundings rather than the plasma. The wavelength of this stray light does not differ from the laser wavelength. Due to the low electron temperature the Doppler shift of Thomson scattered light is very small and measurements must be done close to the wavelength of the laser and stray light. Therefore, the combination of a high stray light level and a low electron temperature is often problematic.
Summary

In order to address this problem, a triple grating spectrograph has been designed. The first two gratings and a mask between them serve as a stray light filter. The third grating disperses Thomson scattered light, like in a conventional Thomson scattering system. The triple grating spectrograph reduces the fraction of stray light per spectral range in the measured spectra from $10^{-3}$ nm$^{-1}$ (for a conventional system) to about $10^{-9}$ nm$^{-1}$. Due to the large stray light reduction and the large dispersion of the system, plasmas with electron temperatures between 2000 and 45 000 K can be studied. The electron density detection limit lies below $10^{16}$ m$^{-3}$. The system has a spatial resolution of about 0.1 mm, a spectral resolution of about 0.06 nm, and a time resolution of 20 ns.

The first plasma that was considered is a spectrochemical Inductively Coupled Plasma (ICP). This RF (100 MHz) plasma, which can be used to analyse the atomic composition of samples, operates with argon at atmospheric pressure at a power of about 1 kW. The plasma parameters under standard conditions were estimated from the operational conditions of the plasma. This estimate shows good agreement with experimental results and values in literature. In addition, trends of $n_e$ and $T_e$ for changes in the operational settings can be explained qualitatively from the electron particle and energy balances.

The response of $n_e$ and $T_e$ to a short power interruption of the ICP was studied as well. In this way, insight into electron production and loss processes was obtained. It turns out that atomic processes cannot account for the observed loss rates. Formation and destruction of molecular ions are shown to provide a possible explanation.

Another plasma under study is the Philips QL lamp. This is a low-pressure gas discharge lamp (argon-mercury) that is powered inductively. The absence of electrodes extends the lamp’s life time while preserving its high efficacy. Laser scattering experiments were done at various positions and for various argon and mercury pressures. Again experimental results agree reasonably well with predictions on the basis of the operational conditions of the plasma.

Finally, a capacitively coupled helium plasma at atmospheric pressure was studied. The plasma power is on the average around 35 W, but is strongly modulated with a frequency of 112 kHz. This, together with the high mobility of helium, leads to strong modulations in $n_e$ and $T_e$, which were measured by Thomson scattering. In addition, $T_e$ was determined from the absolute intensity of line emission from the plasma. The difference in the temperatures obtained by both techniques indicates that the electron energy distribution is not entirely Maxwellian. The time dependence of the electron density was calculated on the basis of the operational conditions and the measured electron temperatures. A reasonable agreement was found with the measured electron density, although molecular processes are likely to play a role in this plasma as well.

This work demonstrates the possibility to determine, in a number of cases, the characteristic parameters of a plasma in a relatively simple way from the operational conditions. Furthermore, Thomson scattering with a high spatial, spectral, and temporal resolution has been made applicable to plasmas in the proximity of a wall, such as low-pressure gas discharge lamps and very small plasma sources.
Samenvatting

Plasma’s, typisch reactieve en licht emitterende gassen, worden steeds vaker toegepast in het dagelijks leven en in de industrie. Voorbeelden hiervan zijn plasma’s als warmtebron voor lassen en snijden, als lichtbron in gasontladingslampen en lasers of als deeltjesbron in corona gasreiniging en depositie van zonnecellen. Om plasma’s voor deze toepassingen te optimaliseren of nieuwe toepassingen te ontwikkelen is het uiteraard zinvol om hun gedrag te begrijpen.


De elektronen spelen een speciale rol in plasma’s. Door hun kleine massa in vergelijking met “zware” deeltjes zoals ionen, atomen en moleculen worden zij het meest beïnvloed door externe elektromagnetische velden. Het zijn dan ook primair de elektronen die energie kunnen opnemen uit deze velden. Daardoor is de elektronentemperatuur doorgaans veel hoger dan de zware-deeltjestemperatuur. Een conventionele TL-buis heeft bijvoorbeeld een zware-deeltjestemperatuur die nauwelijks boven kamertemperatuur ligt, maar een elektronentemperatuur van ongeveer 10 000 K. Door deze hoge temperatuur zorgen de elektronen voor excitatie en ionisatie van zware deeltjes en zijn daarmee (mede) verantwoordelijk voor lichtemissie en reactiviteit van het plasma. Vanwege de belangrijke rol van elektronen zijn hun dichtheid en temperatuur belangrijke parameters voor plasmakarakterisatie.

Een van de meest betrouwbare en nauwkeurige meettechnieken om de elektronendichtheid en -temperatuur te bepalen is Thomson-verstrooing: verstrooing van (laser)licht door de elektronen in het plasma. Het aantal verstrooide fotonen is evenredig met de elektronendichtheid, en hun Dopplerverschuiving hangt af van de elektronentemperatuur. Hoewel Thomson-verstrooing zeer directe en eenvoudig te interpreteren resultaten geeft, is de complexiteit en kostbaarheid van de benodigde apparatuur een nadeel van deze meetmethode. Bovendien vereisen de metingen een stabiele, trillingsarme omgeving. Daardoor is het gebruik van Thomson-verstrooing vaak beperkt tot het wetenschappelijk onderzoek.

In de industrie is men doorgaans aangewezen op eenvoudigere meettechnieken. Bovendien wil men de belangrijke plasmaparameters vaak continu kunnen volgen. Directe metingen, bijvoorbeeld met Thomson-verstrooing, zijn dan nauwelijks mogelijk. Exacte
gegevens over de instelparameters van het plasma (zoals samenstelling, druk, afmetingen en vermogen) zijn echter wel voorhanden of eenvoudig te bepalen. Deze studie toont aan dat in een aantal gevallen de relevante plasmaparameters geschat kunnen worden op grond van deze instelparameters, mits men beschikt over een globale kennis van de belangrijkste processen in het plasma. Dit kan door de plasmaparameters te relateren aan de productie en het verlies van deeltjes en energie, die mede bepaald worden door de instelparameters.

Het doel van dit onderzoek is tweeledig. Het eerste doel is de methode om plasmaparameters af te leiden uit de instelparameters van het plasma in een aantal gevallen te verifiëren. Dit is gedaan door resultaten van deze methode te vergelijken met resultaten van Thomson-verstrooiingsexperimenten. Deze verificatie leidt tot inzicht in de belangrijkste processen in het plasma, zoals productie en transport van elektron-ionparen. Met deze kennis kunnen ook plasma’s in industriële omgevingen of plasma’s die minder toegankelijk zijn voor gedetailleerde metingen worden gekarakteriseerd.

Het tweede doel van dit onderzoek is het uitbreiden van de toepasbaarheid van Thomson-verstrooiing naar plasmagebieden die een lage elektronentemperatuur (< 3000 K) hebben en zich dicht bij een wand bevinden. De nabijheid van een wand leidt tot een grote hoeveelheid vals strooilight, d.w.z. laserlicht dat niet door de elektronen in het plasma verstrooid wordt, maar door de wand. De golflengte van dit vals strooilight verschilt niet van die van het laserlicht. Door de lage elektronentemperatuur is echter de Dopplerschuingvinding van Thomson-verstrooide fotonen gering en is het vals strooilight moeilijk te onderscheiden van Thomson-verstroooid licht. Daarom is de combinatie van een hoog vals strooilightniveau en een lage elektronentemperatuur vaak problematisch.

Om dit probleem te omzeilen is een spectrograaf met drie tralies ontworpen. De eerste twee tralies en een masker daartussen worden gebruikt als filter om het vals strooilight uit het spectrum te verwijderen. Het derde tralie wordt gebruikt om het spectrum van het Thomson-verstrooide licht zichtbaar te maken, zoals dat ook in een conventionele opstelling gebeurt. De fractie strooilight per specraal gebied in gemeten spectrum is hierdoor verlaagd van $10^{-3}$ nm$^{-1}$ (voor een conventionele opstelling) tot ongeveer $10^{-9}$ nm$^{-1}$. Door deze strooilightreductie en de grote dispersie van de opstelling kunnen plasma’s met elektronentemperaturen tussen 2000 en 45 000 K bestudeerd worden. De detectielimiet (laagst meetbare elektronendichtheid) ligt beneden $10^{16}$ m$^{-3}$. Met de opstelling kan een plaatsresolutie van ongeveer 0.1 mm, een golflengteresolutie van 0.06 nm en een tijdresolutie van 20 ns bereikt worden.

Het eerste plasma dat onderzocht werd is het spectrochemisch inductief gekoppeld plasma (ICP). Dit RF (100 MHz) plasma, dat gebruikt wordt voor de analyse van de atomaire samenstelling van stoffen, “brandt” op een argonstroom in de open lucht (atmosferische druk) met een vermogen van rond de 1 kW. De plasmaparameters onder standaardcondities zijn bepaald uit de instelparameters van het plasma. Er is een goede overeenstemming gevonden met gemeten waarden en waarden uit de literatuur. Verder is het plasma onderworpen aan een aantal veranderingen in de instelparameters. Trends in de plasmaparameters zijn kwalitatief goed te begrijpen met de toegepaste theorie.
Samenvatting

Ook is de reactie van het ICP op een korte onderbreking van het vermogen bestudeerd. Op die manier is informatie verkregen over de productie- en verliesprocessen van vrije elektronen. Het blijkt dat aan de rand van het plasma veel grotere elektronenverliezen plaatsvinden dan aangenomen werd. Waarschijnlijk wordt dit veroorzaakt door moleculaire argon-ionen, die gevormd kunnen worden door de relatief lage temperatuur aan de rand van het plasma.

Een ander plasma dat bestudeerd werd is dat in de Philips QL-lamp. Dit is een lagedruk gasontladingslamp (argon-kwik) die inductief van energie voorzien wordt. Daardoor kunnen elektroden ontbreken, hetgeen de levensduur van de lamp ten goede komt terwijl de hoge efficiëntie gehandhaafd blijft. Om de laserbundel voor Thomson-verstrooiing door de lamp te leiden is een aantal veranderingen aan de lamp aangebracht. Er is gemeten op verschillende plaatsen en voor verschillende argon- en kwikdrukken. Deze metingen zijn wederom vergeleken met voorspellingen op basis van de externe parameters en ook hier is een goede overeenstemming gevonden.

Tenslotte is nog een ander spectrochemisch plasma bestudeerd. Dit plasma werkt op helium bij atmosferische druk, maar de energie wordt capacitief ingekoppeld door twee elektroden. Het vermogen is gemiddeld rond de 35 W, maar het is sterk gemoduleerd met een frequentie van 112 kHz. Door deze relatief lage frequentie en de kleine massa van heliumatomen treden ook sterke modulaties van de elektronentemperatuur en -dichtheid op. Deze zijn weer gemeten door middel van Thomson-verstrooiing. Ook is de elektronentemperatuur bepaald uit de absolute intensiteit van de lijnemissie van het plasma. Op grond van het verschil tussen de met deze twee technieken gemeten elektronentemperaturen is geconcludeerd dat de elektronen-energieverdeling in het plasma niet Maxwells is. Het tijdsverloop van de elektronendichtheid is berekend aan de hand van productie- en verliesprocessen op basis van de gemeten elektronentemperaturen. Er is een redelijke overeenstemming gevonden met de gemeten elektronendichtheid, hoewel ook hier moleculaire ionen van belang kunnen zijn.

Dit werk vormt een bevestiging van de mogelijkheid om in een aantal gevallen op relatief eenvoudige wijze de karakteristieke parameters van een plasma te schatten op grond van de instelparameters van het plasma. Bovendien is Thomson-verstrooiing met een hoge plaats-, golflengte- en tijdresolutie toepasbaar gemaakt op plasma's met een lage elektronentemperatuur en in de nabijheid van een wand die leidt tot een hoog strooilicht niveau. Daardoor kan Thomson-verstrooiing bijvoorbeeld gebruikt worden voor lagedruk gasontladingslampen en zeer kleine plasmabrullen.
Dankwoord

Ondanks dat het schrijven van een proefschrift vele uren in eenzaamheid vraagt, is een promotie zeker niet het werk van één persoon alleen. Een woord van dank aan alle betrokkenen is daarom op zijn plaats.

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Dankwoord

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Stellingen

behorende bij het proefschrift

Laser scattering on
low temperature plasmas
High resolution and stray light rejection

door

Marco van de Sande
I

Ook in niet-ioniserende plasma’s kan gelden dat doorexcitatie van een aangeslagen toestand naar een hogere toestand waarschijnlijker is dan deëxcitatie naar een lagere toestand.

II

De tijdsafhankelijkheid van “stationaire” plasma’s die geproduceerd worden door microgolffoortsen heeft een wezenlijke invloed op zowel de deeltjes- als energiebalansen van het plasma.

III

De benaming “gradiëntlengte” als karakteristieke lengteschaal bij de beschrijving van deeltjesverliezen door diffusie werkt verwarrend.

IV

In het bedrijfsleven wordt onderzoek gedaan om geld te verdienen; op universiteiten is dat precies andersom.

V

De plaats die het milieu in de harten van de mensen inneemt komt niet overeen met de bereidheid om daar offers voor te brengen.

VI

De achteruitgang van het dialectgebruik is voor een belangrijk deel te wijten aan de vooruitgang van de techniek.
VII
In tegenstelling tot wat de huidige internationale politiek doet vermoeden, is het uitvoeren van een militaire vergeldingsactie als antwoord op een terroristische aanslag geen recht, en vormt het eerder een voedingsbodem dan een afschrikking voor terreur in de toekomst.

VIII
Grafische programmeeromgevingen zoals LabVIEW vormen zelfs voor niet-programmeurs een zeer duidelijke illustratie van de term “spaghetti-programmeren”.

IX
Kalmte in een drukke tijd kan ten onrechte worden geïnterpreteerd als luiheid of desinteresse.

X
De oprechtheid van een compliment neemt meestal af naarmate er meer woorden aan worden gespendeerd.

XI
Er is niets “micro” aan microgolven.

XII
De uitvinding die wetenschappelijke vooruitgang het meest zou helpen is een bandrecorder voor gedachten.