Poly-diagnostic Validation of Spectroscopic Methods

In-depth monitoring of microwave induced plasmas

PROEFSCHRIFT

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The author's idea about the relation between models and experiments is perfectly illustrated by the lithograph “Drawing Hands” of the Dutch artist M.C. Escher.

Представата на автора за връзката между експеримент и теория, перфектно илюстрирана с картината “Рисуващи ръце” на холандският артист М.К. Ешер.
1

General introduction
Chapter 1.

The purpose of this introductory chapter is to provide a short survey of the field of microwave plasmas and to show how the subject of this thesis is embedded in that field. A brief discussion about the nature of these plasmas will be presented. This is followed by introducing various applications of microwave plasmas. In addition, the microwave plasmas employed in this thesis are given in a gallery-form.

1.1 The nature of plasma energy sources

One of the amazing features of plasmas is that they emit light. Since light is a form of energy, plasmas need energy sources to be sustained. According to the wide variety of energy natures, we can expect that several different types of plasma energy sources can be distinguished.

In the case of the sun and the stars, energy is provided by the nuclear reactions taking place in the stellar core. In the case of lightning, the light production during thunderstorms, the energy is supplied by the electrical potential between the earth and a cloud; whereas the plasma around a falling star is powered by the kinetic energy of the asteroid. The same energy-type drives polar light.

The plasmas in technology are mainly driven by electromagnetic (EM) energy. A classification of these plasmas can be made according to the frequency of the power supply. For increasing frequency we get the sequence: direct current driven, capacitively coupled, inductively coupled, microwave induced and laser produced plasmas.

Since this experimental study is performed on microwave induced plasmas (MIPs), the rest of the chapter is focused on providing more information about this type of plasma.

1.2 Microwave induced plasmas (MIPs)

The term microwaves is used to describe EM waves with wavelengths ranging from 1 cm to 1 m: wavelengths that are comparable to the dimensions of technological applications. This implies that by adjusting the EM field using slits, chokes and dielectric materials, these plasmas can be shaped and sized.

The MIPs exhibit several specific characteristics that make them distinctive
General Introduction

not only in terms of technology but also in physics. Some of their features are listed below:

- High plasma purity – especially due to electrode-less operation.
- Good reproducibility and stability.
- Large diversity in the choice of plasma launching devices.
- Variability in the plasma length – from cm to several m.
- Pulsed or continuous mode of operation.
- The resulting wide range of operational conditions:
  - variety of gases – atomic and molecular
  - pressure – from a few pascal to several atmospheres
  - frequency – from MHz to GHz
  - applied power – from a few W to MW.
- Widely varying plasma parameters (electron density, electron temperature, gas temperature, ionization degree and chemical composition).

In section 1.1, the light emitting nature of plasmas was emphasized; and certainly an important application of plasmas is the creation of light. Moreover the key-item of this study is to develop a method of light interpretation by which a maximum of information of the internal plasma conditions can be obtained.

Apart from being sources of photons, plasmas can also be used for the generation of radicals. Radicals that can for example be used to clean air, to kill bacteria, or to deposit layers. The latter is known as plasma chemical vapor deposition (PCVD). Although this study is initiated by the quest to get more insight into PCVD, an application primarily related to the production of radicals, the light generated by plasmas still plays an important role. By analyzing the light emitted from the plasma, information about its properties can be deduced. So the key question is: How does the plasma light provide insight into the plasma inside?

The PCVD technique is used for the deposition of different types of materials in many applications. Popular nowadays are silicon film deposition for thin-film solar cell production, deposition into quartz tubes for the production
Chapter 1.

of optical fibers, as well as the deposition of diamond films. In the category of surface treatment one can classify semiconductor processing, modification of bio-polymers, plasma spraying for the fabrication of thick coatings and the sterilization of surfaces.

The use of MIPs as ion sources has found applications in the production of beams of negative ions; for instance the pulsed mono-energetic-ion-sources make beams that are suitable for space experiments. For the generation of light, we can think of spectral lamps designed for optical absorption measurements or the sulfur lamp. Furthermore, we can mention the applications of microwave plasmas as excitation and atomization sources in spectrochemical analysis.

It is not easy to give a complete list of all the possible applications of microwave plasmas here. Although the field of microwave plasma applications can nowadays be considered as being well developed, the opportunities for development of new devices, techniques and applications are still open.

1.3 The MIPs in this thesis

This thesis reports on a study performed in the framework of the STW project:

Exploring the compositional freedom in space and chemistry of Microwave Induced Plasmas; An object oriented approach

which is co-sponsored by the company Draka Communication. At Draka, MIPs are employed in the PCVD process that is used in the production of optical fibres.

Figure 1.1 shows a scheme of the plasma setup at Draka. This plasma is confined in a quartz tube that is placed into a furnace. This enclosure implies that many diagnostic methods, like laser spectroscopy, can not be applied. As a consequence, we have to restrict ourselves to methods based on the detection of light emitted by the plasma.

The non-equilibrium nature of plasmas makes the theoretical description extremely complicated. Subsequently, most technological applications are explored by trial and error. Thus the empirical exploration of the parameter space of the control settings is application driven. This means that, for a given requested plasma product, the best combination of control settings is searched for by using several trial and error steps (cf. figure 1.2). In the case of PCVD the
control settings are the vessel shape $R$ and volume $V$, power $P$, pressure $p$ and filling-gas composition while the plasma product is the deposited layer of the requested composition and morphology.

In order to avoid excessive empiricism a more systematic approach is required. In this approach, one should first study how changing the control settings effects the plasma. The next step then is to understand, how that in turn changes the plasma product. Thus, for achieving better understanding of the
relation between the control settings and the plasma product, the knowledge of plasma features is required.

<table>
<thead>
<tr>
<th>Input</th>
<th>Internal</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>control settings</td>
<td>plasma features</td>
<td>plasma products</td>
</tr>
<tr>
<td>R, V, P, p, φ,...</td>
<td>nₑ, Tₑ, n*, n**,...</td>
<td>depo-layer</td>
</tr>
</tbody>
</table>

**Figure 1.3:** The aim of this thesis is to get better insight into the internal plasma features; these are matched in between the two blocks, input and output of figure 1.2. Empirical zig-zag is replaced by the direct arrows of causal understanding.

Figure 1.3 gives an example of *internal* plasma features, such as the electron temperature $Tₑ$ and the density of electrons $nₑ$, radicals $n^*$ and radiating species $n^{**}$. The *internal* plasma features is the stage where experiments for model-validation play the most important role.

As stated before, the configuration of the plasma setup at Draka does not allow easy observation of internal plasma features. This for instance means that the application of laser spectroscopy is impossible. As a consequence, the research on this configuration has to be restricted to passive spectroscopic methods solely.

For this reason, we have decided to take an indirect route: rather than studying the Draka setup directly, we have investigated a number of microwave induced plasmas that are expected to have similar properties, but that are more easily accessible experimentally. In particular, these plasmas have experimental setup configurations that lend themselves for active spectroscopic methods, like Thomson and Rayleigh scattering. The experimental methods developed in this way can then be used to interpret the light emitted by industrial plasmas and to understand and improve the plasma features of the Draka setup.

### 1.4 A gallery of the MIPs studied

Like the Draka plasma, all microwave plasmas studied in this thesis are created and sustained by microwaves of 2.45 GHz. They also have in common that the microwave power is transferred from the magnetron towards the plasma field applicator via a coaxial line or a waveguide system. EM energy is absorbed by free electrons, which transfer energy to atoms and molecules via elastic and inelastic collisions.
The plasmas studied in this thesis can be divided into two categories: surface-wave sustained plasmas and freely expanding atmospheric plasmas. Examples of the first category are the surfatron and waveguide-surfatron. Representatives of the second category are the Torche à Injection Axiale (TIA) and the atmospheric surfatron. The following plasmas are operational in our laboratories\(^1\) (cf. figure 1.4):

- **Low pressure surfatron:** the microwaves are coupled into the plasma via a launching gap and can travel in both axial directions along the interface between plasma and dielectric (quartz tube). The plasma has no clearly localized active zone and can extend far beyond the field applicator.

\(^1\)This also includes the laboratory in Edificio Einstein, Rabanales, Cordoba, Spain.
• Waveguide-surfatron; operates basically the same as the surfatron except that the energy coupling takes place by means of a waveguide system. This allows the waveguide-surfatron to operate at higher powers and in larger volumes than the surfatron. The waveguide surfatron strongly resembles the Draka plasma setup.

• Atmospheric surfatron; the generated plasma is a flame similar to that obtained with the TIA. The plasmas have low gas temperatures and have the practical advantage that there is no need for a complicated vacuum system.

• TIA; a high power plasma torch that can produce atmospheric plasmas in various gases. It is a plasma source that is suitable for many applications. It can function as an excitation source for spectrochemical analysis and for cleaning of large gas volumes.

1.5 Poly-diagnostic validation

In well-exploited fields of science measurement precisions of 1 part in $10^{10}$ can be achieved; however, plasma measurements are frequently considered successful when a precision of 1 part in 10 is reached. The availability of different methods to determine plasma quantities at the same location simultaneously opens up a number of interesting opportunities. When different methods are employed to measure the same plasma parameter, the results might substantially differ from each other. Thus, before measurements can be used to validate models, the experimental diagnostic methods have to be validated against each other and effort must be made to explain the differences in the results. Along the same lines, one method can be used to calibrate another one.

Overall, this so-called poly-diagnostic validation has the aim

\begin{itemize}
  \item to determine for each method the validity range and
  \item to find a \textit{minimum} of easily measurable quantities from which a \textit{maximum} of plasma-information can be deduced.
\end{itemize}

A spin-off of poly-diagnostic validation is in-depth plasma-monitoring. That is: \textit{to employ validated measurement-techniques to follow essential plasma parameters and processes in real-time}. In this study poly-diagnostic validation is applied by means of \textit{active} and \textit{passive} spectroscopic methods and techniques.
An example is the quasi-simultaneous application of Thomson scattering and optical emission spectrometry on the same plasma location. The Thomson scattering technique has the advantage that it yields direct and reliable information of the local electron temperature and density. The interpretation of the results is straightforward and independent of the state of equilibrium departure. A disadvantage of the Thomson scattering technique is that it requires expensive and complex optical and laser systems and that it is experimentally demanding. The optical emission spectrometry (OES) method is much simpler; by intensity measurements average densities \( \langle n^* \rangle \) of light-emitting species can be obtained easily. Nevertheless, the translation from these densities to basic plasma properties like the electron density \( n_e \), the electron temperature \( T_e \) and the densities \( n^* \) of radicals is complicated and strongly depends on the state of equilibrium-departure. Furthermore, optical emission spectrometry is based on line-of-sight measurements and as a result average values are obtained. Deduction of essential local plasma information out of this global information requires non-trivial post-processing steps. For instance, the absolute continuum intensity method (chapter 3), requires a post-processing step that involves a theoretical model, for the plasma under study, to obtain results. The Thomson and Rayleigh scattering results (chapters 5 and 6) can be used to check if the assumptions that underly such model apply: it can be used to validate the method (chapter 7).

Summarizing, we need the active spectroscopic techniques to guide the interpretation of passive spectroscopy.

1.6 This thesis

The following chapter 2, gives a detailed introduction into the methods and techniques applied in this work.

The remainder of this thesis is devoted to the results of different diagnostic methods and techniques, as applied to argon MIPs at low and atmospheric pressure.

Chapters 3 and 4 present passive spectroscopy methods, based on the absolute measurements of line and continuum radiation. The method described in chapter 3, based on the continuum radiation, is used to determine the electron density of argon surfatron plasmas; while in chapter 4 the continuum method is applied in combination with absolute line intensity measurements. This de-
livers the electron density and electron temperature simultaneously. This novel method is applied to a plasma created by the TIA at atmospheric pressure.

In chapters 5 and 6 two active spectroscopy techniques are performed, namely Thomson scattering and Rayleigh scattering. The Thomson scattering technique is used to deliver the electron temperature and density, whereas the Rayleigh scattering gives insight into the heavy particle density and temperature.

In chapter 7 new insights into the interpretation of the absolute continuum intensity method are presented. The method is validated by the use of results obtained by Thomson and Rayleigh scattering.

Chapter 8 is devoted to a discussion of the inequality of the temperatures as determined by the Thomson scattering technique and the absolute line intensity method.

The results from chapters 3, 4 and 5 have been published as papers, while chapters 6, 7 and 8 are aimed to be submitted in the near future. As a consequence, most of the chapters can be read separately.

Finally, in chapter 9, general concluding remarks and recommendations for future work are provided based on the findings generated in this study.
An overview of the applied experimental methods
Chapter 2.

2.1 Introduction

This chapter gives an overview of the various spectroscopic techniques that have been employed in this thesis. Most of the chapters have been written as articles. As a consequence, not all the technicalities of the methods could be given. This chapter is aimed to compensate for that and to provide additional details of the used procedures, methods and techniques.

In general, plasma spectroscopic diagnostics can be divided in passive and active spectroscopy. The first case, considers the spectroscopic features of the radiation of the plasmas “as they are”, i.e. without any plasma-irradiation. In the second case, the response of the plasma to the irradiation of an external source, for instance a laser, is studied.

Passive spectroscopic diagnostics can be subdivided in relative and absolute intensity measurements. Relative measurements are very popular, basically because they are easy to perform. However, more insight into the plasma parameters and the degree of equilibrium departure can be obtained if spectroscopic measurements are performed in an absolute way. This leads to much more valuable results, but also demands for substantially more effort than in the case of relative measurements.

In view of the division into passive and active spectroscopy, this chapter will have two main parts devoted to the passive methods and active techniques as applied in this thesis.

2.2 Passive spectroscopy

A plasma emits line and continuum radiation and both spectral components can be used as information sources from which important plasma properties can be deduced. Most popular are the relative methods; these are based on the assumption that the population of the different plasma constituents is ruled by Saha-Boltzmann (SB) distribution law. Examples of these methods are the $2\lambda$-method from which a temperature-value is determined via the ratio of the intensities of two lines. The line-continuum ratio is another example of a relative spectroscopy method.

However, in the plasmas under study large deviations from SB can be expected due to the large effluxes of electron-ion pairs. This implies that most of
the methods based on ratios break down. Under these circumstances it is more appropriate to use methods based on absolute intensity measurements. In order

\[ \ln \eta_i \]

\[ \ln \eta \]

\[ T_e \alpha \frac{1}{k_B T_e} \]

\[ \eta \]

\[ \text{Saha jump} \]

\[ \eta_{\infty} = \eta_i \frac{h^3}{(2\pi m_e k_B T_e)^{3/2}} \]

Figure 2.1: A scheme of a Boltzmann-Saha plot for the ASDF in two adjacent systems under equilibrium conditions. It can be seen that the slopes in the atomic and ionic systems are the same and proportional to \( \frac{1}{k_B T_e} \), while the so-called Saha jump \( \left( \eta_i \frac{h^3}{(2\pi m_e k_B T_e)^{3/2}} \right) \) gives the transition between the two systems.

to understand the effect of the efflux of charged particles on the atomic state distribution function (ASDF) and how this changes on the relation between line and continuum radiation, we start with figure 2.1. The figure gives the logarithm of the occupation of the excited states as a function of energy for a system under equilibrium condition. The representation shows the ASDF for an atomic and that of the adjacent ion system described by the Saha-Boltzmann balance. The lines in the atomic and ionic systems are parallel, both having the slope \( \frac{1}{k_B T_e} \) while the discontinuity between the systems is known as the Saha jump. It is given by

\[ \frac{\eta_{\infty}}{\eta_i} = \eta_i \frac{h^3}{(2\pi m_e k_B T_e)^{3/2}} \]

where \( m_e, k_B, h \) and \( T_e \) are the mass of the electron, the Boltzmann and Planck constants and the electron temperature respectively. The parameter \( \eta \) corresponds to the state density (cf. section 4.2).
The radiation escaping from the plasma tends to bring the ASDF out of equilibrium. Nevertheless, assuming that the mean frequency of transitions between levels induced by electron impact is (much) higher than that of the radiative transitions, one can expect that the escape of radiation will not effect the ASDF seriously. However, this does not imply that the ASDF will attain its equilibrium shape. Another condition that has to be satisfied for the presence of Saha equilibrium is that also the outward transport of electron-ions pairs is relatively small.

Figure 2.2: The effect of the efflux of ei pairs on the ASDF is that the continuum level $\eta_{\infty}$ will be pushed down from $\eta_{\text{equil}}$ to $\eta_{\text{efflux}}$ (cf. figure 4.1). As a consequence the slope will be variable and steeper. This implies that the temperature obtained with the $2\lambda$-method and the temperature obtained from the line to continuum ratio will give values that are too low. In case that departures from equilibrium are present it is better to work with absolute intensity methods.

Figure 2.2 clarifies schematically the impact of the escape of electron-ion pairs on the atomic ASDF. It shows that this efflux will change the ratio of the occupation of any couple of excited levels and the ratio between line and continuum radiation. In general we can say that, due to the electron-ion (ei) efflux, the slopes will become steeper. So the derivation of the temperature using a Boltzmann plot leads to temperatures that are lower than the electron temperature. In order to distinguish between the temperature determined by the slope in a SB plot and the actual electron temperature, the former is often denoted by the excitation temperature. Concluding, we may state that the
The experimental methods

efflux of ei pairs in an ionizing plasma will lead to $T_{\text{exc}} < T_e$.

Figure 2.3 gives an example of the ASDFs for argon systems as detected in the atmospheric and low pressure surfatron induced plasmas (SIPs) (cf. [1, 2]). It can be seen that the ASDF cannot be specified by just one line with a constant slope. Applying absolute intensity measurements we are able to relate the densities of the excited states to that of the ground state. Evidently, the latter cannot be determined spectroscopically, since the ground state is not emitting light. However, the ground state population $n_1$ can be determined via the gas law. Written as $p = n_1 k_B T_a$, it expresses that the pressure is predominantly realized by the ground state atoms. The reason is that $n_1$ is more than 4 orders of magnitude larger than that of the sum of the excited states and the densities of ions and free electrons.

So, in order to get insight in the main plasma properties, like the electron temperature, the electron density, the ASDF and the departure from equilibrium, it is desirable to achieve absolute measurements. The methods based on ratios are not valid.

Figure 2.3: Examples of the ASDF of ionizing argon systems. Left: the ASDF typical for atmospheric plasmas like the atmospheric surfatron and the Torche à Injection Axiale (cf. figure 4.2). Right: an ASDF typical for the low pressure surfatron. In both cases it is impossible to specify the ASDF by just one line with a constant slope.
2.2.1 Absolute intensity calibration

The aim of this section is to show how plasma properties can be determined from absolute line and continuum measurements. From the continuum we can, among others, obtain the electron density while the absolute line intensity (ALI) can be used to construct the atomic state distribution function. With the help of collisional radiative models (CRMs), the ASDF can give information on the electron temperature $T_e$, electron density $n_e$ and the degree of equilibrium departure. The study of radiation generation, radiation transport and the calibration procedure will be guided by the radiation transport equation:

$$\frac{dI_{\lambda}(\lambda)}{ds} = j_{\lambda}(\lambda) - k(\lambda)I_{\lambda}(\lambda),$$

(2.2)

which describes how the spectral intensity $I_{\lambda}(\lambda)$ (in Wm$^{-1}$ m$^{-2}$ sr$^{-1}$) of a beam changes along its path through a medium due to absorption and emission processes. The importance of these processes determined by the medium is given by the absorption coefficient $k(\lambda)$ (in m$^{-1}$) and the emission coefficient $j_{\lambda}(\lambda)$ (in Wm$^{-1}$ m$^{-3}$ sr$^{-1}$). The quantity $I_{\lambda}(\lambda)$, the monochromatic intensity or spectral intensity, is the most fundamental radiation quantity and plays a central role in the calibration procedure.

Notes

1. In the used notation difference is made between the functional dependence of a quantity on $\lambda$ and the differentiation of a quantity with respect to $\lambda$. In the former case, such as for $k(\lambda)$, we put $\lambda$ between brackets; in the latter case e.g. for $j_{\lambda}$ it appears as a subscript. For instance $j_{\lambda}(\lambda)$ refers to the emission per $\lambda$ generated at a certain value of $\lambda$. This difference between the per and at notation is not always followed strictly. Where omitting $\lambda$ does not lead to ambiguity the notation can be simplified.

2. For a more general representation, we have to extend the right-hand-side (rhs) of equation (2.2) with a reflection term. However, we assume that it is justified to neglect this term for the plasmas under study.

3. As said $I_{\lambda}(\lambda)$, is the most fundamental radiation quantity. It represent the power of the radiation per unit of area, solid angle and wavelength interval as measured through a surface placed perpendicular to the emission.
direction. In physics it is usually denoted by the radiance, here we follow the astronomical nomenclature and use the indication spectral intensity.

4. In contrast to the flux (W) and flux density (Wm$^{-2}$), the intensity of a beam does not change during propagation other than due to emission and absorption (and reflection) processes. That is why $I_\lambda(\lambda)$ plays a central role, among others, in the calibration procedure.

To explore the properties of equation (2.2), it is solved here for the case of a homogeneous medium, that is, a medium for which $j_\lambda(\lambda)$ and $k(\lambda)$ are not position dependent. In that case we can write

$$\frac{dI_\lambda(\lambda)}{ds} = -k(\lambda)[I_\lambda(\lambda) - S_\lambda(\lambda)]. \quad (2.3)$$

In this equation, we used $S_\lambda(\lambda) \equiv j_\lambda(\lambda)/k(\lambda)$, the so-called source function, a quantity of the medium with the same dimensions as $I_\lambda(\lambda)$ that, in turn, describes the properties of the beam. So in fact equation (2.3) demonstrates the competition between the medium $S$ and the beam $I$; it gives the change in $I$ due to local value of $S$.

For a beam with initial intensity $I_\lambda(\lambda, 0)$ that enters the medium with constant $S$ value and depth $D$, we get the solution

$$I_\lambda(\lambda, D) = I_\lambda(\lambda, 0) \exp(-\tau) + S_\lambda(\lambda)\{1 - \exp(-\tau)\}, \quad (2.4)$$

where

$$\tau(\lambda, D) = \int_0^D k(\lambda)ds \quad (2.5)$$

is a dimensionless quantity known as the optical depth. In our case of a homogeneous plasma slab of depth $D$, we can then write $\tau(\lambda, D) = k(\lambda)D$. We now apply equation (2.4) to the case for which $I_\lambda(\lambda, 0) = 0$, i.e. to a non-back-lighted medium. There are two limiting cases.

1. The medium is optically thin for the radiation: $\tau(\lambda, D) = k(\lambda)D \ll 1$.

   In this situation we obtain

   $$I_\lambda(\lambda, D) = S_\lambda(\lambda)k(\lambda)D = j_\lambda(\lambda)D. \quad (2.6)$$
2. The medium is optically thick for radiation, $\tau(\lambda, D) = k(\lambda) D \gg 1$. This leads to

$$I_\lambda(\lambda, D) = S_\lambda(\lambda) = \frac{j_\lambda(\lambda)}{k(\lambda)} = B_\lambda(\lambda),$$

where the Kirchoff relation is used to transform $S$ into the Planck function

$$B_\lambda(\lambda, T) = \frac{2hc^2\lambda^{-5}}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1},$$

which in the frequency representation reads

$$B_\nu(\nu, T) = \frac{2h\nu^3}{c^2(\exp\left(\frac{h\nu}{k_B T}\right) - 1)}.$$

This division as given above in $\tau \ll 1$ and $\tau \gg 1$ gives the difference between the plasma and the calibration lamp. The plasma is optically thin, i.e. $\tau \ll 1$, for the radiation under study. On the other hand, the standard radiation source employed in this study is ruled by $\tau \gg 1$ radiation.

Due to the high material density in the emitting ribbon of the standard lamp the spectral features can be reasonably well approximated by the Planck function. To express deviations from Planck’s law the emissivity $\varepsilon(\lambda, T)$ is introduced so that, for the radiation generated by the standard source, we can write

$$I_{RB}^\lambda(\lambda, T) = \varepsilon(\lambda, T) B_\lambda(\lambda, T).$$

A typical value of the emissivity of the tungsten ribbon is $\varepsilon(\lambda, T) = 0.45$. We come back to this in subsection 2.2.4.

### 2.2.2 Continuum radiation

The continuum radiation can be used in combination with line radiation and this line-continuum ratio method gives the electron temperature. However, it is only applicable to systems close to equilibrium; e.g. thermal plasmas. Characteristic for this class of plasmas is the high value of $n_e$ and the high degree of ionization $\alpha = n_e/n_a$. However, the plasmas dealt with in this thesis have low $\alpha$-values while large deviations from equilibrium are present. Both features imply that the

\[\text{In our plasmas we can replace the atom density by the density of the atoms in the ground state, hence } n_a = n_1.\]
The experimental methods

The line-continuum ratio method cannot be used. Another typical property of the plasmas under study is that the main contribution to the continuum generation comes from electron-atom (ea) rather than from electron-ion (ei) interactions.

In general, the continuum contributions can be classified according to the nature of the kind of interacting species. In this way we can distinguish between the radiation generated by collisions of free electrons with atoms (ea, free-free), free electrons with ions (ei, free-free) and by free-bound radiation (ei, free-bound)\(^2\).

\[
j_{\lambda}(\lambda) = j_{\lambda}^{\text{ea, ff}}(\lambda) + j_{\lambda}^{\text{ei, ff}}(\lambda) + j_{\lambda}^{\text{ei, fb}}(\lambda) .
\]

In the latter case, the initially free electrons are captured by ions. It was found [3] (also cf. chapter 3) that for our conditions, for which the ionization ratio \(n_e/n_a\) is small (in most cases \(n_e/n_a < 10^{-4}\)), the ea free-free gives by far the most dominant contribution.

A full description of the various terms can be found in chapters 3. Here we reproduce the formula for the \(j_{\lambda}^{\text{ea, ff}}(\lambda)\) as it describes the main continuum contribution for our type of plasmas. The expression

\[
j_{\lambda}^{\text{ea, ff}}(\lambda) = c_2 T_e^{3/2} n_e n_a \lambda^2 
\times \left\{ Q_{\text{Ar}}(T_e) \left( 1 + \frac{h c}{\lambda k_B T_e} \right)^2 \exp \left( - \frac{h c}{\lambda k_B T_e} \right) \right\}
\]

shows the dependence of the emission coefficient on \(n_a\) and \(T_e\). This means that a \(n_e\) determination can only be applied if \(n_a\) and \(T_e\) are known (cf. chapter 7). The meaning of the other symbols can be found in chapter 3.

In order to find \(T_e\) we combined the absolute continuum intensity (ACI) method with the absolute line intensity (ALI) method using an iterative procedure. This method is described in [1] and chapter 4 of this thesis.

The calibration of the continuum radiation

If the atom density \(n_a\), the electron temperature \(T_e\) and the intensity \(I\) of the continuum radiation are known (for certain wavelengths) we can, by combining

\(^2\)In a more complete notation, one should write \(j_{\lambda}(\lambda, T_e, n_e, n_a)\). However, for the sake of brevity, we will often denote the emission coefficient by \(j_{\lambda}(\lambda, T_e)\) or \(j_{\lambda}(\lambda)\).
equation (2.6) with equation (2.12), write

\[ n_e = \frac{j^o \lambda^2 G(T_e, \lambda)}{n_o c Q^2 T_e^{3/2}} = \frac{(I/D) \lambda^2 G(T_e, \lambda)}{n_o c Q^2 T_e^{3/2}}, \quad (2.13) \]

where it is assumed that \( j \) is homogenous along the intersection \( D \) of the line-of-sight of the detection system and the plasma. The function \( G(T_e, \lambda) \) can easily be deduced from equation (2.12) and is given in equation (7.4). An important part in the determination of \( I \) is the calibration of the setup. For that a tungsten ribbon lamp (TRL) is used. The procedure is as follows: The photons emitted by the TRL, radiating with a spectral intensity \( I_{S,\lambda}(\lambda) \), are collected by a monochromator during an exposure time \( t_S \). Transmitted to the CCD array they generate in that time \( h_S(\lambda) \) counts per pixel. Now, if the plasma radiation creates via the same optical path during \( t_P \) a number of \( h_P(\lambda) \) counts on the same CCD pixel we find for the spectral intensity at \( \lambda \)

\[ I_{P,\lambda}(\lambda) = I_{S,\lambda}(\lambda) \frac{h_P(\lambda)}{h_S(\lambda)} \frac{t_S}{t_P}. \quad (2.14) \]

This procedure is depicted in figure 2.4 giving the \( h_P/t_P \) and \( h_S/t_S \) as a function of \( \lambda \). The ratio of \( h_P/t_P \) and \( h_S/t_S \) gives the ratio between \( I_{P,\lambda}(\lambda) \) and \( I_{S,\lambda}(\lambda) \).
In the studies that were done in relation to the chapters 3, 4 and 7 the continuum radiation is analyzed over a broad wavelength range. In those studies reliable $\lambda$ regions were found to be centered around $\lambda = 648$ nm for the low pressure plasmas and $\lambda = 439$ nm for the case of atmospheric pressure. The reason is that in these parts of the spectrum the radiation is free from contributions of bound-bound transitions (spectral lines) for the plasmas under study.

### 2.2.3 Line radiation

The spontaneous decay of an atom from an upper state to a lower state

$$A_u \rightarrow A_l + h\nu_{ul}$$

(2.15)

is accomplished by the emission of a photon $h\nu_{ul}$. In a plasma this leads to line radiation for which the corresponding emission coefficient $j_{ul}(\lambda)$ ($\text{Wm}^{-1}\text{m}^{-2}\text{sr}^{-1}$) reads

$$j_{ul}(\lambda) = \frac{A(u, l)E_{lu}n(u)\varphi(\lambda)}{4\pi},$$

(2.16)

where $n(u)$ is the density of the radiating (upper) level $u$, $E_{lu} = E_u - E_l = h\nu_{ul}$ is the photon energy which equals the energy difference between the upper and lower state, $A(u, l)$ ($\text{s}^{-1}$) the transition probability and $\varphi(\lambda)$ the line shape of the transition. This is normalized in such a way that

$$\int_T \varphi(\lambda) d\lambda = 1 .$$

(2.17)

Here, the subscript $T$ refers to the fact that the integral is carried out over the complete spectral line (the whole transition).

The line shape as described by the function $\varphi(\lambda)$ contains interesting information about the plasma parameters. The Stark-broadening of the $H_\beta$ line, for instance, can be used to determine the electron density. Here, we will not further deal with the line broadening.

The basic parameter to determine the ASDF is the transition integrated emission coefficient that reads

$$j_{ul} = \int_T j_{ul}(\lambda) d\lambda = \frac{A(u, l)E_{lu}n(u)}{4\pi},$$

(2.18)

where the last step is justified due to the fact that $\varphi(\lambda)$ is normalized. In optically thin homogeneous plasma, we can deduce $j_{ul}$ from the transition-integrated...
intensity $j_{ul} = I_{ul}/D$ so that density $n(u)$ of the radiating level can be obtained via

$$n(u) = \frac{4\pi (I_{ul}/D)}{A(u,l)E_{lu}}.$$  \hspace{1cm} (2.19)

Note that $I_{ul} = \int \rho I_{ul}(\lambda) d\lambda$, is the quantity deduced from the measurements after the calibration of line radiation. One should keep in mind that the basic property in radiation transport is the spectral intensity $I_{\lambda,ul}(\lambda)$; that is the quantity that has to be calibrated using a standard lamp (medium $S$). Thus, in computing the transition integrated intensity $I_{ul}$, the starting point is to determine $I_{\lambda,ul}(\lambda)$ for the several $\lambda$ values in the line. In fact, the procedure done for the continuum has to be performed for the different $\lambda$ values that are in the line (cf. figure 2.5). After that, integration over the spectral line must be performed. A short recipe of the procedure:

1. select a proper integration time $t_p$
2. determine $h_P$ for several $\lambda$ in the transition $T$
3. do the same for the calibration source
4. apply equation (2.14) for several $\lambda$ values in the line
5. perform the integration over the spectral line (the transition). This gives
\[ I_{ul} = \frac{I_{S,\lambda}(\lambda_0)}{h_S(\lambda_0)} t_P \int P h_P(\lambda) d\lambda. \] (2.20)

Here, the assumption is used that \( I_{S,\lambda}(\lambda)/h_S(\lambda) \) is constant over the spectral line-profile so that \( I_{S,\lambda}(\lambda)/h_S(\lambda) \) can thus be replaced by \( I_{S,\lambda}(\lambda_0)/h_S(\lambda_0) \) where \( \lambda_0 \) refers to the central wavelength of the transition.

For the CCD the integration can be replaced by a summation giving

\[ I_{ul} = \frac{I_{S,\lambda}(\lambda_0)}{h_S(\lambda_0)} t_P \sum P h_P(\lambda) \Delta \lambda_{\text{pix}}, \] (2.21)

where \( \Delta \lambda_{\text{pix}} \) is the bandwidth of the CCD pixels, a quantity that can be assumed to be constant along the spectral line-width.

Inserting the \( I_{ul} \) value into equation (2.19) gives the density of the level \( u \).

We stress the fact that the plasma needs to be optically thin for the radiation of interest.

The ASDF construction

After the \( n(p) \) values of various radiating levels are determined the ASDF can be constructed. This is done by plotting \( \eta(p) = n(p)/g(p) \), where \( g(p) \) is the statistical weight of the level\(^3\) (being the number of states per level), as a function of excitation energy in a semi-log plot.

A typical shape of the ASDF is depicted in figure 2.3, showing that the ASDF of ionizing plasmas can be divided roughly in a lower and upper part. The lower part is formed by the ground state ‘1’ and the states in level ‘3’. This is the level (group) formed by the 4p block, the lowest easy observable states\(^4\).

In \([1, 4]\) a method is described by which the ratio of \( \eta(1) \) and \( \eta(3) \), providing the temperature \( T_{13} \), can be used to calculate the electron temperature \( T_e \). The translation of \( T_{13} \) into \( T_e \) is based on the theoretical knowledge of the effect of

---

\(^{3}\)A distinction is made between (energy) level and “state”. The degeneration of a state is unity: \( g(\text{state}) = 1 \). For a level that is not the case, in general. Since Ar is a noble gas the atom ground level is a state. Meaning that \( n(1) = \eta(1) \).

\(^{4}\)The lowest excited level group of Ar is the 4s group consisting of two metastables and two radiative levels. However the radiation, having a wavelength of about 100 nm, is not easy to observe. Moreover the plasma is optically thick for this radiation so that detection of this radiation will not provide information of the 4s occupation.
the departure of equilibrium on the lower part of the ASDF. This theory is used to construct a so-called collisional radiative model (CRM) (cf. figure 4.1).

It is often assumed that the upper part of the ASDF is in equilibrium with the continuum, thus in so-called partial local Saha equilibrium (pLSE). In that case $\eta_\infty$ can be determined by extrapolating the ASDF to the continuum ($I = 0$). The $\eta_\infty$ in turn gives a value of the electron density $n_e$ (cf. equation (2.1)). This method was used in [5] where the results were compared to those obtained by Thomson scattering, the absolute continuum method and the $H_\beta$ line broadening method. It was found that by applying the extrapolation method the derived values of $n_e$ are too high. The underlying reason is that the detectable upper part is not ruled by pLSE but by the excitation saturation balance (ESB) [6]. A feature of the ESB is that the local excitation temperature, the slope temperature $T_{\text{slope}}$, nearly scales with the ionization potential (the location in the excitation space) and approximately obeys $T_{\text{slope}} = I_p/3$. So in contrast to what figure 2.3 suggests, the slope of the upper ESB part is not constant but becomes steeper and steeper until it reaches pLSE.

2.2.4 The calibration source

In the previous section, it is made clear that the intensities emitted by the plasma must be determined in an absolute way. Therefore, a calibration source is needed. The task of this source is to provide known $I_{S,\lambda}(\lambda)$ values as a function of $\lambda$ for the $\lambda$-range of interest. The detector signal $I_{P,\lambda}(\lambda)$, generated by the plasma intensity can then be compared to the signal generated by $I_{S,\lambda}(\lambda)$. In our case, where $\lambda$ is in the range of $400 - 800$ nm, we work with tungsten ribbon lamps (TRL). The TRL is a secondary standard, meaning that it must be calibrated against a primary standard. The result of the TRL calibration, however, does not lead to $I$ values (in W$m^{-1}m^{-2}sr^{-1}$) for a series of $\lambda$ values but rather to one single temperature (for only one $\lambda_0$ value).

Two types of temperatures can be specified: the true temperature $T_{\text{true}}$ and the radiance temperature $T_{\text{rad}}$. In general they are given as functions of the current $i$ through the ribbon. The two temperature types are defined as follows:

The true temperature $T_{\text{true}}$ of a source is the same temperature as that measured with a thermometer in perfect contact and in thermal equilibrium with that source.

The radiance temperature $T_{\text{rad}}$ of a source at a wavelength $\lambda_0$ is the tem-
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perature of a Planckian radiator that for \( \lambda_0 \) delivers the same intensity as the source does. The relation between \( T_{\text{true}} \) and \( T_{\text{rad}} \) can be expressed as

\[
B_\lambda(\lambda_0, T_{\text{rad}}) = \tau_w(\lambda_0) \varepsilon(\lambda_0, T_{\text{true}}) B_\lambda(\lambda_0, T_{\text{true}}) .
\] (2.22)

The product of the two last factors at the rhs of the above equation, \( \varepsilon(\lambda_0, T_{\text{true}})B_\lambda(\lambda_0, T_{\text{true}}) \) expresses that the ribbon having a temperature \( T_{\text{true}} \) generates an spectral intensity (at \( \lambda_0 \)) that deviates with a factor \( \varepsilon(\lambda_0, T_{\text{true}}) \) from the values prescribed by the Plank function \( B_\lambda(\lambda_0, T_{\text{true}}) \) (cf. equation (2.10)). The transmission \( \tau_w(\lambda_0) \) accounts for the fact that only the fraction \( \tau_w(\lambda_0) \) of the Ribbon radiation leaves the source via the bulb. Usually \( \tau_w \) is in the order of 90\%. In the calibration procedure of the TRL this intensity is compared to that of a primary standard of which the spectral intensity at a given wavelength \( \lambda_0 \)\(^5\) is expressed in the \( B \)-function (the lhs of the above equation). This is done for several values of the current \( i \) through the lamp.

Literature inspection reveals that there are two main routes.

1. The calibration of the TRL gives (apart form the \( T_{\text{rad}} \)) the true temperature \( T_{\text{true}} \) for several \( i \) values.

2. The calibration only gives \( T_{\text{rad}} \) at a certain \( \lambda_0 \) for several \( i \) values.

The case 1, above, can be seen as a special service of a calibration institute, since an extra step is needed. The rest of the procedure of the calibration of the plasma radiation is then quite straightforward. By using equation (2.22) and the Planck function \( B_\lambda(\lambda, T_{\text{true}}) \) the spectral intensity can be calculated for any wavelength. The only extra information that is needed is the transmission \( \tau_w(\lambda) \) and the emissivity \( \varepsilon(\lambda, T_{\text{true}}) \). It can be assumed that the \( \tau_w(\lambda) \) is nearly constant as a function of \( \lambda \). For \( \varepsilon(\lambda, T_{\text{true}}) \) we can use the tables of De Vos [7] from which we constructed figure 2.6 together with the value of the fit function \( \varepsilon(\lambda, T) \)

\[
\varepsilon(\lambda, T) = (2.22 \times 10^{-5} T - 1.26 \times 10^{-1}) \lambda^2 \\
+ (-4.62 \times 10^{-5} T + 5.69 \times 10^{-2}) \lambda + 0.5 \\
= (2.22 \times 10^{-5} \lambda^2 - 4.62 \times 10^{-5} \lambda) T \\
+ (-1.26 \times 10^{-1} \lambda^2 + 5.69 \times 10^{-2} \lambda + 0.5). \quad (2.23)
\]

\(^5\)The value of \( \lambda_0 \) is normally around 655 nm and the exact value comes with the calibration report accompanying the calibration source.
Figure 2.6: Emissivity of tungsten for different temperatures with the corresponding fitting function (the solid lines), the data is obtained from [7].

This reproduces the table values in the range $400 < \lambda < 1000 \text{ nm}$ within 1%. The temperature $T$ is expressed in K and the wavelength $\lambda$ in µm.

In case 2, there are two options:

- By exposing the detection system (tuned at $\lambda_0$) to the TRL we can determine the sensitivity of the system. For instance the number of counts per unit of time and pixel as generated by the known $B_\lambda(\lambda_0, T_{\text{rad}})$. If the transmission function $\tau_s(\lambda)$ of the system is known, we can calculate the sensitivity at other $\lambda$ values as well. Only information of the relative $\tau_s$ value is needed.

- Using equation (2.8) and applying the Wien limit, meaning that the $[\exp\left(\frac{hc}{(\lambda k_B T_e)}\right) - 1]^{-1}$ in equation (2.8) can be replaced by $\exp\left(-\frac{hc}{(\lambda k_B T_e)}\right)$, one gets

$$\frac{1}{T_{\text{rad}}} = \frac{1}{T_{\text{true}}} - \left(\frac{k_B}{h\nu_0}\right) \ln (\mathcal{E}(\lambda_0, T_{\text{true}})).$$

Assuming that $\mathcal{E}(\lambda_0, T_{\text{true}})$ has a linear dependence on $T_{\text{true}}$ around a certain $T^*$
value, we can write $\varepsilon = \varepsilon^*(1 + r(T_{\text{true}} - T^*))$, where $r = \Delta \varepsilon / (\Delta T \varepsilon^*)$. Using the approximation $\ln (1 + x) \approx x$ equation (2.24), leads to

$$\frac{1}{T_{\text{rad}}} = \frac{1}{T_{\text{true}}} - \left(\frac{k_B}{h\nu_0}\right) rT_{\text{true}} + \left(\frac{k_B}{h\nu_0}\right) \{rT^* - \ln \tau_w \varepsilon^*\}. \quad (2.25)$$

It can be solved iteratively or as square root equation. The latter has the solution

$$T_{\text{true}} = \frac{1 - pT_{\text{rad}}}{2qT_{\text{rad}}} \left(1 - \left(1 - \frac{4qT_{\text{rad}}^2}{(pT_{\text{rad}} - 1)^2}\right)^{1/2}\right). \quad (2.26)$$

Equation (2.26), where $q = -(k_B/h\nu_0)$ and $p = (k_B/h\nu_0)(rT^* - \ln \tau_w \varepsilon^*)$, gives a direct translation $T_{\text{rad}} \rightarrow T_{\text{true}}$.

Now, when $T_{\text{true}}$ is known (for several $i$ values) we can find the intensity for other $\lambda$ values as well. Hereafter, the steps given above under case 1 can be performed.

As stated before the temperature of the ribbon is derived from the $i - T_{\text{RB}}$ relation; i.e. the relation between the current through the lamp and the $T_{\text{true}}$ value of the ribbon. The relation is determined during the calibration procedure of the ribbon lamp.

2.2.5 Error analysis of the calibration method

The error in the $I$-determination is via equation (2.14) and (2.20) among others determined by the absolute intensity measurement procedure and thus to the knowledge of the temperature and emissivity $\varepsilon$ of the ribbon of the standard lamp. We can assume that the $\varepsilon$ value is accurately known over a large range so that the most important error in $I$ stems from the Planck function due to the $T$ inaccuracy. This in turn comes from possible variations in the current through the ribbon. Taking a typical value of the temperature of $T_{\text{RB}} = 2000 \text{K}$ we find for $\lambda = 760 \text{nm}$ that $hc/(\lambda k_B T_{\text{RB}}) \approx 10$ which implies that we are in the Wien limit of the Planck function. So, we can write

$$B_\lambda(\lambda, T) = \frac{2hc^2}{\lambda^5} \exp \left(-\frac{hc}{\lambda k_B T}\right). \quad (2.27)$$

Taking the derivative of $\ln(B_\lambda(\lambda, T))$ with respect to the temperature we get

$$\Delta \ln(B_\lambda(\lambda, T)) = \frac{\Delta B}{B} = \frac{hc}{\lambda k_B T} \frac{\Delta T}{T}. \quad (2.28)$$
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Using $hc/(\lambda k_B T) = 10$, we see that uncertainties in the temperature of the ribbon lamp are amplified by a factor of 10.

The inaccuracy in the temperature is determined by that of the current and thus depends on the $i - T_{RB}$ relation. If we assume that the current-temperature relation is roughly determined by the power balance: ohmic power = radiative power, we get $i^2R = \varepsilon_{eff} \sigma_{SB} T_{true}^4 A_{eff}$, where $A_{eff}$ is the effective surface of the ribbon, $\sigma_{SB}$ Stefan-Boltzmann coefficient and $\varepsilon_{eff}$ an effective emissivity. This means that the temperature and the current through the ribbon are linked to each other as $T_{true} \propto \sqrt{i}$ and thus

$$\frac{\Delta T}{T} \approx \frac{1}{2} \frac{\Delta i}{i} \quad (2.29)$$

so that

$$\frac{\Delta B}{B} = \frac{hc}{2\lambda k_B T} \frac{\Delta i}{i}. \quad (2.30)$$

The above means that in view of the factor $(hc/2\lambda k_B T)$ the calibration procedure must be performed with care. First of all, we need a stable current source. Second, we should carefully select the surface part of the ribbon that will be employed for the calibration (cf. figure 2.7).

![Figure 2.7: Pictures of the tungsten ribbon for three different current values. In case a) the current is $i = 0 \text{ A}$, b) $i = 4.5 \text{ A}$ and in c) $i = 9.5 \text{ A}$. Especially in case b) a temperature gradient along the ribbon length is clearly visible. This indicates that it is very important that the observation point is always at the same position, thus in the middle of the ribbon.](image)

With respect to the first condition we selected a highly stabilized current source with a stability of 0.01% which means, applying equation (2.30), that $\Delta B/B = 0.05\%$. To cope with the second aspect, i.e. allocating the appropriate surface spot of the ribbon, we performed the calibration several times and with
two different ribbon lamps. This led to an error of 3%, which is larger than the current variability and thus determines the error in the \( I \) values.

For absolute line intensity measurements the main uncertainty is due to the inaccuracy of the \( A \) values; typically \( \Delta A / A = 25\% \). For the absolute continuum intensity measurements the uncertainty is determined by the use of the cross section \( Q \) used in equation (2.12), (cf. subsection 4.5.1). This means that the error induced by the calibration step is relatively small; provided of course that the calibration is done with care.

2.2.6 Practical issues

The error analysis makes clear that special attention must be paid to the treatment of the TRL and the setup. This can be translated in guidelines for the maintenance of the TRL and for the proper use during operation [7].

Maintenance

- Recalibrate the lamp periodically.
- Keep the lamp envelope clean with ethanol or another suitable solvent, using a soft cloth or lens tissue.
- Reverse the current frequently, this will prevent grooving; typically each ten working hours is recommended. Operation on alternating current from time to time is a good option.
- Avoid overloading or too high current pulses.
- It is advised not to use the lamp for long time at high temperatures; for a gas-filled lamp high temperature means 2800 K and for a vacuum lamp 2400 K.

During operation

- Use very well current-stabilized power supplies; better than \( 10^{-4} \).
- The electrical polarity must be the same as that given in the calibration report.
• Apply the desired current by increasing it in small steps (for instance around 2 minutes per 1 A) from current zero to the current that is wanted. After reaching the desired current wait approximately 15 minutes till equilibrium is settled.

• The tungsten ribbon lamp must be operated in a good ventilated and (if possible) thermostrated room.

• The orientation of the TRL must be the same as that given in the calibration report; this is especially important in the case of gas-filled TRL.

• The optical axis should not deviate more than $5^\circ$ from the normal on the surface of the strip.

• Use the same portion of the ribbon as that on which the calibration is performed, this position normally is marked by the producer.

• The optical path from plasma to detector must be the same as that from the standard source to the detector.

• Make sure that the CCD or photomultiplier tube are used in the linear domain.
2.3 Active spectroscopy; laser scattering

The first part of this chapter was devoted to passive spectroscopic methods. The advantage of these methods is that the plasma information is deduced from the radiation generated by the plasma itself; so that these techniques are intrinsically non-intrusive. The disadvantage is that they are based on line-of-sight observations so that the deduction of spatially resolved information is not straightforward. Moreover, the interpretation of the spectroscopic information in terms of main plasma properties is far from simple and strongly dependent on the (local) degree of equilibrium departure.

The active spectroscopic methods, dealt with in this thesis, do not have these disadvantages. The information does not (strongly) depend on state of equilibrium departure while spatially resolved information is obtained at once. The findings obtained with these methods can be used to guide the interpretation of the passive observation.

Three types of laser scattering methods have been applied:

- Thomson scattering (TS)
- Rayleigh scattering (RyS)
- Raman scattering (RnS)

In all types the essence is the scattering of (laser) photons by electrons. In the case of Thomson scattering the electrons are free, in Rayleigh scattering the electrons are bound and in the case of Raman scattering the electrons are bound to molecules while the scattering is accompanied with an internal change of the molecule in rotational and/or vibrational modes. The current study deals with rotational Raman scattering only. In the past, vibrational RnS was applied in our group by [8–10]. Rotational and vibrational RnS are comparable with laser absorption (LA) and laser induced fluorescence (LIF) in the sense that during scattering a bound-bound transition takes place. For Thomson and Rayleigh scattering this is not the case. No further attention to LA and LIF will be assigned, since they are not applied in this thesis.

Thomson scattering plays a central role in this study. It gives the opportunity to determine the density and temperature of the most active plasma species: the free electrons. Raman scattering is used to calibrate the Thomson scattering
experimental setup for absolute density measurements, while the Rayleigh scattering is used to determine the density and temperature of the principal density reservoir: the ground state atoms. The main objective of Rayleigh scattering is to find out how much heat the ground state atoms receive from the electrons.

The spectral power $P_x^\lambda(\Delta \Omega(\theta, \varphi))$, unit $\text{Wnm}^{-1}$, of the scattered radiation collected in the solid angle element $\Delta \Omega$ around the direction specified by $\theta$ and $\varphi$ depends linearly on the incident laser power $P_i$, the length $L$ over which the laser-medium interaction takes place, the density $n_x$ of the scattering particles, the size of the solid angle $\Delta \Omega$ and the differential cross section $d\sigma^x/d\Omega$. The relation reads

$$P_x^\lambda(\Delta \Omega(\theta, \varphi)) = P_i n_x L S^\lambda(\lambda) \Delta \Omega(\theta, \varphi) \frac{d\sigma^x}{d\Omega}$$

where $S^\lambda(\lambda)$ contains the spectral information; the unit is nm$^{-1}$ and we assume that it satisfies normalization, meaning that $\int S^\lambda d\lambda = 1$.

A double perpendicular scattering geometry is used in our studies meaning that for all scattering experiments the observation direction is perpendicular to the direction of the incident radiation ($\theta = 90^\circ$) and that the incident radiation is polarized perpendicularly to the plane of scattering ($\varphi = 90^\circ$).

Below we will focus on the three different techniques Thomson, Rayleigh and Raman scattering separately.

### 2.3.1 Thomson scattering

For the relatively low values of electron density $n_e$ and high electron temperatures $T_e$ observed in the plasmas under study we deal with non-collective scattering [10, 11]. This means that electrons respond individually to the laser photons and that $S^\lambda(\lambda)$ is directly related to the velocity distribution of the electrons. If this distribution is Maxwellian, the Thomson scattering spectrum has a Gaussian shape from which $T_e$ can be determined using the formula

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

Here, $\lambda_i$ is the wavelength of the incident radiation, $\theta$ the angle between the scattered wave vector and the incident wave vector, $m_e$ the electron mass, $c$ the speed of light, $k_B$ the Boltzmann constant while $\Delta \lambda_{1/e}$ is the half of the 1/e width of the TS spectrum.
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![Image](image_url)

**Figure 2.8:** An iCCD image and the corresponding of Thomson signal. Left: A typical iCCD image obtained by the accumulation of TS photons. The vertical direction reflects the spatial dimension along the laser plasma interaction zone; the horizontal direction is the direction of the wavelength dispersion. Right: binning of the iCCD image along the vertical direction gives a Gaussian distribution. The gap around the central wavelength is the result of the (home-made) notch filter (cf. subsection 2.3.5).

Considering the double perpendicular geometry (i.e. $\theta = 90^\circ$ and $\varphi = 90^\circ$) and the wavelength of the incident radiation used (532 nm), equation (2.33) can be simplified to

$$T_e = 5238 \times (\Delta \lambda/\text{e})^2 \text{ K nm}^{-2}.$$  \hspace{1cm} (2.33)

So the spectral analysis of the scattered photons gives the electron temperature.

The electron density can be obtained after integrating expression (2.31) over the spectrum. Since $\int S_\lambda d\lambda = 1$ we get

$$n_e = \frac{P_e(\Delta \Omega(\theta, \varphi))}{P_e L \Delta \Omega(\theta, \varphi)} \left( \frac{d\sigma^e}{d\Omega} \right)^{-1},$$ \hspace{1cm} (2.34)

where $P_e(\Delta \Omega(\theta, \varphi))$ is the spectral integrated power associated with Thomson scattering (collected in $\Delta \Omega$). The denominator is determined in the calibration procedure [12, 13]. Figure 2.8 presents an iCCD image of collected Thomson scattering photons and the corresponding spectral profile.
2.3.2 Raman scattering

Figure 2.9 gives a typical example of the Raman signal as a function of wavelength. It can be seen that due to the different transitions the spectrum is rather broad and the width is comparable with the spectrum of TS for our plasmas. This implies that after removing the signal at the central wavelength part, an action that is often applied to eliminate the strong scattering signal created by RyS and false stray light, still enough information is left to perform the calibration of TS with RnS.

In [12] and [10] rotational Raman scattering was applied to individual rotational transitions; so for instance the transition $4 \rightarrow 6$ and $14 \rightarrow 16$, where employed in [10], to determine the gas temperature of the plasma edge. In that application the $n_x$ in equation (2.31) represents the density of the nitrogen molecules in the rotational states 4 and 14 whereas the $S_\lambda$ corresponds to the Gaussian function related to the velocity distribution of these rotational excited molecules. However, since the expected Doppler width equals 0.006 nm at 2000 K whereas our detection system is not capable to resolve better than 0.02 nm we can only look at the spectrally integrated signals of these transitions. This gives an expression for $n(J)$, the density of $N_2(J)$ for $J = 4$ or $J = 14$, 

![Figure 2.9: An iCCD image and sketch of Raman signal. Left: A typical iCCD image obtained by accumulating the RnS photons on pure N$_2$ (pressure equals to 50 mbar and temperature 300 K). Right: A sketch of the result of vertical binning.](image-url)
similar to the one for $n_e$. It reads

$$n(J \to J + 2) = \frac{P_{\text{RnS}}(\Delta \Omega(\theta, \varphi))}{P_L \Delta \Omega(\theta, \varphi)} \left( \frac{d\sigma_{J \to J+2}}{d\Omega} \right)^{-1}. \quad (2.35)$$

As stated above we only use rotational Raman scattering to calibrate the Thomson scattering setup. So we could employ one of the transitions discussed above, for instance $4 \to 6$ under standard condition (e.g. 300 K and 1 atm) for which the occupation of $n_{J=4}$ is known and use this to calibrate the system. After this the $n_e$ can be determined. Instead we used the complete Raman spectrum (cf. figure 2.9) which after spectral integration gives

$$P_{N_2}(\Delta \Omega) = P_L \Delta \Omega n(N_2) \sum n(J) \frac{d\sigma_J}{n(N_2) d\Omega}. \quad (2.36)$$

Here the factor in $\sum$ is the weighted sum of the differential cross sections of all individual rotational transitions in which the weight factor accounts for the occupation of the rotational levels at room temperature; the summation runs over all the rotational levels. Combining equation (2.34) and (2.36) gives

$$n_e = n(N_2) \frac{P_e}{P_{N_2}} \Gamma_{\text{RnS}}, \quad (2.37)$$

where $P_e$ and $P_{N_2}$ are the power of the Thomson and Raman scattering, respectively. The parameter $\Gamma_{\text{RnS}}$ represents the ratio between the (averaged) RnS and TS cross sections.

For the perpendicular geometry the value of $\Gamma_{\text{RnS}}$ calculated in [10] was found to be $\Gamma_{\text{RnS}} = 8.15 \times 10^{-5}$. Since the Raman measurements are taken at room temperature with a controlled pressure, the density of scattering molecules, $n(N_2)$, is known by means of the ideal gas law. So, once the total TS($P_e$) and Raman($P_{N_2}$) intensities are experimentally measured, equation (2.37) can be used to deduce $n_e$ from the known $n(N_2)$ value.

### 2.3.3 Rayleigh scattering

Figure 2.10 gives a sketch of a typical Rayleigh scattering spectrum. The RyS signal is compared with RnS signal to show the difference in spectral shape. In analogy with what has been done to get equation (2.34) and equation (2.35)
we can integrate equation (2.31) for the case of RyS and obtain for the atom density
\[ n_a = \frac{P^a(\Delta \Omega(\theta, \varphi))}{P_L \Delta \Omega(\theta, \varphi)} \left( \frac{d\sigma^a}{d\Omega} \right)^{-1}. \] (2.38)

Here \( P^a \) refers to the spectral integrated power of Rayleigh scattering. Just as in the case of Raman scattering we are not able to obtain spectral resolution so that the Doppler broadening can not be determined for gas temperature determination. Instead the gas temperature \( T_a \) is obtained by the comparison of the \( P^a \) value of a plasma to that obtained for a gas filling at room temperature and a known pressure. For more details we refer to chapter 6.

### 2.3.4 The signal strength

The cross section for the photon-electron interactions in Thomson, Rayleigh, and Raman scattering are small. This has implication for the use of these techniques. As an example we first take TS for which the differential cross section, for perpendicular scattering (\( \theta = 90^\circ \)) equals
\[ \frac{d\sigma}{d\Omega} = r_e^2 = 7.9 \times 10^{-30} \text{ m}^2 \text{ sr}^{-1}, \] (2.39)

with \( r_e = e^2/(4\pi \varepsilon_0 m_e c^2) \) the classical radius of an electron. Taking some typical values for the interaction length of \( L = 0.012 \text{ m} \), a solid angle \( \Delta \Omega = 2.2 \times 10^{-2} \text{ sr} \)
The experimental methods

and \( n_e = 1 \times 10^{19} \text{nm} \) we see that only a fraction \( 2.1 \times 10^{-14} \) will reach the detector. This implies that:

- Thomson scattering can only be performed with lasers that are sufficiently powerful.
- The Thomson signal can easily be lost in the signal created by plasma background radiation, Rayleigh scattering and false stray-light FS. The latter refers to the photons that are created by the scattering of the laser (side) beam(s) by dust particles by the wall.

The relative importance of RyS can be determined by comparing the product of the gas density and differential Rayleigh cross section with the corresponding product for TS. This gives

\[
\frac{P_{\text{RyS}}}{P_{\text{TS}}} = \frac{n_a (d\sigma^a/d\Omega)}{n_e (d\sigma^e/d\Omega)} = 6.8 \times 10^{-3} \frac{n_a}{n_e},
\]

where we insert for atomic argon the differential cross section \( d\sigma^a/d\Omega = 5.4 \times 10^{-32} \text{ m}^2 \text{sr}^{-1} \) (scaled for \( \lambda_i = 532 \text{ nm} \) and \( \theta = \vartheta = 90^\circ \)). Note that \( d\sigma^a/d\Omega \) strongly depends on \( \lambda \).

For the typical value of \( n_a/n_e = 10^4 \) the strength of RyS is about 70 times stronger than that of TS. Thus it is advised to remove RyS during TS measurements. Since RyS is generated at the laser wavelength \( \lambda_i \) it can be removed together with FS by using a notch filter centred around \( \lambda_i \).

On the other hand, if RyS is the objective of study, using a notch filter makes no sense and precautions must be taken to reduce the generation of FS. Therefore changes have to be made to the detection system. This is addressed in chapter 6. The above makes clear that RyS measurements can be performed in a much smaller measurement time than TS.

The relative importance of RnS with respect to TS can be deduced from equation (2.37), which leads to

\[
\frac{P_{N_2}}{P_e} = \frac{n(N_2)}{n_e} \Gamma_{\text{Rn}} = 8.15 \times 10^{-5} \frac{n(N_2)}{n_e},
\]

where the last member is only valid for room temperature condition.
2.3.5 The experimental setup

The experimental setup, depicted in figure 2.11, shows a three fold structure: the laser setup, the scattering medium and the detection branch.

![Figure 2.11](image)

**Figure 2.11:** The three-fold structure of the setup, composed of laser (left), plasma source (bottom) and detection branch (top). The numbered components have the following meaning: 1 – 45° mirror; 2 – beam dump; 3 – beam splitter; 4 – 1m plano-convex lens; 5 – Brewster window; 6 – achromatic lens; 7 – entrance slit; 8 – image rotator; 9 – grating; 10 – mask; 11 – intermediate slit.

The lasers

Two different lasers systems are used:

1. A frequency doubled Nd:YAG Continuum Laser, model Precision II 8010, producing 8 ns pulses with a repetition rate of 10 Hz; the maximum pulse energy is approximately 700 mJ@532 nm.

2. An Edgewave class IV that produces laser pulses @532 nm with duration of 10 ns and energy of 4 mJ with a repetition rate of 5 kHz.
The specifications of these systems are compared with each other in table 2.1. The main difference is that the Continuum laser generates pulses of much higher energy (maximum 700 mJ versus 4 mJ) but with a much lower repetition rate (10 Hz versus 5 kHz). The advantage of the Edgewave laser is that higher mean powers can be achieved so that the measurement time can be reduced. Moreover, shooting with less energy per pulse means that there is less risk to damage optical elements or to create plasma-heating. The disadvantage is that due the low energy per pulse the plasma background is more important. Finally, we mention that the laser beam profile of the Edgewave is less Gaussian than that of the continuum.

Both laser systems deliver vertically polarized radiation. So the laser beam can be guided directly into the scattering medium (e.g. plasma) while having the perpendicular geometry needed for TS. This is a difference to the Expla laser [14] used in the past in our group for which the polarization is horizontal.

In order to study the influence of the laser beam on the plasma, TS was performed for different values of the laser pulse energy $E$. For instance working with the Continuum laser we selected $E$ values of 50, 110 and 180 mJ. Working with the low pressure surfatron induced plasma we found variation in $n_e$ and $T_e$ values within 3%, thus comparable to the random error margins. This means that for the low pressure conditions Thomson scattering can be seen as non-intrusive. In the case of atmospheric plasmas it was found that laser plasma heating can not be neglected (cf. chapter 8). For those types of plasmas it is better to work with the high repetition rate laser (Edgewave) or to correct for the laser heating.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Continuum laser</th>
<th>Edgwave laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy per pulse</td>
<td>700 mJ</td>
<td>4 mJ</td>
</tr>
<tr>
<td>Repetition frequency</td>
<td>10 Hz</td>
<td>5 kHz</td>
</tr>
<tr>
<td>Mean power</td>
<td>7 W (max)</td>
<td>20 W (max)</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>8 ns</td>
<td>10 ns</td>
</tr>
</tbody>
</table>

Table 2.1: The main parameters of the two laser systems used in the thesis.
Chapter 2.

The scattering media

The laser is directed along the axis of a tube that can be moved along its own axis while keeping the alignment with the laser intact. The tube has an inner radius of 3.0 mm and an outer radius of 4.0 mm. Brewster windows are attached to both tube-ends with the aim to minimize laser reflections. In this tube plasmas can be generated due the absorption of electromagnetic waves of 2.45 GHz in an argon flow. The gas temperature of these plasmas is determined using RyS (cf. chapter 6); the electron temperature and density are measured by means of TS. For the calibration of TS (cf. chapter 5), Raman scattering is used. To that end the tube was filled with nitrogen at room temperature and a known pressure. The Raman calibration is also applied to measure the spectral dispersion of the setup. Since all the Raman transitions for nitrogen are well-known, the dispersion can be obtained measuring the distance between two of the Raman peaks. The dispersion is found to be 119.88 ± 0.46 pixels/nm for the present setup. Obtaining the width of the TS spectrum and using this dispersion, the electron temperature \( T_e \) can be calculated employing equation (2.33).

For the calibration of Rayleigh scattering we used fillings of argon at variable pressures. By changing the pressure we could determine the level of false stray light (chapter 6).

The detection branch

For the detection and the analysis of the TS signal a triple grating spectrograph (TGS) is used. The TGS is designed with the purpose to reject false stray-light and Rayleigh scattered photons, and to disperse and collect the TS signal.

Nevertheless, by a simple action the TGS can easily be adjusted so that RyS can be measured. The combination of the first two gratings form a notch filter whereas the final dispersion is performed by the third grating that sends the dispersed image to an iCCD. The iCCD (model Andor DH534) can be cooled so that, by reducing the noise level, better detection limits can be obtained. The same setup can be used for RyS by removing the mask by which the notch filter function is switched off.

The iCCD camera is 2D giving spectral information in the horizontal and spatial information in the vertical direction.

Figure 2.12 shows a typical example of a 2D iCCD-image as published in [15].
Figure 2.12: Left: A photograph of a plasma created by a microwave plasma torch investigated by Thomson scattering; the arrow depicts the position of the laser beam. Right: The accumulation of scattered photons of 600 laser shots as collected by the 2D-iCCD. The horizontal dimension corresponds with the wavelength (dispersion); the black band is the result of blocking the central wavelength $\lambda_i$. The vertical dimension is the spatial dimension along the laser beam. The structures at top and the bottom show the Raman scattering just outside the plasma, the two branches in the middle are TS photons corresponding to the upper and lower part of the laser-plasma intersection (cf. the left photograph).

In this image, the detected photons of 600 subsequent laser shots are accumulated. The vertical direction is the spatial dimension, i.e. the length along the laser beam, the horizontal direction gives the wavelength dimension, exhibiting the dispersion. The black central vertical band is the result of blocking the central wavelength $\lambda_i$; the action of the notch filter. At both sides of the central black line we first observe, coming from above, a strong Raman spectrum, caused by the scattering of the laser light on $N_2$ and $O_2$ molecules in air. Further downwards, the Raman spectrum disappears and makes place for the TS spectrum; so apparently the molecules are not present in regions where electrons can be detected. Here we observe two TS branches in vertical direction. These reflect two intersection zones of the laser with the mantle of the plasma cone [15].

References

Chapter 2.


Absolute measurements of the continuum radiation to determine the electron density in microwave-induced argon plasmas

Abstract.
A method for the determination of the electron density \( n_e \) using the continuum radiation is presented. The radiation is calibrated with a standard tungsten ribbon lamp and thus expressed in absolute units. This method is applied to a microwave induced argon plasma, created by a surfatron (2.45 GHz), for which the standard settings are: a wavelength region at 648 nm, input power of 60 W, pressure of 15 mbar, gas flow of 70 sccm and axial distance from the launcher of 3 cm. Due to the low degree of ionization the influence of electron-ion interactions can be neglected; the radiation is predominantly generated by free-free interactions between electron and atoms. The method provides electron density values in the order of \( 10^{19} \text{ m}^3 \) for different plasma settings. It is observed that the measured \( n_e \) follows the well known trends: it decreases in the direction of the propagating surface wave and increases with power.

3.1 Introduction

Surface wave sustained discharges, first described in the early 1970s [1], are stable and reproducible electrode-less plasmas that can operate under a broad range of working conditions. This is the reason why they are used in a wide variety of applications [2, 3]. In order to further improve these applications, insight is needed into plasma properties which can be obtained by means of experiments, modeling or a combination of both.

The experimental methods can be divided into electronic and optical diagnostics. The first category comprises the various (single, double electrical) probe techniques; the second category can be divided into passive and active spectroscopy. The active spectroscopic methods are mainly based on the use of an external light source, in most cases a laser. A famous example is Thomson scattering where the scattering of laser photons on free electrons gives insight into the electron density $n_e$ and electron temperature $T_e$. The experimental setup is expensive and the method not easy. However, the results are usually easy to interpret, do not depend on the state of equilibrium departure of the plasma and straightforwardly lead to the simultaneous determination of the main plasma parameters, $n_e$ and $T_e$. A well known example of the passive spectroscopy method is line intensity measurements. Here we meet with the opposite situation. The experimental costs are low but the results are not easy to establish. Of course, the absolute measurement of line intensities leads to the densities of excited species, and thus the atomic state distribution function (ASDF), but the classical way to deduce the main plasma parameters like $n_e$ and $T_e$ out of the ASDF is in most cases based on doubtful equilibrium assumptions [4].

In a recent study [5] we presented a method for the $T_e$ determination in low pressure argon surfatron plasma, based on the combination of passive spectroscopy and a non-equilibrium model. In the first step the excitation temperature, $T_{13}$ is deduced from the ratio of the density of ground level ‘1’ and that of the lowest easily observably excited level ‘3’. The density of the ground level $n_1$ is determined via the pressure, $n_1 = p/k_B T_h$, where $T_h$ is the heavy particle temperature. The density of level ‘3’ which stands for one of the Ar-4p levels, is determined by using absolute emission spectroscopy. In the second step a collisional radiative model (CRM) is used to transfer $T_{13}$ into $T_e$.

The CRM calculates the argon ASDF of strongly ionizing plasmas as a function of input parameters such $n_e$ and $T_e$. Two ASDF parts can be distinguished:
the bottom part for which the CRM predicts a $T_{13}-T_e$ relation and the upper part for which the CRM prescribes how the ASDF merges into the energy distribution of the free electrons. The dependence of the $T_{13}-T_e$ relation on $n_e$ and $T_e$ turns out to be limited while the weak dependence of $T_e$ can be taken into account via an iterative procedure. The electron density, having only a minor influence on the $T_{13}-T_e$ relation, is determined by extrapolating the experimentally determined upper part of the ASDF to the continuum. This is justified only if the upper part of the ASDF is in partial local Saha equilibrium (pLSE) [6], thus in equilibrium with the continuum. In the case of the plasma under investigation this assumption is doubtful, so that only a rough estimate of $n_e$ is obtained. Therefore, to improve the method of the $T_e$ determination, a better method for the determination of $T_e$ is needed.

Here, a method for the $n_e$ determination is presented using absolute measurements of the continuum radiation. In a certain sense this novel $n_e$ method is complementary to the $T_e$-method discussed above. The absolute line method gives $T_e$ and weakly depends on $n_e$ whereas the absolute continuum mainly delivers $n_e$ in a way that depends on $T_e$. So they have to be used in conjunction with each other. It is a plan for the future to perform this combination of methods on different plasmas. The results of the continuum method on the plasma for which the line method was used recently [5] will be discussed.

In the past, continuum measurements were used in several studies [7–11]. Most of these studies dealt with relative measurements; that is to say, with the ratio of the continuum and line radiation. With this line-continuum ratio, the electron temperature can be determined if the level that produces the atomic line is in pLSE. This method is valid for plasmas of high $n_e$ values that are close to equilibrium and for which the continuum is generated mainly by electron-ion (ei) interactions. Other studies [12–14] are based on absolute measurements of the continuum of completely ionized plasmas. For these plasma types, the ei interactions are responsible for the generation of continuum solely. The plasmas we deal with are strongly ionizing, so that strong deviations from pLSE are present. These pLSE deviations are certainly present in the lower part of the ASDF where strong line transitions are generated and where it is seductive to apply this line-continuum ratio method. This, however, would certainly lead to erroneous results. Another consequence of dealing with strongly ionizing plasmas is that these are under-ionized: the electron density is lower than what can be expected using the Saha relation on the ground state density. This
means that the degree of ionization is relatively low. Consequently, the most important contribution to the continuum is generated by electron-atom (ea) collisions. This stands in sharp contrast to the plasmas for which the line-continuum ratio method is applied. These plasmas are close to equilibrium and the continuum radiation is predominantly generated by ei interactions. This means that the success of our application depends on the knowledge of the ea cross section of momentum transfer. In this study the method is applied to argon for which it is known that, due to the sharp Ramsauer minimum, this cross section strongly varies as a function of energy.

This paper can be seen as a proof of principal for this continuum-based n_e determination and is organized as follows. In section 3.2 the theory and the relevant equations are presented. Section 3.3 is devoted to the description of the experimental setup, section 3.4 gives the experimental results whereas section 3.5 deals with an error analysis. Conclusions are given in section 3.6.

3.2 Theory

The starting point is the radiation transport equation [15]

\[ \frac{dI_\lambda(\lambda)}{ds} = j_\lambda(\lambda) - k(\lambda)I_\lambda(\lambda), \]  

(3.1)

which describes how the spectral intensity \( I_\lambda(\lambda) \) of a beam changes along its path through the plasma due to the absorption and emission processes. The importance of these processes is determined by the absorption coefficient \( k(\lambda) \) and the emission coefficient \( j_\lambda(\lambda) \). Note that we make a notational distinction between \( \lambda \) in parentheses, such as in \( k(\lambda) \), and \( \lambda \) as a subscript; e.g. in \( j_\lambda \). In the first case, \( \lambda \) is the argument of a function (\( k(\lambda) \) is the \( k \) value at a certain wavelength). In the second case, \( \lambda \) is the parameter to which differentiation is carried out (\( j_\lambda \) is the emission power density per unit of solid angle and per wavelength interval). Where it does not lead to ambiguity, simplified expressions are used, in which the “at” and/or “per” notation is/are omitted.

The continuum radiation originates from free electrons colliding with atoms and ions. If a free electron remains free after the collision, it is called a free-free collision. If an electron is captured by an ion, it is called a free-bound collision or a recombination collision.
In the case that the plasma is optically thin for continuum radiation this radiation can fully escape and self-absorption can be neglected. This implies that only the first term of equation (3.1) is relevant and that the spectral intensity created by the plasma is

$$I_\lambda(\lambda) = \int_0^D j_\lambda(\lambda) ds,$$

where the integration is done over a path of length $D$ through the plasma. If we assume that the plasma is homogeneous along the plasma size $D$, we get

$$I_\lambda(\lambda) = j_\lambda(\lambda) D.$$  

The emission coefficient $j_\lambda(\lambda)$, for the case of continuum, has three contributions \[11, 13, 16, 17\],

$$j_\lambda(\lambda) = j_{\lambda}^{ei,fb}(\lambda) + j_{\lambda}^{ei,ff}(\lambda) + j_{\lambda}^{ea,ff}(\lambda).$$

The first contribution, given by $j_{\lambda}^{ei,fb}(\lambda)$, is generated by the recombination of $\text{ei}$ pairs, the second, $j_{\lambda}^{ei,ff}(\lambda)$, by the free-free interactions between electrons and ions and the third $j_{\lambda}^{ea,ff}(\lambda)$, by electron-neutral interactions.

The three contributions are related to the main plasma parameters (such as $n_e$ and $T_e$) as determined by the following expressions \[17\]:

$$j_{\lambda}^{ei,fb}(\lambda, T_e) = c_1 Z^2 \frac{n_e n_i}{\lambda^2 T_e^{1/2}} \left(1 - \exp \left(- \frac{hc}{\lambda k_B T_e}\right)\right) \xi_{fb}(\lambda, T_e),$$

$$j_{\lambda}^{ei,ff}(\lambda, T_e) = c_1 Z^2 \frac{n_e n_i}{\lambda^2 T_e^{1/2}} \exp \left(- \frac{hc}{\lambda k_B T_e}\right) \xi_{ff}(\lambda, T_e),$$

$$j_{\lambda}^{ea,ff}(\lambda, T_e) = c_2 \frac{n_e n_a T_e^{3/2}}{\lambda^2}$$

$$\times \left\{ Q_{\lambda}^{At}(T_e) \left(1 + \left(1 + \frac{hc}{\lambda k_B T_e}\right)^2 \right) \exp \left(- \frac{hc}{\lambda k_B T_e}\right) \right\},$$

with constants

$$c_1 = \frac{16\pi}{3 m_e c^2 (6\pi m_e k_B)^{1/2}} \left(\frac{e^2}{4\pi\varepsilon_0}\right)^3$$

$$= 1.6321 \times 10^{-43} \ (\text{Jm}^4\text{K}^{1/2}\text{s}^{-1}\text{sr}^{-1}),$$

$$47$$
and

\[
c_2 = \frac{32e^2}{12\pi \varepsilon_0 c^2} \left( \frac{k_B}{4\pi m_e} \right)^{3/2} = 1.026 \times 10^{-34} \text{ (Jm}^2\text{K}^{3/2}\text{s}^{-1}\text{sr}^{-1}),
\]

with \(m_e\) the mass of the electron, \(\varepsilon_0\) the permittivity of vacuum, \(c\) the speed of light, \(k_B\) the Boltzmann constant, \(e\) the elementary charge and \(Z\) the charge number of the ion. The plasma properties are given by \(n_e\) for the electron density, \(n_i\) for the ion density, \(n_a\) for the atom density while \(T_e\) refers to the electron temperature in K.

Figure 3.1: The cross section \(Q^A(E)\) (–––– Milloy [19], · · · · Phelps [20]) of the momentum transfer in e-Ar collisions as a function of energy \(E\) compared with the mean value \(Q^A(T_e)\) (–––·– Milloy, –Phelps) as a function of electron temperature as determined by equation (3.10). The solid line is the analytical fit function of equation (3.11) for interval 0.5 – 2eV. Both \(E\) and \(T_e\) are given in electronvolt.

In this study that deals with plasmas in which only singly charged argon ions are present, we take \(Z = 1\) and use for \(Q^A(T_e)\) the mean cross section
Figure 3.2: The total Biberman coefficient $\xi_{\text{total}}^\text{ei}(\lambda)$ as a function of $\lambda$ for four different values of $T_e$. It can be seen that the approximation $\xi_{\text{total}}^\text{ei}(\lambda) \approx 1.2$ holds within 20% for the visible wavelength range 400 – 800 nm and the temperature range 0.5 – 2 eV.

for momentum transfer of electrons with argon atoms $Q^{\text{Ar}}(T_e)$. This is defined as [18]

$$Q^{\lambda}(T_e) = \frac{2}{3} \int_0^\infty x^2 e^{-x} Q^{\text{Ar}} \left( \sqrt{\frac{2k_B T_e}{m}} x \right) \, dx,$$  \hspace{1cm} (3.10)

the energy-weighted average of the speed-dependent rate for momentum transfer in electron-atom collisions, divided by the mean electron speed $\langle \nu \rangle = \sqrt{\frac{8k_B T_e}{\pi m_e}}$.

For the integration parameter in equation (3.11) $x = \frac{E}{k_B T_e}$ is used. The cross section $Q^{\text{Ar}}(E)$ for momentum transfer in electron-argon (e-Ar) collisions as a function of energy $E$ and the mean value $Q^{\text{Ar}}(T_e)$ as a function of electron temperature are shown in figure 3.1. For this, we used data from Milloy and Phelps [19, 20]. The analytical fit of $Q^{\text{Ar}}(T_e)$ for the temperature interval from 0.5 to 2 eV

$$Q^{\text{Ar}}(T_e) = -20.64 + 2.31 T_e - 1.11 T_e^2 + 0.2 T_e^3$$  \hspace{1cm} (3.11)

reproduces the part of equation (3.7) applied to $Q^{\text{Ar}}(E)$ within 2% for the temperature range 0.5 eV $< T_e < 2$ eV. Due to the averaging procedure, $Q^{\text{Ar}}(T_e)$
shows much less dependence on $T_e$ as that of the non-averaged value $Q_{Ar}^r(E)$ on the electron energy $E$. Nevertheless, it should be kept in mind that $Q_{Ar}^r(T_e)$ cannot be regarded as a constant in our temperature range of interest.

The $\xi_{\text{ei}}^r(\lambda, T_e)$ and $\xi_{\text{ff}}^r(\lambda, T_e)$, used in equations (3.5) and (3.6), are the so-called Biberman factors. These are dimensionless parameters that are functions of the wavelength and temperature and depend on the ion type.

In the case of a mono-atomic singly ionized ($Z = 1$) plasma, the continuum contributions of free-free and free-bound $\text{ei}$ interaction can be combined in one term. The resulting emission coefficient reads

$$j^\text{ei}_\lambda(\lambda, T_e) = c_1 \frac{n_e n_i}{\lambda^2 T_e^{1/2}} \xi_{\text{total}}^{\text{ei}}(\lambda, T_e),$$

where

$$\xi_{\text{total}}^{\text{ei}}(\lambda, T_e) = \left( 1 - \exp \left( -\frac{hc}{\lambda k_B T_e} \right) \right) \xi_{\text{fb}}^r(\lambda, T_e)$$

$$+ \exp \left( -\frac{hc}{\lambda k_B T_e} \right) \xi_{\text{ff}}^r(\lambda, T_e).$$

Figure 3.2 gives $\xi_{\text{total}}^{\text{ei}}$ as a function of $\lambda$ for four different $T_e$ values [20], $\xi_{\text{ff}}^r(\lambda)$ is taken constant [19] and the data for the free-bound Biberman factor $\xi_{\text{fb}}^r(\lambda)$ is obtained from [21].

If we further assume quasi neutrality, i.e. $n_e = n_i$, we can after some substitutions recast equations (3.5)-(3.7) into

$$j_\lambda^{\text{ei}}(\lambda, T_e) = n_e^2 f_\lambda(\lambda, T_e)$$

and

$$j_\lambda^{\text{ea}}(\lambda, T_e) = n_e n_a g_\lambda(\lambda, T_e),$$

where the functions $f_\lambda(\lambda, T_e)$ and $g_\lambda(\lambda, T_e)$ are, respectively,

$$f_\lambda(\lambda, T_e) = \frac{c_1}{\lambda^2 T_e^{1/2}} \xi_{\text{total}}^{\text{ei}}(\lambda, T_e)$$

and

$$g_\lambda(\lambda, T_e) = \frac{c_2}{\lambda^2 T_e^{3/2}}$$

$$\times \left\{ Q_{Ar}^r(T_e) \left( 1 + \left( 1 + \frac{hc}{\lambda k_B T_e} \right)^2 \right) \exp \left( -\frac{hc}{\lambda k_B T_e} \right) \right\}. \ (3.17)$$
By performing absolute continuum measurements, we get the calibrated continuum signal $I_\lambda(\lambda)$. Dividing this by $D$ the mean value of the emission coefficient $j_\lambda(\lambda) = I_\lambda(\lambda)/D$ along this plasma chord can be determined. This is related to the sum of the three contributions in the following way:

$$j_\lambda(\lambda) = n_e^2 f(\lambda, T_e) + n_e n_a g(\lambda, T_e),$$

which leads to the square root equation

$$f(\lambda, T_e)n_e^2 + n_e n_a g(\lambda, T_e) - j_\lambda(\lambda) = 0,$$

that has two mathematical solutions of which only one has a physical meaning. It reads

$$n_e = \frac{g(\lambda, T_e)n_a}{\sqrt{1 + \frac{4f(\lambda, T_e)j_\lambda(\lambda)}{(g(\lambda, T_e)n_a)^2}} - 1}.$$

In the limit of high $n_a$ values we have

$$\frac{4f(\lambda, T_e)j_\lambda(\lambda)}{(g(\lambda, T_e)n_a)^2} \ll 1$$

so that, using the well known approximation $(1 + x)^{1/2} \approx 1 + 1/2x$, the solution is

$$n_e = \frac{j_\lambda(\lambda)}{g(\lambda, T_e)n_a}.$$

This is of course the same solution as that we get from equation (3.19) by neglecting the first term, i.e. the contributions of ei interactions.

Substituting equation (3.22) into (3.21) we get a criterion for the dominance of the ea contribution in terms of the ionization ratio $\alpha = n_e/n_a$. This reads $\alpha \ll \alpha_{crit}$ with

$$\alpha_{crit}(\lambda, T_e) = \frac{g(\lambda, T_e)}{4f(\lambda, T_e)}.$$ 

The formula for $\alpha_{crit}(\lambda, T_e)$ can be obtained by combining equations (3.23) and (3.13). The critical value of $\alpha$ is dependent on $T_e$ which mainly comes in via $Q^{Ai}(T_e)$ and only slightly via $\xi_{ei total}(\lambda, T_e)$. For $T_e = 1.2$ eV it is found that $\alpha_{crit} = 5 \times 10^{-4}$. In the cases where high values of $\alpha$ can be expected we applied equation (3.20) in full form. It was found that for our plasma conditions the difference between the $n_e$ value found by means of equation (3.22) and that found with equation (3.20) is less than 5%.

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3.3 Experimental setup

The plasma is generated in a quartz tube surrounded by a surface wave launcher for which a surfatron is used (cf. figure 3.3). This is an integrated surface wave plasma launcher that performs both field shaping and impedance matching. The microwave coupled into the plasma can travel in both axial directions in the interface between plasma and dielectric. By means of a conductor installed at one side of the launcher, the wave propagation is obstructed in that direction and directed towards the opposite side. Along the wave propagation each plasma slab gets a fraction of the energy carried by the wave; this is used to sustain the plasma. As a consequence the energy content in the wave will decrease, which implies that the power density at which energy is coupled to the plasma decreases as well. This implies that the electron density goes down along the wave: the plasma is not uniform in the axial direction. The EM waves in this study have been generated by a magnetron device (Microtron 200 Mark III Microwave power generator) that can deliver a maximum power of 200 W at a fixed frequency of 2.45 GHz. The generated plasma is confined in a quartz tube with an inner radius of $r_{\text{inner}} = 3.0 \text{ mm}$. The light emitted by the plasma is collected by an optical fibre that conducts the photons towards the entrance.
Absolute continuum intensity measurements

slit of a 1 m monochromator. After dispersion the radiation illuminates a two dimensional CCD camera. In this way the spectrum is recorded as a function of lateral position (the direction perpendicular to the axial direction).

The number of collected photons per unit of time and per CCD pixel can be compared with those obtained by positioning the fibre in front of a tungsten ribbon lamp, which operates at a known electric current. In this way calibration will lead to the spectral intensity $I_\lambda(\lambda)$ from which an average of $j_\lambda(\lambda) = I_\lambda(\lambda)/D$ can be determined (cf. section 3.2). In this study $D$ is taken as $D = 2r_{\text{inner}}$ and thus obtain a mean value of $n_e$ for the diameter of the plasma. In future work, we plan to do Abel inversion to reconstruct the radial value of $n_e$. However, in order to get an insight into the radial distribution of $n_e$ it is better to use a tube with a larger inner diameter. In this way the effect of refraction by the quartz wall can be reduced.

The neutral gas density $n_a$, which is used in equations (3.7) and (3.22) is obtained using the gas law $n_a = p/k_B T_h$ in which an estimated value of heavy particle temperature $T_h$ is introduced [5]. The $T_e$ value used in the above equations is derived from the two-step method, described in the introduction, in which absolute density measurements of the argon 4p levels are combined with a CRM (cf. section 4.2).

For more details about the $T_e$ determination and the optical and microwave system we refer to [5].

Since the continuum gives a small signal it will be easily overruled by lines and bands, created not only by the main plasma constituent but also by trace elements. This means that the purity of the system is very important for continuum measurements.

The monochromator has been initially used to explore the continuum part of the spectrum in order to find the most suitable wavelength range. This leads to the decision to do most of the measurements at $\lambda = 648$ nm. The results were compared with those from the continuum at $\lambda = 423$ nm and 569 nm. The trends are the same and the resulting $n_e$ values agree within a few percent. Filters have been used to avoid the second-order effects of the grating. Background measurements have been done to subtract the noise from the continuum signal.

---

1In this thesis, sometimes we replace the notation for the atom density $n_a$ by $n_1$, which is justify since most of the atom density is delivered by the ground state density $n_1$. Replacing $T_h$ by $T_a$, is allowed since there is no difference between the temperature of the atoms $T_a$ and the rest of the heavy particles.
Different working conditions of the argon plasmas have been obtained by changing the incident power $P$, the gas flow rate $\phi$, the pressure $p$ and the axial distance from the launcher $z$. A standard condition is selected: an input power $P = 60 \text{ W}$, a gas pressure of $p = 15 \text{ mbar}$ and an argon flow rate of $\phi = 70 \text{ sccm}$. The standard position is taken at a distance of $z = 3 \text{ mm}$ from the launcher. For the direction and the origin of the axial coordinate $z$, see figure 3.3. Note that in contrast to most of the surfatron literature where the axial direction is taken anti-parallel to the wave propagation direction, we take the $z$ direction in this study parallel to the wave propagation, whereas $z = 0$ is taken next to the launcher and not at the plasma end.

![Figure 3.4](image.png)

**Figure 3.4:** Two CCD image frames for distances $z = 3$ and $33 \text{ cm}$ from the launcher for an input power $P = 60 \text{ W}$, pressure $p = 15 \text{ mbar}$ and flow $\phi = 70 \text{ sccm}$. The central $\lambda$-position of $648 \text{ nm}$ is selected such that the saturation of the Ar lines is limited to such a level that blooming does not give an overflow into the adjacent continuum.

### 3.4 Results

The method for the electron density determination is used as a function of position and the control parameters such as power, pressure and gas flow.
3.4.1 Position dependence

It is found that close to the launcher the continuum could be observed easily, whereas at the plasma edge (large \( z \) values) the signal is rather weak. Thus to get a better record of the continuum signal at the plasma edge, longer exposure times must be used. As an illustration two frames of the CCD camera are shown in figure 3.4, one obtained close to the launcher (at a distance of \( z = 3 \) cm with an integration time of \( \tau = 300 \) s, the other at a distance of \( z = 33 \) cm from the launcher for \( \phi = 600 \) s. Note that these integration periods are much larger than the periods that are needed for the determination of line intensities (these are typically between 0.5 and 15 s). A first glance clearly shows that the continuum, and thus the electron density, decreases along the wave. In order to verify the linearity of the CCD response we did measurements with the tungsten ribbon lamp for several integration periods. Grey filters were used to avoid over-exposure. The trend that \( n_e \) decreases in the wave propagation direction is confirmed in more detail in figure 3.5, which shows the electron density as a function of the axial position \( z \). The \( n_e \) decreases in an almost linear way along the wave propagation direction, as observed by [22, 23]. This

![Figure 3.5: Electron density as a function of the axial distance from the launcher for a pressure \( p = 15 \) mbar, power \( P = 60 \) W and gas flow \( \phi = 70 \) sccm. The continuum at wavelength \( \lambda = 648 \) nm is used.](image)
tendency can be understood from the electron energy balance, which for this
type of plasma can be put in the simplified form [4, 24]

\[ \varepsilon = n_e n_1 S_{\text{heat}} (k_B T_e - k_B T_h) + n_e n_1 S_{\text{ion}} \left( I_1 + \frac{3}{2} k_B T_e \right), \]  
(3.24)

which can be approximated as

\[ \varepsilon \approx n_e n_1 S_{\text{heat}} k_B T_e + n_e D_a R^* -2 I_1 \text{ elastic} \to \text{heat} \quad \text{inelastic} \to \text{creation}. \]  
(3.25)

The upper line shows that the power density \( \varepsilon = \Delta P / \Delta V \), in which \( \Delta P \) refers to the power delivered to the electrons in volume \( \Delta V \), is divided over two channels: (1) the heat channel by which heavy particles gain kinetic energy due to elastic collisions and (2) the plasma creation channel through which the energy flow associated with excitation and ionization takes place.

Equation (3.25) is a further simplification based on the fact that \( k_B T_h \ll k_B T_e \ll I_1 \), the ionization energy, while the creation frequency \( n_1 S_{\text{ion}} \) is replaced by \( D_a R^* -2 \), where \( R^* \) is (in the order of) the plasma radius and \( D_a \) the ambipolar diffusion coefficient. The latter substitution is obtained using an approximation of the electron particle balance \( \nabla \cdot (n_e w_e) = n_e n_1 S_{\text{ion}} \), where \( S_{\text{ion}} \) is the rate of ionization (including stepwise ionization) while the efflux can be equated to the ambipolar form: \( n_e w_e = D_a \nabla n_e \). The divergence term can be approximated by

\[ \nabla \cdot n_e w_e = \nabla \cdot (D_a \nabla n_e) \approx n_e D_a R^* -2. \]  
(3.26)

Note that this last step of the simplification is justified only if (most of) the energy lost in inelastic collisions leads to the diffusive efflux of ei pairs.

For the rate of heat transfer we used

\[ S_{\text{heat}} = \frac{3 m_e}{M} \sqrt{\frac{8 k_B T_e}{\pi m_e}} Q^{A^e}(T_e) \]  
(3.27)

with \( M \) the mass of the argon atom, and \( Q^{A^e}(T_e) \) the cross section for momentum transfer between electrons and heavy particles (cf. equations (3.10) and (3.11)).
The local value of $\varepsilon$ is a fraction of the electromagnetic power density stored in the wave. Due to the energy transfer from the wave to the plasma-electrons the EM power will decrease in the wave propagation direction, which implies that the power density $\varepsilon$ will go down as well. Since equations (3.24) and (3.25) state that $\varepsilon$ is linear in the electron density, the $n_e$ value will also decrease. That is experimentally confirmed by figure 3.5.

3.4.2 Pressure dependence

The electron density at the position $z = 3$ cm is measured for several pressures in the range $9 - 20$ mbar (cf. figure 3.6). A slight increase in $n_e$ can be observed for increasing pressure. Theoretically the pressure increase has two opposite effects that can be attributed to the competition between the elastic and the inelastic loss channel (cf. equations (3.24) and (3.25)). Due to the associated increase in the atom density the exchange of elastic energy of electrons to the heavies will increase; this means that more power per electron is needed for heat generation and thus, at constant power (density), the electron density will
decrease. The inelastic channel behaves in the opposite manner. The increase in the atom density will reduce the diffusion so that the residence time will increase. Therefore less energy per ei pair is needed which pushes the electron density upwards. Figure 3.6 shows that apparently the inelastic term is slightly larger than the elastic one, at least for the lower pressures under study.

3.4.3 Power dependence

Three different values for the input power have been used to investigate the influence of the launched power on the electron density. The experiment shows that by increasing the power, the plasma increases in length and so does the value of the electron density close to the launcher (cf. figure 3.7). This is in agreement with equations (3.24) and (3.25). By increasing the power new plasma will be added at the launcher side while the old part corresponding to the plasma with lower power is pushed forward into the wave propagation direction. The new added plasma has a higher $\varepsilon$ value and thus higher $n_e$ value.

Figure 3.7: Electron density close to the launcher ($z = 3$ cm) as a function of the input power for pressure $p = 15$ mbar and gas flow $\phi = 70$ sccm.
3.4.4 Flow dependence

The Ar gas flow was changed from 40 to 80 sccm at a power of 60 W and a pressure of 15 mbar. The results presented in figure 3.8 show that the influence of the change in the gas flow on the electron density is not detectable. We may state that the flow has no influence, at least not in the range we investigated and we can use the scatter in figure 3.8 as a measure of the stochastic error of the method. Theoretically, we can expect some second-order effect of the flow $\phi$ on the $n_e$ value. Due to the extra cooling as induced by an increase in $\phi$, the gas temperature will go down, which thus leads, at constant pressure, to an increase in the atom density. However, the gas temperature is already close to the room temperature so that the additional flushing will not reduce $T_h$ substantially.

Figure 3.8: The electron density measured at different gas flow rates shows that there is no dependence of $n_e$ on $\phi$. The measurements are done at axial position $z = 3$ cm, with a power of $P = 60$ W and pressure $p = 15$ mbar.

3.5 Error analysis

The random errors of this method of $n_e$ determination can be deduced from repeated measurements on the same plasma conditions and taking the standard
deviation of the scatter obtained. It was found that the day-to-day reproducibility was in the order of 5% and thus in the same order as the accuracy that can be deduced from figure 3.8. In order to get insight into the errors as induced by the calibration step we performed the calibration with two different radiation sources. The differences in the results of the electron density were found to be within a few percent.

Of more importance are the systematic errors of the method that is related to the reliability of equations (3.7), (3.10), (3.11) and (3.22). The continuum radiation has until now mainly been used in relation to the intensities of adjacent lines (line-continuum ratio) for plasmas close to equilibrium. For these plasmas the degree of ionization is large and there is no need to know the absolute value of the \( n_e \) contribution with high precision. In our case we deal with feebly ionized plasmas and the accuracy of the \( n_e \) determination directly depends on that of the equation for \( j^{\text{ea}} \) (equations (3.7), (3.10), (3.11) and (3.22)). All references we found go back to the work of Chapele and Cabbanes [17]. There it can be found that the \( j^{\text{ea}} \) expression is based on the mean cross section for momentum transfer in the \( \text{ea} \) collision assuming that this is a hard-sphere collision.

It is known that the cross sections of billiard-ball type collisions are constant as function of energy and it is also known that the momentum transfer cross section for \( \text{ea} \) collision is not constant at all. This \( \text{e-Ar} \) cross section has a deep Ramsauer minimum of \( Q_{\text{min}}(E) \approx 1 \times 10^{-21} \text{m}^2 \) at \( E \approx 0.22 \text{eV} \) after which it sharply increases (cf. figure 3.1). So especially for our plasma conditions we can hardly say that the elastic \( \text{ea} \) interactions are hard-sphere collisions. This means that this method needs a future calibration with other methods of \( n_e \) determination performed on the same plasma conditions. Possibilities are the \( \text{H}\beta \) line-broadening method and Thomson scattering.

Due to the Ramsauer shape the choice of the electron temperature is important. This means that an accurate value of the \( T_e \) is needed. Here we use the \( T_e \) values that were found in [5] for the same plasma conditions. However, in that study we needed for the \( T_e \) determination a \( n_e \) value that was determined from an inaccurate method; by assuming that the ASDF top is in pLSE.

In future studies we plan to use the absolute line method and the continuum method in conjunction with each other in an iterative procedure.

Another point of concern is the possible presence of departure from the Maxwell equilibrium. Due to the relatively low degree of ionization we may expect deviation in the tail of the electron energy distribution function (EEDF);
that is for kinetic energy values above 12 eV. How far this will affect the emission of the continuum around $\lambda = 648\,\text{nm}$ is a matter that needs further study.

Finally, we recall that we did not apply any method to convert the lateral intensities into radial resolved emission coefficients. Instead, the intensity of the central lateral position was divided by the diameter of the plasmas. This implies that only a mean value of the emission coefficient and thus $n_e$ value is obtained. By using an Abel inversion procedure we can, in a future study, obtain spatial resolved $n_e$ values. For that we need a plasma with a larger diameter.

3.6 Conclusions

This paper introduces a method to determine the electron density based on the absolute value of the continuum part of the spectrum. The method is applied to a surfatron plasma in argon of a low degree of ionization. It is observed that the measured $n_e$ follows the well known trends, such as the decrease in $n_e$ in the propagation direction and the increase in $n_e$ with increasing power. Due to the low degree of ionization of the argon surfatron plasma, the continuum is dominated by free-free interactions of electrons with atoms. It is therefore strongly related to the momentum transfer collisions of electrons with argon atoms. This cross section has a pronounced Ramsauer minimum which means that a careful description of the interaction should be applied. The method described follows a quasi hard-sphere approach where an averaged cross section is assumed that varies with temperature. Since the well known dependencies of $n_e$ as a function of power and distance were found we believe that the method is correct, in principle, but that it needs to be validated in the future with other diagnostic methods. Another consequence of the strong dependence of the interaction cross section on energy is that a precise value of the electron temperature is needed. We employed the results of the $T_e$ method as published in [5]. This method, which is based on absolute line intensities, weakly depends on the electron density so that in the future both methods have to be employed in conjunction with each other.

The method is by no means limited to surfatrons and can easily be applied to other plasma sources. Moreover, there are no reasons why the method would be limited to argon plasmas; it is expected to work on plasmas of other chemical compositions as well. However, the following have to be taken into account:
• in the case if other gases the corresponding ca cross sections for momentum transfer have to be used,
• for mixtures an averaged cross section must be applied and
• for molecular plasmas precautions have to be taken for molecular bands in the spectrum; if these are erroneously interpreted as part of the continuum this will lead to an overestimation of \( n_e \).

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References


A novel method to determine the electron temperature and density from the absolute intensity of line and continuum emission: application to atmospheric microwave induced argon plasmas

**Abstract.** An absolute intensity measurement (AIM) technique is presented that combines the absolute measurements of the line and the continuum emitted by strongly ionizing argon plasmas. AIM is an iterative combination of the absolute line intensity-collisional radiative model (ALI-CRM) method and the absolute continuum intensity (ACI) method. The basis of ALI-CRM is that the excitation temperature $T_{13}$ determined by the method of ALI is transformed into the electron temperature $T_e$ using a CRM. This gives $T_e$ as a weak function of electron density $n_e$. The ACI method is based on the absolute value of the continuum radiation and determines the electron density in a way that depends on $T_e$. The iterative combination gives $n_e$ and $T_e$. As a case study the AIM method is applied to plasmas created by Torche à Injection Axiale (TIA) at atmospheric pressure and fixed frequency at 2.45 GHz. The standard operating settings are a gas flow of 1 slm and a power of 800 W; the measurements have been performed at a position of 1 mm above the nozzle. With AIM we found an electron temperature of 1.2 eV and electron density values in the order of $10^{21}$ m$^{-3}$. 

Chapter 4.

4.1 Introduction

During the last decade an enormous interest has been developed in plasmas working in open air. These plasmas find their applications, for instance, in the field of spectrochemistry, waste treatment and biomedicine. Especially popular are the micro plasmas, a category for which, due to the small size and relatively low power consumption, large deviations from equilibrium can be expected. But also plasmas of larger sizes get a lot of attention nowadays. In some cases they are robust in volume like the spectrochemical inductively coupled plasma or filamentary in shape like the plasma produced by the Torche à Injection Axiale (TIA) and microwave plasma torch (MPT).

The fact that they all have the same pressure might suggest that the category of atmospheric plasmas is rather limited. In contrary, there is a wide variety of plasmas resulting from the possible variation in control parameters such as the gas composition, gas flow rate, the frequency of the driving field and the optional presence of dielectrics.

In order to understand the relation between the external control parameters and the resulting plasma conditions, (numerical) models have to be constructed. These models have to be validated with experiments.

The experiments can be based on several different diagnostic techniques that can be classified in probe measurements and spectroscopic methods. The latter category, can be further divided into active and passive spectroscopy. In the first case, the response of the plasma to the irradiation of an external source, for instance a laser, is studied. In the second case, the spectroscopic features of the radiation of the plasmas is studied as it is (i.e. without plasma-irradiation). The passive spectroscopy can be subdivided in relative and absolute intensity measurements. Particulary the relative measurements are very popular because they are easy to perform. For instance, by taking the ratio of two line intensities one can find “a” value of the excitation temperature. Somewhat, more elaborated is to measure several lines (relatively) and to construct a Boltzmann plot which again gives “an” excitation temperature. However, the central question remains: what is the relation between that slope and the basic plasma properties like the electron temperature and density. The answer is strongly related to the degree of equilibrium departure of the plasma under study.

Recently, we [1–3] showed that more insight in the plasma parameters and the degree of equilibrium departure can be obtained if spectroscopic measurements
are performed in an absolute way. This leads to much more valuable results, but also implies that more effort must be made than for relative measurements. In [1, 2], we presented two spectroscopic methods for the electron temperature $T_e$ and electron density $n_e$ determination in low-pressure argon plasma created by a surfatron.

The method introduced in [1] determines $T_e$ as a (weak) function of $n_e$. It is based on the combination of passive spectroscopy, namely absolute line intensity (ALI) measurements, and a collisional radiative model (CRM). The CRM supports the interpretation of the measurements and accounts for the influence of the departure from equilibrium on the density of the excited states. Thus, the so-called ALI-CRM technique can be seen as a two-stage method. The ALI measurement gives the excitation temperature $T_{13}$, the temperature as determined by the population ratio of the states in the ground level (denoted by level ‘1’) and those of the first (group of) easily observed excited levels (denoted by ‘3’); for argon the levels of the 4p group. In the second stage, the CRM is used to correct for the non-equilibrium aspects and to transform $T_{13}$ into the electron temperature $T_e$. This gives $T_e$ as a function of $n_e$.

The method presented in [2], determines the electron density $n_e$ as a function of $T_e$. This method, hereafter denoted by absolute continuum intensity (ACI) measurements, is based on the absolute value of the continuum radiation. It is applied to argon plasmas with a low degree of ionization so that extra attention had to be paid to the continuum radiation as originated by electron-atom (ea) collisions. Due to the Ramsauer effect the cross section of e-Ar interactions strongly depends on the electron energy; this is one of the reasons why the $n_e$ determination depends on the electron temperature.

To summarize, ALI-CRM gives $T_e$ as a (weak) function of $n_e$, whereas ACI delivers $n_e$ in a way that depends on $T_e$.

In both cases, the methods were applied to an argon surfatron plasmas. However, since they are based on fundamental principles, it is to be expected that these methods are applicable to other plasma types as well.

In this study, we apply the combination of ACI and ALI-CRM on plasmas created by the TIA; that is, a microwave induced plasma (MIP) created in open atmosphere. By applying this combined method, briefly denoted as AIM (absolute intensity measurements) to the TIA in argon, we expect to get more insight not only into the AIM method but also into atmospheric argon plasmas.
After the TIA was introduced in [4], it has been studied by various groups [5–12] in order to understand the applicability of this plasma launcher as excitation source for spectrochemical analysis and cleaning of hazardous effluent gases.

To determine the gas temperature $T_g$ several techniques were applied. So, for instance, the rotation spectra of OH and $N_2$ have been measured; these give values of around 2000 K. In [13], results of Rayleigh scattering are reported for which values of below 1000 K were found. There is a considerable spread in the results but in any case these $T_g$ values are lower than those found for the electron temperature $T_e$. These are in the range of 0.8 – 1.8 eV. So, the widely accepted statement is that the plasmas created by the TIA are far from equilibrium and that the value of the temperature depends on the used method.

The lowest values for the electron temperature were found [14] by equating the electron temperature to the excitation temperature in the argon system; the highest given is in [13] and based on Thomson scattering (TS). These relatively high $T_e$ values are in the same range as those found with the Stark intersection method SIM [15]; a method based on the combination of the widths of atomic hydrogen lines.

The results of the AIM presented in the current study are compared with those of other methods. It is found that the electron temperature as obtained by AIM is about 30% lower than the values found using TS [13] and the SIM [15] but higher than the values based on relative intensity measurements [14]. The electron density is in reasonable agreement with the values found in [13, 15].

This paper is organized as follows: In section 4.2, the theory is presented that is relevant for the interpretation of the measurements. Section 4.3 deals with a description of the experimental setup and operating conditions. The results are shown in section 4.4. Discussion and conclusions are given in section 4.5 and section 4.6, respectively. For the explanation of symbols, acronyms and abbreviations we refer to the Appendix. The background of the absolute measurement procedure is dealt with in chapter 2.

4.2 Theory

The radiation generated by a plasma can be seen as a combination of line and continuum contributions. Apart from the intensity of the lines one could also use the shapes of the various lines, in order to find plasma features, for instance
as in the SIM [15]. In this study, we confine ourselves to the intensities of the lines and the continuum. Several studies in the past dealt with the combination

![Figure 4.1: The ASDF, i.e. In $\eta$ versus the excitation energy $E$ or ionization potential $I$ for a LTE and non-LTE ionizing plasma. The upper dashed line represents the ASDF in LTE; from the constant slope the temperature can be determined. The curved line represents the ASDF of an ionizing plasma. In that case the electron density and thus $\eta_{\infty}$ is lowered due to the efflux of (ei) pairs. This results into a curved shape and makes that the lower levels are overpopulated w.r.t. Saha which is usually expressed by the overpopulation factor $b(p) = \eta(p)/\eta^{S}(p)$. The value of $b(p)$ approaches unity for decreasing values of $I$; this upper part is in pLSE. The relative population coefficient $r^{1}(3)$ is determined by the CRM and plays, as depicted in the figure, a crucial role in the transformation of $T_{1,3}$ into $T_{e}$.](image)

of line and continuum radiation [16–21]. However, these are mostly based on line/continuum ratios, so on relative intensities and only applicable to plasmas that are close to LTE. Here, we measure both the line and continuum in an absolute way and develop a method that can be used for plasmas that are not in local thermodynamic equilibrium (LTE). The added value of the combination is that results from the line method are used in the continuum interpretation and vice versa.

We start with the study of absolute line intensities; subsection 4.2.3 will be devoted to the continuum radiation. By measuring the absolute intensities of several lines the atomic state distribution function (ASDF) can be constructed.
If the plasma (part) is in LTE, equilibrium exists for any collisional process, meaning that the number of forward processes equals that of the corresponding backward processes. As a consequence, all material particles will have a Maxwellian kinetic energy distribution ruled by one and the same temperature, while the ASDF obeys the Saha-Boltzmann distribution law. A sketch of the ASDF in LTE is given as the upper line in figure 4.1; it is described by the Saha-Boltzmann formula

\[
\eta^S(p) = \eta_e \eta_i \frac{h^3}{(2\pi m_e k_B T_e)^{3/2}} \exp \left( \frac{I_p}{k_B T_e} \right) \tag{4.1}
\]

that relates the state density \(\eta(p) = n(p)/g(p)\), i.e. the level density \(n(p)\) divided by the statistical weight \(g(p)\), to the \(\eta\) value of the ion ground state (\(\eta_i\)) and the electrons (\(\eta_e\)). In the equation above, \(k_B\) and \(h\) are the constants of Boltzmann and Planck, \(m_e\) is the electron mass, while \(I_p\) is the ionization potential of the atomic excited level \(p\) (\(I_p = E_p - E\)). By taking the natural logarithm of equation (4.1) we get

\[
\ln(\eta(p)) = \exp \left( \frac{I_p}{k_B T_e} \right) + \ln \eta_\infty, \tag{4.2}
\]

where

\[
\eta_\infty = \eta_e \eta_i \frac{h^3}{(2\pi m_e k_B T_e)^{3/2}}. \tag{4.3}
\]

By plotting \(\ln(\eta(p))\) versus \(I_p\) (cf. figure 4.1), \(T_e\) can be deduced via the slope and \(\eta_\infty\) by a linear extrapolation of \(\eta(p)\). This value of \(\eta_\infty\) provides the electron density, assuming that \(n_e = n_i\).

Note that in the case of LTE the relation \(T_e = T_g = T\) holds. Nevertheless, we used in equation (4.1) \(T_e\), and not \(T\). The reason is that equation (4.1), in principle, stays applicable for the upper part of the ASDF in non-LTE plasmas. This part of the atomic system close to the continuum is in so-called partial local Saha equilibrium (pLSE) [22].

In ionizing plasmas, electron-ion (ei) pairs are removed from the active plasma zone, the ionization and excitation are no longer balanced by the corresponding reverse processes and especially the lower part of the ASDF will not obey the Saha-Boltzmann equation (4.2). The curve in 4.1 schematically shows the ASDF of an ionizing plasma. It can be seen that the slope is no longer constant. The slope or excitation temperature changes gradually and the deduction
of the electron temperature from the slope of the Saha-Boltzmann plot is far from trivial.

In figure 4.2, we present an ASDF of a TIA, as published in [23], operated at a power of 330 W and a flow of 3.0 slm. It can be seen that the slope is not constant. Following [23], we denote the lower excitation temperature by \( T_{13} \) and the temperature for the ASDF top as “the” spectroscopic temperature \( T_{\text{spec}} \). To determine \( T_{13} \) we need absolute densities of the states in the first easy observable levels (denoted by ‘3’) since these have to be combined with the ground state density that cannot be determined spectroscopically but follows from the pressure and gas temperature \( T_g \). The \( T_{\text{spec}} \) can be determined by spectroscopic means solely.

The measured levels are in the so-called excitation saturation balance (ESB) [22, 24] and the slope of the ASDF in ESB changes (cf. 4.1) gradually. In [25] it was proven that the corresponding slope temperature (in eV) follows approximately \( T \sim I/3 \). The slope of the line segment through 4p and higher levels has its tangent point at about 14 eV, that, being about 1.5 eV below the continuum, leads to the so-called spectroscopic temperature of about \( T_{\text{spec}} = 0.5 \text{ eV} \). The low value of \( T_{\text{spec}} \) between 0.4 and 0.5 eV is often found in ionizing argon plasmas and in many cases erroneously interpreted as the electron temperature [25]. In this paper, we use the following terminology and symbols (cf. also Appendix). The density of an excited atomic level labeled with \( p \) is denoted with \( n(p) \); the statistical weight (degeneracy) of that level, \( g(p) \), is the number of states in that level. So a state has a statistical weight of \( g = 1 \) and \( \eta(p) = n(p)/g(p) \) is the mean number density of the states in level \( p \). The ground level is labelled by ‘1’. Since we deal with the noble gas argon we have \( g(1) = 1 \), so that \( n(1) = \eta(1) \); the group of the first easily observable levels is denoted by ‘3’, for argon that are the levels of the 4p group (10 levels containing in total 36 states). The density of these states is denoted by \( \eta(3) \). The levels in the 4p group decay spontaneously to levels in the 4s group. These levels are denoted by ‘2’.

### 4.2.1 Absolute line intensity; ALI

The determination of the densities \( \eta(4p) \equiv \eta(3) \) of the states in the 4p level group goes along the following procedure. The radiation of the transition from one particular level in 4p to one of the levels in the 4s group of argon, schemat-
Figure 4.2: A sketch of the ASDF of an argon system as determined by means of the ALI method for an Ar-TIA plasma and published in [23]. The ground state follows from the pressure (1 bar) and the gas temperature while all the other densities are determined spectroscopically. The densities of the 4s levels (levels '2') were not measured; the ratio between the population density of the ground state density and some of the 4p levels (level '3') gives the temperature $T_{13}$. Using the relative population coefficient $r^3(3)$, as provided by the CRM, $T_{13}$ can be converted into $T_e$ (cf. equation (4.12)). The measured levels are in the so-called excitation saturation balance (ESB) and the slope of the ASDF in ESB changes gradually (cf. figure 4.1) and follows $T \sim I/3$. The tangent of the curved part of the ASDF for the 4p and higher levels leads to the so-called spectroscopic temperature; here about $T_{\text{spec}} = 0.4$ eV.

\[
A_3 \rightarrow A_2 + h\nu_{32}, \quad (4.4)
\]
generates photons of energy $h\nu_{32}$ spread around the energy distance $E_{23} = E_3 - E_2$ between the lower and higher level. The corresponding frequency and thus wavelength distribution is described by the line-form function $\phi_\lambda(\lambda)$ that is
normalized, meaning that \( \int \phi_\lambda(\lambda) d\lambda = 1 \). Here the subscript ‘T’ indicates that the integral is carried out over the complete spectral line (the whole transition). The spontaneous transitions of the type given above contribute to the emission coefficient

\[
j_{\lambda}^{32}(\lambda) = \frac{A(3, 2)E_{23}n(3)\phi_\lambda(\lambda)}{4\pi}.
\]

If we deal with a homogeneous plasma with depth \( D \) we can deduce \( j_{\lambda}^{32}(\lambda) \) in a simple way from the calibrated intensity \( I_{\lambda}^{32}(\lambda) \) by equating \( I_{\lambda}^{32}(\lambda) = j_{\lambda}^{32}(\lambda)D \) and \( n(3) \) can be obtained via

\[
n(3) = \frac{4\pi}{A(3, 2)E_{23}D} I_{32},
\]

where \( I_{32} = \int_T I_{\lambda}^{32}(\lambda) d\lambda \) is the transition integrated intensity and \( D \) the depth of the plasma along the line of sight.

It should be realized that the wavelength ‘\( \lambda \)’ can be placed in two different notational positions; placed between parenthesis, like in \( k(\lambda) \) it is the argument of a function, positioned as lower index it refers to differentiation with respect to the wavelength. So for instance, \( j_\lambda(\lambda_0) \) is the emitted power (per volume and per unit of solid angle) per wavelength interval at the value \( \lambda_0 \). If it does not lead to ambiguity we will omit \( \lambda \) in the “at” and/or “per” form.

### 4.2.2 The task of the CRM: the transformation of \( T_{13} \) into \( T_e \)

To account for the effect of equilibrium departures on the spectroscopic properties of plasmas and to understand the relation between \( T_{13} \) and \( T_e \), we have to use collisional radiative models (CRMs).

A CRM solves a set of particle balance equations \([22, 26, 27]\) with result that the population density \( \eta(p) \) of the excited level \( p \) of an atomic system can, in most cases, be described as an addition of two contributions, one from the atomic ground level \( \eta^1(p) \) and the other from the ionic ground level \( \eta^+\) \( p) \) i.e.

\[
\eta(p) = \eta^1(p) + \eta^+(p).
\]

The two contributions can be related to the Boltzmann \( \eta^B(p) \) and Saha \( \eta^S(p) \) populations densities via the relative population coefficient \( r(p) \)

\[
\eta^1(p) = r^1(p)\eta^B(p)
\]

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and
\[
\eta^+(p) = r^+(p)\eta^S(p). \tag{4.9}
\]
In the case of a strongly ionizing plasma, the ion contribution can be neglected for lower excited states (\(\eta^+(p) \ll \eta^1(p)\)) and equation (4.7) reduces to \(\eta(p) = r^1(p)\eta^B(p)\). So for the density of the states in '3' we get
\[
\eta(3) = r^1(3)\eta^B(3) = r^1(3)\eta(1) \exp\left(\frac{-E_{13}}{k_B T_e}\right). \tag{4.10}
\]
where \(\eta(1) \equiv \eta^B(1)\) is the ground state density. This means for the electron temperature that
\[
k_B T_e = \frac{E_{13}}{\ln(r^1(3)\eta(1)/\eta(3))} \tag{4.11}
\]
or
\[
T_e = \frac{T_{13}}{1 + (k_B T_{13}/E_{13}) \ln(r^1(3))}. \tag{4.12}
\]
Equation (4.11) gives \(T_e\) as a function of \(\eta(3), \eta(1)\) and \(r^1(3)\). Equation (4.12) gives the transformation from \(T_{13}\) into \(T_e\), where we used the definition of the excitation temperature
\[
k_B T_{13} = \frac{E_{13}}{\ln(\eta(1)/\eta(3))}. \tag{4.13}
\]

Figure 4.3: The value of the relative population coefficient \(r^1(3)\) as a function of \(n_e\) for different values of \(T_e\) using the CRM of [28]. It can be seen that \(r^1(3)\) is, for high \(n_e\) values, almost independent of \(n_e\).
The value of $T_e$ can now be found by inserting for $\eta(3)$ the value as determined via ALI and for $\eta(1) = n(1) = p/k_B T_g$. So the gas temperature $T_g$ must be known but the dependence of $T_{13}$ on $T_g$ is quite insensitive.

Figure 4.3 shows $r^1(3)$ as a function of $n_e$ for some typical values of $T_e$. These are the results obtained from the CRM constructed in [28]. It can be seen that $r^1(3)$ is, for high $n_e$ values, almost independent of $n_e$.

### 4.2.3 Absolute continuum intensity; ACI

In general, the continuum contribution can be classified according to the nature of the interacting species. In this way, we can distinguish between radiation generated by collisions of free electrons with atoms (ea, free-free), free electrons with ions (ei, free-free) and by free-bound radiation (ei, free-bound). So, we get the following general structure of the emission coefficient

$$j_\lambda^{cont}(\lambda) = j_\lambda^{ei,ff}(\lambda) + j_\lambda^{ei,ff}(\lambda) + j_\lambda^{ea,ff}(\lambda).$$

The first two terms of the above equation can be combined and in the case of a singly ionized plasmas for which $n_e = n_i$, this combination reads

$$j_\lambda^{ei}(\lambda) = c_1 \frac{n_e^2}{\lambda^2 T_e^{1/2}} e^{ei}_\lambda(\lambda, T_e),$$

where $T_e$ must be expressed in K and $\lambda$ in m. The constant equals:

$$c_1 = \frac{16\pi}{3m_e c^2 (6\pi m_e k_B)^{1/2}} \left( \frac{e^2}{4\pi \varepsilon_0} \right)^3 = 1.6321 \times 10^{-43} \text{ (Jm}^4\text{K}^{1/2}\text{b}^{-1}\text{sr}^{-1})$$

with $\varepsilon_0$ the permittivity of vacuum, $c$ the speed of light, $m_e$ the mass of electron and $e$ the elementary charge. An expression and a graphical representation of $\xi^{ei}_\lambda(\lambda, T_e)$ are given in [2]. It is found that for the visible wavelength range of $350 < \lambda < 750$ nm and temperature range $1 < T_e < 2$ eV, the variation of $\xi^{ei}_\lambda(\lambda, T_e)$ factor ranges from 1.2 to 1.8.

The emission coefficient of the radiation generated in ea interactions is given
by

\[ j_\lambda^{ea, \text{eff}} (\lambda) = c_2 \frac{n_e n_a}{\lambda^2} T_e^{3/2} \]

\[ \times \left\{ Q^{\lambda \text{r}}(T_e) \left( 1 + \left( 1 + \frac{\hbar c}{\lambda k_B T_e} \right)^2 \right) \exp \left( - \frac{\hbar c}{\lambda k_B T_e} \right) \right\}, \]  

(4.17)

where

\[ c_2 = \frac{32e^2}{12\pi \varepsilon_0 c^2} \left( \frac{k_B}{4\pi m_e} \right)^{3/2} \]

\[ = 1.026 \times 10^{-34} \text{ (Jm}^2\text{K}^{3/2}\text{s}^{-1}\text{sr}^{-1}) \]  

(4.18)

with \( Q^{\lambda \text{r}}(T_e) \) the energy-weighted average of the speed-dependent rate for momentum transfer in electron-atom collisions, divided by the mean electron speed \( \langle \nu \rangle = \sqrt{8k_B T_e / \pi m_e} \) (cf. [2, 29]).

In the case of a homogenous plasma, we find the emission coefficient of the continuum by dividing the (calibrated) intensity of the continuum by the plasma size \( D \), i.e.

\[ j_\lambda^{\text{cont}} (\lambda) = \frac{I_\lambda^{\text{cont}} (\lambda)}{D}. \]  

(4.19)

By equating this absolute value of \( j_\lambda^{\text{cont}} (\lambda) \) to the theoretical expression for the sum of the contributions we get quadratic equation of the form

\[ j_\lambda^{\text{cont}} (\lambda) = n_e^2 f(\lambda, T_e) + n_e n_a g(\lambda, T_e), \]  

(4.20)

where we used \( f(\lambda, T_e) = j_\lambda^{ei}(\lambda, T_e)/n_e^2 \) and \( g(\lambda, T_e) = j_\lambda^{ea}(\lambda)/n_e n_a \). The result for the electron density is

\[ n_e = \frac{g(\lambda, T_e) n_a}{2 f(\lambda, T_e)} \left( \sqrt{1 + \frac{4f(\lambda, T_e) j_\lambda^{\text{cont}} (\lambda)}{(g(\lambda, T_e) n_a)^2} - 1} \right). \]  

(4.21)

In [2] it was found that for \( n_e/n_a \) below \( 5 \times 10^{-4} \) the ea-contribution will dominate. As we will see this applies for the current plasma as well. Nevertheless, we will solve equation (4.21) in its full glory; that is, including both ei and ea contributions.
4.3 Experimental setup and settings

4.3.1 Setup configuration

To validate the AIM method we performed a case-study on plasmas created by the Torche à Injection Axiale. For details of this type of microwave induced plasma we refer to [4]. Here only the features are reported that are relevant for this study. The electromagnetic waves are generated by a power supply that operates with maximum power of 1000 W. The power supply is connected to one end of a rectangular waveguide of which the other end is shortened by a moveable plunger. This facilitates to find the optimal power coupling. The microwave frequency is fixed at 2.45 GHz. The gas flows through an inner coaxial conductor and the plasma is created above the nozzle in an argon flow into the open air, so, without making use of a discharge tube (cf. figure 4.4).

Different plasma conditions can be achieved by changing the incident power and the gas flow rates. For the spectroscopic diagnostics, an optical arrangement

![Figure 4.4](image-url)

**Figure 4.4:** A sketch of the microwave setup and the detection system. The microwaves, initially in the TE_{01} mode, enter the waveguide at the left hand side; at the launcher the waves are converted into the TEM mode; by means of the stubs and the movable plunger an optimum in energy coupling can be reached for the plasma created in an atmospheric flow of argon. The light is collected and projected onto the entrance of a monochromator using the combination of two achromatic lenses and a Dove prism.

is used to focus the light emitted by the brightest zone of the plasma flame onto the entrance slit of a 1 meter focal length monochromator (THR 1000 Jobin-
Chapter 4.

Yvon) with 1200 grooves mm\(^{-1}\) grating and dispersion of 0.08 nm mm\(^{-1}\) (at 500 nm). To that end two achromatic lenses are used with a Dové prism in between. The Dové prism is used to rotate the image on 90°. In this way, the light from the plasma emitted at a certain \(z\)-position is collected by lenses and focused onto the entrance slit of the monochromator (cf. figure 4.4). The setup is not lateral selective, hence, we are not able to get spatially resolved results. Instead by employing equations (4.6), (4.19) and (4.21) we find line-of-sight averaged values of \(n(3)\) and \(T_e\). The measurements are done at \(z = 1\) mm above the nozzle, which is the axial position with maximum emission intensity under the used operating conditions.

The optical system is calibrated by replacing the TIA by a standard tungsten ribbon lamp, operated at an accurately known electric current.

4.3.2 Plasma conditions

Spectroscopic measurements have been performed on different argon plasmas that have been composed by selecting between the applied power settings of 600, 800 and 1000 W, and argon gas flow of 0.5 and 1 slm. The observed plasmas position is \(z = 1\) mm above the nozzle. The selected exposure time is 1000 ms for the continuum measurements and 300 ms for the argon lines.

First, we performed a complete scan of the visible spectrum of the plasma; that is in the range from 350 to 750 nm. The most reliable wavelength regions were selected for the continuum method, which are the regions free of intensive lines. It is found that the region around 439 nm is the most suitable for continuum measurements in this study.

The selected atomic argon lines for ALI-CRM method are 763.5 (13.17 eV) and 706.7 (13.3 eV) nm. They both belong to the 4p-4s transition. The value between parenthesis gives the energy in eV of the emitting sublevel of the 4p group, that is the energy distance between these levels and the argon ground state.

For the selection of the gas temperature we follow \[30\] where \(T_g\) was determined by means of Rayleigh scattering. A whole field of \(T_g\) values was found ranging from 800 to 4500 K. A remarkable finding is that in the active plasma zone, the region where the electrons are, the gas temperature is low and on the order of 900 K. A different study \[31\] reports higher \(T_g\) values by equating the gas temperature to the rotational or vibrational temperature of molecules. How-
ever, most likely these molecules are not located in but are at the periphery of the active plasma zone. This bring us to the decision to take $T_g = 1500 \text{K} \pm 40\%$.

To determine the $D$ value we took photographs of the plasma flame from which sizes of around 0.28 mm could be deduced. From the electron density profile of [13] the same value of about 0.3 mm can be deduced. This is the same value as that reported in the paper on single shot Thomson scattering measurements on the MPT [32]. So apparently, there is not much variation in the plasma size, even if we change the torch type from TIA to MPT. This might be related to the fact that $D = 0.3$ mm is close to the skin depth of the plasma for waves with 2.45 GHz.

In conclusion we take for the plasma depth $D = 0.3 \text{mm} \pm 10\%$ and for the gas temperature $T_g = 1500 \text{K} \pm 40\%$.

4.3.3 The iterative procedure; AIM

In section 4.2, two methods are presented for the determination of $T_e$ and $n_e$. The first one, deals with the processing of the absolute line intensity measurements together with a collisional radiative model (ALI-CRM), giving the electron temperature assuming a value of the electron density $n_e$. The second, based on the continuum radiation, is used to calculate the electron density assuming an electron temperature, thus $T_e$ value. Here, both methods are combined in an iterative procedure that can be applied for given values of the plasma depth $D$ and the gas temperature $T_g$.

The recipe used is as follows:

1. Take a starting value e.g. $n_e = 10^{21} \text{m}^{-3}$ and $T_e = 1 \text{eV}$.
2. Calculate $r^1(3)$ (cf. figure 4.3).
3. Determine $n(3)$ via ALI, equation (4.6).
4. Combine this with $n(1) = p/k_BT_g$ and calculate $T_{13}$.
5. Use the $r^1(3)$ value to translate the $T_{13}$ into $T_e$ using equation (4.12).
6. Calculate $n_e$ using the $T_e$ value obtained at step (5) and equation (4.21) for the continuum.
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7. With the new values of \( n_e \) and \( T_e \) return to step (1) and repeat the procedure until convergence is reached.

The number of iterations to get convergence is typically 6 reaching a precision of 0.1 %. We performed the recipe for the two 4p lines 763.5 (13.17 eV) and 706.7 (13.3 eV) nm independently and found a variation in \( T_e \) of 5 % and in \( n_e \) of 14 %.

4.4 Results

The iterative procedure given in subsection 4.3.3 is applied to different plasma conditions giving \( n_e \) and \( T_e \) values. The calculations are based on the \( D \) and \( T_g \) values of \( D = 0.3 \) mm and \( T_g = 1500 \) K. The observation position is always \( z = 1 \) mm where \( z \) is the distance above the nozzle. The input power is varied between 600 and 1000 W and for the argon gas flow we selected 0.5 and 1.0 slm.

![Figure 4.5](image)

**Figure 4.5:** The electron density as a function of power \( P \). Only a slight increase in \( n_e \) is observed for increasing \( P \) values.

Figure 4.5 shows results for \( n_e \) as a function of input power keeping the gas flow constant at 1 slm. For the continuum measurements we selected \( \lambda = \)
439 nm. It can be seen from the figure that \( n_e \) slightly increases with increasing power, a trend that was also observed in the surfatron study [2]. This tendency can be understood from the electron energy balance, which neglecting convection and heat conduction can be put in the simplified form

\[
\varepsilon = n_e n_1 S_{\text{heat}} (k_B T_e - k_B T_h) + n_e n_1 S_{\text{ion}} (I_1 + 3/2 k_B T_e) \approx n_e n_1 S_{\text{ion}} I_1, \tag{4.22}
\]

which expresses that the power density of the plasma energy coupling (\( \varepsilon = \text{power/volume} \)) is divided over the elastic and inelastic channels; \( S_{\text{heat}} \) and \( S_{\text{ion}} \) are the rate coefficients for heat transfer and effective ionization. By using an argon CRM it can be shown [30] that \( S_{\text{ion}} \) is very close to the rate coefficient \( k_{12} \), of electron induced excitation of the first excited state \( 1 \rightarrow 2 \). This near equality \( S_{\text{ion}} \approx k_{12} \) is based on the fact that due to the relatively high \( n_e \) value the transition \( 1 \rightarrow 2 \) is immediately followed by a ladder-climbing-like sequence of processes like \( 2 \rightarrow 3 \rightarrow 4 \cdots \rightarrow + \). In the last step of the above equation we performed further simplifications that are based on the fact that \( I_1 \gg 3/2 k_B T_e \) and that for the higher \( T_e \) values the inelastic processes are dominant over the elastic interactions [32]. The proportionality between \( \varepsilon \) and \( n_e \) suggests that by increasing the power \( n_e \) will also increase. However, care must be taken. By increasing the power the flame becomes longer so that power density in the

Figure 4.6: The electron temperature as a function of power \( P \); no change in the temperature could be found.
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region close to the nozzle will not increase in direct proportionality to the power. The variation of the gas flow rate gives no clear change in the electron density; again in agreement with the finding reported in [2].

The value of the electron temperature as a function of power is presented in figure 4.6. It can be seen that no substantial change is found in the $T_e$ values. The flow has no measurable consequence for both $n_e$ and $T_e$. The $T_e$ values are derived from $T_{13}$ values of around 8700 K, using the CRM as explained in section 4.3.2. The $T_{13}$ values we found are close to the value that was reported in [23] and shown in figure 4.2. The fact that $T_{13}$ is substantially lower than $T_e$ is based on non-equilibrium aspects: the plasma is strongly ionizing.

4.5 Discussion

4.5.1 Error analysis

The error analysis will be guided by table 4.1 giving a schedule of how $n_e$ and $T_e$ depend on measurable quantities and elementary parameters. For the first category, the plasma depth $D$, the gas temperature $T_g$ and intensity $I$ are presented. For the second, the transition probabilities $A$ and the cross section $Q_{Ar}(T_e)$. The $n_e$ and $T_e$ determination have in common that both go along the determination of the emission coefficients $j_{\lambda}^{cont}(\lambda)$ and $j_{\lambda}^{32}(\lambda)$. The difference is that $T_g$ is important for $j_{\lambda}^{cont}(\lambda)$ but not for $j_{\lambda}^{32}(\lambda)$. We start in the right-most column dealing with the relative errors in $I$, $D$ and $T_g$ and study how they affect the accuracy of $n_e$ and $T_e$. The errors in $D$ and $T_g$ were already addressed in subsection 4.3.2 where we found that $\Delta D/D \approx 10\%$, and $\Delta T_g/T_g \approx 40\%$. Due to the relationship as given by equations (4.5) and (4.20) we see that this leads to an inaccuracy in $j_{\lambda}^{cont}(\lambda)$ of 42% and 10% in $j_{\lambda}^{32}(\lambda)$. The difference originates from the fact that $T_g$ will not affect $j_{\lambda}^{32}(\lambda)$ while $j_{\lambda}^{cont}(\lambda)$ depends on $T_g$ via the gas density; especially since ea interactions give the most dominant contribution to the continuum radiation.

The error in the absolute intensity $I$ is determined by the calibration procedure for which we refer to chapter 2. There it is shown that the main error source is the allocation of the appropriate surface spot on the ribbon of the calibration lamp. By performing the calibration several times using two different tungsten ribbon lamps we could establish that the typical error in the $I$ determination is about 3%. This is smaller than the uncertainty in the plasma depth (10%)
Table 4.1: Schedule of the dependence of \( n_e \) and \( T_e \) on elementary parameters and measurable quantities.

<table>
<thead>
<tr>
<th>( n_e )</th>
<th>( j_{\lambda}^{\text{cont}}(\lambda) )</th>
<th>( I_{\lambda}(\lambda) )</th>
<th>( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_a )</td>
<td>( Q^{\text{Ar}}(T_e) )</td>
<td>( Q^{\text{Ar}}(T_g) )</td>
<td></td>
</tr>
<tr>
<td>( T_e )</td>
<td>( \eta(3) )</td>
<td>( j^{32} )</td>
<td>( I_{\lambda}(\lambda) )</td>
</tr>
<tr>
<td>( A_{32} )</td>
<td>( D )</td>
<td>( T_g )</td>
<td></td>
</tr>
</tbody>
</table>

and the gas temperature (40%). The inaccuracy in the \( I \) determination is just as that of \( D \) directly transferred into that of the \( j \) calculation. However, since \( \Delta D/D \) is, with 10%, smaller, we can state that the inaccuracy of the \( j \) value of \( j_{\lambda}^{\text{cont}}(\lambda) \) is determined mainly by the error in \( T_g \) and thus approximately 40%, while for \( j^{32}(\lambda) \) the estimated error is 10%, being the error in \( D \).

We now make the step from \( j_{\lambda}^{\text{cont}}(\lambda) \) to \( n_e \) and assume that \( j_{\lambda}^{\text{ea}}(\lambda) \) is the most important contribution. In that case we are faced with the inaccuracy of \( Q^{\text{Ar}}(T_e) \) which brings us to the discussion as given in [2] where it was stated that the validity of equation (4.17) is highly questionable. It is based on a hard-sphere collision approach while, due to the Ramsauer effect, we know that e-Ar collisions are certainly not constant as a function of energy. So, the application of equation (4.17) will lead to a systematic error and the search for a more appropriate collision theory asks for a separate study.

In conclusion, the random relative error in the \( n_e \) is determined mainly by the inaccuracy of the gas temperature and is about 40%. The use of the hard-sphere collision type expression for the ea interactions is questionable and needs further study.

For the \( T_e \) error we have to look to the influence of the transition probabilities, these are known to be on the order of 25%. The gas temperature error is not manifest in the determination of \( \eta(3) \) but in \( \eta(1) \). However, due to procedure of taking the logarithm we find that the influence of the various quantities on \( \Delta T/T \) is reduced.
From equation (4.11) we can derive the following relation between the relative errors:

\[
\frac{\Delta T}{T} = \Delta \ln \left( \frac{\eta(3)}{r^1(3)\eta(1)} \right) \times \left( \frac{k_B T_e}{E_{13}} \right)
\]  

(4.23)

showing that the error in the logarithm is diminished by a factor \(k_B T_e/E_{13}\), which is about 0.1. Since \(\eta(3)\) is fairly well known we may state that the error in the logarithm is mostly determined by the uncertainties in \(\eta(1)\) and the \(r^1(3)\) coefficient. The uncertainty in \(\eta(1)\) is the same as that in \(T_g\) and thus 40%. The error in \(r^1(3)\) is mainly systematic and thus difficult to determine. Here we will follow [1] by taking \(\Delta r^1(3)/r^1(3) = 50\%\). By pythagorean averaging we get for the logarithm a total error of 64%. This being reduced of the factor \(k_B T_e/E_{13} \approx 0.1\) leads to an error in the temperature of about \(\Delta T/T = 7\%\).

In conclusion we may state that the \(T_e\) is with a margin of 7\% more accurate than \(n_e\) (40\%) and that the systematic errors as introduced by the \(r\)-coefficient ask for future studies.

4.5.2 Comparative overview

In table 4.2 we compare the results of the current study with those of previous investigations. Apart from the \(n_e\) and \(T_e\) values different working conditions are also given; i.e. the gas flow rate, the input power and the type of microwave torch: TIA or MPT.

The following conclusions can be drawn.

1. The \(n_e\) value is relatively low but in view of the estimated error of 40\% it is not far from the values obtained by the other techniques. Nevertheless, even increasing the AIM value of \(n_e\) with 40\% results in values that are lower than those found with TS and SIM; the finding that the continuum gives low values for \(n_e\) are in agreement with our previous study [33].

2. The electron density is more or less independent of the power, flow rate and even the torch type.

3. The \(T_e\) value (1.2 eV) is higher than the value obtained by equating the \(T_e\) to the excitation temperature (0.4 – 0.8 eV) but lower than the values obtained using TS (1.9 eV) and SIM (1.8 eV).
4. There is much scatter on the $T_e$ values which is noticeable in view of the low estimated error of 7% in our $T_e$ determination.

The large difference between the $T_e$ value as obtained from TS and SIM on the one hand and our AIM method on the other hand remains a puzzle. Nevertheless, we may put some questions about the validity of the high $T_e$ values obtained by TS and AIM; questions and doubts that are based on the energy balance.

In equation (4.22) we related the power density to the effective ionization rate of the plasma:

$$\varepsilon = n_e n_1 S_{\text{ion}} I_1.$$  \hspace{1cm} (4.24)

The rate coefficient for effective ionization in this equation is given by [32]

$$S_{\text{ion}} = 7.3 \times 10^{-15} \hat{T}^{0.5} \exp \left( \frac{-12.06}{k_B T_e} \right),$$  \hspace{1cm} (4.25)

where $\hat{T}$ is expressed in eV. The strongest temperature dependence originates from the exponential form. For instance the change from $T = 1.2$ to 1.9 eV would result in an increase in $S_{\text{ion}}$ of more than a factor 40. Since $n_e$ and $n_1$ are more or less constant, it would mean that the volume of the plasma in the case of 1.9 eV would be about 40 times smaller. This is in violation of basic observations.

One of the reasons for the discrepancy of TS and SIM on the one hand and AIM on the other hand could be the deviation of the electron energy distribution (EEDF) from the Maxwell form. Due to the low degree of ionization we can expect that the tail of the EEDF is under-populated with respect to Maxwell. With TS and SIM we measure the bulk whereas AIM (more particular ALI-CRM) is much more dependent on the tail and will thus be affected (lowered) by a possible tail depletion.

The comparison of all the different techniques asks for further studies. In such a study we should perform all the different measurement techniques at the same time and at the same plasma location. This method of “poly-diagnostics calibration” was recently applied to low pressure plasmas (in the range of 10 mbar) created by the surfatron [33].
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<table>
<thead>
<tr>
<th>Methods</th>
<th>MIP</th>
<th>Power W</th>
<th>Flow slm</th>
<th>z mm</th>
<th>n_e m^{-3}</th>
<th>T_e eV</th>
<th>Ref</th>
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<td>1</td>
<td>1.2 \times 10^{21}</td>
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<tr>
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<td>2</td>
<td>2 \times 10^{21}</td>
<td>1.5</td>
<td>[23]</td>
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<tr>
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<td>2</td>
<td>2 \times 10^{21}</td>
<td>1.9</td>
<td>[13]</td>
</tr>
<tr>
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<td>TIA</td>
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<td>1.8</td>
<td>5</td>
<td>1.5 \times 10^{21}</td>
<td>1.7</td>
<td>[13]</td>
</tr>
<tr>
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<td>TIA</td>
<td>600</td>
<td>1</td>
<td>1</td>
<td>1.46 \times 10^{21}</td>
<td>1.8</td>
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<td>2</td>
<td>2.1 \times 10^{21}</td>
<td>1.5</td>
<td>[34]</td>
</tr>
<tr>
<td>SSTS</td>
<td>MPT</td>
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<td>2</td>
<td>2 \times 10^{21}</td>
<td>1.4</td>
<td>[32]</td>
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<td>0.4 - 0.8</td>
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Table 4.2: Results of the current study in comparison with other works: TIA refers to Torche à Injection Axiale and MPT to microwave plasma torch; in the bottom line we present the temperature values that are found when \( T_e \) is equated to the spectroscopic or excitation temperature (cf. figure 4.2). SSTS stands for single shot Thomson scattering.

4.6 Conclusions

This paper presents a novel method to deduce the properties of the electron gas from the emission spectrum. The method is applicable to (strongly) ionizing plasmas, and based on a combination of the absolute intensity measurement (AIM) of the continuum and the 4p lines of argon. The so-called AIM method is based on the iterative combination of the ACI and ALI-CRM method. The ACI method is based on the absolute value of the continuum radiation and determines \( n_e \) in a way that depends on \( T_e \). The bases of ALI-CRM is that the excitation temperature \( T_{13} \), determined by the method of absolute line intensity (ALI) measurements, is transformed into the electron temperature \( T_e \) using a collisional radiative model (CRM).

As a case study the AIM method is applied to plasmas produced by the Torche à Injection Axiale (TIA) but, as stated before, it can easily be applied to other ionizing plasmas as well. The restriction “ionizing” stems from the applicability of the CRM. The essential parameter of the CRM that is used in the \( T_{13} \rightarrow T_e \) conversion, is the \( r_{13}(p) \) coefficient; also known as the Boltzmann decrement. It gives the ratio at which the excited level in question is underpopulated with respect to the value as prescribed by the Boltzmann equation.
In order to apply the AIM method to other atomic plasmas we need a CRM for the atomic system in question. The same applies mutatis mutandis to molecular plasmas but an extra difficulty might be that it is not easy to find the pure continuum; that is the part of the spectrum that is not populated by molecular (and atomic) transitions.

The error analysis of the method indicates that the calibration procedure is quite accurate. Employing a well-stabilized current source and applying the same spot on the ribbon as that at which the calibration procedure of the standard lamp was performed, we can reduce the inaccuracy to below 3%. This is much lower than the uncertainty in the transition probabilities (25%), the size (10%) of the plasma and the gas temperature (40%). Especially the improvement of the $T_g$ determination deserves much attention in the future. The difficulty is that most $T_g$ determination techniques are based on vibrational or rotational transitions in molecules and that it is not certain which part of the radiation comes from the active plasma zone; the zone where the electrons are created.

The fact that the $T_e$ determination goes along a logarithmic procedure leads to a relatively accurate result. However, this small resulting spread in $T_e$ is amplified back again in the computation of plasma creation, using the rates of excitation and effective ionization. These rates strongly depend on $T_e$ via a Boltzmann exponent. 

Apart from the measurement-related errors systematic errors were also addressed. There is doubt about the applicability of the formula of the continuum contributions due to ea interactions. The formula is based on a hard-sphere collision approach and this is highly questionable in view of the Ramsaur effect of the e-Ar collisions. Another systematic issue is that more attention has to be paid to the determination of the CRM. First of all it should be better validated for the pure Ar case, secondly the influence of the entrainment of the ambient air and its effect on the population of the 4s and 4p levels must be investigated. Finally, one should include the influence of a possible non-Maxwellian tail of the electron distribution function.

The results show that $n_e$ and $T_e$ do not change much as a function of the power and gas flow rate. Moreover, comparing the present values with those in the literature shows that the difference between the results of the TIA and its little sister MPT completely lies in the large spread of the TIA results. Remarkable is the spread that is found in the non-AIM $T_e$ values as provided
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by TS and SIM.

For a better comparison between the various methods, it is recommended to perform the methods at the same plasma location at the same time. We plan to perform this method of poly-diagnostic calibration in the near future.

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References

Absolute Intensity Measurements

Thomson scattering on argon surfatron plasmas of intermediate pressure: axial profiles of the electron temperature and electron density

Abstract.

The axial profiles of the electron density $n_e$ and electron temperature $T_e$ of argon surfatron plasmas in the pressure range of 6 to 20 mbar and microwave power between 32 W and 82 W have been determined using Thomson scattering of laser irradiation at 532 nm. For the electron density and temperature we found values in the ranges $5 \times 10^{18} < n_e < 8 \times 10^{19}$ m$^{-3}$ and $1.1 < T_e < 2.0$ eV. Due to several improvements of the setup we could reduce the errors of $n_e$ and $T_e$ down to 8% and 3%, respectively. It is found that $n_e$ decreases in the direction of the wave propagation with a slope that is nearly constant. The slope depends on the pressure but not on the power. Just as predicted by theories we see that increasing the power leads to longer plasma columns. However, the plasmas are shorter than what is predicted by theories based on the assumption that for the plasma-wave interaction electron-atom collisions are of minor importance (the so-called collision-less regime). The plasma vanishes long before the critical value of the electron density is reached. In contrast to what is predicted by the positive column model it is found that $T_e$ does not stay constant along the column, but monotonically increases with the distance from the microwave launcher. Increases of more than 50% over 30 cm were found.

5.1 Introduction

Microwave induced plasmas (MIPs) are successfully applied in atomic spectrometry where they can act as excitation sources for optical emission spectrometry, ion sources in mass spectrometry and chromatography or as components of tandem plasmas. There is a wide variety of MIPs [1, 2] that can be classified as cavities (resonators) [3, 4], surface wave plasmas [5], torches [6, 7] or micro plasmas [8].

This paper is devoted to the axial non-uniformity of surface wave plasmas a sub class of MIPs that can be characterized by the common feature that the plasma creating electromagnetic wave propagates along the interface between the plasma and a dielectric, for instance a quartz tube. In this way stable discharges can be created of different lengths in a wide range of pressures. Some examples of surface wave launchers are the surfatron [9], the surfaguide and the waveguide surfatron [10].

The easiest way to produce surface wave-sustained plasmas at low and intermediate pressure is offered by the surfatron, the launcher dealt with in the current study. Its flexibility is one of the reasons why surfatron induced plasmas (SIPs) are extensively used and studied. Several theoretical models have been developed to understand the fundamentals of SIPs and to predict their operational properties [11–15]. Particularly [16] gives an extensive and recent review. Various experimental studies have been performed among others to validate the models [17–24]. Many experiments are based on spectroscopy; they can be divided into passive and active methods. Passive spectroscopy has the advantage that only the light produced by the plasma is analysed. So, in contrast to e.g. electrical probe measurements, the method is not intrusive. However, the interpretation of line radiation in terms of the main plasma properties, the electron density $n_e$ and electron temperature $T_e$, is not simple. For that purpose models are needed that account for the state of equilibrium departure. In the case of low pressure SIPs, the discharge is far from equilibrium so that indeed models are indispensable. In [25, 26] we presented a collisional radiative model to interpret the absolute intensities of the argon 4p lines. Less sensitive to the degree of equilibrium departure is the method of absolute continuum measurements [27]. In [28] we recently published a method based on the simultaneous measurements of the absolute line and continuum intensities from which $n_e$ and $T_e$ can be obtained in an iterative way. This method was applied to atmospheric argon
plasmas created by the Torch à Injection Axiale but can easily be applied to other plasmas as well.

Another way to determine $n_e$ and $T_e$ is Thomson Scattering (TS). This is an active spectroscopic method based on the scattering of laser photons by the free plasma electrons. It is a direct way of measuring the properties of the electron gas in the sense that it does not need any model that accounts for the state of equilibrium departure. Moreover, this technique also gives accurate results of $n_e$ and $T_e$ with high spatial and temporal resolution, and it can be applied over a wide variety of discharges [29–33]. In [34] an overview is given by Warner and Hieftje on Thomson scattering performed on analytical plasmas dealing with studies before 2001. Later studies on spectrochemical plasmas were published related to high precision TS [35] and single shot TS [36].

Disadvantages of TS are that it is expensive and experimentally demanding. The main reason for the latter is that the cross section for the photon-electron interaction is very small ($\sim 10^{-29} \text{ m}^2$). This implies that the TS process is very inefficient and that TS photons are easily lost in the signal created by Rayleigh scattering or false stray light; that is light coming from the laser reflections on the plasma vessel window and/or dust particles.

In [37] TS was for the first time applied to intermediate-pressure SIPs. For that purpose a new experimental setup was constructed and built to tackle the specific experimental challenges. The plasma tube was sealed by Brewster windows to minimize laser reflections; a high quality laser with a Gaussian beam profile was used to avoid direct contact of the laser (side beams) with the quartz tube. A triple grating spectrograph (TGS) [38] was used to block the Rayleigh and false stray light photons and to disperse the remaining Thomson photons.

The work done in [37] led to several interesting results. Investigating the region close to the launcher we obtained values for $n_e$ and $T_e$ in the order of $10^{19} \text{ m}^{-3}$ and 1.3 eV, which are in reasonable agreement with the results of older measurements [18, 21, 24, 26, 27]. It was proved that for a given geometry $T_e$ mainly depends on the pressure while $n_e$ increases with the microwave power. In [39] we performed a poly-diagnostic study; a method that determines $n_e$ and $T_e$ using several different experimental techniques at the same time and on the same plasma position (again close to the launcher). Apart from TS also the Stark broadening of $\text{H}_\beta$ and absolute line and continuum measurements were performed. In this way we could determine the validity regime of the different methods. As a by-product we could extrapolate the Stark broadening
The $H_β$ method down to values of $n_e = 10^{19} \text{ m}^{-3}$. That is a factor 10 lower than the application limit of Stark broadening theories that are commonly used.

As stated before, most the results obtained in [37] in which plasma regions close to launcher were investigated were in reasonable agreement with (global) plasma models and other diagnostics techniques. However, one of the main characteristics of a SIP, namely the axial dependence of plasma properties, could not be studied with the setup used at that time since it was not possible to perform accurate measurements as a function of axial position.

In this paper, we present axial TS measurements applied for the first time on intermediate-pressure surfatron plasmas. For this purpose we designed and built a new setup based on the previous one, but improved so that axial measurements could be accomplished precisely. In the new setup the whole plasma tube and the supporting table can be translated while the plasma remains aligned along the laser beam. This allows TS measurements on any position of the plasma column without changing other parts of the optical setup. Other improvements are the use of laser that delivers more energy per pulse and a more sensitive iCCD camera; both contribute to the reduction of the measurement time and to an improvement of the accuracy.

The experiments have been performed on pure Ar surfatron plasmas created in a tube with inner radius of 3.0 mm, in the pressure range of $6 - 20 \text{ mbar}$ and for microwave power between 30 and 80 W.

The axial $n_e$ profiles show a quasi-linearly decreasing behavior along the column, that is $\partial n_e / \partial z \approx \text{Cnst}$. This constant increases with pressure but is independent of the power. The effect of the power is that when it increases the plasma becomes longer. These findings are in agreement with the trends predicted by models. However, extrapolating the axial $n_e$ profile assuming a constant slope leads to $n_e$ values at the end of the column that are much larger than the critical density; the $n_e$ value obtained by equating the (modified) frequency of the wave to the plasma frequency.

The $T_e$ profiles obtained with TS show that, in agreement with model predictions, the $T_e$ values at the launcher, increase when the pressure drops. However, we found that $T_e$ does not stay constant along the column, but monotonically increases with the distance from the wave launcher.

This paper is organized as follows: section 5.2 deals with the experimental setup, with special emphasis on the improvements made to measure axial de-
pendencies accurately; in section 5.3 the results are presented, discussed and compared with previous studies; the results are followed by the conclusions in section 5.4.

5.2 Experiment

5.2.1 Thomson scattering

Thomson Scattering is the scattering of photons on free electrons. For an in-depth treatment we refer to [34, 37, 38].

In case of the relatively low values of $n_e$ and high $T_e$ observed in the plasmas under study we deal with non-collective scattering. This means that electrons respond individually to the laser photons. Just as in our previous works [37, 39] we used a double perpendicular scattering geometry, meaning that the observation direction is perpendicular to the direction of the incident radiation ($\theta = 90^\circ$) and that the incident radiation is polarized perpendicularly to the plane of scattering. Considering the double perpendicular geometry, the wavelength of the incident radiation used (532 nm), and assuming a Maxwellian electron energy distribution function for the bulk part of the electrons, the TS spectrum has a Gaussian shape. From this $T_e$ can be determined using the expression:

$$T_e = 5238 \times (\Delta \lambda)_{T_e}^2 (\text{Knm}^{-2}).$$

The electron density can be obtained from the fact that in our case of incoherent TS the total scattered power, $P_T$, is directly proportional to $n_e$. In order to calibrate the TS setup, rotational Raman scattering on nitrogen is used [40, 41]. By combining the expressions for Thomson and Raman scattered power one gets:

$$n_e = n_m \frac{P_T}{P_{Rm}} \frac{\Gamma_{Rm}}{\Gamma_{Tm}},$$

where $P_{Rm}$ is the power of the Raman scattering, $n_m$ the density of scattering molecules while $\Gamma_{Rm}$ represents the ratio between the Raman and TS cross sections. This factor is calculated by taking the weighted sum of the differential cross sections of all individual rotational transitions in which the weight factor accounts for the occupation of the rotational levels at room temperature. This sum is subsequently divided by the differential Thomson cross section.
For the Raman we used $N_2$, and for the perpendicular geometry the value of $\Gamma_{Rm}$ was calculated in [42] and found to be $\Gamma_{Rm} = 8.15 \times 10^{-5}$. Since the Raman measurements are taken at room temperature under a controlled pressure, the density of scattering molecules, $n_m$, is known by means of the ideal gas law. So, once the total TS ($P_T$) and Raman ($P_{Rm}$) intensities are experimentally measured, equation (5.2) can be used to deduce $n_e$ from the known $n_m$ value.

![Figure 5.1: Schematic view of the setup showing the three-fold structure of laser (left), plasma source (bottom) and detection branch (top). The horizontal bolded arrows along the plasma tube indicate that it can be translated along its own axis; an essential feature of this renewed setup. The vertical bolded arrows refer to micrometric screws that can tune the transversal tuning of the tube position. The numbered components have the following meaning: 1 – 45° mirror; 2 – beam dump; 3 – beam splitter; 4 – 1m plano-convex lens; 5 – Brewster window; 6 – achromatic lens; 7 – entrance slit; 8 – image rotator; 9 – grating; 10 – mask; 11 – intermediate slit.]

5.2.2 The setup

The experimental setup, depicted in figure 5.1, shows a three fold structure: the laser setup, the plasma source and the detection branch. Most of the components are discussed in detail in [26, 27, 36]. Here, we confine ourselves to
Thomson scattering

the information that is essential for the changes in the setup together with the explanation needed to make the paper self-contained.

The laser

The SL312 Expla laser used in [37] is replaced by a laser with higher power, a Continuum Laser, model Precision II 8010. It is a frequency doubled Nd:YAG laser producing 8 ns pulses with a repetition rate of 10 Hz; the maximum pulse energy is approximately 700 mJ at 532 nm. With this laser the measurement time can be shortened by a factor of 2 and now accounts 16 min for the determination of $n_e$ and $T_e$ at one plasma position. Moreover, it is easier to investigate the influence of the laser power. The power level can be selected by using different beam splitters. For safety reasons the route of each laser (side) beam is terminated with a beam dump. Another improvement that greatly simplifies the current setup is that, contrary to the previous laser system, this version produces vertically polarized radiation. So the laser beam can be guided directly into the surfatron plasma while having the perpendicular geometry needed for TS.

The surfatron setup

The plasma is generated by the absorption of electromagnetic waves of 2.45 GHz in an argon flow. The microwave generator is a Muegge type MG0300D-200TC. The flow rate and the pressure inside the quartz tube can be measured and controlled using a mass flow controller and pressure meters. The tube has an inner radius of 3.0 mm and an outer radius of 4.0 mm. Brewster windows are attached to both tube-ends with the aim to minimize laser reflections.

An essential change is that the whole surfatron setup can be translated along its own axis as indicated in figure 5.1 by the arrows (anti-) parallel to the wave propagation direction. The axis coincides with the laser beam. An accurate parallel co-axial translation is required to keep the alignment of the system unchanged and to avoid scattering of laser light on the tube wall. Fine-tuning for correcting the tube position in the directions transversal to the laser beam can be achieved via micrometric screws; in figure 5.1 the function of these micrometer adjustment screws are indicated by the vertical arrows.
The detection branch

For the detection of the TS signal a home-made triple grating spectrograph (TGS) is used [42]. The TGS is designed with the purpose to reject false stray light and Rayleigh scattered photons, and to disperse and collect the signal. The combination of the first two gratings form a notch filter whereas the final dispersion is performed by the third grating that sends the dispersed image to an iCCD. The 4Picos (Stanford computer optics) iCCD used in [37] is replaced by an Andor type DH534 that can be cooled so that by reducing the noise level better detection limits can be obtained.

5.2.3 The experimental procedure

Once the surfatron is aligned along the laser beam and the TGS is focused onto the detection volume, the setup is ready to perform TS experiments. Each TS measurement is obtained by accumulating the photons of $10^4$ laser shots. A dark current and background measurements are subtracted in order to get the pure TS spectrum. The spectrum is processed to find the best Gaussian fit. The width and area of the resulting fitting curve are used to find $T_e$ (equation (5.1)) and $n_e$ (equation (5.2)) respectively.

To perform Raman scattering, the tube is filled with nitrogen at a control pressure, normally 50 mbar. Then for the same laser power, number of shots, exposure time, and alignment conditions the Raman spectrum is collected. Measuring the total intensities of the Raman and TS spectra the electron density can be obtained using equation (5.2). The Raman calibration is also used to measure the spectral dispersion of the setup. Since all the Raman transitions for nitrogen are well-known, the dispersion can be obtained measuring the distance between two of the Raman peaks. The dispersion is found to be $119.88 \pm 0.46$ pixels/nm for the present setup. Obtaining the width of the TS spectrum and using this dispersion, $T_e$ can be calculated employing equation (5.1).

When the setup is aligned, meaning that the mechanical axis of the surfatron table is parallel to the laser beam and that the beam coincides with the central axis of the surfatron tube, the whole surfatron setup can be translated along its own axis, keeping for all the positions the laser-alignment in tact. So the laser path is never changed and the detection volume (that is the volume observed by the TGS) remains at the same position in the laboratory frame.
We simply move the plasma tube along its axis to place the detection volume at different plasma positions. It is important to realize that the measurements are taken on the axis of the discharge. In contrast to many spectroscopic and interferometric methods [21, 26] they do not provide radially averaged results but deliver the plasma properties of the small detection volume that is formed by the intersection of the laser beam and the optical axis of the detection system.

The process to perform TS measurements at different axial positions is rather simple once the setup is aligned. Beginning at a certain position the tube is filled with nitrogen at a pressure of \(50 \text{ mbar}\) for Raman calibration. Later the tube is filled with argon at the chosen pressure and the discharge can be ignited. For the subsequent measurement the discharge is switched off and the setup is translated to the next axial position. If necessary, minor (radial) realignments can be done. The discharge can now be re-ignited under the same pressure and power conditions. After a stable plasma condition is reached new TS measurements can be done at that new axial position. Raman calibration could be taken for every axial position, but we have checked that the different Raman spectra measured at different positions give practically the same intensity values.

Taking in average six TS measurements to cover a plasma column at a certain pressure and microwave power, the time needed to finish with one discharge condition is about five working hours.

Since the setup is mainly the same as the one used in [37] the error analysis is similar. The main differences come from the use of a different iCCD camera with a smaller pixel size and therefore a higher number of pixels per nanometer. With the new setup the total random error for the electron density is 7\%. There is also a systematic error in \(n_e\) caused by the uncertainty in the cross-section for Raman scattering. This systematic error is equal to 8\% [43]. The total random error for the electron temperature is estimated to be 6\%.

The emitted plasma signal is collected by a two-dimensional iCCD camera giving spectral information in the horizontal and spatial information in the vertical direction. Each TS frame covers a plasma length of 1.2 cm. A pixel binning process is applied in spatial and spectral direction in order to reduce the noise and smooth the spectra. After pixel binning the frame is divided in 15 different spectra, each one of them is processed separately and produces a result of \(n_e\) and \(T_e\) with the relative errors given previously. To obtain the final result for one TS measurement, the 15 results are averaged. This averaging reduces the random errors with a factor \(\sqrt{15}\). In conclusion the averaged result for any
TS measurement has a final relative error of 8% for $n_e$ and 3% for $T_e$.

In order to study the influence of the laser beam on the plasma we performed TS for 3 different values of the laser pulse energy 50, 110 and 180 mJ. The variation in the $n_e$ and $T_e$ values was within 3%, thus comparable to the random error margins. This means that for the plasma under study, TS can be seen as non-intrusive.

5.3 Results and discussion

TS measurements are done on surfatron argon plasmas in the pressure range of 6 – 20 mbar realized with an argon flow rate of 50 sccm. The absorbed powers were selected in the range between 32 – 82 W. The precise value was determined by subtracting the reflected from the forward (= applied) power. The result was reduced by 5% accounting for the absorption in cables and connections.

The positions in the plasma on which TS are performed are specified by their distance to the end of the column (DEC). This is in contrast to what was done in [37], where the positions were expressed in their distances to the launcher. The advantage of working with the DEC coordinate is that this representation is the same as that used in most of the previous models and experiments [11, 15, 17, 22]. According to the theories, increasing the power implies that a new, more energetic plasma slab is added at the launcher side while the “old” plasma (as sustained with the previous lower power level) is shifted towards the end. During this shift the properties of “old” plasma remain the same. This assumed behaviour, denoted the “DEC congruence”, has been validated several times with different diagnostic techniques [17–20, 22]. However, in [44] deviations from DEC congruence were found. It was observed that the axial profile of the electron density in a hydrogen plasma is a function of the absorbed power; a peculiarity that can be related to the change in the gas temperature when the power is changed.

A disadvantage of the DEC coordinate is that the zero point, $z = 0$, located at the end of the plasma column, is not an exact position. The reason is that the plasma is rather fuzzy at the end. First, we explore and discuss the general properties of the axial $n_e$ and $T_e$ profile for the standard condition of 32 W and 20 mbar. After that, the trends are studied when the power and pressure are changed.
5.3.1 The axial $n_e$ profile for standard condition

In figure 5.2, the axial $n_e$ profile is shown for the standard condition with a pressure of $p = 20$ mbar and power of $P = 32$ W. Under these conditions the plasma was found to have a length of 25 cm while the profile shows a linear decrease of $n_e$ within the measured accuracy. The almost constant slope, $\partial n_e / \partial z = \text{Cnst}$, found in the current study has been measured many times for instance by means of interferometric methods [17–21] and the absolute continuum intensity method [27].

![Figure 5.2: The axial electron density profile for an argon plasma; gas pressure 20 mbar and microwave absorbed power 32 W. The $n_e$ values are given as function of the distance to the end of the column $z = \text{DEC}$, the position of the surfatron launcher is at the left side of the graph ($z = 25$ cm).](image)

Sample code is given in figure 5.2.

The decrease of $n_e$ along the tube can be understood realizing that the energy transfer from wave to plasma reduces the power content of the wave. As a consequence the less energetic wave can not create plasmas of the same $n_e$ value. The plasma power density, $\varepsilon$, associated to the energy transfer can be related

\[ \text{Note that in contrast to other chapters, where } z \text{ refers to the distance from the launcher here it gives the distance to the end of the column (DEC).} \]
to the electron density via
\[ \varepsilon = n_e \theta, \]  
(5.3)
where \( \theta \), the power to sustain an electron-ion pair in the plasma, is (almost) constant along the plasma column. Now, since the EM power decreases along the wave, \( \varepsilon \) goes down as well. This leads via equation (5.3) to a decrease in \( n_e \). That is what we see in figure 5.2. To obtain a quantitative expression for the slope \( \partial n_e / \partial z \) one has to solve the plasmas equations in combination with the wave equation; for this we refer to [11, 12].

Close to the launcher a deviation from the \( \partial n_e / \partial z = \text{Cnst} \) trend is present; a behavior that was also found in our previous studies [26, 27], where \( n_e \) was determined from the continuum emission intensity. In literature [22] this deviation is attributed to the fact that in this wave-shaping region the wave is not yet developed to a pure surface wave. Since this plasma region is strictly speaking not part of a surface wave plasma we will not pay further attention to it.

Of more interest is the region at the end of the column, \( z = 0 \), the reference point of the other axial positions. Note that the \( z = 0 \) position is determined from the visual inspection of the end of the plasma. A method that is far from accurate since the plasma edge is rather fuzzy. However, we had no other way to locate \( z = 0 \).

In general treatments of surface wave sustained plasmas it is assumed that the wave will propagate creating and sustaining the discharge until \( n_e \) reaches a critical density. The value of this critical \( n_e \) value depends on the plasma conditions that can be divided in two regimes depending on the ratio \( \nu / \omega \), where \( \nu \) is the collision frequency for electron-atom momentum transfer and \( \omega \) is the angular frequency of the wave. In the low pressure case for which \( \nu \ll \omega \), the plasma-wave interaction is called collision-less, and the value of the critical density is determined by the expression:

\[ n_c = 3.14 \times 10^{-4} \omega^2 (1 + \varepsilon_g), \]  
(5.4)
with \( \varepsilon_g \) the relative permittivity of the discharge tube material. In the case under study \( \varepsilon_g = 3.84 \) for a quartz tube and \( \omega = 2\pi \times 2.45 \) GHz, we have \( n_c = 3.5 \times 10^{17} \, \text{m}^{-3} \).

In literature e.g. [18, 21] the plasma is assumed to be in the collision-less regime for similar geometries and pressures up to 15 mbar. Thus, most of our measurements were done in or close to the collision-less regime. This means that according to theory the plasma column should finish at \( n_e = 3.5 \times 10^{17} \, \text{m}^{-3} \).
However, extrapolating figure 5.2 gives a much higher $n_e$ value for $z = 0$; with $n_e = 1.5 \times 10^{19} \text{m}^{-3}$ it is close to 40 times larger than $n_e$. This implies that the $\partial n_e / \partial z = \text{Cnst}$ trend can not be extrapolated till $n_e$ is reached and that apparently some low density plasma is missing at the plasma end. This “missing plasma” has a length of about 12 cm.

This is in agreement with the results of the measurements presented in [18, 21], where for a similar range of pressures, a simple extrapolation to the plasma edge does not give the critical value as predicted by equation (5.4). This deserves further experimental and theoretical studies.

5.3.2 The axial $T_e$ profile for standard condition

The temperature values for the various plasma conditions and positions were obtained using a Gaussian fitting procedure based on the following recipe

1. find the baseline of the TS spectrum in question,
2. subtract the baseline,
3. fit the remaining spectrum with a Gaussian function,
4. determine $\Delta \lambda / \epsilon$, the half width of the distribution,
5. use equation (5.1) to determine $T_e = 5238 \times (\Delta \lambda)^2 / \epsilon$.

Figure 5.3 demonstrates the results obtained for a typical example. It gives the Gaussian fit of the number of counts $P(\delta \lambda)$ as a function of the wavelength shift $\delta \lambda = \lambda - \lambda_0$, the base line and the residue. The latter shows apart from positive also negative values, as should be. In the wings the residue can be larger than the corresponding value of the Gaussian fit. These negative values should be treated with care in the interpretation of the experimental results [30].

An alternative way to determine the electron temperature is to plot the logarithm of the signal $P$ as a function of $\delta \lambda = |\lambda - \lambda_0|$. As a Maxwellian EEDF leads to [34]:

$$P(\delta \lambda) = A \exp \left( -\frac{m_e c^2 (\delta \lambda)^2}{4 \lambda_0^2 k_B T_e} \right)$$

(5.5)

where $A$ is a constant and $c$ the velocity of light, we may expect that $\ln P(\delta \lambda)$ versus $(\delta \lambda)^2$ gives a linear trend. This method was used in the past in [33] not
Figure 5.3: The number of counts \( P(\delta \lambda) \) as a function of the wavelength shift \( \delta \lambda = |\lambda - \lambda_0| \) (Experimental) fitted by a Gaussian (Gauss fit) superimposed on a base line (Base line). The gap in the central region around \( \delta \lambda = 0 \) is due to the blocking of the signal around the central wavelength, an action of the TGS that is needed to reduce the influence of Rayleigh photons and false stray light. The residue of the fitting given just above the \( x \)-axis (Residue) shows apart from positive also negative values, as should be.

only to determine the \( T_e \) values but also to control whether the electron energy distribution function is Maxwellian.

Figure 5.4 gives the result of this linear fitting procedure applied to the right wing of the curve given in figure 5.3. It is evident that the scatter increases with \( \delta \lambda \) and that only the signal corresponding to relatively small \( \delta \lambda \) values can be used to determine the temperature. Note that for large \( \delta \lambda \) values several data points are missing; they create gaps in the graph. The reason is that the base line subtraction leads, apart from positive also, to negative numbers and these cannot enter into the logarithm. From this we may conclude that the distribution can only be constructed from the first 3 nm of wavelength shift or so, which corresponds to kinetic energies of 4.5 eV [34]. Since the excitation of the argon ground state demands energies of at least 12 eV it can be expected that deviations of the EEDF from the Maxwell distribution will appear for higher
energies. In particular it is expected that the tail ($>12\ eV$) of the EEDF will be under-populated. However, this tail-depletion can not be observed. Hereafter we present the $T_e$ values as obtained with the Gaussian fit procedure.

Figure 5.4: Logarithm of the number of counts $P(\delta \lambda)$ as a function of the square of the wavelength shift, $(\delta \lambda)^2$, after the baseline subtraction. The result shows the expected linear tendency for the first $7\ nm^2$. For higher wavelength shifts the noise obscures the signal. For $(\delta \lambda)^2 > 13\ nm^2$ there are in total of 13 points, 8 of them have negative values and do not appear in the figure since the logarithm of a negative value can not be taken.

Figure 5.5 gives the axial $T_e$ profile for the standard condition, thus the condition corresponding to figure 5.2. In the first $10\ cm$ close to the launcher $T_e$ increases slightly, but around $z = 15\ cm$ it increases fast from 1.2 to 1.4 eV. This axial gradient in $T_e$ is in contradiction with experimental findings and theoretical predictions given by the so-called positive column (PC) approach [10, 11]. This PC approach used in the microwave modeling community is often used as the bases of global models for other kind of plasmas [36, 45, 46] and based on the electron particle balance. In simplified form this balance can be written as

$$n_e N k_{ion}^*(T_e) = -\nabla \cdot (D_{amb} \nabla n_e),$$

(5.6)
where $N$ is the density of the argon ground state while $k^*_\text{ion}(T_e)$ stands for the effective ionization rate. Since the coefficient for ambipolar diffusion, $D_\text{amb}$, is inversely proportional to the gas density we can transform the above equation into

$$k^*_\text{ion}(T_e) = D^*_\text{amb}(Na^*)^{-2}, \tag{5.7}$$

where $D^*_\text{amb} = D_\text{amb}N$, and $a$ the effective diffusion length which is in the order of the plasma radius. The latter comes into play by applying the divergence and gradient operator to a certain assumed profile.

At reasonable high $n_e$ values the effective ionization rate is equal to the rate of ground state excitation; i.e. $k^*_\text{ion}(T_e) = k_{\text{ex}}(T_e)$. The reason is that all excitation processes are followed by subsequent step-wise ionization processes since radiative decay is overruled by electron excitation. This ladder-like excitation towards the continuum makes $k^*_\text{ion}$ independent of the electron density [25, 36, 45, 47]. However, $k^*_\text{ion}$ is a strong function of the electron temperature so that equation (5.7) states that $T_e$ is determined by the product $Na$. Since both $N$ and $a$
are constant as function of axial position its is expected that \( T_e \) will be constant as well.

Our observation that \( T_e \) increases approaching the plasma end is in violation with these theoretical considerations. A possible explanation for the discrepancy might be that, in contrast to the assumption used in global models [36, 37, 45], \( k^*_{\text{ion}} \) is not independent of the electron density and that, under certain conditions, a lower \( n_e \) leads (for the same \( T_e \) value) to a smaller \( k^*_{\text{ion}} \) value. Traveling along the axis towards the plasma end \( n_e \) decreases so that the associated negative effect on \( k^*_{\text{ion}} \) can only be compensated by an increasing \( T_e \).

Two mechanisms may be responsible for the \( n_e \) dependence of \( k^*_{\text{ion}} \):

- For low \( n_e \) values radiative transitions will block the step-wise ionization process.
- For low values of \( n_e/N \) the tail of the electron distribution function (EEDF) will be depleted.

In both cases a decrease in \( n_e \) (or \( n_e/N \)) leads to a decrease in \( k^*_{\text{ion}}(T_e) \) and in order to keep the creation of e-i pairs on level (as requested by the right hand sight of equation (5.7) the plasma has to attain a higher \( T_e \) value.

In [26] we applied a hybrid method to a comparable SIP. The absolute line intensity (ALI) measurements of the 4p emission combined with a collisional radiative model (CRM) gave \( T_e \) values for various axial positions. The result of this ALI-CRM method supports the global model results: i.e. \( \partial T_e/\partial z \approx 0 \). And therefore it is in violation with the TS findings reported here. In the CRM procedure the escape of radiation for low \( n_e \) cases is taken into account. What is not corrected for is the influence of the EEDF tail depletion; the excitation and ionization rate coefficients used in the CRM are based on a Maxwellian EEDF. So most likely the origin of the discrepancy between ALI-CRM together with the global model at the one hand and TS on the other hand must be searched in tail depletion of the EEDF. It should be realized that TS measures the bulk temperature while the global model and ALI-CRM give a temperature based on a mixture of the bulk and tail.

In [14, 15] a model for a surfatron induced plasma is developed in which also an axial temperature gradient is found \( \partial T_e/\partial z \neq 0 \). In the more advanced model [15], the axial behaviour of \( T_e \) is attributed to the axial variation of the EEDF, which deviates from the Maxwellian distribution as the electron density...
goes down towards the column end. These results seem in agreement with our suggestion that the EEDF tail depletion is responsible for the $T_e$ gradient. However, the behaviour in [15] is found for a $n_e$ range that is approximately 10 times lower than what was found experimentally. Moreover, this $n_e$ range could not be found experimentally (sections 5.3.1 and 5.3.4). The topic of the axial $T_e$ gradient needs more investigation.

5.3.3 Dependence on the microwave power

Figure 5.6 shows the axial $n_e$ and $T_e$ profiles for increasing microwave powers for the constant pressure of $p = 20$ mbar. The applied powers are 32 W, 59 W and 82 W, and the corresponding column lengths are 25 cm, 36 cm and 45 cm respectively.

Figure 5.6(a) shows that the axial $n_e$ profiles do not change in slope as the microwave power increases; they only get enlarged. This is in agreement with the DEC congruence assumption: when more power is introduced, a new high-$n_e$ plasma segment is added at the position of the launcher while the old plasma shifts in the wave propagation direction in unaltered form. Figure 5.6(b) shows that in the new added high-$n_e$ plasma slaps $T_e$ goes down, albeit slowly, so an asymptotic tendency is found. This asymptotic value should be considered as a theoretical value at a position far away from the end of the column, $z \to \infty$.

5.3.4 Dependence on the gas pressure

Figure 5.7 shows the dependence of the axial values of $n_e$ and $T_e$ on the pressure. The absorbed microwave power is kept constant at 32 W, and the gas pressures are 20 mbar, 10 mbar and 6.5 mbar. The corresponding column lengths are 25 cm, 32.5 cm and 34 cm respectively; thus for decreasing pressures the plasma length increases. Moreover, figure 5.7(a) suggests that there is a tendency that the slope increases with pressure. Both observations are in global agreement with previous studies [18–20, 22, 26].

An interesting observation is that by reducing the pressure from 20 mbar to 10 mbar the extrapolated $n_e$ value found at the plasma end approaches the critical density $n_c$ more closely. To state it differently, in the case of 10 mbar we are missing only 1.5 cm plasma whereas this is 12 cm for $p = 20$ mbar. However, this trend is not continued; if we further reduce the pressure from 10 to 6.5 mbar
the missing plasma length increases again from 1.5 to 5 cm.

Figure 5.7(b) again shows that $T_e$ is not constant along the column and approaches a sort of asymptotic value at the launcher. This asymptotic $T_e$ value increases as the pressure decreases. This can be explained using equation (5.6); if the pressure goes down (or better: $N$ goes down), the losses by diffusion

Figure 5.6: Axial profiles of $n_e$ (a) and $T_e$ (b) for gas pressure 20 mbar and different microwave absorbed power. The results are presented as function of the distance to the end of the column. The arrows mark the position of the surfatron launcher for every condition; cf. note related to figure 5.2.
increase and therefore a higher $T_e$ is needed to sustain the discharge.

To obtain a representative value for the temperature of each column we take the asymptotic value of the profiles for $z \to \infty$. The asymptotic temperatures values are $1.08\,\text{eV}$, $1.28\,\text{eV}$ and $1.31\,\text{eV}$ for the pressures of 20 mbar, 10 mbar and 6.5 mbar respectively. These values are in good agreement with those ob-
tained by passive spectroscopy techniques [24, 26] and with the predictions of the positive column model equations (5.6), (5.7) and [10, 17].

5.4 Conclusions

An essential feature of surface wave discharges is that the plasma parameters change along the wave-propagation direction. Many theoretical and experimental studies have been employed in the past to study this behaviour, but direct insight in the properties of the electron gas could not be obtained. This forms a serious shortcoming in the understanding of these types of plasmas since the electrons are the most essential particles: they absorb the wave EM field.

In this study, we report the measurements of the electron density, \( n_e \), and electron temperature, \( T_e \), of argon surface wave induced plasmas created in the pressure range of \( 6 - 20 \) mbar and for microwave power between \( 32 \) and \( 82 \) W for a plasma with a radius of \( 3 \) mm. These essential plasma parameters, \( n_e \) and \( T_e \) were obtained by applying Thomson scattering in a way that was found to be non-intrusive.

In order to measure the axial profiles \( n_e \) and \( T_e \) we had to rebuild our Thomson Scattering setup. In the new setup the whole plasma and the supporting table can be translated while the plasma remains aligned to the laser beam. The detection volume remains at the same position in laboratory frame. This implies that for changing the axial plasma position the whole plasma setup has to be moved such that the new axial plasma position is brought into the spatially fixed detection volume. This method largely favours the plasma-reproducibility so that the values and trends in \( n_e \) and \( T_e \) as a function of axial position could be obtained with great precision. It is our strong believe and hope that the results of this experimental study can be used to boost future theoretical studies.

With respect to the axial \( n_e \) profiles we report that an almost linear behaviour is found that can be expressed as

\( n_e(z) = Az + B, \)  

(5.8)

where \( z \) is measured from the plasma end in the contra-wave propagation direction. The slope \( A \equiv \partial n_e/\partial z \) is close to constant for any plasma setting under study and depends on the pressure; increasing the pressure gives larger \( A \) values. Extrapolation of the found axial \( n_e \) curve towards the plasma end shows that

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\[ B \equiv n_e(z = 0) \] is much larger than the critical value \( n_c \), as predicted by theories based on the assumption of a collision-less wave-plasma interaction. This value of \( n_c \), being close to the value that is obtained by equating the plasma frequency to frequency of the exciting wave, equals \( n_c = 3.5 \times 10^{17} \text{ m}^{-3} \). It is found that \( B \) depends on the pressure. For 20 mbar we found \( B = 1.5 \times 10^{19} \text{ m}^{-3} \) while for 6.5 mbar a value of \( B = 4.2 \times 10^{18} \text{ m}^{-3} \) was found. This points to a deviation from the theories based on the collision-less approach. The density behaviour at the plasma-end remains an interesting topic for future investigations.

With respect to the \( T_e \) profiles we report that close to the launcher i.e. far away from the column end, \( T_e \) values are found that are more or less equal to the results predicted by global models. They follow the trend that an increase in pressure leads to a decrease in \( T_e \). However, and that is the most striking result of this study, we found that \( T_e \) is gradually increasing in the direction of decreasing \( n_e \). Increases of about 50\% over 30 cm were found. From the two possible explanations, namely the role of radiation escape or the EEDF-depletion the latter one is the most likely. This interesting and counter-intuitive behaviour of the electron temperature deserves much more attention in future studies.

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References

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Axial profiles of the atom density and gas temperature of intermediate pressure surfatron plasmas found with Rayleigh scattering

Abstract. The axial profile of the heavy particle density and temperature of surface wave plasmas are determined using Rayleigh scattering. The plasma is generated at a frequency of 2.45 GHz in argon by a surfatron operating under the standard settings of a power of 100 W, a flow rate of 50 sccm and a pressure of 20 mbar. To investigate the effect of the pressure on the axial gas temperature we also investigated 6 and 10 mbar plasmas. By using a 2 dimensional intensified CCD array we could determine and eliminate the influence of false stray light; a mayor disturbing factor in the determination of the Rayleigh signal. In order to trace the energy fluxes that determine the gas temperature we performed Thomson scattering so that the properties of the electron gas are known. It is found that the gas temperature mainly depends on the pressure and follows axially the electron density, meaning that it is highest at the launcher and decreases monotonically in the wave propagation direction. The maximum gas temperature of around $T_a = 800$ K is found close the launcher for the highest pressure of 20 mbar. For lower pressures we find lower $T_a$ values. In all cases, the extrapolation of $T_a$ toward the end of the plasma column leads to a temperature of about 350 K which is close to room temperature.
6.1 Introduction

Surface-wave discharges, form a special type of microwave induced plasmas, that have been studied and investigated systematically. Due to their broad range of operating conditions, stability and reproducibility they have received many technological applications. In order to further improve these applications, insight into plasma parameters is needed. This can be achieved by modeling and experiments or even better by a combination of these methods.

In many experimental and theoretical methods a lot of attention is paid to the properties of the free electrons. They deserve attention as they are the most active particles and so it is important to know their temperature and density. However, it is also important to know the density and the temperature of the main plasma constituent. Dealing with atomic plasmas of low degree of ionization this is the collection of atoms in the ground state. The density and temperature hereafter denoted by \( n_a \) and \( T_a \) are connected to each other by the pressure \( p = n_a k_B T_a \), a quantity that is usually easy to measure. This implies that only one of the parameters \( n_a \) of \( T_a \) has to be determined; knowing (at given \( p \)), \( n_a \) gives \( T_a \) and vice versa\(^1\).

The knowledge of \( n_a \) or \( T_a \) is important for models and experiments. For instance in the method of absolute line intensities (ALI) the density of the ground state is combined with that of excited radiating species. From this density ratio the electron temperature can be deduced by employing the results of a collisional radiative model \([1]\). The measurement of the continuum of atomic plasmas can give the electron density \([2, 3]\). In case the degree of ionization is small the atoms are the main scatter partners of the electron so that again the \( n_a \) value is needed for a correct interpretation of the continuum spectrum.

In modeling plasmas \( n_a \) is an essential parameter. It is an important factor in the determination of the rate of the elastic and inelastic collisions and thus for a proper understanding of the plasma heating and the creation of light and radicals.

In literature several methods can be found to measure \( n_a \) or \( T_a \). Generally they can be divided as based on emission spectroscopy \([4]\), laser absorption

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\(^{1}\)In this thesis, sometimes we replace the notation for the atom density \( n_a \) by \( n_1 \), which is justified since most of the atom density contribution is delivered by the ground state density \( n_1 \). Replacing \( T_h \) by \( T_a \), is allowed since there is no difference between the temperature of the atoms \( T_a \) and the rest of the heavy particles.
spectroscopy [4–7] and laser scattering [8]. In case of emission spectroscopy the \( T_a \) can for instance be obtained from the rotational temperature of excited molecular species. A disadvantage of applying this method to atomic plasmas is that an addition of molecules is required and this will change the plasma properties substantially. The same applies to the Doppler broadening experiments for which small amounts of \( \text{H}_2 \) are introduced. Apart from the fact that the addition of \( \text{H}_2 \) changes the plasma drastically it is also found that the different H-lines give different temperatures [9]. This makes the method far from reliable.

In [10, 11] also Regt the \( T_a \) is derived from the Doppler width of the absorption transition \( 4s \rightarrow 4p \) in argon. This method, for which an accurately tunable narrow band laser is needed gives line-of-sight information. Methods are needed to convert the lateral spectral profiles into spatially resolved temperatures.

In this work, we determine the main gas properties using Rayleigh scattering (RyS). That is the elastic scattering of (laser) photons by electrons bound to heavy particles. RyS is familiar to TS in the sense that both are related to scattering of photons on electrons. In the case of TS the electrons are free whereas in the case of RyS they are bound.

The RyS measurements are performed on a low-pressure surfatron induced plasma in argon at intermediate pressure and fixed frequency at 2.45 GHz. The standard conditions are an absorbed power of 100 W, an argon gas flow of 50 sccm and a gas pressure of 20 mbar. Apart from that, plasmas realized in 6 and 10 mbar argon at 100 W are investigated as well for comparison.

The surfatron induced plasma (SIP) belongs to the class of surface-wave produced plasmas with the common feature that, since the wave loses energy while traveling along the plasma column, the electron density decreases in the wave propagation direction. This implies that the heat transfer from electrons to the heavy particles will decrease as well in the wave propagation direction. The precise knowledge of this process is of importance for a proper understanding for these types of plasmas. Therefore the knowledge of the behaviour of \( n_a \) (or \( T_a \)) along the discharge column is indispensable and it should be measured together with the properties of the electron gas, \( n_e \) and \( T_e \).

The current study can be seen as an extension of the work reported in [12] on measurements that were performed in our laboratories. There are three essential differences

1. We apply RyS to a plasma with a much smaller radius (3.0 mm versus
implying that it is much more difficult to handle false stray-light (FS); i.e. the light generated by the scattering of the laser (side-beams) on dust particles or the wall. However, since we use a 2D iCCD array instead of a 1D photo diode array in the detection system as in [12] we get better insight into the role and strength of FS.

2. In the current work we observe different axial positions of a plasma operated at a constant power whereas in [12] the plasma position is fixed (7 cm from the gap) while the power is changed. The last method is based on the assumption that by increasing the power a new, more energetic, plasma part is added at the launcher side whereas the “old plasma”, that is already measured, is simply pushed further away in the wave propagation direction while retaining its plasma properties. In our approach this assumption is not needed.

3. Our RyS scattering experiments are done in conjunction with TS so that apart form the properties of \( h \) also \( n_e \) and \( T_e \) are obtained. In this way we can trace the energy flow from \( e \) to \( h \). In [12] the properties of the electron gas were not known.

This chapter is organized as follows: section 6.2 gives a theoretical background by comparing RyS with TS. Section 6.3 describes the experimental setup and experimental procedure for RyS measurements followed by an error analysis. The results are presented and discussed in section 6.4. Finally, section 6.5 provides concluding remarks.

### 6.2 Theory

Laser scattering can deliver substantial information about the main plasma parameters such as the temperature of the electrons and the densities of the electrons and heavy particles. The interpretation of the experimental results is rather straightforward and does not depend on the degree of equilibrium departure. Moreover the methods are non-intrusive provided the laser power is not too high.

During the laser-plasma interaction the electrons oscillate in the electric field of the laser beam. Due to this oscillation the accelerated electrons will emit electromagnetic radiation, which can be seen as the scattering of the incident
laser radiation. In the case of free electrons the process is known as Thomson scattering and if the electrons are bound we speak of Rayleigh (or Raman) scattering. The fact that RyS and TS have much in common implies that the same setup initially developed for TS [13–15], can also be employed for RyS. Only minor adjustments are needed (cf. section 6.3). The same applies for the theoretical treatment which will be given here.

The spectral power $P_\lambda^x(\Delta\Omega)$ of the scattered radiation collected in the solid angle element $\Delta\Omega$ reads

$$P_\lambda^x(\Delta\Omega) = P_i n_x L S_\lambda(\lambda) \frac{d\sigma^x}{d\Omega} \Delta\Omega d\Omega.$$  \hspace{1cm} (6.1)

Here, $P_i$ is the incident laser power, $L$ the length over which the laser-medium interaction takes place, $n_x$ the density of the scattering particles, $d\sigma^x/d\Omega$ the differential cross section while $S_\lambda(\lambda)$ contains the spectral information. We assume that $S_\lambda(\lambda)$ is normalized, meaning that $\int S_\lambda(\lambda) d\lambda = 1$. In the case of TS the spectral information comes from the thermal motion of free electrons, $S_\lambda(\lambda)$ can be resolved and gives the electron temperature\(^2\). In the case of RyS this is not possible (with our setup) since the thermal velocity of the heavy particles is much smaller. We can only work with the spectral integrated form of equation (6.1) which, using the normalization of $S_\lambda(\lambda)$, gives

$$P^x(\Delta\Omega) = P_i n_x L \Delta\Omega \frac{d\sigma^x}{d\Omega}.$$ \hspace{1cm} (6.2)

This expression can be used to obtain both $n_e$ and $n_a$ by inserting the corresponding value of $(d\sigma^e/d\Omega)$.

The relative importance of RyS with respect to TS can be determined by comparing the product of the gas density and differential Rayleigh cross section with the corresponding product for TS. This gives

$$\frac{P_{RyS}}{P_{TS}} = \frac{(n_a d\sigma_a/d\Omega)}{(n_e d\sigma_e/d\Omega)} = 6.8 \times 10^{-3} n_a/n_e \hspace{1cm} (6.3)$$

where we inserted the value $d\sigma^e/d\Omega = 7.94 \times 10^{-30} \text{ m}^2 \text{ sr}^{-1}$ for TS (for $90^\circ$ of observation and polarization) and for RyS on argon $d\sigma^a/d\Omega = 5.4 \times 10^{-32} \text{ m}^2 \text{ sr}^{-1}$

\(^2\)In the plasmas under study the TS is non-collective meaning that the electrons respond individually on the laser light (cf. [13–15]).
for $\lambda_i = 532$ nm. Note that the differential cross section $d\sigma^a/d\Omega$ for RyS strongly depends on $\lambda$. The differential cross section of TS is wavelength-independent.

In both RyS and TS we apply a double perpendicular scattering arrangement meaning that the detection takes place in a direction at 90° to the incident laser beam while the polarization is perpendicular to the plane formed by the laser and the detection direction.

Equation (6.3) shows that for the typical ionization ratio of $n_e/n_a = 10^{-4}$ the strength of RyS is about 70 times stronger than that of TS. Thus, it is advised to remove RyS during TS measurements. Since RyS is generated within a small spectral band around the laser wavelength $\lambda_i$, this removal can be done by using a notch filter centered around $\lambda_i$. An advantage is that by removing RyS also the false stray light (FS) is removed.

If RyS is the study objective a notch filter makes no sense since we are interested in the photons at and in the immediate vicinity of the laser wavelength. However, apart from the RyS the signal will contain FS as well, so that extra precautions must be taken to reduce the generation of FS and to find a method to disentangle RyS signal from FS.

The above also makes clear that RyS measurements can be performed in a much smaller measurement time than TS. A typical TS measurement needs 20 minutes, while for RyS this is around 2 minutes.

The setup used for the measurements of RyS is derived from the TS setup. This implies that RyS and TS can be done just after each others. The change from TS to RyS is realized by removing the mask of the TGS (cf. figure 6.1). This mask is an essential part of the notch filter so that removing-the-mask implies that the notch filter is “switched off”.

6.3 Experiment

6.3.1 The experimental setup

The experimental setup (cf. figure 6.1) consists of three main parts: the laser setup (on the left) the plasma tube (bottom right) and the detection system (top right). Since the setup was discussed in previous publications [13–15] and in subsection 2.3.5 we will only mention the main changes and give the information that are needed to make the chapter self-contained. For the laser we used an
Edgewave class IV that produces laser pulses @532 nm with a repetition rate of 5 kHz, a duration of 10 ns and energy content of 4 mJ. This replaces the laser in [15] (cf. chapter 5), where the repetition rate was 10 Hz, while the pulse energy was typically 100 mJ.

This means that with the present setup the number of collected photons per unit of time will be 20 times larger.

The measurements have been performed on microwave induced argon surfatron plasmas. The EM waves are generated by a magnetron, that can deliver a maximum power of 200 W at a fixed frequency of 2.45 GHz. The generated plasma is confined in a quartz tube with an inner and outer radius of $r_{\text{inner}} = 3.0 \text{ mm}$ and $r_{\text{outer}} = 4.0 \text{ mm}$. Brewster windows are attached on both sides of the tube to minimize laser reflections and to assurance a maximum transmission. The argon pressure can be controlled by mass flow controllers.
and is measured by two pressure meters. The plasma tube can be translated along its own axis. During this translation the central axis remains coincident with the laser beam.

The scattered light is collected by an optical system of two parallel lenses that focuses the photons onto the entrance slit of a triple grating spectrograph (TGS). The TGS was designed [13, 16] with the purpose to reject the false stray light and Rayleigh scattered photons and to disperse and collect the remaining TS signal. The combination of the first two gratings and the mask in the middle form a notch filter whereas the final dispersion is performed by the third grating that sends the dispersed image to an iCCD. In the present study the setup is used to perform both TS and RyS. Changing from one to the other can be done by simply (re)placing or removing the mask between the first two gratings (cf. figure 6.1). By removing the mask the function of the notch filter is switched off.

The emitted plasma signal is collected by a two-dimensional iCCD camera giving spectral information in the horizontal and spatial information in the vertical direction. Each iCCD frame covers a plasma (or gas) length of 1.2 cm. A pixel binning process can be applied in spatial and spectral direction in order to reduce the noise and smooth the spectra.

Figure 6.2 compares two iCCD images. The top frame is obtained by TS the bottom by RyS+FS. The number of shots, needed to get the TS frame is about 20 times longer since much less TS than RyS+FS photons are collected per unit of time; therefore the central wavelength must be blocked, that is, the notch filter must be in function for the detection of TS photons. The TS spectrum is much broader so that it can deliver the Te value. In the lower frame the notch filter is switched off so that the scattering photons with λ values at and around the central wavelength of 532 nm are collected. The vertical strip gives a mixture of photons generated by RyS and FS. Apart from the “glow-like” regions also spots can be seen. These are the result of laser scattering on dust particles, small impurities carried by the gas flow and deposited on the wall tube. Since the laser is very intense and the tube radius with 3 mm rather small, there is a reasonable chance that one of the laser side-beams interacts with one of these particles. It is very important to choose zones from the central signal-strip that are free of false stray light. These dust-free zones are selected for the determination of the FS level.

In figure 6.2 an example of 4 different glow regions is given; they are bound by
Rayleigh scattering

Figure 6.2: Typical iCCD images of TS (a) and RyS+FS (b); the horizontal direction gives the wavelength dispersion the vertical the position along the laser beam-medium interaction zone. The central wavelength is blocked (notch filter “switched on”) for the TS measurements, in order to avoid over-exposure due to RyS+FS. In the lower frame (b) the notch filter is “switched off” so that the scattering around the central wavelength of 532 nm is manifest; the central strip shows that apart from “glow-like” regions also spots can be seen.

4 pairs of black horizontal lines. By bringing the pressure to the lowest possible value we reduce RyS so that only the FS is left. This is subsequently subtracted from the mixed spectrum of RyS+FS under plasma condition. We stress the fact that this exploration of the RyS and FS signal and the elimination of strong FS zones is the benefit of working with a 2D iCCD. In the experiment reported in [12] use was made of a 1D iPhoto diode array. Apart form the fact that an
iCCD is much more sensitive it can also be used to study the composition of RyS and FS by iCCD-picture inspection.

### 6.3.2 The plasma density determination

For the TS procedure we refer to chapter 5, were the axial dependence of TS and the associated determination of $n_e$ and $T_e$ are given for comparable plasma conditions. For more details and an in-depth comparison of the laser scattering techniques we refer to section 2.3. Here we confine ourselves to the description of the RyS procedure.

The RyS measurements consist of three steps. In the first step RyS is performed on a plasma with a known gas pressure. This gives a signal with RyS and FS components, hereafter denoted by $S(\text{RyS}_{\text{plasma}} + \text{FS})$. The second measurement is done on an argon flow at room temperature. The plasma is off while the pressure and thus $n_a(\text{gasfill}) = p/k_B T_{\text{room}}$ is known. The signal of this measurement is denoted by $S(\text{RyS}_{\text{gasfill}} + \text{FS})$. The third measurement is again with plasma-off but now under vacuum conditions; the signal is supposed to be equal to the signal of the FS and denoted by $S(\text{FS})$. In all the three steps the same number of shots (with the same energy per pulse) is applied. The signal $S(\text{FS})$ of the third step can be subtracted form the signal obtained in the first and second steps giving the RyS for the plasma and the room temperature Ar gas. Employing equation 6.2 on both the plasma and room temperature and taking the quotient we can eliminate the factor $P_I L(\frac{d\sigma}{d\Omega})\Delta\Omega$. This gives the relation

$$\frac{n_a(\text{plasma})}{n_a(\text{gasfill})} = \frac{S(\text{RyS}_{\text{plasma}} + \text{FS}) - S(\text{FS})}{S(\text{RyS}_{\text{gasfill}} + \text{FS}) - S(\text{FS})} \quad (6.4)$$

from which $n_a(\text{plasma})$ can be determined since $n_a(\text{gasfill})$, the density of the gas at room temperature, can be determined using the ideal gas law and the known gas pressure. The gas temperature $T_a$ of the plasma can be deduced from $n_a$ using the ideal gas law at known pressure. Note that the RyS method gives radial-resolved results since only photons generated in the intersection region of the laser beam and the optical axis of the detector optics are detected. This gives insight into the axial properties of the plasmas; more precisely for the region of 250 µm around $r = 0$. 

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6.3.3 The experimental procedure

The experimental procedure starts with aligning the plasma tube along the laser beam. The alignment implies that not only the tube but the whole surfatron supporting table is positioned correctly. This means that the tube-axis coincides with the laser beam, and that this remains unaltered when the table is translated. So by translating the table the volume observed by the TGS remains at the same position in the laboratory frame but changes position in the plasma frame.

Another aspect of the alignment is that the detection volume is focused onto the entrance slit of the TGS. The detection volume has a size of 1.2 cm along the laser beam and a width of 250 µm. The former is the length of the iCCD, the latter the width of the slit.

After the alignment, the discharge tube is filled with argon gas and the plasma is launched. The gas pressure and gas flow are settled at the desired values. Hereafter the three steps given above can be performed so that we get for the position and condition in question the values of the triplet $S(RyS_{\text{plasma}} + FS)$, $S(RyS_{\text{gasfill}} + FS)$ and $S(FS)$.

For a new set of measurements the plasma table is translated so that the detection branch is focused onto a new plasma position. If necessary, minor radial realignments can be done. The discharge can now be re-ignited under the same pressure and power conditions, and a new triplet of RyS measurements can be performed. The standard pressure is 20 mbar. For comparison we also performed measurements on plasmas of 10 and 6 mbar. After one plasma setting is studied for different axial positions we move to the next pressure condition. In all cases the input power is kept constant at 100 W.

6.3.4 Error analysis

The largest error in the RyS method comes from the false stray light $FS$. The impact of this error source on the final quantities $n_a$ and $T_a$ will be analyzed using equation 6.4, which for convenience is denoted here as $Q = N/D$, while the signal and the absolute error in $FS$ will be denoted by $F$ and $\Delta F$.

First, we look to error in the numerator $N = S(RyS_{\text{plasma}} + FS) - S(FS)$, were indeed $FS$ plays an important role as it contributes to both signals. As stated above we determine the $S(FS) \equiv F$ from the “glow” zones in the central
iCCD strip and skip the dots; this, with the aim to reduce $\Delta F$. Figure 6.2 gives an example from which we could deduce that the relative error typically equals $\Delta F/F = 7\%$. Since the absolute error in $S(\text{RyS}_{\text{plasma}} + \text{FS})$ is more or less equal to $\Delta F$, we find for the absolute error in $N$ that $\Delta N = \sqrt{2}\Delta F$.

To determine the relative error in $N$ we first express the Ry signal in $F$ by stating that $S(\text{RyS}_{\text{plasma}} + \text{FS}) = \xi F$. This means that $N = (\xi - 1)F$ and thus that the error due the subtraction leads to $\Delta N/N = (\sqrt{2}/(\xi - 1))(\Delta F/F)$. For the relative error in the denominator $D = S(\text{RyS}_{\text{gasfill}} + \text{FS}) - S(\text{FS})$ we find accordingly $\Delta D/D = (\sqrt{2}/(\varsigma - 1))(\Delta F/F)$ where we introduced the parameter $\varsigma$ as $\varsigma = S(\text{RyS}_{\text{gasfill}} + \text{FS})/S(\text{FS})$. Putting things together results into

$$\frac{\Delta Q}{Q} = \frac{\Delta F}{F} \sqrt{\frac{2}{(\xi - 1)^2} + \frac{2}{(\varsigma - 1)^2}}. \quad (6.5)$$

For the $20 \text{ mbar}$ case it was found that $\xi \approx 2$ while $\varsigma$ is larger. Taking $\Delta F/F = 7\%$ and the worst case scenario of $\xi = \varsigma$ we find that $\Delta Q/Q = 2\Delta F/F = 14\%$. It should be realized that the errors in the lower pressure cases of $p = 6$ and $10 \text{ mbar}$ will be larger. The reason is that $\xi$ will be smaller under these conditions.

This error caused by the FS is much larger than any other error source such as the error related to the fluctuation of the laser power, the plasma reproducibility and the reading of the pressure meter.

### 6.4 Results and discussions

Figure 6.3 gives the gas density $n_a$ as a function of axial position. The position $z = 0$ corresponds to the exit of the launcher while the direction of increasing $z$ is that of the surface wave propagation. The end point of the plasmas is in all cases denoted by signs, corresponding to the pressure legend. The plasmas were all operated at an absorbed power of 100 W. Apart form the standard condition of $20 \text{ mbar}$, we also give the results for two different pressures namely $6$ and $10 \text{ mbar}$.

Figure 6.4 gives the corresponding $T_a$ values as a function of the distance $z$. We see that in the case of $20 \text{ mbar}$ the highest gas temperature value of about $T_a = 800 \text{ K}$ is measured at the closest position to the launcher-exit. For $p = 6 \text{ mbar}$ the highest value is about $500 \text{ K}$. The reason of this pressure dependence of $T_a$ is that for high $n_a$ values the heat exchange between electrons
and atoms is higher while the heat conductivity is \( n_a \)-independent. We come back to that in the discussion part below. Note that the extrapolation of the \( T_a \) toward the end of the plasma column leads in all cases to a temperature of about 310 K which is close to room temperature; as should be. In contrast with the work published in [12] we do not see a plateau in the region of the launcher. According to that work the gas temperature is more or less constant along the tube and only changes drastically in the region close to the plasma end.

The temperature of the gas is determined by the energy flow

\[
EM \rightarrow e \rightarrow h \rightarrow \text{environment}
\]

showing that the electrons receive energy form the EM field and pass that over to the heavy particles. These in turn transfer their heat to the environment.

Thus, for a proper understanding of the plasma heating and the resulting gas temperature \( T_a \) we should know the properties of the electron gas \( e \) at each relevant axial position. For that purpose we performed TS measurements. The results given in figures 6.5(a) and 6.5(b), show the same trends as reported in [15], namely that the electron density decreases more or less linearly in the direction of the traveling wave whereas the electron temperature goes up. Note

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{argon.png}
\caption{Axial profiles of the \( n_a \) in case of gas pressure at 6, 10 and 20 mbar, input MW power of 100 W, laser power of 12 W and argon gas flow at 50 sccm.}
\end{figure}
that the accuracy in $n_e$ and $T_e$ obtained by TS is quite high (cf. chapter 5). The random errors in both quantities are less than 3% and in the order of the errors resulting from the fluctuations in the laser pulse energy and the plasma non-reproducibility. This high-level accuracy can be reached since, due to the notch filter, the determination of the TS signal is not hindered by FS.

Discussion

The gas temperature in the plasma is determined by the energy balance of the heavy particles. This balance equates the heat transfer from the electrons to the heavy particles to the transport due to heat conduction and convection.

Since the flow rate is small we may neglect the convection so that the energy balance reads

$$n_e n_a S_{\text{heat}} k_B (T_e - T_a) = - \nabla \cdot (\lambda_h \nabla T_a),$$

(6.6)

where $k_B$ is Boltzmann’s constant and $\lambda_h$ the thermal conduction coefficient. The coefficient of heat transfer $S_{\text{heat}}$ is related to that of electron-atom momentum transfer $S_{\text{mom}}$ by means of $S_{\text{heat}} = (3m_e/M)S_{\text{mom}}$, where $m_e$ and $M$ are the mass of the electron and the argon atom, respectively. Since $T_e \gg T_a$, we
Figure 6.5: The electron density $n_e$ (5a) and temperature $T_e$ (5b) as functions of the axial position obtained with TS experiment for three different pressures. The condition is: an argon gas flow of 50 sccm and input power of 100 W. The signs on the right bottom side point the end of the plasma column; they corresponds to the pressure legend.

may equate $T_e - T_a = T_e$. So that, substituting $n_a = p/k_B T_a$ equation (6.6) turns into

$$S_{\text{heat}} n_e T_e p = \frac{\lambda_h (T_a - T_w) T_a}{R^2},$$

(6.7)

where $T_w$ is the wall temperature whereas $R^*$ is the thermal diffusion length,
a distance comparable to the radius of the plasma tube. To arrive at this equation we neglected the dependence of $\lambda_h$ on radial position. This expression is a quadratic equation for $T_a$ with solution

$$T_a = \frac{T_w}{2} (1 + \sqrt{1 + 4Cp_e/p_w^2}),$$

(6.8)

where $C = S_{\text{heat}} (k_B \lambda_h)^{-1} R^2$. This solution shows that the axial temperature roughly depends on $p_e p$, i.e. the product of the electron pressure and the pressure of the heavy particles i.e. the gas pressure. The dependence on the gas pressure can be seen (cf. figure 6.4) by comparing the $T_a$ values at the launcher for different $p$ values. The highest $T_a$ value is obtained at the highest pressure of 20 mbar. The reason is that for increasing $n_a$ the transfer between electrons and heavy particles (lhs of equation (6.6)) will increase whereas the heat conduction (rhs) is $n_a$ independent. The dependence on the electron pressure is manifest in the decay of $T_a$ along the axis. Along the wave propagation direction the electron pressure goes down and as a consequence the heavy particles will receive less heat.

Figure 6.6 gives a comparison between the $T_a$ values obtained from equation (6.8) and experiments. We inserted the $n_e$ and $T_e$ values obtained from TS

![Figure 6.6: Comparison of $T_a$ values derived from the experimental RyS (circles) measurements and the calculation (line) based on equations (6.6)-(6.8).]
measurements (cf. figure 6.5). Since these are values for \( r = 0 \) we divided the \( n_e \)
value by 1.5. For the value of \( C \), we used \( R = 3 \) mm, \( \lambda_h = 0.017 \) W(mK)\(^{-1}\) (this
corresponds to 300 K) and \( S_{\text{heat}} = 6.7 \times 10^{-19} \) m\(^3\)s\(^{-1}\). It can be seen that the
agreement between theory and experiment are reasonable and fall in between
the error bars.

6.5 Concluding remarks

To understand the heating mechanism in argon surfatron plasmas at intermediate
pressures we performed Rayleigh scattering experiments for various axial
positions. To that end we used a set-up in which the plasma can be measured
on various positions while the power applied to the plasma remains the same,
namely 100 W. This, in contrast with the method described in [12] were the
plasma was shifted by increasing the power so that more energetic plasmas parts
are brought into the detection volume. This method is based on the assumption
that for the surface wave discharges (at a given settings) the plasma characteristics
are only dependent on the distance to the end of the plasmas column.

Another major improvement is that we could use the same setup for the
determination of the electron density and temperature using Thomson scattering.
In that way we could obtain more precise insight into the heat transfer
mechanisms in the plasma that follow a chain in which electrons, accelerated by
the field, pass (part of their) heat to the heavy particles that are subsequently
cooled by the environment. In contrast to the work of [12], where a steep axial
gradient in the gas temperature was found at the end of the plasma column
and a nearly constant \( T_a \) in the bulk plasma we find that the gas temperature
decreases gradually in the direction of the wave propagation. This confirms
that the gas is not directly heated by the microwave but via the electrons. So if
the electron density is large the heavy particles receive more heat. The gradual
decrease of \( T_a \) along the wave propagation direction is the result of the fact that
\( n_e \) goes down in that direction.

The method can be improved in future if the quality of the laser beam profile
is enhanced. In the present set-up the laser has side-beams. If these hit the wall
they will remain propagating in the quartz in much the same way as happens
in a glass fibre. This makes the tube glowing and it creates a continuous con-
tribution of background lighting. More seriously is the interaction of the laser
with dust particles. They give lead to intense spots on the iCCD images. It is the advantage of the use of a 2D iCCD that, due to image inspection, these point-like sources can be eliminated in the determination of the pure RyS signal.

The accuracy of the present method is estimated to be 14% for 20 mbar. For conditions with lower pressure the error will be larger. However, for our standard condition of 20 mbar, we see that the agreement between theory and experiment is reasonable and that the heat transfer via elastic electron-atom collisions is responsible for the gas heating.

The method is by no means limited to argon surfatron plasmas and can be employed to other plasma sources and plasma gases. It is interesting to employ the same setup to argon plasmas with admixtures of molecular gases and to find out how these will change the heat balance of the plasma.

References

Rayleigh scattering


Abstract. The continuum emission of plasmas can under certain circumstances be used to determine the electron densities $n_e$. This is the basis of the absolute continuum intensity (ACI) method as developed in a recent study [1]. When ACI was introduced, we made use of simple theoretical considerations and passive spectroscopic means to determine the density of atoms $n_a$ and the temperature of the electrons $T_e$. The values of these quantities are needed in the ACI method of $n_e$ determination since the intensity of the continuum generated by plasmas of low ionization degree depends on the product of $n_e$, $n_a$ and a function of $T_e$. In the current study, we use new insights as obtained by Thomson and Rayleigh scattering to recalculate the electron density by the use of ACI method. The results are compared to the $n_a$ value obtained by Thomson scattering. The comparison between the different results validates the ACI method but at the same time shows that precise values of $n_a$ and $T_e$ are needed in order to get accurate results. Moreover, deeper theoretical insight into the electron-atom cross section for continuum generation is required.
Chapter 7.

7.1 Introduction

In a recent paper [1] we introduced a spectroscopic method to determine the electron density $n_e$ based on absolute continuum intensity measurements (ACI). The ACI method was applied to surfatron induced plasmas (SIPs) operated in argon at the pressure range of 6 – 20 mbar and input power-values between 40 and 75 W.

One of the findings of that research is that for this plasma type the continuum radiation is predominantly generated by electron-atom collisions. Due to the small degree of ionization, these interactions are much more important than electron-ion collisions.

The aim of the ACI method is to investigate one of the most important features of surface wave plasmas namely the values and the axial behavior of the electron density $n_e$. Models [2–5] for SIPs predict that the $n_e$ decreases along the wave propagation direction. The reason is that the electron density scales with the power carried by the EM wave while the wave loses energy propagating along the plasma. The knowledge of the actual shape of $n_e$ as a function of the axial coordinate $z$ is of crucial importance to validate models, since $dn_e/dz$ gives insight into the wave damping mechanisms as provided by plasma phenomena such as elastic and inelastic collisions.

Since the radiation intensity of the continuum depends on the product of the densities of the interacting species and some function of the electron temperature $T_e$; thus in the form $n_e n_a G(T_e)$, it is obvious that we can only determine $n_e(z)$ if the electron temperature $T_e(z)$ and the gas density $n_a(z)$ are known. In [1] these quantities were determined from theoretical considerations and measurements predicting that $n_a$ and $T_e$ are more or less constant along the plasma column. As a result the ACI method led to axial $n_e$-profiles that were only gradually decreasing along the wave propagation direction.

Recently, we have applied active spectroscopy diagnostics (cf. chapters 5,6) to the same microwave induced argon surfatron plasma as to which ACI was employed. The active diagnostic methods are Thomson scattering (TS) and Rayleigh scattering (RyS). These measurements can be used to validate the ACI results, more specifically to determine the $|dn_e/dz|$, and to understand the potential shortcomings of the ACI method.

The TS technique is based on the scattering of photons by free electrons and can be used to determine $n_e$ and $T_e$ simultaneously. In the case of non-
collective scattering, the $T_e$ value directly follows from the spectral width while the $n_e$ can be deduced from the calibrated spectral integrated intensity of the scattered light. Other benefits are that TS gives spatially resolved $n_e$ and $T_e$ values and that the interpretation of the results is independent on the plasma-state of equilibrium departure. Moreover, the accuracy of TS is high; the random errors related to the $n_e$ and $T_e$ determination were found to be as low as 3%. This is determined by the in-accuracy of the plasma reproduction. For the $n_e$ determination there is a systematic error of about 8% [6] and chapter 5 that originates from the intensity calibration procedure that is based on Raman scattering [7]. The systematic error stems from the uncertainty of the Raman cross section.

These advantages make TS a suitable technique to validate the $n_e(z)$ as initially found with the ACI method. Besides, it indicates whether the $T_e$ values used in the ACI method were correct. We recall that in the first application of ACI on the SIP it was assumed that $T_e$ is constant along the axis. The TS method shows that this is not the case, as observed in chapter 5 (cf. also [6]).

The second active diagnostic method announced above, Rayleigh scattering (RyS), is based on the elastic scattering of (laser) photons by electrons that are bound to heavy particles. The intensity of the RyS delivers the heavy particle density in the plasma. So, this method gives insight into the validity of the assumption that $n_a$ is constant along the plasma tube; an assumption that was used in the first application of ACI on the SIP. As we have seen in chapter 6, RyS shows that $n_a$ is not constant but increases in the wave propagation direction.

Applying TS, RyS and ACI to the same plasma type gives the opportunity to compare the methods and to determine the validity regime of the ACI method.

The remaining of this chapter is organized as follows: section 7.2 is devoted to the theoretical part needed to introduce the absolute continuum method; section 7.3 shows results obtained after the revision of the method. Discussion and conclusions are given in section 7.4.

7.2 Theory

In general the continuum radiation has three contributions depending on the pairs of interacting particles and the nature of the process; these are the free-free interaction between electron and atoms (ea), the free-free collisions between
electron and ions (ei), and the free-bound interaction of electrons and ions that lead electron-ion recombination. The total emission coefficient is the sum of these contributions and reads:

$$j^\text{cont}_\lambda(\lambda, T_e) = j^{\text{ea, ff}}_\lambda(\lambda, T_e) + j^{\text{ei, ff}}_\lambda(\lambda, T_e) + j^{\text{ei, fb}}_\lambda(\lambda, T_e).$$  

(7.1)

As stated before, it was found [1] that for our plasma conditions the free-free ea term is dominant, since the ionization ratio $n_e/n_a$ is small (in the order of $n_e/n_a < 10^{-4} \text{m}^{-3}$). Therefore, we confine ourselves here to the dominant $j^{\text{ea, ff}}_\lambda$ term solely, which can be written in the form [8]

$$j^{\text{ea, ff}}_\lambda(\lambda, T_e) = \frac{c_2}{\lambda^2} \frac{n_e n_a T_e^{3/2}}{c^2 Q^A(T_e)} \times \left\{ Q^A(T_e) \left( 1 + \left( 1 + \frac{hc}{\lambda k_B T_e} \right)^2 \right) \exp \left( -\frac{hc}{\lambda k_B T_e} \right) \right\},$$  

(7.2)

where $c_2 = \frac{32 e^2}{12 \pi \varepsilon_0 c^2} \left( \frac{k_B n_e}{4 \pi m_e} \right)^{3/2} = 1.026 \times 10^{-34} \text{(Jm}^2\text{K}^{3/2}\text{s}^{-1}\text{sr}^{-1})$, in which $c$ is the speed of light, $k_B$ the Boltzmann constant, $m_e$ the mass of an electron, $\varepsilon_0$ the permittivity of vacuum and $e$ the elementary charge. The plasma properties are given by $n_e$ for the electron density, $n_a$ for the atom density while $T_e$ refers to the electron temperature in K. The parameter $Q^A(T_e)$ is the cross section for momentum transfer in electron atom collisions. In our case of an argon plasma we take $Q^A(T_e) = Q^{Ar}(T_e)$, for which we refer to [1].

Since the ACI method was used as a line-of-sight method, it gave $j_\lambda(\lambda, T_e)$ via an averaging procedure in which the measured intensity $I_\lambda(\lambda)$ was divided by the plasma’s diameter $D$; thus $\langle j(\lambda) \rangle = I_\lambda(\lambda)/D$. This implies that the radial averaged electron density is determined by the equation

$$n_e = \frac{(I/D) \lambda^2 G(\lambda, T_e)}{n_a T_e^{3/2} c_2 Q},$$  

(7.3)

where

$$G(\lambda, T_e) = \frac{\exp \left( \frac{hc}{\lambda k_B T_e} \right)}{1 + \left( 1 + \frac{hc}{\lambda k_B T_e} \right)^2}$$  

(7.4)

is a function that only varies 5% if $T_e$ changes 30% around 1 eV. So, the changes in $n_e$ can mostly be attributed to the variation in the product $n_a T_e^{3/2}$. In the
recalculations of $n_e$(ACI) in which new values of $T_e$(TS) and $n_a$(RyS) are used we perform the complete calculation of equation (7.2).

We use expression (7.3) to guide us through the analysis of the validity of the assumptions made in the ACI method as introduced and used in [1].

The first assumption made in [1] was related to the heavy particle density; i.e. the $n_a$ value. This was determined (cf. [9]) from a simple heat balance equation, the measured wall temperature and the ideal gas law ($n_a = p/k_BT_a$), which led to the simplification that $n_a$ is more or less constant along the plasma column axis. An assumption that according to the new insights obtained in chapter 6 is not valid.

The second assumption was related to the electron temperature. Based on the experimental results published in [10], where the electron temperature was derived from measured densities of the 4p levels and a collisional radiative model, we found that the electron temperature is nearly constant along the plasma column. However, TS results show that the $T_e$ increases in the wave propagation direction.

The third important assumption was based on the proposal given in [8] to treat the cross section $Q$ for momentum transfer in equation (7.2) as if the elastic e-Ar collision is a hard sphere-like collision. As discussed in [1] we have severe doubts on the validity of this assumption since the strong influence of the Ramsauer effect on the e-Ar collisions predicts that the cross section strongly depends on the electron energy (thus $T_e$). This is in contrast to the fact that the cross section of hard-sphere collision is energy independent. However, since we have no alternative for $Q^{Ar}(T_e)$ at the moment we will not consider the influence of possible changes in $Q$ on the outcome of the ACI method.

Thus we will confine ourselves to the comparison between the electron density as obtained by Thomson scattering (briefly $n_e$(TS)) and the ACI method ($n_e$(ACI)) and we will investigate how new insights as obtained by TS and RyS, giving $T_e$(TS) and $n_a$(RyS) can be used to recalculate the values of $n_e$(ACI) and therewith the slope $dn_e$(ACI)/dz.

7.3 Results

This section starts with the comparison of the results for the electron density derived from the absolute continuum method $n_e$(ACI) as published in [1] to-
together with \( n_e(TS) \) obtained from (cf. chapter 6). After that we will present \( T_e(TS) \) and \( n_a(RyS) \) and investigate how these values are going to change the \( n_e(ACI) \) values and whether or not the agreement between \( n_e(TS) \) and \( n_e(ACI) \) is improved.

![Figure 7.1](image)

**Figure 7.1:** Comparison between \( n_e(TS) \) and \( n_e(ACI) \), both given as a function of axial position \( z \), for the settings given in the text. It is clear that close to the launcher \( n_e(TS) \) is more than a factor of 3 larger than \( n_e(ACI) \) and that the slope of \( n_e(TS) \) is steeper than that of \( n_e(ACI) \).

The conditions used in the ACI method are a gas pressure of \( p = 15 \text{ mbar} \), an applied power \( P = 60 \text{ W} \) and a gas flow \( \phi = 70 \text{ sccm} \). The settings for the TS and RyS measurements are given by \( p = 10 \text{ mbar} \), \( P = 100 \text{ W} \), and \( \phi = 50 \text{ sccm} \). As it can be seen, there are some differences between the plasma settings of the ACI experiment on the one hand and the TS and RyS experiments on the other hand. However, we found in the ACI method that the dependency of \( n_e(ACI) \) on the pressure and the flow is weak.

Figure 7.1 compares the \( n_e(ACI) \) as published in [1] with \( n_e(TS) \) (cf. chapter 6). It is clear that the slope of \( n_e(TS) \) is steeper than that of \( n_e(ACI) \)\(^1\)

\(^1\)Note that there is a difference between the \( n_e \) values given here and those published in [1]. This is based on a difference in the \( n_a \) value; here \( n_a \) is determined from the gas-law

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whereas the $n_e$(TS) values are larger, in general. We recall that the $n_e$(ACI) values as found in [1] were initially based on the assumption that both $n_a$ and $T_e$ are constant along the plasma column; for the gas density this constant value was $n_a = 2.7 \times 10^{23} \text{ m}^{-3}$ (corresponding to a constant gas temperature of 400 K) while for the electron temperature the value of $T_e = 1 \text{ eV}$ was employed.

Figure 7.2 gives the values of $T_e$(TS) as a function of axial position $z$ showing that the electron temperature is not constant but increases along the wave propagation direction. There is a substantial increase of about 50%. To facilitate the comparison the constant value of $T_e(z)$ used in [1] is given in the same figure. Figure 7.3 gives $n_a$(RyS) showing that also the gas density is not constant along

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7.2.png}
\caption{Comparison between $T_e$(TS) and $T_e$(ALI), both given as a function of axial position $z$.}
\end{figure}

the plasma axis; it was found in chapter 6 that $n_a$(RyS) increases in the wave propagation direction. The total reduction of the typical value for $n_a$ as found with RyS is about a factor of 2 compared to the value assumed in ACI. The $n_a$(ACI) obtained from the ideal gas law $p = n k_B T$ is added for comparison.

These findings of the behavior of the electron temperature obtained from TS
\((p = 15 \text{ mbar and } T_a = 400 \text{ K}),\) in [1] the round value $n_a = 10^{23} \text{ m}^{-3}$ was taken.

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and the atom density given by RyS can now be used to recalculate the $n_e(\text{ACI})$.
The results are given in figure 7.4 where they are again compared to the $n_e(\text{TS})$
values already presented in figure 7.1. It is found that inserting the new values
of $T_e$ and $n_a$ (obtained by TS and RyS respectively) gives a much better match
both in value and in slope. In the region close to the launcher the $T_e$ is more or
less constant; but since $n_a$ is almost 2 times smaller the corresponding $n_e$ value
will be 2 times higher (cf. equation (7.3)). As we move away from the launcher
both the increase in $n_a$ and $T_e$ results in lower $n_e$ values. This makes the slope of
$n_e(z)$ substantially steeper. The discrepancy in the absolute value still reaches

![Figure 7.3: Comparison between the $n_a$ initially used for ACI, “old” $n_a(\text{ACI})$
and $n_a(\text{RyS})$ as determined by RyS, both given as a function of axial position $z$.](image)

a factor of about 1.5. It can be further reduced if the comparison is applied to
the central values of the quantities, thus the values for $r = 0$. We remind that
TS and RyS give spatial resolved values for positions along the central axis of
the plasma (hence $r = 0$) whereas ACI is a line-of-sight method. The $\langle j \rangle$ is
obtained by dividing the intensity by the plasma diameter. To get an idea of
the difference between the central value and the line averaged value we assume
that $j(r)$ has a parabolic profile given by $j(r) = j_0(1 - (r/R)^2)$. By integrating
this expression along the plasma diameter we find the relation between the line
averaged and central value, $\langle j \rangle = 2/3j_0$; meaning that the central value of the
The absolute continuum intensity method revised

Figure 7.4: Comparison between $n_e$(ACI) (corrected via $T_e$(TS) and $n_a$(RyS)) and $n_e$(TS).

emission coefficient $j_0$ will be 1.5 larger than the diameter-averaged value $\langle j \rangle$. The exact influence of the averaging along the line of sight depends on the shape of $j(r)$ and needs additional attention in a future study.

7.4 Discussion and conclusion

The continuum radiation generated by atomic plasmas of low degree of ionization is mainly generated by elastic electron-atom collisions. Therefore it depends on the product of the electron density, the atom density and some function of the electron temperature; thus it has form $n_e n_a G(T_e)$. This fact was used in [1] to develop a method to determine the electron density based on measuring the absolute value of the continuum radiation. However, in order to perform the method properly the values of $n_a$ and $T_e$ must be known with some precision. When the ACI method was introduced it was employed to get insight into the axial behavior of the electron density; this provides a useful mean to validate the models of SIPs. The values and the axial behavior of $n_a$ and $T_e$ were obtained from simple methods and considerations and as a result we obtained low values
of $n_e$ and the slope $|dn_e/dz|$. By employing recent results obtained with the active spectroscopic techniques TS and RyS better data is obtained for $n_a(z)$ and $T_e(z)$. Moreover, we get a new method to compare the $n_e$ as obtained with ACI.

It is found that the low value of $n_a$ close to the launcher leads to an increase of the $n_e$(ACI) value at that position. Furthermore, the increase of both $n_a(z)$ and $T_e(z)$ along the wave propagation direction makes the slope $|dn_e/dz|$ steeper. This results in a significantly better agreement between the $n_e$ values of the ACI and the TS method. Especially the axial increase in $T_e$ leads to a drastic change that improves the agreement.

The increase of $T_e$ in the wave propagation direction came as a surprise in the study (cf. chapters 5 and 6). It is in contradiction with existing theories and results of earlier measurements. This poly-diagnostic calibration can thus also be used in the opposite direction; the fact that we need a substantial axial gradient of $T_e$ to get a better match between $n_e$(TS) and $n_e$(ACI) gives an a posteriori validation of the strong axial dependency found in $T_e(z)$ by means of TS.

This mutual comparison between various diagnostic techniques can be improved in future studies. From the experimental point of view it is needed that the experimental methods are applied to exactly the same plasma settings and positions and that Abel inversion is performed to get the central value of $n_e$(ACI). From the theoretical point of view it is of interest that more research will be done on the mechanisms behind the ea continuum radiation generation. Since the Ramsauer effect is important in electron-atoms collisions, it is indispensable that a full quantum mechanical approach must be applied.

The ACI method is by no means confined to argon plasmas. It can be applied to other atomic plasmas as well. In case when molecules are present, one should first locate the spectral regions free from molecular bands. Moreover, the relevant cross section for the continuum generation must be known and employed.

References


Abstract. The discrepancy between the values of the electron temperature as found with Thomson scattering (TS) and absolute line intensity (ALI) measurements is studied systematically. By analyzing both low and atmospheric argon plasmas, a general trend is found showing that the discrepancy mainly depends on the ionization factor $\alpha$. Most likely the discrepancy is based on the depletion of the tail of the electron energy distribution function that increases for decreasing $\alpha$. A depleted tail gives lower rates for excitation and ionization. This leads to a relative low plasma emission that is interpreted as a low temperature. Thus the tail depletion gives ALI temperatures that are too low. Another aspect that is relevant when comparing the two temperature methods is the laser heating that might take place during TS. Especially focusing substantial laser energy into a high atom density plasma will lead to an increase of the electron temperature. This leads to TS temperatures that are too high.
Chapter 8.

8.1 Introduction

The aim of this thesis project was to get a more in-depth understanding of the relation between the light emitted by plasmas and the underlying plasma conditions. So the leading question is: *in how far does the plasma-light provide insight into the plasma inside.* The idea is that a proper understanding of the plasma light might be helpful in the on-line monitoring of plasmas. This study is guided by a request of Draka Communications, that uses microwave discharges for the fabrication of optical fibers to get better control over the plasma production process. In the chain between the plasma control parameters and the plasma products an essential role is played by the electrons. So in answering the question given above we are especially interested in the deduction of the electron density and temperature out of the plasma light.

The class of plasmas studied in this thesis are just as in the case of Draka microwave induced plasmas. Our plasmas are operated in argon in atmospheric or intermediate pressures\(^1\). The latter means, pressures in the range \(5 - 30\) mbar. These plasmas have in common that the ionization factor \(\alpha = n_e/n_a\) is rather low (in the order of \(n_e/n_a < 10^{-4}\)). Characteristic for these plasmas is that electron-atom (ea) collisions are dominant over electron-ion (ei) collisions. That means that the conductivity is not determined by Coulomb collisions, that the continuum is generated by ea collisions rather than ei interactions and that severe deviations from equilibrium can be expected.

The light generated by plasmas can be divided in continuum and line radiation. We have found that, globally speaking, the *continuum* gives the *electron density* \(n_e\) while the (optically thin) *line* radiation gives the *electron temperature* \(T_e\), provided that in both cases absolute intensities are used. In the case of the continuum we talk about absolute continuum intensities (ACI) in the case of spectral lines the method is named absolute line intensities (ALI). The results of these passive spectroscopic methods have been compared with those obtained by laser methods like Thomson scattering (TS) and Rayleigh scattering (RyS). Guided by the aim to construct a method of in-depth monitoring and realizing that industrial plasmas are not accessible for laser diagnostics we use the active spectroscopical techniques to calibrate the passive methods. In the industrial environment optical emission spectrometry has to operated in a

\(^1\)In the comparison with atmospheric condition the intermediate pressure is, for convenience sometimes denoted by low pressure or shortly low-p.
stand-alone mode.

To facilitate the discussion below we will use abbreviations like \( n_e(\text{ACI}) \) and \( n_e(\text{TS}) \) to express the method by which a quantity is determined.

## 8.2 The discrepancy between the two temperature methods

To deduce the electron density from the continuum, \( n_e(\text{ACI}) \), we need to know \( T_e \) and the ground state density, \( n_1 \). If we use \( T_e \) from TS and \( n_1 \) from RyS we find that \( n_e(\text{ACI}) \) follows the same trends as \( n_e(\text{TS}) \). There is a mismatch of a factor \( n_e(\text{ACI})/n_e(\text{TS}) \approx 0.7 \), but this factor is approximately constant and seems to be independent on the plasma settings, like the pressure (cf. figure 7.4). This mismatch can be determined experimentally and used in the future to derive the true \( n_e \) value out of \( n_e(\text{ACI}) \) obtained by monitoring. This suggests that \( n_e \) can be determined by passive spectroscopy solely and that complicated laser systems are not needed in industrial practice. However, as stated above, the ACI method is based on known values of \( n_1 \) and \( T_e \). Can these quantities also be determined by pure passive means? In chapter 6 we found that \( n_1 \) can be determined via the gas temperature by modeling the heavy particle heat balance (HHB), but what about \( T_e \)?

For the \( T_e(\text{ALI}) \) the situation is completely different. There is a mismatch between \( T_e(\text{ALI}) \) and \( T_e(\text{TS}) \) and this mismatch, denoted by \( T_e(\text{ALI})/T_e(\text{TS}) \neq 1 \), strongly depends on the plasma condition. This becomes clear by figure 7.2 of chapter 7, that is reproduced here for convenience as figure 8.2. It shows that in the region close to the launcher of the low pressure SIP, a good agreement exists between \( T_e(\text{ALI}) \) and \( T_e(\text{TS}) \). However, it is also shown that in the wave-propagation direction \( T_e(\text{ALI}) \) remains more or less constant while the \( T_e(\text{TS}) \) increases monotonically as function of the distance, so \( T_e(\text{TS})/T_e(\text{ALI}) \) increases in the wave-propagation direction.

There are good reasons to believe that for low-\( p \) plasmas the determination of \( T_e(\text{TS}) \) is reliable so that the reason for the discrepancy must be searched in the \( T_e(\text{ALI}) \)-determination. We recall that the \( T_e(\text{ALI}) \) is derived from the atomic state distribution function (ASDF) that is interpreted with the use of a collisional radiative model (CRM). This CRM accounts for the departure of equilibrium (cf. figure 4.1). It is not impossible that the CRM fails and/or that the influence of the state of equilibrium-departure is different in nature or more
severe than what was known when the CRM was constructed.

It is general recognized that for decreasing \(n_e\) large deviations from equilibrium can be expected. The reason is that most of the equilibrium restoring processes scale with \(n_e\). However, there are several mechanisms that might create equilibrium departure. In case that the equilibrium departure is generated by the escape of radiation we find conditions in the form

\[ n_e \gg n_e^{\text{crit}}(\text{CR}) \quad \text{with} \quad n_e^{\text{crit}}(\text{CR}) = \frac{A}{K} \]  

(8.1)

where \(A\) is a transition probability for radiative decay (Einstein coefficient), \(K\) stands for the rate of electron induced processes, while CR refers to the competition between collision and radiative processes. This criterion, known as the Griem criterion, is discussed among others in [1, 2] where precise values of the right hand side \(A/K\) can be found.

So, if the condition \(n_e \gg n_e^{\text{crit}}(\text{CR})\) is not fulfilled the escape of radiation could be responsible for the discrepancy \(T_e(\text{TS})/T_e(\text{ALI}) > 1\). However, the CRM applied in the interpretation of the ASDF already corrects for the radiation
The discrepancy between two temperature methods

Ar, 74 W

\[ n_a/n_e \quad T_e(TS)/T_e(ALI) \]

\[ 4.7 \times 10^3 \quad 0.9 \]

Ar+0.3% H₂, 88 W

\[ 1.03 \times 10^4 \quad 1.2 \]

Ar+0.3% H₂, 55 W

\[ 2.9 \times 10^4 \quad 1.5 \]

Table 8.1: Results obtained at atmospheric SIP.

escape. So the cause of the discrepancy \( T_e(ALI)/T_e(TS) \neq 1 \) must be searched for somewhere else.

If this discrepancy is related to the departure of the electron energy distribution function (EEDF) from its equilibrium form as given by Maxwell, the critical parameter is the ionization degree \( \alpha = n_e/n_1 \) rather than to the electron density \( n_e \). In [1, 2] we find the following condition for the presence of Maxwell equilibrium

\[ \alpha \gg \alpha^{\text{crit}} \quad \text{with} \quad \alpha^{\text{crit}} = C_s(S) \frac{1}{2 \ln \lambda_c} \left( \frac{k_B T_i}{E_{12}^*} \right)^2 \]  

(8.2)

In the case of Ar we have \( C_s(Ar) = 0.3 \) and \( E_{12}^* = 12 \text{ eV} \). Inserting for the Coulomb logarithm a typical value of \( \ln \lambda_c = 7 \), and \( k_B T_i = 1.2 \), we find \( \alpha^{\text{crit}} = 2 \times 10^{-4} \).

In order to establish the nature of the equilibrium departure we take a look to table 4.2, where an overview of \( T_e \) (and \( n_e \)) values is given for different atmospheric plasmas using different methods. It is obvious that despite the fact that the \( n_e \) values are larger than in the low-p surfatron induced plasmas (SIP) case, we can still find large values of \( T_e(TS)/T_e(ALI) \) in this table. Large \( n_e \) values imply that condition (8.1) is fulfilled. This suggests that the nature of the discrepancy \( T_e(TS)/T_e(ALI) > 1 \) is an equilibrium departure created by depletion of the EEDF tail. In order to confirm the presence of larger \( T_e(TS)/T_e(ALI) \) values under large \( n_e \) conditions we make use of the values obtained by experiments on an atmospheric SIP [3]. A picture of this plasma can be found in plasma gallery presented in chapter 1. The values of \( T_e(TS)/T_e(ALI) \) are given
in table 8.1 for various $\alpha$ values. These are determined by RyS, TS and ALI performed on an atmospheric SIP. The change in the $\alpha$ values is obtained by adding $\text{H}_2$ to the plasma and/or reducing the power. It is seen that just as in the case of the low-p SIP an increase in $T_e(\text{TS})/T_e(\text{ALI})$ is observed for decreasing $\alpha$ values. The pressure independence of the $T_e(\text{TS})/T_e(\text{ALI})$ discrepancy becomes evident by figure 8.2. the figure gives $T_e(\text{TS})/T_e(\text{ALI})$ as a function of $\alpha^{-1}$ for different plasmas. This figure suggests a universal trend.

So we come to the proposition that $T_e(\text{TS})/T_e(\text{ALI})$ is a function of the ionization ratio; stated formally

$$\frac{T_e(\text{TS})}{T_e(\text{ALI})} = F(\alpha) \quad (8.3)$$

The precise form of $F(\alpha)$ has to be determined in future studies. But if it is available we can construct a recipe for in-depth plasma monitoring based on the following ingredients: the results from ALI, ACI, $F(\alpha)$ and HHB. The latter gives the gas temperature and thus, via the pressure the ground state density. The recipe could have the following structure:

1. Take realistic initial values for $n_e$ and $T_e$
2. Find using the HHB the $n_a$ value
3. Measure the 4p density, determine $T_{13}$
4. determine from this $n_e$ a $T_e$ value (ALI method)
5. measure the continuum and use $T_e$ to calculate $n_e$ (ACI method)
6. use this together with $n_a$ to determined $\alpha$
7. use $F(\alpha)$ to find $T_e$
8. return to 3) and repeat until convergence is reached.

With this recipe we can determine the electron properties using passive spectroscopy solely. This method is applicable to Ar plasmas but extension to other plasmas must be possible.
8.3 How non-intrusive is Thomson scattering?

In the discussion above TS is promoted as the most reliable method to determine the properties of the electron gas. It is even used as a standard to calibrate passive spectroscopy methods. However, we should not forget that TS uses an external source to irradiate the plasma; so that a question should rise whether the method is really non-intrusive.

The table 4.2 of chapter 4 shows that there is scatter in the $T_e$(TS) value. So for instance it was found in [4] that $T_e = 1.4$ eV, while in [5] values of $T_e = 1.9$ eV are given. In [5] the laser was focused. This scatter in $T_e$(TS) values raises the question: how reliable TS actually is and can laser focusing lead, in our conditions, to heating of the electron gas.

![Figure 8.2](image)

**Figure 8.2:** The discrepancy between $T_e$(ALI) and $T_e$(TS) as a function of $\alpha^{-1}$ as obtained from experiments on both low pressure and atmospheric pressure. Included are the results given in chapter 5, table 4.2 and the atmospheric SIP [3].

Assume that a laser with beam-diameter $A$ and pulse energy $E_L$ travels through the plasma over a length $L$ and let the absorption coefficient be given by $k_L$ (in $\text{m}^{-1}$). Than the energy absorbed by the plasma will be $k_L E_L$. Now, if the electron density and the absorption coefficient of the plasma are not
changed by the laser and if the electrons keep the energy for themselves than the increase in electron temperature follows from the balance
\[
\frac{3}{2} n_e V \Delta k_B T_e = k_L E_L. \tag{8.4}
\]
Using for the volume of the laser-plasma interaction region \( V = LA \) this leads to
\[
\Delta k_B T_e = \frac{2 k_L E_L}{3} \frac{n_e}{A} \tag{8.5}
\]
this is basically the equation as found in [6], where the absorption coefficient for inverse bremsstrahlung
\[
k_L = k_{IB} = \left( \frac{\omega_{pl}}{\omega_l} \right)^2 \frac{\nu_{ei}}{c} \tag{8.6}
\]
was employed. Here \( \omega_{pl} \) and \( \omega_l \) are the circular frequency associated to the plasma and laser respectively, while \( \nu_{ei} \) is the collision frequency for momentum transfer from electrons to ions. This expression is valid for the case when \( \omega_l \gg \nu_{ei} \). However, we must also take electron-atom collisions into account so that in general \( \nu_{ei} \) should be replaced by
\[
\nu_{eh} = \nu_{ei} + \nu_{ea}. \tag{8.7}
\]
In plasmas with low degree of ionization and thus \( \nu_{ei} \ll \nu_{ea} \) we have
\[
\nu_{eh} = \nu_{ea} = n_a k_{ea}, \tag{8.8}
\]
where \( k_{ea} \) is the rate coefficient for momentum transfer in \( ea \) collisions. Inserting
\[
\omega_{pl}^2 = \frac{n_e e^2}{m_e \varepsilon_0} \tag{8.9}
\]
into equation 8.6 and replacing \( \nu_{ei} \) by \( \nu_{ea} = n_a k_{ea} \) we get
\[
\Delta k_B T_e = \frac{2 n_a k_{ea} E_l}{3} \frac{e^2}{A} \frac{1}{m_e \varepsilon_0 \omega_l^2 c} = 5.7 \times 10^{-37} \frac{n_a k_{ea} E_l}{A} \tag{8.10}
\]
where we used \( \omega_l = 3.54 \times 10^{15} \text{s}^{-1} \) corresponding to a laser wavelength of \( \lambda = 532 \text{ nm} \). For example: in a cold atmospheric plasma for which \( n_a = 10^{20} \text{ m}^{-3} \),
The discrepancy between two temperature methods

penetrated by a laser with cross section \( A = 1.25 \times 10^{-7} \), \( \lambda = 532 \text{ nm} \) and pulse energy \( E_l = 100 \text{ mJ} \), we find, taking \( k_{ea} = 10^{-14} \) [7]

\[
\Delta T^e_e = 0.3 \text{ eV}. \tag{8.11}
\]

This is an increase in the order of 20%!!

The derivation given above shows that \( \Delta T_e \) linearly scales with \( n_a \) and the laser energy \( E_l \) whereas it is inversely proportional to the laser beam cross section \( A \). So that we may conclude that:

- in the low pressure case (cf. chapter 5) laser heating plays no role \( (n_a \approx 10^{23} \text{ m}^{-3}) \);
- the laser beam should not be focused too much, (the laser beam cross section \( A \) should not be too small);
- the energy per pulse must be limited.

It is striking that the same fact that makes the \( ea \) interaction the most dominant mechanism for the generation of continuum radiation is also responsible for laser heating.

8.4 Concluding

In the chain between the plasma control parameters and the plasma products an essential role is played by the plasma-properties; more specifically, by the features of the electron gas (cf. 1.3). So, in view of the principal aim of this project; i.e. to build a method of in-depth light-interpretation from which an advanced technique of on-line monitoring of plasma processes can be constructed, we are especially interested in the deduction of the electron density and temperature out of plasma light. Therefore, we compared in this thesis the electron density and temperature as obtained from optical emission spectrometry (OES) with the values as determined by laser spectroscopic techniques like Thomson and Rayleigh scattering.

The light generated by plasmas can be divided in continuum and line radiation. Globally speaking, the continuum gives the electron density \( n_e \) while the (optically open) line radiation gives the electron temperature \( T_e \), provided
that in both cases absolute intensities are used. By comparing the results of passive spectroscopic methods (OES) with those obtained by laser methods, we found a fairly good agreement as far as the electron density \( n_e \) concerns. There is a slight disagreement but it is a constant factor. However, with respect to the electron temperature \( T_e \) substantial discrepancies were found. Both in the case of the low pressure surfatron induced plasmas (SIP) and the atmospheric discharges (like the TIA and the atmospheric SIP) we found that in general the \( T_e \) value found by TS is in general larger than the one obtained via OES, that the discrepancy is not constant and that it depends on the ionization degree. The latter implies that most likely the discrepancy is based on the depletion of the tail of the electron energy distribution function that increases for decreasing degree of ionization. A depleted tail gives lower rates for excitation and ionization, this leads to a relative low emission that is interpreted as a (relative) low temperature. Furthermore, the tail depletion gives an OES temperature that is too low.

Another aspect that is relevant in the comparison of the two methods of temperature-determination is the laser heating that might take place during TS. Especially in the case of a high atom densities the focusing of substantial laser energy will lead to an increase of the electron temperature. This leads to TS temperatures that are too high. We found that, for the laser pulse energies used in this thesis, heating is not important for the low pressure SIP but that for the investigation of high pressure discharges TS must be handled with care.

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General concluding remarks
9.1 Introduction

The goal of this research project was to study the non-equilibrium mechanisms behind the light emission of microwave induced plasmas; to find out what information is carried by the plasma light and to construct methods to come to a more in-depth interpretation of plasma radiation. More specifically this means that the method of optical emission spectrometry was analyzed and refined such that it can deliver insight into the main plasma parameters like the electron density and electron temperature. The results of optical emission spectrometry were compared with those of laser-scattering methods. We believe that this poly-diagnostic approach provides substantial steps forward in the development of a general method for in-depth plasma monitoring.

Each chapter of this thesis is devoted to specific topics and gives relevant conclusions. Here an overview and general concluding remarks will be given. In addition, recommendations for future investigations will be served.

9.2 Methods and techniques

- Active and passive spectroscopic methods have been employed on the plasmas under study.

- Passive spectroscopy of non-equilibrium plasmas is only useful if the intensity is measured in an absolute way; this implies that the intensity of the plasma emission is calibrated against the radiation generated by a standard light source.

- In accordance with the fact that the plasma spectrum contains both continuum and spectral line contributions two procedures have been developed: Absolute continuum intensity (ACI) and absolute line intensity (ALI) measurements. Only optically thin radiation was investigated.

- The method based on the absolute continuum intensities is introduced and employed to determine the electron density $n_e$ (cf. chapter 3).

- The method of ALI-CRM has been refined and applied to obtain the electron temperature $T_e$ (cf. chapter 4). The bases is that the excitation temperature $T_{13}$ determined by absolute line intensity measurements
Concluding remarks

is transformed into the electron temperature $T_e$ employing a collisional radiative model (CRM).

- An absolute intensity measurement (AIM) method has been developed based on the simultaneous application of ALI-CRM and ACI. This iterative procedure determines both the electron density ($n_e$) and electron temperature ($T_e$) in strongly ionizing argon plasmas (cf. chapter 4).

- Active spectroscopy techniques are performed in order to validate the passive methods. Three laser scattering techniques have been used. The first one is Thomson (TS) scattering for the determination of $n_e$ and $T_e$; the second, Rayleigh scattering (RyS), delivers information for the heavy particles density and temperature. The third, Raman scattering, has been used for calibration purposes (cf. chapters 2, 5 and 6).

9.3 Plasma conditions and parameters

- The methods and the techniques listed above are performed on different types of argon microwave induced plasmas. The microwave frequency is fixed and in all cases equals 2.45 GHz.

- The ACI method has been implemented on a low pressure microwave induced plasmas created by a surfatron. Several wavelength regions were found to be reliable for this method. Standard settings: an applied power of 60 W, pressure of 15 mbar, gas flow of 70 sccm. The electron density was found to decrease in the wave propagation direction from $2.4 \times 10^{19}$ to $1 \times 10^{19} \text{m}^{-3}$.

- The AIM method has been applied to plasmas created by the Torche à Injection Axiale (TIA) at atmospheric pressure. Standard settings are: a gas flow of 1 slm and a power of 800 W; the measurements have been performed on a position of 1 mm above the nozzle. Typical values are, for the electron density $1.2 \times 10^{21} \text{m}^{-3}$ and the electron temperature $1.2 \text{eV}$.

- The TS technique has been performed on plasmas created by a low pressure surfatron. Standard settings: in the pressure range of 6–20 mbar and microwave power range 30 – 80 W. Typical values that were found: for
the electron density $4 \times 10^{18} - 7 \times 10^{19} \text{ m}^{-3}$ and the electron temperature $1.1 - 2.1 \text{ eV}$.

- TS and AIM have been used in the case of atmospheric argon surfatron plasmas. Standard settings: applied power of 74 W and gas flow 1.45 slm.
- The RyS technique is applied on surfatron plasmas. Standard settings: power of 100 W, flow rate of 50 sccm and pressure of 20 mbar. Typical values: the atom density varies in the range of $8 \times 10^{22} - 3 \times 10^{23} \text{ m}^{-3}$, while the atom temperature is found to be in the range of $350 - 800 \text{ K}$.

### 9.4 Findings

The findings listed below are the results of the application of the methods developed in this thesis.

- The ACI method, for the first time applied on low pressure surfatron plasmas, was found to be successful. It gives the electron density in a rather simple and straightforward way. Close to the microwave launcher the continuum radiation could be observed easily whereas at the plasma end the signal is weak so that longer exposure times are required. This confirms the results predicted by theories that the electron density decreases in the wave propagation direction. However, we could not find plasmas with electron densities close to the critical value; that is the value found by equating the (modified) plasma frequency to the frequency of the driving EM field.

- The ALI method applied to intermediate-pressure surfatron plasmas suggests that the electron temperature is more or less constant. This $T_e(\text{ALI})$ agrees rather well with the results of global modeling and close to the launcher it fits with the value obtained with Thomson scattering.

- The AIM method performed on an atmospheric torch suggests values of $n_e$ and $T_e$ that are rather constant. The variations with input power are rather limited.

- For the first time axial Thomson scattering has been performed successfully on intermediate pressure induced argon surfatron plasmas. The temperature and the density of the electrons are determined as functions of
axial position. The values are derived directly from experimental data; there is no need for a non-equilibrium model to interpret the results. These results are of great help to get a proper interpretation of the results of optical emission spectrometry (cf. chapter 5).

• Just as in the case of ACI we found with TS that at the end of the plasma column the electron density is much higher than the critical density; this is in contrast to what models predict.

• Along the wave propagation the $n_e$ decreases, so that the departure from Maxwell increases. Due to the decreasing ionization ratio, the tail fraction decreases. This implies that a higher $T_e$ (bulk temperature) is needed to sustain the plasma. This is most likely the reason behind the discrepancy of temperatures as measured with TS and ALI.

• For the first time Rayleigh scattering has been applied successfully to measure the heavy particle density and temperature in intermediate pressure surfatron plasmas with small radius. Axial profiles of the heavy particles density and temperature are obtained (cf. chapter 6).

• By comparing the results of ACI with those of RyS and TS we found that for a proper application of the ACI method as a tool to determine $n_e$, the heavy particles density and the electron temperature should be known (cf. chapter 7).

• The heavy particle temperature in a low pressure surfatron plasmas decreases gradually in the direction of the wave propagation. This confirms that the gas is not directly heated by the microwaves but via the electrons. The decrease of the atom temperature along the wave propagation results from the fact that the electron density goes down in the same direction.

• The increase of the atom density in the wave-propagation direction implies that the elastic collision frequency increases as well. This, together with the fact that the electron temperature increases as the wave propagates, means that the power that is needed to sustain an electron-ion pair (known as the $\theta$ parameter) is not constant.
9.5 Recommendations for future studies

- The experimental results should, in future, be compared more thoroughly with numerical models. The experiments will facilitate the validation of the models while the models will guide the interpretation of experimental results.

- An EEDF solver has to be employed to get a better understanding of the rise in electron temperature as found in regions close to plasma edges.

- The absolute continuum intensity method is by no means limited to argon surfatron plasmas and can be employed to other plasma sources and plasma gases. To that end we need the relevant cross sections for electron-atom momentum transfer interactions. In cases of gas mixtures an average value has to be used. The influence of molecular bands has to be addressed appropriately; for instance by a subtraction method. The contributions of the electron-ion interactions (free-free and free-bound) have to be taken into account if the method is applied to plasmas with higher degree of ionization.

- For a better comparison between the various methods and techniques and to come to an even better interpretation of plasma light it is recommended to perform (quasi) simultaneously the various diagnostic techniques at the same plasma-location and at the same time.
Appendix
## Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Meaning</th>
</tr>
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<tbody>
<tr>
<td>ACI</td>
<td>Absolute continuum intensity</td>
</tr>
<tr>
<td>AIM</td>
<td>Absolute intensity measurements</td>
</tr>
<tr>
<td>ALI</td>
<td>Absolute line intensity</td>
</tr>
<tr>
<td>ASDF</td>
<td>Atomic state distribution function</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>CRM</td>
<td>Collisional radiative model</td>
</tr>
<tr>
<td>DEC</td>
<td>Distance to the end of the column</td>
</tr>
<tr>
<td>EEDF</td>
<td>Electron energy distribution function</td>
</tr>
<tr>
<td>ESB</td>
<td>Excitation saturation balance</td>
</tr>
<tr>
<td>FS</td>
<td>False stray (light or signal)</td>
</tr>
<tr>
<td>LTE</td>
<td>Local thermodynamic equilibrium</td>
</tr>
<tr>
<td>MIP</td>
<td>Microwave induced plasma</td>
</tr>
<tr>
<td>MPT</td>
<td>Microwave plasma torch</td>
</tr>
<tr>
<td>OES</td>
<td>Optical emission spectrometry</td>
</tr>
<tr>
<td>PCVD</td>
<td>Plasma chemical vapor deposition</td>
</tr>
<tr>
<td>pLSE</td>
<td>partial local Saha equilibrium</td>
</tr>
<tr>
<td>RnS</td>
<td>Raman scattering</td>
</tr>
<tr>
<td>RyS</td>
<td>Rayleigh scattering</td>
</tr>
<tr>
<td>SIM</td>
<td>Stark intersection method</td>
</tr>
<tr>
<td>SIP</td>
<td>Surfatron induced plasma</td>
</tr>
<tr>
<td>SSTS</td>
<td>Single shot Thomson scattering</td>
</tr>
<tr>
<td>TGS</td>
<td>Triple grating spectrograph</td>
</tr>
<tr>
<td>TIA</td>
<td>Torche à injection axiale</td>
</tr>
<tr>
<td>TRL</td>
<td>Tungsten ribbon lamp</td>
</tr>
<tr>
<td>TS</td>
<td>Thomson scattering</td>
</tr>
</tbody>
</table>

**Table 1:** Acronyms used in the text.
Summary

Poly-diagnostic Validation of Spectroscopic Methods

*In-depth monitoring of microwave induced plasmas*

This thesis deals with poly-diagnostic investigations of microwave induced plasmas. Poly-diagnostic refers to the procedure in which more than one experimental method is used to determine the same plasma quantity.

Microwave induced plasmas have been studied and investigated systematically both theoretically and experimentally. Due to their broad range of operating conditions, stability and reproducibility they have received many technological applications. In order to improve these applications and to get a better understanding of the relation between the external control parameters and the resulting plasma properties and plasma products, insight into plasma mechanisms is required. To that end (numerical) models have been constructed and these have to be validated with experiments.

However, also the experimental methods need to be calibrated. Hence a poly-diagnostic study is indispensable. The aim of this procedure is to determine for each method the validity range and to help to find a minimum of easily measurable quantities from which a maximum of plasma-information can be deduced. In this way we are able to provide a firm base to plasma monitoring, a method already used in industry, by which the radiation emitted by plasmas is used to follow the plasma features and to control the plasma application process on-line.

In this work spectroscopic diagnostic methods have been applied to different microwave plasma sources, including the surfatron, the waveguide surfatron and the axial induced torch. The frequency of these microwaves equals in all cases
Different plasma settings are realized by changing the pressure, input power, gas flow and composition.

The applied spectroscopic methods can be divided into active and passive techniques.

Active spectroscopy refers to laser spectroscopy; more specifically to Thomson scattering and Rayleigh scattering. The Thomson scattering technique is used to determine the electron density and electron temperature, while Rayleigh scattering delivers information about the heavy particle density and temperature. These laser techniques are expensive and experimental demanding. Nevertheless, the interpretation of the results is in most cases straightforward.

For passive spectroscopy the opposite applies. The methods are experimentally relatively easy to perform but the interpretation is complicated and strongly depends on the degree of equilibrium departure. One of the ways to improve the interpretation of passive spectroscopy is to use absolute intensity measurements; meaning that the emitted and detected plasma radiation is calibrated against the radiation generated by a standard light source. This is done for both line and continuum radiation. Absolute line intensities give the electron temperature whereas the electron density can be deduced from absolute continuum measurements. To take the departure from equilibrium into account a collisional radiative model has been used. The iterative combination of (the absolute measurements of) line and continuum radiation provides a new method to obtain the values of electron density and electron temperature simultaneously.

An important role in our poly-diagnostic study is played by Thomson scattering. Since it simultaneously provides information of both electron density and temperature, while the interpretation of the data is straightforward it can be used to guide the interpretation of plasma emission. In this way the relation between plasma light and plasma properties can be established more firmly and the insights obtained can be used in industrial environments where plasmas are not accessible for laser techniques.
Acknowledgements

Our life is a study and practice. We spend our days at the University of Life. Every single day we learn something new, every day we win or lose a small battle, but in any case we earn life experience. I spent many days at the University of Science and I believe I learnt a lot. I believe, my life changed in a better direction thanks to my experience during the last three years at the TU/e. In personal scale, my PhD work is Something. In general scale, who knows how important it is? I did not discover the telephone or the lamp, but I filled in small parts of a big puzzle that at some moment will lead to new discoveries.

First at all, I would like to thank Joost van der Mullen. Joost, thank you for the wonderful time we worked together. You were supporting not only my scientific work but helping me always when I had hard time in personal scale. Thank you for showing optimistic mood at difficult moments. Everything starts with ABC...and at the moment, thanks to you, I end with writing the Acknowledgements of a PhD thesis! Blagodaria for everything Joost! My big reverence to you!

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Now, I switch to Bulgarian to thank my family.
Животът ни е учение и практика. Прекарваме дните си в университета, наречен Живот. Всеки ден научаваме нещо ново, всеки ден печелим или губим малка битка. Но винаги печелим житейски опит. Аз прекарах много дни от живота си в университета, наречен Наука. Вярвам, че научих много. Вярвам, че живота ми се е променил в по-добра насока, благодарение на опита добит през дните ми в университета в Айндховен. В личен план, лично за мен, докторатът ми е Нещо. В обич план, кой знае?. Не съм открила топлата вода или колелото. Попълнила съм само малки парченца от голям пъзел, който един ден ще доведе до нови и велики открития.

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