Spectroscopic study of microwave induced plasmas
Exploration of active and passive methods

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General introduction

1.1 Introduction

A plasma is a complex mixture that consists of atoms, molecules, (molecular) ions and electrons. The atoms can be in all kinds of excited electronic states whereas the molecules and molecular ions can occupy various electronic, vibrational or rotational excited states. In a plasma, part of the electrons are free instead of being bound to atoms or molecules. As a result, positive and negative charges are able to move more or less independently in the plasma. Hence, its behaviour is largely determined by the charged particles. As these properties are not encountered in the three well known states of matter, i.e. the solid, fluid and gas state, the plasma state is considered to be the fourth state of matter. In the universe, over 99% of the visible matter is in the plasma state. This is the case because the stars, nebulae and most of the interstellar matter are in the plasma phase. Besides natural plasmas, plasmas can be created in laboratories. These artificial plasmas can be operated in a large range of operating conditions. Control parameters like the chemical input, pressure, wall geometry, electromagnetic field structure, discharge configuration (plasma volume) and temporal behaviour (pulsed or continuous) can easily be modified [1]. This offers a tremendous freedom in the physical and chemical properties of plasmas. Due to these aspects, plasmas are used in a large variety of industrial applications like deposition and etching, materials treatment, lamps, light creation, waste treatment and materials analysis [2].

Plasmas can be classified by the pressure at which they operate. Three pressure ranges can be distinguished, namely low pressure (< 10^{-3} mbar), moderate pressure (~ 1 mbar) and high pressure (atmospheric or higher). The pressure is an important parameter since it largely determines the equilibrium state of the plasma. Generally, high pressure plasmas are in local thermodynamic equilibrium (LTE) whereas plasmas at low and moderate pressure are not in LTE. LTE is present when the particles are in thermal and chemical equilibrium. Thermal equilibrium implies that the temperatures of the different species are equal and that their energy distribution functions are Maxwellian. Chemical equilibrium is settled when the excited state distribution is given by Boltzmann, the relation between the densities of subsequent ionic states is according to Saha, and dissociation degree is described by the Guldberg Waage relation.
In industrial applications, plasmas are often used for the production of photons and particles. Due to the extraction of particles, momentum or energy from the plasma it is required to supply power in order to sustain the discharge. Most of the times, an externally applied electromagnetic field is used for this purpose. In order of increasing frequency, the following plasma types can be distinguished: direct current (DC), Radio Frequency (RF) (100 kHz – 1 GHz) and microwave (1 GHz – 100 GHz). In a DC plasma, a continuous current flows through the discharge as a result of constant potential difference between two electrodes. An example of a DC plasma at moderate pressure is the fluorescent lamp [3]. The RF waves can be coupled capacitively or inductively to the plasma. In capacitively coupled RF plasmas, an alternating potential difference is applied between the anode and the cathode causing the electrons to oscillate in the plasma between the electrodes. The parallel plate reactor [4] and the high pressure plasma needle [5, 6] are examples of capacitively coupled RF plasmas. In inductively coupled plasmas, the RF waves are coupled to the plasma using coils. Examples of these electrode-less plasmas are the spectrochemical inductively coupled plasma (ICP) and the Philips QL lamp [7]. In a microwave induced plasma (MIP), microwaves are produced by a magnetron and transported to a waveguide or cavity filled with gas. As is the case with RF plasmas, MIPs are also operated without the use of electrodes. A famous application of microwaves is the microwave oven, a kitchen appliance where the microwave radiation emitted from a magnetron is primarily absorbed by the water molecules inside the food. An example of a MIP is the microwave driven sulfur lamp [8].

The microwave induced plasmas form a special class of plasmas. As the wavelength of the microwaves is comparable to the geometrical dimensions, the wave propagation can be manipulated with slits, chokes and dielectrics [9–11]. Due to these aspects, MIPs can be operated electrode-less and the plasma can be sustained far away from the launcher. A special feature of MIPs is the wide range of operating conditions that can be used. Depending on the source, the frequency range is 300 MHz – 10 GHz, the pressure ranges from less than 10^{-2} mbar to several times atmospheric pressure (\sim 10\text{ bar}) and both atomic and molecular gases can be used. For these reasons, MIPs are often preferable to other types of plasmas. Three types of MIPs can be distinguished; the first are the expanding atmospheric plasma torches (TIA and MPT) [9], the second are plasmas produced by resonant cavities like the Beenakker cavity and the last are the surface wave sustained discharges (SWD) [12–14]. The resonant cavities and SWDs are confined in a quartz tube and can be operated at reduced or high pressures.

At the company Draka, a microwave deposition plasma at moderate pressure is used for the production of optical fibres [10, 11, 15]. The deposition technique is called \textit{Plasma activated Chemical Vapour Deposition}, abbreviated to PCVD. This molecular plasma is generated inside a quartz tube located inside a cylindrical microwave resonator [16]. In order to improve the deposition process, Draka has a large interest in obtaining more fundamental insight in MIPs at the same operational conditions as their deposition plasma. However, due to the moderate pressure (\sim 10\text{ mbar}) this plasma is far from LTE. Moreover, the complex atomic and molecular chemistry and the complicated electromagnetic coupling realized by the various microwave components (waveguides, slits, chokes) makes it difficult to obtain a thorough understanding of the microwave induced deposition plasma.

For these reasons, a joint research project including both experimental and numerical studies of MIPs was started by the Eindhoven University of Technology (TU/e) and Draka.
This STW project ETF6265 started in 2004 and will continue for at least two more years. The main purpose of the total project is to design an experimentally validated grand model for the microwave deposition plasma. Another aspect is to come to global models which can focus on more specific aspects like the complex chemistry.

This thesis describes a part of the work done within this research project and focusses on the experimental aspects and the use of global plasma models. Because the PCVD plasma was difficult to study experimentally, two other microwave induced plasma sources, the surfatron and the waveguide surfatron, were designed and constructed at the TU/e. This chapter starts with a description of the PCVD process (section 1.2), followed by the surface wave sustained plasma launchers in section 1.3. Section 1.4 contains a short overview of the different methods that can be employed to obtain information about the plasma. The scope and conclusions are respectively given in sections 1.5 and 1.6.

1.2 Plasma chemical vapor deposition

The setup of the PCVD used at the company Draka [15, 16] is schematically shown in figure 1.1. The substrate tube is made of quartz and mounted between a gas supply system and a pump. A gas mixture which consists of SiCl$_4$, GeCl$_4$ and O$_2$ flows through the tube under low pressure conditions (10 – 20 mbar). The tube is partially surrounded by a moving microwave cavity, also called resonator, which is connected to a magnetron.

![Setup of the PCVD used for the manufacturing of a preform.](image)

The resonator operates at a frequency of 2.45 GHz and high power (~ 6000 W) and couples the microwave energy directly into the tube. In this process, a plasma is created. The most important overall chemical reactions which occur in the plasma are

$$\text{SiCl}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{Cl}_2,$$
and

\[ \text{GeCl}_4 + \text{O}_2 \rightarrow \text{GeO}_2 + 2\text{Cl}_2. \]

During each pass of the traversing resonator, a thin layer of glass \( \text{SiO}_2 \), doped with a small amount of \( \text{GeO}_2 \), is deposited on the inner wall of the quartz tube. In time, the ratio of \( \text{SiCl}_4 \) and \( \text{GeCl}_4 \) is changed and a radial refractive index profile is obtained. To prevent the formation of chloride bubbles in the deposition layers, which occurs at temperatures below 1100 K, the complete system is placed inside an oven. Due to the deposition process, the tube is transformed to the so-called preform. Further heating of the preform causes the hollow tube to collapse into a solid rod, from which an optical fibre can be drawn. In this process, the refractive index profile of the preform is transformed into the optical fibre. The performance of the optical fibre is largely determined by the refractive profile of the preform.

### 1.3 Surface wave sustained plasma sources

Surface waves sustained (SWS) plasmas are a special type of MIPs that have several resemblances with the microwave induced deposition plasma used at Draka. In both cases, the microwaves that sustain the plasma are launched into a quartz tube via a circular gap. The electromagnetic waves propagate along the quartz-plasma boundary and ionize the gas. The microwave frequency, gas pressure, power density and flow velocity are of the same order. A difference is the position of the circular gap. For the microwave induced deposition plasma, the gap is more or less in the centre and the plasma is more confined. For SWS plasmas, the launching gap is on the end of the structure and most of the plasma is launched into a preferred direction. In this way, the SWS plasma can be extended far outside the field applicator. This aspect makes SWS plasmas easily accessible for optical spectroscopic methods.

Although several surface wave launchers are available, they all use a circular gap via which the microwave energy is coupled into a (quartz) tube filled with gas from which the plasma is created. The surface waves propagate along the tube at the interface between the quartz and plasma boundary and sustain the plasma. The shape of the electric and magnetic field components is determined by the mode in which these electromagnetic waves propagate. For a tube with a small radius, the surface waves propagate along the plasma column in the so called azimuthal symmetric \((m = 0)\) mode. This is a pure transverse magnetic (TM) mode, where the magnetic field in the direction of propagation is equal to zero. In cylindrical coordinates, the surface wave propagates in the axial \((z)\) direction. As a result, only the electric field components \(E_r, E_z\) and the magnetic field component \(B_\phi\) are unequal to zero. The azimuthal dependence of these components is described by the integer \(m\) via the field amplitude factor defined by \(\exp(jm\phi)\) [17]. This shows that the field components are independent on the azimuthal angle \(\phi\) for the \(m = 0\) mode. The dipolar mode \(m = 1\) can also occur in SWS plasmas. This mode is a linear combination of both TM and TE (transverse electric) waves where the amplitude of the components depends on the azimuthal angle. Experimentally, it is found that the propagation mode is related to the product of frequency and tube radius [17]. Generally, at the microwave frequency of 2.45 GHz, the \(m = 0\) mode is launched when the radius is smaller than \(\sim 1\) cm [12]. Although it is still possible to launch the pure \(m = 0\) mode for a larger tube radius, this is much harder to accomplish.
Two types of surface wave launchers are studied in this thesis, namely the \textit{surfatron} and the \textit{waveguide surfatron}, respectively shown in the figures 1.2 and 1.3. The surfatron is used in combination with coaxial cables and components and is suitable for low microwave powers ($< 300$ W), whereas the waveguide surfatron setup is based on waveguide components and can be used for high microwave powers. The surfatron is relatively small and flexible and is used in combination with experimentally demanding spectroscopic setups. The waveguide surfatron has a closer resemblance (tube radius, power) with the deposition plasma. To deal with high microwave powers, the waveguide surfatron is cooled with flowing water. These high powers are required to sustain molecular plasmas. Due to these aspects, the waveguide surfatron is more suitable for the use of molecular plasmas than the surfatron. In the following, a short description of both launchers is given.

![Figure 1.2: Schematic drawing of the surfatron (not to scale).](image1)

![Figure 1.3: Schematic drawing of the waveguide surfatron (not to scale).](image2)

The surfatron \cite{18} is an integrated surface wave plasma launcher which performs both field shaping and impedance matching. Electromagnetic waves with a fixed frequency of 2.46 GHz are generated in a magnetron and are guided towards the surfatron using coaxial cables, where
the coupler transports the waves to the launching gap. The radial position of this capacitive coupler can be adjusted in order to minimize the reflected power [13]. The microwaves are coupled into the plasma via a circular launching gap and can travel in both axial directions between the boundary of the plasma and the quartz tube. Inside the surfatron a metal tube is placed around the quartz tube which significantly increases the impedance for the propagation of the microwave. As the impedance for the wave propagation in air is much smaller, the main part of the waves are launched in the direction opposite to that of the closed metal tube [19]. In this way, the plasma can extend far outside the surfatron. Because the inner radius of the tube is relatively small ($a = 3$ mm), only the azimuthally symmetric mode ($m = 0$) is excited.

The waveguide surfatron consists of waveguide and coaxial elements [20]. Rectangular waveguides are used to transport the microwaves from the microwave generator to the waveguide surfatron. The waveguide section is terminated with a movable waveguide plunger that can be used to optimize the impedance matching. The coaxial section is placed perpendicularly to the waveguide components and provides an extra tuning capability. The position of the coaxial plunger determines the propagation mode of the surface waves. This makes it possible to launch the $m = 0$ mode when using a relatively large tube radius ($\sim 2$ cm). In this work, the waveguide surfatron is used to launch the $m = 0$ into a quartz tube with a radius of 13 mm. Note that this is not possible with the conventional surfatron as shown in figure 1.2.

1.4 Plasma characterization

Information of plasma properties can be obtained via (optical) diagnostics and plasma modelling. Both methods are discussed below, in which the emphasis lies on the optical diagnostics and the global plasma models.

1.4.1 Optical plasma diagnostics

Several spectroscopic diagnostic techniques have been applied to MIPs in order to determine important plasma properties like the electron density, electron temperature, gas temperature, atomic state distribution function (ADSF) and rotational temperature. The applied techniques can be categorized into two types, namely passive and active optical diagnostics. Passive means that only the spectrum emitted by the plasma is studied. Therefore, passive methods are non-intrusive, experimentally relatively easy and inexpensive. Main disadvantages are that the measurements are integrated over a line of sight through the plasma and that the processing of the experimental data is indirect. In active methods, the plasma is irradiated by a light source and the emitted, scattered or absorbed light is recorded. In general, active diagnostics might disturb the plasma, are expensive and experimentally demanding. The major advantage of these active methods is that they often provide direct information of the plasma properties. Therefore, active results do not rely on all kinds of equilibrium assumptions and can be used to validate the results obtained with the passive methods. The applied optical diagnostics are presented in table 1.1, where also the obtained properties, the type of the method and the chapters in which they are described are given. In the following, a short description of the applied methods is given. More detailed descriptions can be found in the chapters referred to in table 1.1.
Table 1.1: Overview of the applied spectroscopic methods. The abbreviation ASDF stands for atomic state distribution function; $n_e$ and $T_e$ refer to the electron density and temperature while $T_h$ stands for the gas temperature.

<table>
<thead>
<tr>
<th>Method</th>
<th>Parameters</th>
<th>Type</th>
<th>Chapters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute line intensity measurements</td>
<td>ASDF, $T_e$</td>
<td>passive</td>
<td>2,6,7,8</td>
</tr>
<tr>
<td>Absolute continuum measurements</td>
<td>$n_e$</td>
<td>passive</td>
<td>6,8</td>
</tr>
<tr>
<td>Line broadening measurement</td>
<td>$n_e$, $T_h$</td>
<td>passive</td>
<td>4,6,8</td>
</tr>
<tr>
<td>Rotational band measurements</td>
<td>$T_h$</td>
<td>passive</td>
<td>9,10</td>
</tr>
<tr>
<td>Thomson scattering</td>
<td>$n_e$, $T_e$</td>
<td>active</td>
<td>3,6,8,11</td>
</tr>
</tbody>
</table>

Absolute line intensity measurements

*Absolute line intensity* (ALI) measurements are commonly used to determine the density of excited states. The radiation emitted during the optical transition is measured using a spectrometer and calibrated absolutely with a tungsten ribbon lamp. The density of the upper level is proportional to the absolute intensity of an optical transition. The absolute measurement of various spectral line transitions allows the construction of the ASDF, where the excited states are plotted as function of the excitation energy. For a plasma in LTE, the slope of the ASDF is related to the electron temperature and the electron density can be determined from the Saha balance. For plasmas that are not in LTE, collisional radiative models can be used to relate the ASDF to the main plasma parameters $T_e$ and $n_e$.

Absolute continuum measurements

Besides spectral lines, the spectrum emitted by the plasma also contains *continuum radiation*. An absolute measurement of this continuum allows the determination of the electron density. Continuum radiation is created by Bremsstrahlung or recombination processes. Bremsstrahlung is generated by elastic collisions between electrons and other particles like atoms or ions. During the interaction, the electron is slowed down and a photon is emitted. Besides Bremsstrahlung processes, continuum radiation is also created in the process where a free electron is captured by an ion which leads to recombination.

Line broadening measurements

The *line shape* of a spectral transition contains information about the plasma properties. A spectrometer with a high resolution is required in order to measure the shape with sufficient accuracy. The total broadening of a spectral line is caused by a number of different broadening mechanisms. These mechanisms can be split up into two groups; the first are related to the plasma whereas the second are independent of the plasma and are for example caused by the spectrometer or the nature of the transition. In general, a line is broadened by natural broadening, pressure broadening, the fine structure and the instrumental broadening of the employed spectrometer. In our study, the *Stark* and *Doppler* broadening are most relevant. The Stark broadening is caused by the interaction of the emitting particle with the charged particles in the plasma and the Doppler broadening is due to the thermal velocity of the emitting particle. Under certain plasma conditions, Stark broadening results in a Lorentzian line profile of which the half width is related to the electron density. If the velocity distribution
of the emitting particle is Maxwellian, the Doppler broadening results in a Gaussian shape with a width that depends on the atom temperature. The combination of Lorentzian and Gaussian contributions leads to a so-called Voigt profile. Therefore, a measurement of the spectral line shape with sufficient resolution results in a Voigt profile, which can be separated into Gaussian and Lorentzian components. After this so-called de-convolution, plasma tables that relate the Stark width to the electron density have to be employed. For our application, it was necessary to extrapolate the tables to lower electron densities. Therefore, the results are validated with Thomson scattering results.

Rotational band measurements

In a molecular plasma, the emitted spectrum contains spectral lines due to vibrational or rotational transitions. The radiation emitted during such a rotational transition can be measured using a spectrometer of which the resolution has to be high enough in order to resolve the rotational lines. The measured rotational intensities can be plotted as function of the rotational energy. The slope of this graph is related to the rotational temperature that is equal or close to the gas temperature for moderate and high pressures.

Thomson Scattering

Laser Thomson scattering (TS) is an important diagnostic technique based on the scattering of laser radiation by the free electrons in the plasma. It provides direct and spatially resolved information about the electron gas properties, thus local profiles of the electron density and electron temperature. The photons scattered from a focused laser beam are imaged onto the entrance slit of a spectrograph where the TS spectrum is detected by an intensified charge coupled device (iCCD) camera. The TS spectrum has a Gaussian profile when the TS is incoherent (non-collective scattering) and the electron energies have a Maxwellian distribution. The width and the area of the profile are then related to the electron temperature and electron density respectively. Besides incoherent TS, where interference effects between the particles can be neglected, the scattering can also be collective (coherent TS). For coherent TS, the electron motions are influenced by the presence of other electrons in the plasma and the shape of the TS spectrum is not a pure Gaussian anymore. Under certain conditions, the shape of a collective TS spectrum can be described by the Salpeter approximation [21]. The TS spectrum is incoherent when applied onto the low pressure surfatron plasmas whereas the TS on the high pressure mercury lamp is coherent.

1.4.2 Plasma modelling

Plasma modelling is a powerful tool to obtain insight in plasmas and information about the plasma properties. Two types can be distinguished; grand and global plasma models. Both models are discussed below.

Grand plasma modelling

Grand models are two or three dimensional and give a full numerical description of the total plasma, which means that almost all the different aspects of the plasma are taken into account. In this way, detailed information with spatial and temporal resolution can be obtained. The disadvantage of this type of model is that they are very complex and detailed
knowledge of all relevant processes is required. In the past, a numerical simulation tool for plasmas called PLASIMO ("PLAsma SImulation MOdel") has been developed at the TU/e. PLASIMO is a fluid model which divides the plasma into a large number of control volumes for which the conservation equations for mass, momentum and energy are solved [22]. Recently, PLASIMO has been used to construct a grand model for the microwave induced deposition plasma [10, 11]. Hereby, two dimensional profiles of important plasma parameters like the electron temperature, electron density and atom temperature are obtained as function of the experimental control parameters (chemistry, pressure, applied power, geometry). At the moment, this grand model is working properly for argon and the first results are obtained for molecular oxygen [11]. In the next two years, the chemistry will be extended in order to include SiCl$_4$ as well.

Global plasma modelling

Global models are zero dimensional and assume a pre-described spatial distribution of the parameters. This type of model can be valuable to obtain averaged values of the plasma properties in a very short calculation time. An important type of global plasma models relates the experimental control parameters such as the microwave power, tube radius and gas pressure to plasma parameters like the electron density, electron temperature and gas temperature [23]. These zero dimensional plasma models are based on solving the particle and energy balance equations [24]. Because these balance equations are strongly coupled, an iterative solving procedure is generally applied. The results of global plasma models can be used to guide the trends observed from experimental results [25] and can be compared with the experimental results. Also, this type of model gives quick estimates of the plasma properties which can be used as starting conditions for the grand PLASIMO model.

In this thesis, a global model for an atomic argon plasma has been employed in order to compare the experimental results obtained for different control parameters with each other. In an atomic global model, electrons are produced by ionization of atoms, destroyed by two electron recombination and removed from the discharge by ambipolar diffusion. For the experimental conditions of the argon MIPs, it was found that the influence of two electron recombination was negligible. The obtained results are in reasonable agreement with the experimental and grand modelling results. However, the situation drastically changes when molecules and molecular ions$^1$ are present in the discharge. Recombination processes with molecular ions are very efficient and significantly increase the electron temperature. In molecular plasmas, more electron energy loss terms like dissociation and ionization of molecules are present. As a result, the electron density can decrease with more than one order. In addition, the various vibrational and rotational transitions provide a large heating term for the heavy particles. Therefore, the presence of molecules complicates the global models because the particle balances for all relevant particles have to be solved and much more reactions should be taken into account.

$^1$It is expected that the molecular argon ions Ar$_2^+$ plays an important role in surfatron induced argon plasmas.
1.5 Scope of this thesis

This work is focussed on the application of various spectroscopic techniques to microwave induced plasmas. Due to the non-LTE character of the discharge, it is sometimes required to use models for the processing of the experimental data obtained with the passive diagnostics. For this reason, several passive and diagnostic methods are applied to the plasma and the results are compared with each other. This procedure is applied to both atomic and molecular plasmas in order to determine which diagnostic methods can correctly be applied to the microwave deposition plasma. Another important aspect of this study is the application of global plasma models to MIPs. Regarding the chemistry, the following route was followed for both the diagnostics and global models: the study started with the well known argon plasma, advanced to the plasma mixtures argon/hydrogen\(^2\) and argon/oxygen and finally almost pure oxygen plasmas were studied.

The most important experimental purposes of this work are:

- Design and construction of microwave induced plasma sources, the surfatron and the waveguide surfatron, which are accessible for optical diagnostics.
- Development of passive methods based on emission spectroscopy.
- Validation of these passive methods by comparing results of active and passive diagnostics obtained using the surfatron induced plasma with each other (poly-diagnostic calibration).
- Application of the validated passive methods to the waveguide surfatron and the microwave induced deposition plasma.

The global plasma models are used for the following aims:

- Parameter study with an atomic global model for argon to determine the influence of control parameters and the plasma properties.
- Obtain insight in the processes that occur in plasma by comparing global model results with experimental results.
- Determine the influence of the addition of a small amount of molecular gas (hydrogen, oxygen) on the argon plasma.
- First steps towards a molecular global model.

In a later stage of the STW project, the validated experimental results can be used for the validation of the grand Plasimo model. Also, the global models can further be extended so that they can be used to obtain insight in the complex chemistry of the deposition plasma. These aspects are beyond the scope of this thesis.

\(^2\)The hydrogen was added to an argon plasma for spectroscopic purposes, namely to determine the Stark broadening of hydrogen Balmer lines.
1.6 Thesis outline

In chapter two a diagnostic method to determine the electron temperature of a low pressure surface wave sustained argon plasma is investigated. A surfatron was used as a plasma launcher and an explanation of the microwave and optical setup is given. The employed technique is based on absolute line intensity measurements and uses a collisional radiative model for the interpretation of the experimental data. Hereby, axial electron temperature profiles and estimated values of the electron density profiles are obtained.

Chapter three describes the application of Thomson scattering, an active spectroscopic technique, to a surfatron induced argon plasma. These measurements were performed at one spatial position for different plasma conditions.

Chapter four contains a description of the waveguide surfatron and deals with the application of Stark broadening to a low pressure argon plasma to which a small amount of hydrogen was added. Axial profiles for the electron density, electron temperature and atom temperature are given.

In chapter five, an argon plasma with a small amount of hydrogen is studied using a global plasma model. The obtained results are in reasonable agreement with the experimental results.

In chapter six, passive and active spectroscopic techniques are applied simultaneously to a surfatron induced argon plasma and the results of the different techniques are compared. The validated passive methods can now be applied to other microwave plasmas for which Thomson Scattering is not an option.

In chapter seven, a comparative study of the different microwave induced plasmas, i.e. the surfatron, the waveguide surfatron and the resonator plasma, is made. A global model was used to relate the control parameters to the plasma properties. Experimental and global model results are used for this purpose.

Chapter eight deals with argon-oxygen mixtures. Here, the results for an argon/oxygen mixture with approximately 5% of oxygen are compared with pure argon results. Also, by means of a diagnostic study we examine whether the passive diagnostics which work well for argon are still applicable for argon/oxygen mixtures.

In chapter nine, the gas temperature of an oxygen plasma with 1% of argon is determined from molecular spectroscopic measurements.

In chapter ten, the same plasma as in the previous chapter is studied. The gas temperature is used to determine the total particle density. Via a measured intensity ratio of argon/oxygen lines, the dissociation degree is estimated.

General conclusions and recommendations are defined in chapter eleven.

Bibliography

Chapter 1.


A spectroscopic method to determine the electron temperature of an argon surface wave sustained plasma using a collisional radiative model

Abstract. A method is presented to determine the electron temperature in a low pressure argon plasma using emission spectroscopic measurements and a collisional radiative model. Absolute line intensity measurements have been made in order to construct the atomic state distribution function. In addition to the excited states, the ground state density is also taken into account. Because of this, the excitation temperature can be determined with high precision. A collisional radiative model is used to determine the degree of equilibrium departure and to obtain the relationship between the excitation temperature and the electron temperature. This method is applied to a microwave plasma which has been generated inside a quartz tube using a surfatron device. The densities of argon levels close to the continuum are used to get an estimated value of the electron density. These values are used as input data for the collisional radiative model. For an argon pressure of 6 mbar, the 4p-level densities varied between $8 \times 10^{14}$ m$^{-3}$ and $6 \times 10^{15}$ m$^{-3}$. Using the estimated values for the electron density, between $2 \times 10^{19}$ m$^{-3}$ and $3 \times 10^{19}$ m$^{-3}$, the electron temperature is found to range between 1.15 eV and 1.20 eV. An extensive error analysis showed that the relative error in the electron temperature is less than 10\%.

2.1 Introduction

Surface wave sustained discharges (SWD) are a special type of microwave induced plasmas, by which the electromagnetic waves propagate mainly along the interface between the plasma column and a dielectric material [1–5]. Thus the plasma column is both generated and sustained by the surface waves while it guides the wave. The launching of surface waves into the tube can be realized by using a microwave coupler whose axial dimensions are much smaller than the axial length of the plasma column. Examples of surface wave launching devices are the ro-box, the surfatron, the waveguide surfatron and the surfaguide [5]. Using one of these launching devices, an SWD can be sustained in a large pressure range, at different power levels, for various filling gasses, tube diameters and at frequencies ranging from approximately 1 MHz to 10 GHz [1, 5]. Since SWDs are stable and reproducible under a wide range of process conditions, they can be used for a number of applications like material processing (deposition, oxidation, etching), light creation and spectrochemical analysis [6]. In order to improve the various applications, insight into the properties of the plasma is needed. This can be obtained by means of experiments, modeling or a combination of both.

Since the plasma is generally confined in a quartz tube that is transparent for light, emission spectroscopy is a good candidate to obtain information about the main plasma parameters like the electron density, \( n_e \), and the electron temperature, \( T_e \). The advantage of this passive spectroscopic method is that measuring the emitted light is non-intrusive. In this study we determine the electron temperature by using both passive spectroscopy and a model for the interpretation of the measurements.

Several studies can be found in the literature in which a temperature value is derived from the ratio of the intensities of two lines. However, the information of this so-called 2\( \lambda \) method is in many cases limited because of the following two reasons [7, 8]:

1. The excitation temperature, \( T_{ex} \), obtained with the 2\( \lambda \) method is, in many cases, deduced from the ratio of two lines that originate from excited levels which are rather close to each other. The energy difference \( \delta E \) is in the order of 1 eV or even less. This means that the determination of \( T_{ex} \) is generally not very accurate. The accuracy can be improved (partially) by taking more levels into account and by using a larger part of the atomic state distribution function (ASDF). However, as is usually found, the slope of the ASDF is not constant, which points to deviations from equilibrium. This brings us to the second point.

2. Large deviation from equilibrium can be expected for a wide category of plasmas. For these plasmas, it is by no means obvious whether the excitation temperature represents the electron temperature.

In this paper, we will present a method in which both problems are circumvented for argon plasmas. The first one, the inaccuracy in the \( T_{ex} \) determination, can be resolved by taking apart from the excited states also the ground state density into account. In atomic plasmas of low degree of ionization this ground state can be determined via the pressure. Since the energy gap \( \delta E \) for the argon system between the first excited states and the ground state is in the order of 11 eV, we can determine the slope in the ASDF with high precision. An extra demand of this method is that the density of the excited states has to be determined in an
Spectroscopic method to determine the electron temperature

The second step is to determine the degree of equilibrium departure and how this will
affect the relation between $T_{ex}$ and $T_e$. To that end we use a collisional radiative (CR)
model, which calculates the population density of the excited states for a specific set of input
parameters such as the ground level density, the electron density and temperature [9, 10]. In
this work, a CR-model for argon was used of which a detailed explanation is given in [11–13].

In the past, a comparable method was used by Jonkers [14, 15] and Timmermans [16].
They used the combination of the density of the ground state and one of the first excited
states namely those of the 4s group. Since these levels do not radiate in the visible part of
the spectrum (there are transitions at 105 and 107 nm) the 4s level densities were determined
with a laser absorption technique. In our approach we use the combination of the densities
of the ground state and the 4p-level group. This group generates radiation in the range of
668 - 1047 nm. These lines are easily detectable and most of them are not influenced by self-
absorption. Here we will adopt the convention to denote the atom ground state with “1”, the
4s levels with level (group) “2” and the 4p-levels with “3”. So the task of the experimental part
of the present study is to determine the excitation temperature $T_{13}$. This will subsequently
be transformed into $T_e$, using a CR-model. Jonkers and Timmermans used a CR-model to
relate $T_{12}$ to $T_e$. In [17], a CR-model was applied to derive the electron temperature from
measured excited states high in the atomic system. Although the line intensities were abso-
lutely determined, the ground state density was not taken into account so that the energy
distances between the levels in question were small. This introduced large errors.

This article is organized as follows: in section 2.2 a description of the experimental setup
is given. Subsequently, the theory and methods are given in section 2.3, whereas the results
of the absolute line intensity measurements and the CR-model are presented in section 2.4.
In section 2.5 a short discussion of the method and some recommendations are given. An
overview of the measured argon lines is given in the appendix (section 2.6).

2.2 Experimental setup and instrumentation

The microwave and spectroscopic parts of the setup which were used for the spectroscopic
measurements are shown in figures 2.1 and 2.2. The spectroscopic measurements were per-
formed on a microwave induced argon plasma created by a surfatron with a gap diameter of
8.5 mm. The inner radius of the quartz tube with permittivity $\varepsilon_D = 4.3$ equals 3 mm, the
outer radius 4 mm. A metal screen was placed around the tube with a radius of 25 mm. The
argon flow was set at a constant rate of 50 sccm. At a gas pressure of 5 mbar, this corresponds
with an axial flow velocity of 1.2 m/s in the centre assuming a Poiseuille flow profile. The
suratron has been used under two different working conditions. In the first, the averaged
pressure was set at 6.1 mbar, in the second at 9.9 mbar. In both cases, the absorbed power
was equal to 22.5 W. At 6.1 mbar, this resulted in a plasma length of 39 cm, while at 9.9 mbar
a plasma with a length of 38 cm was created. In the first part of this section, the microwave
and vacuum systems are explained; the optical system is shown in the second part.
2.2.1 The microwave and vacuum system

Electromagnetic waves are generated in a magnetron which has a maximum power of 300 W. The frequency of the microwaves is fixed at about 2.46 GHz. A circulator is placed behind the magnetron that guides the reflected waves into a 50Ω dump to prevent that reflected waves enter the magnetron. Coaxial cables are used between the elements to guide the waves towards the surfatron. In order to measure the incident and reflected power, a bidirectional coupler is used to attenuate the incident and reflected waves. For the actual measurement, two power sensors and one power meter have been used (table 2.1). After the bidirectional coupler, a triple stub tuner is used for impedance matching. A surfatron has been used to generate and sustain a plasma inside a quartz tube. The surfatron is an integrated surface wave plasma launcher which performs both field shaping and impedance matching. An antenna is used for the power input of these waves. The radial position of the antenna can be adjusted. This changes the capacitance and inductance and can therefore be used to minimize the reflected power [5]. The microwaves are coupled into the plasma via the launching gap and can travel in both axial directions between the boundary of the plasma and the quartz tube. The impedance for propagation along the plasma through a closed metal tube is larger than the impedance for the propagation in air. Because of this the main part of the wave is launched in the direction opposite to that of the closed metal tube [2]. The plasma is sustained by these waves and can extend far outside the surfatron. A metal (aluminium) screen with a groove over its complete length was placed around the tube to shield the plasma from disturbances from the environment. A mass flow controller is placed before the gas inlet side of the tube and a vacuum pump is placed at the gas outlet side. The gas pressure in the tube is controlled at the pump side by means of a manual valve and is measured both at the gas inlet side and the gas outlet-side. A schematic overview of the setup is shown in figure 2.1.

![Figure 2.1: Representation of the microwave setup.](image-url)
2.2.2 The optical system

The emitted plasma light is focussed by a small lens into an optical fibre, by which the light is guided to the entrance slit of a 1 meter monochromator that is equipped with a grating of 1200 lines/mm. A CCD camera with a horizontal pixel width of 7 μm is attached to the monochromator and has been used to record the spectra. Around a wavelength of 800 nm, the dispersion is about 5.5 pm per pixel and the instrumental broadening was measured to be around 14 pm. The optical fibre and lens can be moved along the axial direction of an optical rail. This setup enables us to measure the emitted plasma light along a radial line of sight at a specific axial position. The measured intensity of a spectral line has to be calibrated with a light source of which the intensity is accurately known. This has to be done for all the transitions under investigation. A tungsten ribbon lamp operated at an accurately known electric current has been used for this purpose. An overview of the optical components can be found in table 2.1 and a sketch is shown in figure 2.2.

Figure 2.2: Overview of the spectroscopic system.

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>Type</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microwave generator</td>
<td>Muegge MW GIR YY 1511</td>
<td>2.46 GHz, 300 W</td>
</tr>
<tr>
<td>Dual directional coupler</td>
<td>HP, model 767D</td>
<td>-19 dB</td>
</tr>
<tr>
<td>Power sensors</td>
<td>8482 H Agilent</td>
<td></td>
</tr>
<tr>
<td>Power meter</td>
<td>HP 438A</td>
<td></td>
</tr>
<tr>
<td>Mass flow controller</td>
<td>Bronckhorst High Tech</td>
<td>100 sccm Ar</td>
</tr>
<tr>
<td>Pressure meters</td>
<td>Capacitance Gauge CMR 262</td>
<td>$10^{-2} - 110$ mbar</td>
</tr>
<tr>
<td>Vacuum pump</td>
<td>Pfeiffer Vacuum (LS80 PR)</td>
<td>$S(N_2) = 10$ m³/h</td>
</tr>
<tr>
<td>Optical fibre</td>
<td>Ocean Optics</td>
<td>0.6 mm</td>
</tr>
<tr>
<td>1m monochromator</td>
<td>BM 100</td>
<td>400 – 1100 nm</td>
</tr>
<tr>
<td>CCD camera</td>
<td>ST-2000XM</td>
<td></td>
</tr>
<tr>
<td>Tungsten ribbon lamp</td>
<td></td>
<td>400 – 1000 nm</td>
</tr>
</tbody>
</table>
2.3 Theory and methods

Spectroscopic measurements enable the construction of the atomic state distribution function (ASDF), which describes the distribution of the atoms over the internal states. Global plasma properties such as the electron temperature, electron density and atom ground state density can be deduced from the ASDF. For an atomic plasma in local thermodynamical equilibrium (LTE), the shape of the ASDF is primarily determined by balances of equilibrating elementary processes; which can be classified in three different types named after Maxwell, Boltzmann and Saha [9]. In the LTE case, the shape of the ASDF is described by the Saha-Boltzmann balance, the slope is related to the temperature and the electron density can be obtained by extrapolating the ASDF to the ion ground state. The shape of the ASDF for an LTE plasma is schematically shown in figure 2.3.

![Figure 2.3: The ASDF of an atomic plasma in LTE. The state density of level p, denoted by η_p, is plotted as a function of the energy. The energy of a level p is denoted in two different ways: via the excitation energy E_p or the ionization potential I_p. The parameters η_p and η_i refers to the atomic and ionic ground state density, respectively.](image)

The Saha balance is in equilibrium when the rate of electron induced ionization processes equals the one of two electron recombination: e + A_p ↔ 2e + A_. In this case the Saha formula describes the shape of the ASDF. It reads

\[
\eta_p = \eta_e \eta_i \left( \frac{h^2}{2\pi m_e k_B T_e} \right)^{3/2} \exp \left( \frac{I_p}{k_B T_e} \right),
\]

where \( \eta_p = n_p / g_p \) is the population density, \( n_p \), per statistical weight, \( g_p \), of an atomic excited level p with ionization energy \( I_p = E_{\text{ion}} - E_p \), while \( \eta_e = n_e / g_e = n_e / 2 \) and \( \eta_i = n_i / g_i \) are the electron, e, and ion, i, densities per statistical weight, respectively. Furthermore, \( h \) refers to Planck’s constant, \( k_B \) to the Boltzmann’s constant and \( m_e \) to the electron rest mass. By taking the natural logarithm of equation 2.1, the following expression is obtained,

\[
\ln (\eta_p) = \frac{I_p}{k_B T_e} + \ln (\eta_\infty),
\]

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Spectroscopic method to determine the electron temperature

in which \( \eta_\infty \) equals

\[
\eta_\infty \equiv \eta_e \eta_i \left( \frac{\hbar^2}{2\pi m_e k_B T_e} \right)^{3/2} .
\]  

(2.3)

By plotting \( \eta_p \) versus \( I_p \) in a semi-logarithmic plot, \( T_e \) can be found via the slope and \( \eta_\infty \) by a linear extrapolation of \( \eta_p \). From this, \( n_e \) can be determined, assuming that \( n_e = n_i \).

For the low pressure surfatron plasma, two reasons for departures from LTE are expected. First, the electrons are heated by the electromagnetic field whereas the atoms are cooled by collisions at the wall. Due to the ineffective energy transfer of electron-atom (ion) collisions, the electron temperature becomes higher than the temperature of the atoms and ions. Second, the transport of charged particles distorts the Saha balance between ionization and two electron recombination \((e + A_p \leftrightarrow 2e + A_+)\) so that the shape of the ASDF can no longer be described with the Saha equation (equation 2.1). Therefore, due to outward diffusion of charged particles, the active plasma zone will be ionizing. The corresponding shape is schematically shown in figure 2.4.

![Figure 2.4](image)

Figure 2.4: Schematic plot of the ASDF of an ionizing plasma. Here, \( \eta_p^B \) and \( \eta_p^S \) are equal to the Boltzmann and Saha state densities, respectively. The parameter \( r_p^1 \) is a relative population factor and is related to the overpopulation of state \( p \) compared to the Boltzmann population.

This figure shows that the slope is variable, so that a single temperature can no longer be defined. Therefore, it is common to define excitation temperatures corresponding to various parts of the ASDF. If the assumption is justified that the Saha balance is valid for levels high in the atomic system, a linear fit can be made in which only these high lying levels are taken into account. Thus by extrapolating the upper part of the ASDF, it is possible to obtain an estimate for the value of \( \eta_\infty \). For the lower part of the ASDF we can not assume that the balances of Saha or Boltzmann are in equilibrium. Therefore, a CR-model has to be applied in order to deduce plasma properties out of this part of the ASDF. In this study we confine ourselves to the determination of the electron temperature out of the lower part of the ASDF. To that end absolute line intensity (ALI) measurements are made in order to construct the
ASDF. The lower lying energy levels are used to determine the excitation temperature $T_{13}$, which is related to the ratio of the density of atoms in level "3" to the atoms in the ground state (state "1"). For argon, the level "3" corresponds to the 4p-group. The upper part of the ASDF is used to estimate the parameter $\eta_{\infty}$. Via the charge neutrality assumption, this leads to $n_e$. The electron temperature $T_e$ can be obtained by using the results of the ALI measurements in combination with a collisional radiative model.

This section is organized as follows: first the principle of the ALI-measurement is explained. This is followed by a description of the collisional radiative model and the method that was used to determine the electron temperature.

2.3.1 Absolute line intensities

The method of ALI measurements is a diagnostic tool to determine absolute densities of atomic states $n_p$ from the absolutely measured intensities of optical thin lines. If the plasma is optically thin for the transition $p \rightarrow q$, the radiation escapes from the plasma and absorption can be neglected. The corresponding spectral emission coefficient as a function of wavelength, $j_\lambda(\lambda)$ [W m$^{-3}$ nm$^{-1}$ sr$^{-1}$], is given by

$$j_\lambda(\lambda) = n_p A_{pq} E_{qp} \varphi_\lambda(\lambda)(4\pi)^{-1},$$

where $n_p$ is the density of the radiating level $p$, $E_{qp} = E_p - E_q$ the energy of the emitted photon and $\varphi_\lambda(\lambda)$ the normalized line shape of the transition. It is defined in such a way that integration over the wavelength gives unity; i.e. $\int \varphi_\lambda d\lambda = 1$. The wavelength integrated spectral density, also called transition integrated emission coefficient and denoted by $j_{pq}$ [W m$^{-3}$ sr$^{-1}$], is defined by

$$j_{pq} = \int j_\lambda(\lambda)d\lambda = \int j_\lambda(\lambda)d\lambda = (1/4\pi) \cdot n_p A_{pq} E_{qp} \varphi_\lambda(\lambda)(4\pi)^{-1}.\quad (2.5)$$

This equation shows that the population density $n_p$ of level $p$ can be found using the emission coefficient $j_{pq}$ of a particular transition and the equation

$$n_p = j_{pq} \frac{4\pi}{A_{pq} E_{qp}}.\quad (2.6)$$

By applying this procedure to various transitions, the ASDF can be constructed by plotting the natural logarithm of $\eta_p = n_p / g_p$ as a function of the energy of the upper level of the transition $E_p$.

2.3.2 A collision radiative model for an atomic plasma

If equilibrium is not present, the ASDF is determined by the combined action of all relevant transport phenomena and elementary collisional and radiative processes. This is described by a collisional radiative (CR) model that solves the set of particle balances. For an atomic state $p$, such a balance is given by the zeroth moment of the Boltzmann transport equation

$$\frac{\partial n_p}{\partial t} + \nabla \cdot n_p w_p = \left( \frac{\partial n_p}{\partial t} \right)_{CR},\quad (2.7)$$
where $n_p$ is the number density of atoms in level $p$ and $w_p$ the mean velocity of these atoms [9]. The terms on the left-hand side describe the change in $n_p$ due to temporal and spatial relaxation. The right-hand side describes the change in state $n_p$ due to electron collisions or radiative processes.

In a large class of plasmas, the typical time scales for transport related processes ($10^{-4}$ s) are much larger than the time scales for radiative and collisional processes, which are approximately $10^{-8}$ s for the excited states [9]. This means that transport related processes can be neglected for most of the excited levels. For these levels, temporal and spatial relaxation can be neglected, so that equation 2.7 reduces to

$$0 = \left( \frac{\partial n_p}{\partial t} \right)_{CR}.$$  \hspace{1cm} (2.8)

This is called the Quasi Steady State Solution (QSSS) and in our case we assume that it is applicable to all excited levels [9] of the Ar-system. For the atom and ion ground levels, the competition between transport and elementary balances has to be described so that the complete particle balance, thus equation 2.7 needs to be solved. The atom ground level density $n_1$, the ion ground level density $n_+$ and the electron temperature are the input parameters for the CR-model. Using this input data, the CR-model is used to solve equation 2.8 for all excited states [11, 13].

The variables $n_1$ and $n_+$ are considered to be mathematically independent. Therefore, the population density $\eta_p$ of an exited level $p$ consists of two contributions, one from the atomic $\eta^1_p$ and the other from the ionic ground state $\eta^+_p$:

$$\eta_p = \eta^+_p + \eta^1_p.$$  \hspace{1cm} (2.9)

These contributions can be related by their equilibrium quantities. The $\eta^1_p$ value can be related to the Boltzmann population density, $\eta^B_p$, and $\eta^+_p$ to the Saha population density, $\eta^S_p$:

$$\eta^1_p = r^1_p \eta^B_p,$$  \hspace{1cm} (2.10)

and

$$\eta^+_p = r^+_p \eta^S_p.$$  \hspace{1cm} (2.11)

The dimensionless quantities $r^+_p$ and $r^1_p$ are known as the relative population coefficients, $\eta^+_p$ corresponds to the CR-model solution for the case that the atom ground level density is put equal to zero, and $\eta^1_p$ with the solution if the ion ground levels are set to zero. The Boltzmann density is given by

$$\eta^B_p = \eta^1_p \exp \left( \frac{-E_{1p}}{k_B T_e} \right),$$  \hspace{1cm} (2.12)

while $\eta^1_p$ is equal to the atomic ground state density $\eta^1_1$.

### 2.3.3 Relative population coefficients

In a strongly ionizing plasma the ion contribution can be neglected for lower excited states so that $\eta^+_p \ll \eta^1_p$ and equation 2.9 can be written as

$$\eta_p = r^1_p \eta^B_p = r^1_p \eta^B_1 \exp \left( \frac{-E_{1p}}{k_B T_e} \right).$$  \hspace{1cm} (2.13)
In this study, a CR-model is applied in order to determine the $r_p^1$-coefficient. This will be used to transform the measured excitation temperature $T_{13}$ into the electron temperature $T_e$ (see subsection 2.3.4). A CR-model for argon was used of which a detailed explanation is given in [11–13]. The excitation temperature $T_{13}$ is associated with the ratio of the lowest easily measurable levels, in our case the 4p-levels in argon, and the ground state.

In order to understand the general structure of $r_p^1$ as a function of $n_e$ and $T_e$, a simplified derivation of the $r_p^1$ value of level "2" will be given. The level "2" refers to the first excited level or group of excited levels, in the case of argon the 4s-group. For this simplified case, the CR-model is based on the particle balance of level "2", which reads

$$0 = n_e n_1 K(1,2) - n_e n_2 K(2,3) - n_e n_2 K(2,1) - n_2 A^*(2,1),$$

where $K(i,j)$ is the excitation or de-excitation rate from a level "i" to a level "j" and $A^*(2,1)$ the product of the radiative transition probability $A(2,1)$ with the optical depth $\Lambda (2,1)$. This particle balance states that level "2" is populated by excitations from the ground level "1" (first term on the right-hand side) and depopulated by excitations to level "3" (second term), de-excitations to level "1" (third term) and radiative transitions to the ground state (fourth term). The density of level "2" can now be expressed as,

$$n_2 = \frac{n_e n_1 K(1,2)}{n_e K(2,1) + n_e K(2,3) + A^*(2,1)}.\quad (2.15)$$

Using the principle of detailed balancing for the "1" → "2" transition [9], i.e. $n_1 K(1,2) = n_2^B K(2,1)$ and dividing by $n_2^B$ results in

$$r_2^1 = \frac{n_2}{n_2^B} = \left[1 + \frac{K(2,3)}{K(2,1)} + \frac{A^*(2,1)}{n_e K(2,1)}\right]^{-1}.$$

From equation 2.16, the following trends can be deduced. First, since $K(2,3)$ is about 1000 times larger than $K(2,1)$, we can expect that $r_2^1$ is in the range of $10^{-3}$. Second, the $T_e$ dependence is determined by $K(2,3)$, which contains the Boltzmann factor $\exp(-E_{23} / k_B T_e)$; on the other hand, $K(2,1)$ is only weakly $T_e$ dependent. For increasing $T_e$, the value of $r_2^1$ will decrease. Third, the $n_e$ dependence is limited if radiative decay is unimportant, thus if $A^*(2,1) \ll n_e K(2,1)$. Moreover, the $n_e$ dependence is tempered due to the fact that the $n_e$ independent term $K(2,3)/K(2,1)$ is in general larger than the $n_e$ dependent term. It can be concluded from this simplified model that $r_2^1$ is independent of $n_e$ when radiative processes are unimportant. The $r_2^1$ weakly depends on $T_e$.

From this consideration, we may expect that $r_2^1$ will also be in the order of $10^{-3}$ and will be only weakly dependent of $n_e$ and $T_e$. However, it is not easy to derive $r_2^1$ analytically. Therefore, a model has to be used which includes all population and depopulation processes to and from level "3", which stands for the 4p-level in argon. Modeling results of the $r_3^1$-coefficient are shown in figure 2.5. This figure show the dependence of $r_3^1$ on $n_e$ and $T_e$, respectively. It shows that the $r_3^1$ coefficient is also dependent on $n_e$ for low electron densities ($< 10^{19}$ m$^{-3}$) and low electron temperatures ($< 0.9$ eV). This is not a limitation to the use of this method, although in this range the electron density has to be determined in a more accurate way. For low $n_e$-values and high $T_e$-values, the $r_3^1$-coefficient is mainly determined.
by the electron temperature. For ground state densities around $10^{23} \text{ m}^{-3}$, it was found that the $r_3^1$-value did not depend on $n_1$.

The results presented in figure 2.5 can be used to estimate the sensibility of the determined $r_3^1$-value when the $n_e$ and $T_e$ values are not accurately known. The $n_e$-values are expected to be in the interval $1.0 \times 10^{19} \text{ m}^{-3} \leq n_e \leq 5.0 \cdot 10^{19} \text{ m}^{-3}$, which gives $\Delta r_3^1/r_3^1 = 4.8 \%$. Allowing $T_e$ to vary between 0.9 eV and 1.3 eV results in $\Delta r_3^1/r_3^1 = 50.8 \%$. Assuming that these errors are independent and that the total error can be determined by quadratic summing, this results in $\Delta r_3^1/r_3^1 = 51 \%$.

![Figure 2.5:](image)

**Figure 2.5:** The left graph shows relative population coefficients $r_3^1$ as a function of $n_e$ for different values of $T_e$ and $n_1 = 9.8 \times 10^{22} \text{ m}^{-3}$. The graph on the right shows $r_3^1$-values as a function of $T_e$. Here, the other input parameters are $n_1 = 9.8 \times 10^{22} \text{ m}^{-3}$ and $n_e = 2.5 \times 10^{19} \text{ m}^{-3}$.

### 2.3.4 Applied $r_3^1$ method

An expression for the electron temperature can now be derived by inserting the Boltzmann equation 2.12 into $r_3^1 = \eta_P/\eta_{PB}$ and rewriting:

$$k_B T_e = \frac{-E_{1P}}{\ln \left( \frac{\eta_{1P}}{\eta_1 r_3^1} \right)}$$  \hspace{1cm} (2.17)

This equation gives an expression for $T_e$ as a function of $\eta_{1P}$, $\eta_1$ and $r_3^1$. The former two values are experimentally determined whereas $r_3^1$ is obtained from the model.

We have applied this method to a $4p$-level in argon ($p = 3$) which has an energy of 13.1 eV, an ionization potential of $I_p = 2.7$ eV and radiates with a wavelength of 801.5 nm. The density of this state, denoted by $\eta_p$, has been determined using ALI measurements and $n_1$ has been found using the ideal gas law combined with the measured gas pressure and an estimated value for the gas temperature. For the determination of $r_3^1$, we need a value of $n_e$. Assuming that levels for which $E_p > 15.1$ eV were in partial local Saha equilibrium (pLSE), $\eta_{\infty}$ has been determined using a linear extrapolation to the ion state. A starting value for $n_e$ has been obtained by using $\eta_{\infty}$ and inserting $T_{13}$ into equation 2.3. For these input values
Chapter 2.

\((T_{13}, n_e, n_1)\), the \(r_{3}^{1}\)-coefficient can be calculated with the CR-model. Applying equation 2.17 gives a value for \(T_e\), which is inserted into the model to recalculate the \(r_{3}^{1}\)-coefficient. These steps have been repeated until \(T_e\) did not change anymore. A new value for \(n_e\) has been obtained by again using \(\eta_\infty\) and inserting the new \(T_e\)-value into equation 2.3. Both iteration procedures have been repeated until convergence for \(T_e\) and \(n_e\) was reached.

2.4 Results

ALI measurements have been made on a surface wave sustained argon plasma at two different pressures, namely 6.1 mbar and 9.9 mbar. The argon mass flow was 50 sccm, and the absorbed microwave power was approximately 22.5 W. Depending on the pressure, the observed plasma column lengths were equal to 38 cm (6.1 mbar) and 39 cm (9.9 mbar). ALI measurements were made at 5 different axial positions along the tube, which corresponded to intersections of about 10 cm. We estimated a gas temperature of about 450 K. For this value, ground state densities were respectively equal to \(n_1 = 9.8 \times 10^{22} \text{ m}^{-3}\) for 6.1 mbar and \(n_1 = 1.6 \times 10^{23} \text{ m}^{-3}\) for 9.9 mbar.

A typical ASDF obtained from ALI measurements is shown in figure 2.6. Here, the population densities of the excited states are plotted as a function of energy for a gas pressure of 6.1 mbar. This figure shows that the lower part of the ASDF, thus the 4p-levels and the atom ground state, can be used to obtain the excitation temperature \(T_{13}\) from a linear fit through the 4p-levels and the atom ground state. Levels high in the atomic system have been used to obtain an estimate of \(n_e\). Therefore, \(\eta_\infty\) has been determined using the argon levels for which \(E_p > 15.1 \text{ eV}\). These levels high in the atomic system are assumed to be in pLSE. The value of \(\eta_\infty\) has been obtained by extrapolation to the ionic ground state. For argon this corresponds with \(E_p = 15.76 \text{ eV}\).

![Figure 2.6: Absolute population densities versus excitation energy of different atomic levels measured in an argon surfatron plasma at a position of 5 cm from the launcher and at a gas pressure of 6.1 mbar.](image-url)
In the left graph of figure 2.7, the density of the measured argon 4p-level is plotted as a function of the axial position for the two different pressures. Maximum values are reached in the region close to the launcher. After the maximum, $\eta_3$ decreases with increasing distance. The $\eta_3$-values are higher for the 6.1 mbar pressure than for the 9.1 mbar pressure. The right plot of figure 2.7 shows the axial profiles of $T_{13}$ for both pressures. It can be seen that the axial excitation temperature profiles are more or less constant for both cases. The results of $\eta_\infty$ are presented in figure 2.8. Maximum values are reached in the region close to the launcher. At a pressure of 6.1 mbar, the value of $\eta_\infty$ at 2 cm is lower than the value of $\eta_\infty$ at 5 cm. This is not as expected, but can be explained because the relative error of $\eta_\infty$ is at least 25%. After the maximum, the values of $\eta_\infty$ decrease with increasing distance from the launcher. Also, the 6.1 mbar case gives higher values for $\eta_\infty$ than for the 9.9 mbar situation.

![Figure 2.7: ](image)

**Figure 2.7:** The state density $\eta_3$ (left) and the excitation temperature $T_{13}$ (right) as function of the axial position $z$. The position $z = 0$ corresponds with the exit position of the launcher. The squares correspond with a gas pressure of 6.1 mbar, the circles with 9.9 mbar.

![Figure 2.8: ](image)

**Figure 2.8:** $\eta_\infty$ as a function of position. The symbols are similar to the ones in figure 2.7.
2.4.1 Results of the $r_p^1$ method

The diagnostic method which is described in subsection 2.3.2 has been applied in order to determine the electron temperature from the results of the ALI measurements. Figure 2.9 shows the obtained axial profiles for the electron density (left) and electron temperature (right).

![Figure 2.9: $n_e$ (left) and $T_e$ (right) as a function of the axial position. The symbols are the same as in figure 2.7.](image)

The axial electron density profile has a maximum close to the launcher and decreases along the tube. The $n_e$-values are slightly higher for the 6.1 mbar case. The electron temperature is constant or weakly descending along the tube and decreases with increasing pressure.

The focus of this work is to determine $T_e$, for which we need an estimated value of $n_e$. Therefore, an accurate error analysis for $n_e$ has not been made. The accuracy of the $T_e$-values is determined in the following subsection.

2.4.2 Accuracy of the $r_p^1$ method

The uncertainty in the ALI measurements is caused by the uncertainty in the transition probability and the emission coefficient $j_{pq}$. We follow [18] for the relative error in the transition rate where a value of 8% is given for the applied transition. The emission coefficient $j_{pq}$ depends on the intensity measurement, the calibration procedure and the plasma diameter. It is estimated that this lead to an uncertainty of 20%. This results in a relative error for $\eta_3$ of 22%. The uncertainty of $\eta_3$ is mainly caused by an unknown value for the gas temperature $T_g$. It is expected that $T_g$ varies between 375 K and 525 K, which corresponds with a relative error of 17%. Applying the ideal gas law gives $|\Delta T_g / T_g| = 17\%$. In subsection 2.3.3, it was shown that $|\Delta r_1 / r_1| = 51\%$. 


Assuming random errors in $\eta_3$, $\eta_1$ and $r_3^1$, the following expression can be derived from equation 2.17:

$$
\frac{\Delta T_e}{T_e} = \left\{ \left( \frac{\Delta \eta_3}{\eta_3} \right)^2 + \left( \frac{\Delta \eta_1}{\eta_1} \right)^2 + \left( \frac{\Delta r_3^1}{r_3^1} \right)^2 \right\}^{1/2} \left\{ \ln \left( \frac{\eta_3}{\eta_1 r_3^1} \right) \right\}^2 . \tag{2.18}
$$

Using $\eta_3 = 1.0 \times 10^{15} \text{ m}^{-3}$, $T_g = 450 \text{ K}$, $\eta_1 = 9.8 \times 10^{22} \text{ m}^{-3}$, $n_e = 2 \times 10^{19} \text{ m}^{-3}$ and $r_3^1 = 7.3 \times 10^{-4}$, results in $\Delta T_e / T_e = 5.2 \%$. Due to the exponent in equation 2.17, the total relative error in $T_e$ is much smaller than the uncertainties in the individual contributions.

Besides these random errors, also systematic errors might be present. These systematic errors can, for example, be caused by the cross section data used in the CR-model. Benoy [11] found that the employed CR-model for argon resulted in $r_3^p$ values that are 35% higher than obtained with other models. Inserting this value into equation 2.18 results in $\Delta T_e / T_e = 3.9 \%$. Therefore, the total inaccuracy of the method is around 9%.

### 2.4.3 Summary of the results

The results obtained in the present work are summarized in table 2.2. The values presented in this table are determined at an axial position of 2 cm from the launcher. The microwave power was equal to 22.5 W in all cases.

<table>
<thead>
<tr>
<th>$p$ [mbar]</th>
<th>$L$ [cm]</th>
<th>$n_3 \pm \Delta n_3$ [m$^{-3}$]</th>
<th>$n_e$ [m$^{-3}$]</th>
<th>$T_e$ [eV]</th>
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<td>$(6.0 \pm 1.4) \times 10^{15}$</td>
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<td>$1.20 \pm 0.11$</td>
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<tr>
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<td>38</td>
<td>$(4.2 \pm 1.0) \times 10^{15}$</td>
<td>$2.6 \times 10^{19}$</td>
<td>$1.09 \pm 0.10$</td>
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Maximum values of the state density $\eta_3$ are reached in the region close to the launcher. After the maximum, the $\eta_3$ values decrease with increasing distance. The $n_3$-values are higher for the 6.1 mbar pressure than for the 9.1 mbar pressure situation. The axial electron density profile also has a maximum close to the launcher and decreases along the tube. The $n_e$-values are slightly higher for the 6.1 mbar case. The electron temperature is constant or weakly descending along the tube and decreases with increasing pressure. The obtained results are in agreement with diagnostic and modeling results performed on a low pressure argon plasma launched using a surfatron setup [19–25].

### 2.5 Discussion and conclusions

A method to determine the electron temperature of a non-LTE argon plasma from the excitation temperature using a CR-model has been presented. The $\eta_3$ state density has been determined with ALI measurements, whereas an estimated value of $n_e$ has been obtained from the high energy part of the ASDF. An error analysis shows that the electron temperature can
be determined with an accuracy of 6%. This high accuracy has been achieved because of the following two reasons:

- The $\eta_3$ state density was measured absolutely and the ground state density has been determined via the pressure. Since the energy gap $\delta E$ between the first excited states and the ground state is in the order of 11 eV for Ar, the slope of the ASDF and thus the excitation temperature could be determined with high precision.

- A numerical CR-model has been used to transform $T_{ex}$ into $T_e$. The ASDF of a non-LTE plasma is determined by the combined action of all relevant transport phenomena and elementary collisional and radiative processes. A CR-model has been used to solve the set of particle balances and takes all these individual processes into account.

The presented method has been applied to determine the electron temperature in a low pressure microwave plasma in argon. The number of measurement points was restricted to four for each pressure because we did not observe a large variation in the determined electron temperatures. It is only useful to take more points into account when $n_e$ and $T_g$ are determined with a higher precision.

The applied method is also applicable to other non-LTE plasmas sustained in noble gases. In order to apply it to molecular plasmas, a complete dissociation of the molecules or a known dissociation rate is required. At this moment, the CR-model is only applicable to atomic plasmas. However, molecular ions might be present in microwave argon plasmas in the low or intermediate pressures. In order to include these molecular processes, the model will be extended in the near future.

In this work it has been shown that the applied method works properly. However, an averaged value for $T_g$ and an estimate value for $n_e$ have been used. Therefore, the applied method can also be improved when it is combined with other diagnostics by which $T_g$ and $n_e$ are determined for different axial positions. These diagnostics are for example Doppler broadening for $T_g$ and Stark broadening or interferometry for $n_e$.

Concluding, an accurate method to determine the electron temperature with an accuracy around 9% has been presented. It has been shown that the principle is working and that it can be improved when it is combined with other diagnostic techniques. In this way, accurate axial electron temperature profiles can be obtained.
2.6 Appendix: argon transitions

In table 2.3 information of argon lines used for the ALI measurements is given. This data is obtained from: http://physics.nist.gov/cgi-bin/ASD/lines1.pl

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<th>$E_j$ eV</th>
<th>$E_k$ eV</th>
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Bibliography

Chapter 2.

Investigations of Thomson Scattering measurements on a low pressure surfatron induced plasma in argon

**Abstract.** Thomson Scattering (TS) experiments have been performed on a low pressure surfatron induced plasma. TS is an active diagnostic method and the experimental results are directly related to important plasma properties like the electron density, $n_e$, and the electron temperature, $T_e$. Therefore, the TS results for $n_e$ and $T_e$ can be used to calibrate passive diagnostic methods which are often based on plasma models. However, the application of TS on a surfatron induced plasma inside a quartz tube is experimentally demanding due to the large amount of stray light and the low intensity of the TS signal. To achieve low detection limits and high stray light rejection, a triple grating spectrograph (TGS) is used in the detection branch and an iCCD is used to record the TS spectrum. For a typical plasma condition with an argon pressure of 10 mbar and an absorbed power of 50 W, the measured electron density was found to be equal to $n_e \approx 4 \times 10^{19} \text{m}^{-3}$ and the electron temperature $T_e \approx 1.2 \text{eV}$. In addition, frame averaged results for 6, 10, 15 and 20 mbar argon plasmas for absorbed microwave powers in between $25 \leq P_{ab} \leq 60 \text{W}$, are presented. The trends found in the dependence of the pressure and power density are according to theory.

---

3.1 Introduction

Surface wave sustained discharges have many characteristics that make them valuable for a range of technological applications [1]. These discharges are stable, reproducible in a wide pressure range and can be used for both atomic and molecular gases. The electromagnetic waves are launched into a quartz tube using a high frequency launcher and create a plasma which extends far away from the launcher [2]. Examples of the HF surface wave launchers are the surfatron, the surfaguide and the waveguide surfatron [3]. A surface wave sustained plasma generated by a surfatron launcher will hereafter be referred to as surfatron induced plasma.

In the past, surfatron induced argon plasmas operating at the microwave frequency of 2.46 GHz have extensively been studied using theoretical plasma models, [4–10], probe measurements [11] and optical diagnostics [12]. Optical diagnostics can be divided into passive and active spectroscopy. Emission spectroscopy is a passive diagnostic method and has often been applied to surface wave sustained plasmas to determine atomic state densities. However, for low pressure argon plasmas, the plasma is not in equilibrium and a collisional radiative model is required to relate the measured atomic state distribution function to main plasma parameters like the electron temperature and the electron density [13–15]. Rayleigh scattering, i.e. scattering of laser photons on the heavy particles, is an active diagnostic technique that can be used to determine the gas temperature [16]. In the past, this technique has been used in our laboratory, in collaboration with the group Laboratoire de Physique des Gaz et des Plasmas (University Paris-Sud), to measure the gas temperature in a low pressure surfatron induced argon plasma [17]. The atom density was determined from the Rayleigh signal for different pressures and microwave powers of an argon plasma. Combined with the measured pressure and the ideal gas law, the gas temperature was obtained.

Thomson scattering (TS) is another active diagnostic technique which can be used to determine the electron temperature and electron density [16, 18–21]. When a laser beam is focussed into a plasma the free electrons are accelerated due to their interaction with the electromagnetic field of the laser and emit an electromagnetic field which is referred to as TS radiation. The spectrum of these TS photons is related to the properties of the electrons in the plasma. For a low pressure surfatron induced argon plasmas, the electron density is around \( n_e \approx 10^{19} \text{ m}^{-3} \) and the electron temperature \( T_e \approx 1.2 \text{ eV} \). For these values and our experimental configuration, the scattering parameter \( \alpha \) is approximately 0.05. For these \( \alpha \) values, TS is non-collective. This makes the interpretation of the data straightforward since the electron density \( n_e \) and electron density \( T_e \) follow directly from the intensity and width of the spectrum [22]. Thus the main plasma properties directly follow from the experimental data without relying on plasma models. Therefore, TS results can be used to calibrate passive diagnostic techniques. In addition, TS gives spatially resolved (local) results, whereas passive diagnostic results are integrated along the tube diameter.

In the past, TS measurements have been made on planar surface wave discharges [23, 24]. Here, the surface waves generate a large area, low temperature plasma which can be used for plasma processing. Due to the experimental difficulties, TS has not yet been applied to low pressure surfatron induced plasmas generated inside a quartz tube. Main problems are the presence of intense stray light caused by scattering of the laser beam on the quartz tube and the low TS intensity due to the relatively low electron densities.
Thomson scattering measurements on a low pressure argon plasma

The aim of this study is to overcome these experimental problems and to perform TS measurements on low pressure surfatron induced argon plasmas generated inside a quartz tube. For this purpose, a new microwave setup was designed and adapted with Brewster windows to minimize reflections caused by the laser beam on the plasma surroundings. Since the inner radius $a$ of the surfatron was small ($a = 3\, \text{mm}$), we had to use a high quality laser with a Gaussian beam profile to reduce the amount of scattering of the laser light on the quartz. In addition, a triple grating spectrograph (TGS) was used to disperse and measure the TS signal. This TGS was built at the Eindhoven University of Technology (TU/e) and designed to reduce the influence of stray light [25] and to block the intense Raleigh signal [22]. With this setup, we were able to make the first TS measurements on a surfatron induced argon plasma generated inside a quartz tube in a pressure range between 6 mbar and 20 mbar.

This chapter starts with a short description of incoherent TS in section 3.2, followed by the experimental configuration and procedures in section 3.3. The TS results are presented in section 3.4, a discussion of the results is given in section 3.5 and is followed by the summary and conclusions in section 3.6.

3.2 Thomson Scattering

Thomson scattering, i.e. the scattering of (laser) light on free electrons, can be used to measure the properties of the electron gas. For the relatively low electron densities and high electron temperatures observed in the plasmas under study, the scattering is incoherent and the intensity of the scattered radiation is directly proportional to the density of the scattered particles, i.e. the electron density. For incoherent Thomson scattering, the TS power $P_T$ radiated by the electrons in a solid angle $\Delta \Omega$ is given by

$$P_T = P_i n_e L \frac{d\sigma_T}{d\Omega} \Delta \Omega,$$

where $P_i$ is the incident laser power, $L$ the length of the beam-plasma interaction zone and $\frac{d\sigma_T}{d\Omega}$ the differential cross-section for TS, which equals

$$\frac{d\sigma_T}{d\Omega} = r_e^2(1 - \sin^2 \vartheta \cos^2 \varphi),$$

where the scattering angle $\vartheta$ is the angle between the incident wave vector and the scattered wave vector, $\varphi$ the angle between the plane of scattering and the polarization of the incident laser beam, and $r_e$ the classical electron radius ($r_e = e^2/4\pi\varepsilon_0 m_e c^2$), with $e$ the electron charge, $\varepsilon_0$ the permittivity of vacuum, $m_e$ the electron mass and $c$ the speed of light. In the basic setup, a perpendicular scattering geometry is used: $\vartheta = 90^\circ, \varphi = 90^\circ$. Equation 3.2 shows that for this case the differential cross-section scattering and thus the scattering probability is at maximum. Rotational Raman scattering [26, 27] was used to calibrate the system. Raman scattering is the inelastic scattering of radiation by molecules. These molecules can undergo a rotational or vibrational transition, thereby changing their internal energy. This results in specific wavelength shifts of the scattered photons. The total Raman scattered power $P_{Rm}$ is obtained when all rotational transitions are taken into account and can be expressed as [22]

$$P_{Rm} = P_i L n_N \frac{d\sigma_{Rm}}{d\Omega} \Delta \Omega$$

33
in which \( \frac{d\sigma}{d\Omega} \) is the total Raman scattering cross-section and \( n_{N_2} \) the molecular nitrogen density. Combining equation 3.1 and equation 3.3 gives an expression for the electron density:

\[
n_e = n_{N_2} \cdot \frac{P_t}{P_{Rm}} \cdot \Gamma_{Rm},
\]

(3.4)

where \( \Gamma_{Rm} \) is per definition equal to the Raman cross-section divided by the differential Thomson cross-section. In our TS experiments, we have used nitrogen at room temperature as a calibration gas. For this particular calibration gas and perpendicular scattering geometry, the value of \( \Gamma_{Rm} \) has been calculated [22] and was found to be equal to \( \Gamma_{RmN_2} = (8.15 \pm 0.65) \times 10^{-5} \). The uncertainty in this value is due to a systematic error of 8\% in the cross-section for Raman scattering.

The spectral width of the TS signal is related to the temperature of the electrons. For incoherent scattering and a Maxwellian electron energy distribution function, the spectrum has a Gaussian shape and the electron temperature \( T_e \) can be determined from the half 1/\( e \) width \( \Delta \lambda_{1/e} \) [22],

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

(3.5)

where \( \lambda_i \) is the incident laser wavelength and \( k_B \) the Boltzmann constant.

### 3.3 Experimental configuration

This section starts with a description of the plasma source, it gives the basic setup that was employed for our measurements and the experimental procedure that we followed. Also, an error analysis is given.

#### 3.3.1 Surfatron setup

The surfatron setup is shown in figure 3.1. The electromagnetic waves (\( f = 2.46 \) GHz) are generated in a magnetron which has a maximum power of 300 W. Coaxial cables are used to transport the electromagnetic waves from the magnetron to the surfatron launcher. The electromagnetic waves are coupled into the plasma via the launching gap of the surfatron. The surface waves travel along the tube-plasma interface and sustains the plasma until a critical electron density is reached. The quartz tube has an inner radius of 3 mm and an outer radius 4 mm. For these experimental configurations, only the symmetric azimuthal mode \( m = 0 \) is excited. To measure the incident and reflected power, a bidirectional coupler, two power sensors and a power meter were used. A triple stub tuner was used to reduce the reflected power and was positioned behind the bidirectional coupler. An argon mass flow controller, in all cases set at a constant value of 50 sccm, is placed before the gas-inlet side of the tube and a vacuum pump is placed at the gas-outlet side. The gas pressure in the tube is controlled at the pump side by means of a manual needle valve and is measured at the gas inlet side and the gas-outlet side. A pressure gradient was not observed in this tube. In order to adapt the setup for TS measurements, Brewster windows are attached to the vacuum equipment on both sides. In contrast to most other studies performed on surface wave sustained plasmas [11, 17], we measure the axial coordinate relative to the position of the surfatron [15, 28] and not to the end of the discharge.
3.3.2 The Thomson scattering setup

The TS setup is shown in figure 3.2. A SL312 frequency doubled Nd:YAG laser produces 150 ps laser pulses at a wavelength of 532 nm with a maximum energy of approximately 115 mJ per pulse and at a repetition rate of 10 Hz [29]. The laser beam is horizontally polarized and has a diameter of approximately 1 cm. To obtain a vertically polarization, the beam is guided two times through a quarter wave plate, after which it is focussed into the plasma by a plano-convex lens with a focal length of 1 m. The waist of the laser beam is about 200 µm. The radiation scattered by the electrons in the plasma is imaged onto the horizontal entrance slit of the triple grating spectrograph (TGS). The TGS is designed and built by M. van de Sande [25] in order to reject false stray light (scattering on the surroundings), Rayleigh scattered photons and to disperse and collect the TS photons. Inside the TGS, dispersion of the scattered light occurs in the horizontal direction. In order to measure spatial and spectral information simultaneously, an image rotator was placed after a horizontal entrance slit. A two dimensional intensified CCD (4Picos, Stanford computer optics) records the spectrum at different axial positions for each laser shot, whereby the horizontal direction contains wavelength (λ), and the vertical direction spatial (z) information. To synchronize the laser pulse and the gating of the camera, the electronic synchronization signal from the SL312 laser was used. The jitter was on the order of 1 ns, which was small enough compared to the gate time of about 10 ns. In one measurement, the TS spectrum is measured along a part of the laser beam. This corresponds to 12 mm, i.e. the length of the entrance slit of the TGS.

To optimize the efficiency of the TGS, we have made some changes compared to the TGS described in [22]. The TS signal has the same polarization as the incident beam (vertical). The image rotator also rotates the polarization of the TS photons from vertical to horizontal. Unfortunately, the efficiency of the gratings used in first order is optimized for vertically polarized light. Therefore, a half wavelength plate (HLP) was placed directly after the entrance
slit, which rotates the polarization by 90 degrees, thus from vertical to horizontal. Due to the image rotator, the photons arrive with a vertical polarization at the first grating. It was found that the use of this HLP increases the Thomson signal by a factor of 7. The polarization properties of the TGS are discussed in more detail in [30].

**Figure 3.2:** Basic setup used for TS experiments on the surface wave sustained plasma. The first and the second spectrometer (left hand side of TGS) of the TGS operates as a notch filter for the rejection of stray light in the center of the spectrum. A third spectrograph (right hand side of TGS) is used for dispersion and focuses the signal onto a two dimensional iCCD detector. HLP refers to the half wavelength plate and IR to the $90^\circ$ image rotator.

### 3.3.3 Experimental procedure

Using this TS setup, a 2-D recording of the iCCD referred to as spectrum, is obtained when the laser beam is guided into the surface induced plasma and the scattered radiation is measured using the iCCD. Each spectrum is integrated over a time interval of 30 minutes, which corresponds to 18000 laser pulses. Due to the fact that the iCCD is two-dimensional, we obtain simultaneously spectral and spatial information. Besides the Thomson spectrum, this total spectrum also contains contributions of dark current of the iCCD, stray light (scattering of the laser beam on the plasma surroundings and the Rayleigh signal), and plasma radiation (background). To obtain the actual Thomson spectrum, the spectra of plasma radiation (laser-off, plasma-on) and stray light (laser-on, plasma-off) were subtracted from the total spectrum. Since both these spectra contain dark current, a spectrum of the dark current has to be added to the results of this subtraction. After this procedure, the spectrum is binned 4 times in the wavelength direction and 30 times in the vertical (axial) direction for accuracy.
reasons. Since the measured dispersion of the spectrometer equals 1.531 mm/nm and the size of a CCD pixel is $26.2 \times 27.2 \mu m$, a binned pixel correspond to 0.069 nm in the horizontal (spectral) and 0.820 mm in the vertical (spatial) direction. Due to this binning, a new area unit of the iCCD is created. A binned pixel will be denoted by a super pixel, shortly $S$-pixel. The image of the entrance slit on the detector has a length of 12 mm, which correspond to 15 S-pixels.

Raman scattering was used to calibrate the total setup in terms of absolute sensitivity. The tube is filled with nitrogen ($N_2$) at room temperature to a pressure of around 50 mbar. The conditions (laser power, exposure time, alignment) are the same as for the Thomson measurement. The stray light has to be subtracted from the Raman measurement in order to obtain the real Raman spectrum. After the $4 \times 30$ 'binning' of the spectrum, the calibration constant can be determined. The total Raman scattered power per spatial channel is determined by summing up the signal over the full width of the spectrum. A 'binned' Raman spectrum is shown in figure 3.3.

![Figure 3.3: The shape of the Raman spectrum of a 50 mbar $N_2$-filling (no plasma). The integration time equals 30 minutes. The known wavelength distance between the $6 \rightarrow 8$ and $8 \rightarrow 6$ transition is used for the wavelength calibration of the detection system.](image)

The dispersion of the optical system was determined by the position of the spectral lines. For this purpose, the spectrum was binned by a factor of 30 in the vertical (spatial) direction, but not in the horizontal (spectral) direction. The most intense Raman peak on the left-hand side of the mask corresponds to the $6 \rightarrow 8$ transition at $\lambda = 533.69$ nm, the most intense Raman peak on the right-hand side is the $8 \rightarrow 6$ transition at $\lambda = 530.32$ nm. Using these peaks results in a dispersion of $d = 14.61 \pm 0.08$ S-pixels per nm for a binning factor of 4 in the wavelength direction, where the error is due to an uncertainty of 2 pixels. This value for the dispersion is a little higher than the value of 14.04 S-pixels per nm as calculated from the parameters of the TGS [22] and the size of a pixel of our iCCD.
3.3.4 Error analysis

The uncertainty in the measured electron densities is mainly determined by the inaccuracy of the Raman calibration. Also, the fitting error of the area under the Gaussian profile gives a small contribution. Due to the long integration times (30 minutes), the pulse to pulse variations of the laser pulses (around 5%) are partly averaged out. The long term stability of the laser (1 day) varied between 1% and 5%. We have used the following values; the numerical value of the cross-section for Raman scattering has an uncertainty of around 8% [31], the inaccuracy of the Thomson scattered power due to the fit inaccuracy is 2%; inaccuracy of the Raman power (offset) 5% and long term (mean) variations in the laser power 5%. Quadratic summing of random errors leads to a total random error of 8%. The systematic error is entirely caused by the numerical value of the cross-section for Raman scattering and is also equal to 8%.

The error in the electron temperature is mainly determined by the accuracy of the fit. The dispersion \( d \) was determined from the measured Raman spectrum and equal to \( d = 14.61 \pm 0.08 \) S-pixel/nm for four times pixel binning in the horizontal (wavelength) direction. The uncertainty in dispersion gives a relative error in \( T_e \) of 1%. We assume that the fitting error is caused by an uncertainty of 1 S-pixel \( a \), thus \( \Delta a = 1 \). At an electron temperature of 15000 K, the Gaussian half width corresponds with 23 S-pixels. Using \( \frac{\Delta T_e}{T_e} = \frac{2 \Delta a}{a} \) results in a relative error of 9%. Thus the total error in the electron temperature obtained using quadratic summing, is approximately 8%.

Due to the binning of pixels and the use of long integration times, the corrected TS signal has an intensity of approximately \( 10^7 \) counts. For this value, photon statistics is not important. In [25], it is discussed that the contribution of the dark current to the total noise level is much smaller than noise on the Thomson and background plasma signal. The uncertainties caused by these contributions are already included in the fit inaccuracies.

3.4 Results

Thomson scattering measurements have been made on argon plasmas in the pressure range of \( 6 \text{ mbar} \leq p \leq 20 \text{ mbar} \). Both the pressure and microwave power were varied. The TS signal was determined in the center of the plasma along an axial distance of 18 mm to 30 mm relative to the gap of the surfatron. The laser energy measured behind the diaphragm (cf. figure 3.2) was kept at a constant value of 75 mJ per pulse. In all cases, an exposure time of 30 minutes, corresponding to 18000 pulses, was used. Before presenting TS results of different powers and pressures, the standard condition will be discussed in more detail.

3.4.1 Standard condition

For the standard condition, we used a pressure of 10 mbar and an absorbed microwave power of 47 W. This results in a plasma with a length of 48 cm in the direction of the wave propagation and 6.7 cm in the opposite site direction. The iCCD images of the measured TS and Raman spectra are shown in figure 3.4. The horizontal direction corresponds with the wavelength direction, the vertical direction with the axial position in the tube. The measured intensity appears to fall of towards the ends of the iCCD in the axial direction. This is caused by
the shape and limited length of the entrance slit. Since the width and intensity of the TS spectrum is more or less the same in the vertical direction, the axial variation in a single measurement is expected to be small.

![Typical iCCD images of TS (left) and Raman scattering (right). The TS spectrum is measured in an argon plasma for a pressure of 10 mbar and an absorbed microwave power of 47 W. The Raman spectrum is measured in nitrogen at room temperature at a pressure of 50 mbar. The central gap is due to the effect of the notch filter, an essential part of the TGS. In both cases, an exposure time of 30 minutes, which corresponds to 18000 pulses, was used.](image1)

**Figure 3.4:** Typical iCCD images of TS (left) and Raman scattering (right). The TS spectrum is measured in an argon plasma for a pressure of 10 mbar and an absorbed microwave power of 47 W. The Raman spectrum is measured in nitrogen at room temperature at a pressure of 50 mbar. The central gap is due to the effect of the notch filter, an essential part of the TGS. In both cases, an exposure time of 30 minutes, which corresponds to 18000 pulses, was used.

Both the Thomson and the Raman images are binned four times in the wavelength and thirty times in the spatial direction. The TS spectrum is shown in figure 3.5.

![Typical shape of the Thomson spectrum measured for a pressure of 10 mbar and a microwave power of 47 W.](image2)

**Figure 3.5:** Typical shape of the Thomson spectrum measured for a pressure of 10 mbar and a microwave power of 47 W.
In figure 3.6, TS results for $n_e$ and $T_e$ are presented as a function of the axial position as obtained for one iCCD frame. Error bars correspond to 9% for both $T_e$ and 8% for $n_e$, respectively. For $n_e$ an additional systematic error of 8%, caused by the uncertainty in the Raman cross-section, has to be taken into account.

In each measurement, the iCCD frame gives a signal of TS photons collected over a distance of 1.1 cm, which corresponds to the length of the entrance slit. In the results presented for this standard condition a minor axial dependence, which was inside the error range, was observed over the iCCD frame. A larger decrease of the electron density was expected, since in surfatron induced plasmas the electron density at the column end is supposed to be equal to the critical electron density \[ n_c = 3.14 \times 10^{-4} \omega^2 (1 + \varepsilon_g), \] (3.6)
with $n_c$ the critical electron density in m$^{-3}$, $\omega$ the radial frequency of the microwaves and $\varepsilon_g$ the discharge tube relative permittivity. For the microwave frequency of 2.46 GHz and $\varepsilon_g = 4.3$ for a quartz tube, we find $n_c = 3.9 \times 10^{17}$ m$^{-3}$. Using the measured $n_e$-value close to the surfatron launcher, the calculated critical density $n_c$ at the end of the plasma column ($z = 29.4$ cm) and assuming a linear dependence of the axial position, we would expect an electron density of $n_e = 2.4 \times 10^{19}$ m$^{-3}$ at the end of the iCCD frame ($z = 2.9$ cm). However, this is lower than the electron densities measured at that position, which was equal to $n_e = 3.3 \times 10^{19}$ m$^{-3}$. Because we did not observe a significant variation of electron density with axial position within the small range of 12 mm, TS results will be presented as frame averaged results.

### 3.4.2 Frame-averaged results

For four different pressures, the microwave power was varied. In figure 3.7, frame-averaged values for $n_e$ and $T_e$ are plotted as a function of the absorbed power for the pressures of...
Thomson scattering measurements on a low pressure argon plasma

6 mbar, 10 mbar, 15 mbar and 20 mbar. The error in the frame-averaged values is obtained by dividing the total random error by \( \sqrt{N} \), where \( N \) is the number of data-points. For \( N = 15 \), the relative error for \( n_e \) is 9% and 2% for \( T_e \).

In figure 3.7, it can be seen that the electron density increases with increasing powers, whereas the electron temperature is more or less constant. For lower powers, \( 25 W \leq P_{ab} \leq 35 W \), we observe a slight increase of \( T_e \) with increasing \( P_{ab} \). Also, figure 3.7 shows that \( n_e \) increases whereas \( T_e \) slightly decreases for increasing pressures.

![Figure 3.7: Frame averaged \( n_e \) (left) and \( T_e \) (right) values as function of the absorbed power for argon pressures of 6, 10, 15 and 20 mbar.](image)

The pressure dependence is shown in figure 3.8, where \( n_e \) and \( T_e \) are plotted as a function of the pressure for absorbed powers of 33 W and 55 W. For a microwave absorbed power of 55 W, \( n_e \) and \( T_e \)-values are shown for pressures of 6 mbar, 10 mbar and 15 mbar. For a microwave absorbed power of 33 W, \( n_e \) and \( T_e \)-values are shown for pressures of 10 mbar, 15 mbar and 20 mbar. The \( n_e \)-values for 6 mbar are much lower, the \( T_e \)-values are all comparable or decrease slightly with increasing pressure. Between 6 mbar and 10 mbar, the \( n_e \)-value increases with pressure whereas the \( T_e \)-values are constant. In the pressure range \( 10 \leq p \leq 20 \) mbar, a small increase in \( n_e \) and a small decrease in \( T_e \) are observed.

Experimentally, it was found that the plasma length decreases with increasing pressures. This means that keeping the input power constant and increasing the pressure increases the power density as well. To determine the influence of the pressure on the plasma properties, we now compare experimental results for which the power per length (instead of the absorbed power) was kept constant. These conditions were obtained by adjusting the power such that for each pressure the plasma gets the same power per length. In figure 3.9, results are shown for different pressures, but in this case the power-density instead of the absorbed power is constant. Between 6 mbar and 10 mbar, the electron density still increases. However, between 10, 15 and 20 mbar, the electron density is more or less constant. A small decrease of electron temperature was observed over the complete pressure range. These results show that when the power density is constant, the electron density is independent of the pressure in the pressure range.
range 10 – 20 mbar. This means that in this pressure range the increased electron density at a constant input power (cf. figure 3.8) is not caused by the pressure but is a result of the increased power density that is obtained due to the decrease in plasma length. In the range 5-10 mbar, the electron density increases with pressure. The electron temperature is slightly lower for higher pressures.

Figure 3.8: Frame averaged $n_e$ (left) and $T_e$ (right) values as a function of pressure for absorbed microwave powers of 33 W and 55 W.

Figure 3.9: Frame averaged $n_e$ (left) and $T_e$ (right) values as a function of pressure for power densities of 0.8 W/cm and 1.0 W/cm.
3.5 Discussion

In this section we will investigate whether the tendencies observed in our experimental results can be explained using global conservation equations such as the electron particle balance and the electron energy equation.

The electron particle balance can be used to relate the ionization frequency $\nu_i$ to the diffusion frequency \[2\]

$$\nu_i = \frac{D_a}{\Lambda^2},$$

(3.7)

where $D_a$ is the ambipolar diffusion coefficient and $\Lambda$ the diffusion length which is proportional to the inner radius of the tube. This equation gives an expression for $T_e$ \[21\]

$$k_{ion}^*(T_e) = \frac{D_{amb}}{\Lambda^2 n_a},$$

(3.8)

where $k_{ion}^*$ is an effective ionization rate and $n_a$ the atom density. For the ambipolar diffusion coefficient we use \[32\], giving

$$D_a = \left(1 + \frac{T_e}{T_a}\right) \frac{2}{3 n_a \sigma_{ia} \sqrt{\frac{k_B T_a}{\pi M_A}}} = \frac{D'_a}{n_a},$$

(3.9)

with $\sigma_{ia}$ the cross-section for ion-atom collisions, $M_A$ the atomic mass of argon, $T_a$ the atom temperature and $D'_a$ an effective ambipolar diffusion coefficient \[33\].

The TS results show that $T_e$ is more or less independent of the absorbed power and slightly decreases with increasing pressures. This can be explained by the fact that $T_e$ is mainly determined by the electron particle balance (equation 3.8), which is independent of the absorbed power but depends on the ambipolar diffusion coefficients and the diffusion length. These parameters are related to the pressure and the radius of the tube. An increase in pressure results in more ground state atoms which decreases the ambipolar diffusion coefficient (cf. equation 3.9) directly. This effect leads to a lowering of the electron temperature. However, it is a relatively small decrease since $k_{ion}^*$ depends on $T_e$ via an exponential form.

The microwave power absorbed by a plasma slab of length $\Delta z$ and radius $a$ equals \[2\]

$$\Delta P_{ab} = \theta \pi a^2 n_e(z) \Delta z,$$

(3.10)

where $\theta$ is the mean power to maintain an electron-ion pair in the plasma and $n_e(z)$ the electron density at position $z$. For low or intermediate pressure discharges, it is generally assumed that $\theta$ is constant over the radial plasma cross section \[34, 35\] and shows only a very small variation along the tube \[34, 36, 37\]. Since the input power is maximum close to the launcher, the absorbed power in that area $\Delta P_{ab}/\Delta z$ has a maximum value and thus gives the highest values for $n_e$. Along the tube, $\Delta P_{ab}/\Delta z$ decreases and thus also $n_e$. Integrating over the total plasma column gives

$$P_{ab} = \theta \pi a^2 \int_0^L n_e(z) dz = \theta \pi a^2 L \bar{n}_e = \theta V \bar{n}_e,$$

(3.11)

with $\bar{n}_e$ the averaged electron density.
with $\bar{\varepsilon}$ the averaged value of $n_e$. The $\theta$-value is equal to the power density $\varepsilon$ divided by the electron density. Employing the electron energy balance [10], we find the following

$$\theta = \nu_{ea} \frac{3 m_e}{m_a} k_B(T_e - T_a) + \nu_{ei} \frac{3 m_e}{m_i} k_B(T_e - T_i) + \sum_j \nu_j \varepsilon_j + \nu_i E_{\text{ion}} \quad (3.12)$$

where $\nu_{ea}$ is the electron-atom collision frequency, $\nu_{ei}$ the electron-ion collision frequency, $m_i$ and $m_a$ the ion and atom mass respectively, $T_i$ the ion temperature, $\nu_j$ the excitation frequency of level $j$ with energy $\varepsilon_j$, $\nu_i$ the ionization frequency and $E_{\text{ion}}$ the ionization energy of argon. The first two terms of equation 3.12 represent elastic collisions. Due to the relatively low ionization degree ($n_e/n_a < 0.1\%$), we can neglect the second elastic term. Equation 3.12 can then be expressed as

$$\theta = \nu_{ea} \frac{3 m_e}{m_a} k_B(T_e - T_a) + \sum_j \nu_j \varepsilon_j + \nu_i E_{\text{ion}}. \quad (3.13)$$

For the observed electron densities, we can assume that each excitation process from the ground state to the first excited state $1 \rightarrow 2$ is followed by an electron induced stepwise process, i.e. $2 \rightarrow 3$, $3 \rightarrow 4$ etc. The net effect of this ladder excitation is that the inelastic processes can be taken together so that we can write $\sum_j \nu_j \varepsilon_j + \nu_i E_{\text{ion}} = n_a k_{3a_i}^k E_{\text{ion}}$ [32, 38–40]. This rate is almost the same as the rate of the $1 \rightarrow 2$ process whereas $E_{\text{ion}}$ is equal to the ionization energy. Inserting this into equation 3.13 and employing the relation $\nu_{ea} = n_a k_{ea}$ with $k_{ea}$ electron-atom momentum transfer coefficient yields,

$$\theta = n_a k_{ea} \frac{3 m_e}{m_a} k_B(T_e - T_a) + n_a k_{3a_i}^k E_{\text{ion}}, \quad (3.14)$$

the first term describes elastic collisions which result in heating and the second term inelastic collisions that leads to the creation of electron-ion pairs. Inserting equation 3.8 into equation 3.14 gives,

$$\theta = n_a k_{ea} \frac{3 m_e}{m_a} k_B(T_e - T_a) + \frac{D_i' E_{\text{ion}}}{n_a L^2}. \quad (3.15)$$

This expression shows that the $\theta$-value depends on the neutral gas density (pressure), electron temperature, atom temperature and diffusion length, which is proportional to the tube radius. Because $T_e$ and $T_a$ [17] are essentially constant in our experiments, the $\theta$-value is more or less constant for a specific plasma condition.

Via $\bar{\varepsilon} = P_{ab}/V$, an increase in microwave power $P_{ab}$ at constant pressure directly results in higher electron densities because the $\theta$-value is more or less constant for specific plasma conditions (constant argon pressure and tube radius). According to equation 3.15, the $\theta$-values increases with atom density when elastic collisions (first term on the right hand side) are important and decrease when inelastic collisions (second term on the right hand side) are dominant. Since the power density is constant, a higher $\theta$ leads to a lower electron density. Thus the electron density decreases with increasing pressure when elastic collisions are dominant and increases with increasing pressure when the inelastic collisions are most important. Looking at the results, we found that for a constant absorbed microwave power density, $n_e$ increases with pressure in the range $6 \text{mbar} \leq p \leq 10 \text{mbar}$ and was constant between $10 \text{mbar}$ and $20 \text{mbar}$. Therefore, it can be concluded that for the lower pressures inelastic collisions are important and for pressures above $10 \text{mbar}$, both contributions are important since the electron densities are constant with pressure.
3.6 Summary and conclusions

In this chapter, TS results of a low pressure surface wave sustained argon plasma have been presented. The $n_e$ and $T_e$-values were directly obtained from the experimental data. This is a main advantage compared to passive diagnostics, where plasma models are required to give an interpretation of the experimental results.

For a surfatron induced argon plasma at a pressure of 10 mbar and an absorbed power of 50 W, the measured electron density was found to be equal to $n_e \approx 4 \times 10^{19} \text{ m}^{-3}$ and the electron temperature to $T_e \approx 1.2 \text{ eV}$. In all cases, the random error bars correspond to 8% for both $n_e$ and $T_e$. For $n_e$ an additional systematic error of around 8%, caused by the uncertainty in the numerical value of the cross-section for Raman scattering, is present.

TS measurements were made in a pressure range between 6 mbar and 20 mbar for different microwave powers in between 25 W and 65 W. The results obtained in these ranges are summarized as follows:

- In the pressure range $6 \text{ mbar} \leq p \leq 20 \text{ mbar}$, $n_e$ increases with absorbed microwave power, $T_e$ is approximately constant when the input power is above a specific value.
- For constant absorbed microwave power, the plasma length decreases and the $n_e$-values increase with increasing pressure in the range $6 \text{ mbar} \leq p \leq 20 \text{ mbar}$. The $T_e$-values decrease slightly with pressure.
- For constant absorbed microwave power density, $n_e$ still increases with pressure in the range $6 \text{ mbar} \leq p \leq 10 \text{ mbar}$, between 10 mbar and 20 mbar these values are constant. The $T_e$-value decreases slightly with pressure.

For the moment, an accurate comparison with previous results obtained with absolute line intensity and continuum measurements is not possible since the experimental conditions are not entirely the same. In chapter 6, active (Thomson scattering) and passive spectroscopic [15, 28] methods will be applied simultaneously to a surfatron induced argon plasma for the same experimental conditions as used in this work. The Thomson scattering results can then be used to calibrate passive diagnostics which are experimentally much easier to use.

Bibliography

Abstract. The broadening of the $H_\beta$ line has been measured in a low pressure ($\sim 10$ mbar) surface wave sustained argon plasma. This line is broadened due to two main contributions, namely a Stark and a Doppler component. For these low pressure plasmas, the components are relatively small; the half-widths are around 5 pm for the Stark and 10 pm for the Doppler broadening. Therefore, a high resolution spectrometer and a sophisticated fitting procedure are required. For high resolution, an Echelle spectrometer with a resolution of about 2 pm per pixel is employed. The fitting routine includes corrections for the instrumental broadening and the fine structure of $H_\beta$. It is assumed that this Doppler broadening gives the gas temperature. Axial profiles of the electron density and gas temperature are determined from the Stark and Doppler broadening of the measured $H_\beta$ spectral line. Electron temperatures as a function of the axial position are obtained by means of an absolute measurement of an argon spectral line at 811 nm and the use of a collisional radiative model. For a pressure of 9 mbar, an electron density of around $10^{19}$ m$^{-3}$, a gas temperature around 1700 K and an electron temperature around 11000 K are found. The obtained results are compared with the results of a zero dimensional global plasma model for argon. The global model electron density value is found to be too high and the atom temperature too low compared to the experimental results. This suggests that the plasma properties are influenced by the small amount of hydrogen (0.5 %) added to the argon plasma in order to measure the $H_\beta$ spectral line.
4.1 Introduction

The plasma column generated by means of electromagnetic surface waves is fairly reproducible and can be sustained over a broad range of experimental conditions. The plasma can be generated for a wide range of frequencies, tube diameters, gas pressures and chemical compositions. For these reasons, RF and microwave surface wave sustained plasmas are often used in industry for various applications. In general, these plasmas are not in equilibrium and it is not easy to measure important plasma properties like the electron density, the electron temperature and the gas temperature.

In the past, Stark broadening of the $H^\beta$ line (486.13 nm) has often been applied to determine the electron density of atmospheric pressure surface wave sustained argon plasmas [1, 2], where the relatively high electron density results in a large value for the Stark broadening. Another technique is the application of Stark broadening to two or more Balmer lines from which both the electron temperature and electron density can be determined simultaneously [3, 4]. In the work presented in these articles, a small amount of hydrogen (about 1%) was added to the discharge or was present as an impurity in the argon gas. It was assumed that the hydrogen addition did not significantly disturb the discharge [4].

The aim of this work is to determine the electron density and gas temperature using the Stark and Doppler broadening of the Balmer $H^\beta$ spectral line in a low pressure surface wave sustained argon plasma. A small amount of hydrogen was admixed into the argon plasma in order to measure this line with an observable intensity. The Stark broadening of spectral lines is caused by collisions of the emitter with charged particles in the plasma, whereas Doppler broadening is caused by the velocity of the emitting particles relative to the observer. The $H^\beta$ line at $\lambda = 486.133$ nm is used because it is sensitive to the Stark broadening and practically independent of ion dynamic processes [2]. To obtain more information of the plasma properties, the electron temperature was determined via absolute intensity measurements of a 4p argon line and the use of a collisional radiative model for argon [5].

In this study, a waveguide surfatron was used to launch the microwaves ($f = 2.46$ GHz) into a large inner diameter $d = 27$ mm tube and generate an argon plasma in the pressure range $9 \leq p \leq 18$ mbar. The waveguide surfatron [6] has extra tuning capabilities compared to the conventional surfatron [7]. This enables the launching of the azimuthal symmetric $m = 0$ mode [8] into a large tube diameter. Moreover, the waveguide surfatron can be used at much higher microwave powers.

For the low pressure plasmas in this work, the electron density ($\sim 10^{19}$ m$^{-3}$) and thus the Stark broadening is much smaller than the values observed in atmospheric plasmas. Therefore, a high resolution spectrometer and a sophisticated fitting procedure to de-convolute the Voigt profile is required. A high resolution spectrometer, the Double Echelle Monochromator (DEMON), was used to measure the line shapes with high resolution. At $\lambda = 486.133$ nm, the width of the instrumental profile is approximately 6 pm. In the fitting procedure, a measured instrumental profile is convoluted with a theoretical profile of $H^\beta$ including the fine structure, and compared with the measured profile. A least square fitting method is applied
to find the best fit. The derived Gaussian part is used to determine the gas temperature\(^1\) and the Lorentzian part is, after a small correction for the van der Waals broadening, used to obtain the electron density.

An important aspect of this study is to extrapolate the tables of [9] and [10] which relate the Stark width to the electron density. For \(H_\beta\), these calculations are made for electron densities of \(10^{20} \text{ m}^{-3}\) and higher whereas the \(n_e\)-values observed for our experimental conditions are about one order of magnitude smaller. This Stark broadening technique has been applied to a low pressure surfatron induced argon plasma and the obtained results for the electron density were in a good agreement with the simultaneously obtained Thomson scattering results [11, 12]. This validates the use of the fitting procedure and the extrapolation to the low \(n_e\)-values in this study since the waveguide surfatron induced plasma has approximately the same values for the pressure and electron density as the values we found in chapter 6 or in [12].

This article starts with a description of the waveguide surfatron and the high resolution spectrometer in section 4.2. In section 4.3, a short overview of the different line broadening mechanisms and theories is presented. This is followed by the fitting procedure, which is explained in section 4.4. Results of temperatures and densities are shown in section 4.5. In section 4.6, a discussion of the experimental results and a comparison with results of an atomic global plasma model is given. The summary and conclusions are given in section 4.7.

4.2 Experimental configurations

4.2.1 Waveguide surfatron

A waveguide surfatron is used to generate a plasma inside a quartz tube. As discussed in [6], this microwave structure can be used to replace the conventional surfatron when high microwave power levels or large tube diameters are needed. The waveguide surfatron is part of the total microwave setup which is shown in figure 4.1. The coaxial part of the waveguide surfatron can be used to select the \(m = 0\) or \(m = 1\) mode of propagation. Therefore, it is possible to launch the azimuthal symmetric mode \(m = 0\) while using a large diameter tube. The experiments in this work are done with the \(m = 0\) mode.

The electromagnetic waves are generated using a magnetron with a maximum power of 2 kW. Waveguide components are used to transport the microwaves to the waveguide surfatron. The microwaves are coupled into the plasma via the launching gap. A triple stub tuner and a movable plunger are used to reduce the reflected power to values below 5 W. The frequency of the microwaves is fixed at 2.46 GHz. The inner diameter of the quartz tube equals 28.1 mm, the outer diameter 31.6 mm. In this work, the argon gas pressure equals 9 mbar or 18 mbar and the input power was in both cases equal to 600 W. At 9 mbar, the plasma length in front of the launcher \(L_1\) was equal to 37 cm and the total plasma length \(L\) was found to be 63 cm. For the 18 mbar plasma, the plasma lengths \(L\) and \(L_1\) were equal to 50 cm and 26 cm, respectively.

\(^1\)For low pressure argon/hydrogen plasmas, it is not certain that temperature derived from the Doppler broadening equals the gas temperature [13]. Also, the hydrogen temperature might be higher than the argon temperature. In this chapter, it is assumed that the temperature obtained from the Doppler broadening is close to the gas temperature.
To obtain a measurable intensity of the $H_\beta$ line, it is necessary to add a small amount of molecular hydrogen to the plasma. In all cases, we used 300 sccm of argon and 1.5 sccm of hydrogen. The molecular hydrogen concentration $C_{H_2}$ can be determined using,

$$C_{H_2} = \frac{Q_{H_2}}{Q_{Ar} + Q_{H_2}}. \quad (4.1)$$

Inserting the argon flow $Q_{Ar} = 300$ sccm and the hydrogen flow $Q_{H_2} = 1.5$ sccm results in $C_{H_2} = 0.5\%$.

4.2.2 High resolution spectrometer

A high resolution spectrometer, called the Double Echelle MONochromator, abbreviated to DEMON, was used to measure the line shapes with high resolution [14]. The DEMON, shown in figure 4.2, consists of a prism pre-monochromator in sequence with a high resolution CCD Echelle spectrometer. The prism pre-monochromator is used for the separation of the different orders from the grating. The Echelle monochromator is the actual high resolution component of the spectrometer. In this configuration, internal order separation and high resolution are received. Both the Echelle grating and the prism are arranged in a Littrow mounting and use parabolic mirror optics (number 2 in figure 4.2). To record the two dimensional spectrum, an Andor DV434 CCD was used (number 6 in figure 4.2). The $1024 \times 1024$ array consists of pixels with a size of $13 \times 13 \mu m$. Thermoelectric cooling results in a negligible dark current.

The plasma light was focussed onto an optical fibre by a quartz lens. The lens had a diameter of $5 \text{mm}$ and a focal length of $10 \text{mm}$, the core diameter of the fibre is $200 \mu \text{m}$. A diaphragm was used to reduce the measured light cone. This is schematically shown in figure 4.3.
4.3 Broadening of spectral lines

The shape of a spectral line contains information of important plasma quantities. The broadening mechanisms in a plasma are natural broadening, Doppler broadening, pressure broadening and Stark broadening. In addition, a spectral line can be broadened by the apparatus profile of the spectrometer. In the case of $H_\beta$, also the fine structure has to be considered.

In this section, the various broadening mechanism are discussed and their contributions to the total line broadening are estimated for typical plasma conditions: electron density $n_e = 10^{19}$ m$^{-3}$, electron temperature $T_e = 15000$ K, atom temperature $T_a = 1000$ K and pressure $p = 10$ mbar.

4.3.1 Natural broadening

Natural broadening is caused by the finite life time of excited states and can be determined from the Heisenberg uncertainty relation; $\Delta E \cdot \Delta \tau \geq \frac{\hbar}{2\pi}$. Without disturbances from other
Chapter 4.

particles, the lifetime $\Delta \tau$ of an atomic state $p$ is determined by the sum of all possible transition probabilities from the emitting level $p$ to all lower lying levels $q$ ($p > q$), and thus given by $A_p = \Sigma_q A_{pq}$. The life time $\tau_p$ of state $p$ due to spontaneous emission is called the natural life time and equals $1/A_p$. Using the Heisenberg relation, we find that the half-width $\Delta \lambda_{\text{nat}}$ due to natural broadening equals

$$\Delta \lambda_{\text{nat}} = \frac{A_p \lambda_0^2}{4\pi c},$$

where $c$ is the speed of light and $\lambda_0$ the central wavelength of the spectral line. For $H_\beta$, the transition probability is approximately $10^7 \, s^{-1}$, which results in a natural broadening of $\sim 10^{-3} \, \text{pm}$. It will be shown that this is much smaller than the other broadening mechanism and can therefore be neglected.

4.3.2 Pressure broadening

Two types of pressure broadening can occur: *resonance broadening* and *van der Waals broadening*. Resonance broadening is caused by collisions of radiating hydrogen atoms with hydrogen ground state atoms of the same kind whereas van der Waals broadening is due to collisions of the radiating excited hydrogen atoms with other atoms.

**Resonance broadening**

As mentioned, resonance broadening is caused by the interaction of the emitting hydrogen particle with hydrogen atoms in the ground state. To estimate the influence of resonance broadening, a broadening coefficient $\gamma_r$ was introduced [15], such that the half-width $\Delta \lambda_r$ equals

$$\Delta \lambda_r = \gamma_r n_H,$$

with $n_H$ as the hydrogen density. Taking $n_H = 10^{21} \, \text{m}^{-3}$ and using $\gamma_r \approx 10^{-26} \, \text{nm}^{-3} \, \text{mm}^{-3}$ [15], equation 4.3 yields $\Delta \lambda_r = 10^{-2} \, \text{pm}$, which is in the same order of the natural line width and thus negligible for our plasma conditions.

**Van der Waals broadening**

Van der Waals broadening is caused by the presence of ground state atoms of a different kind than those of the emitting hydrogen particle. The induced dipole of the ground state argon atoms interacts with the emitting atom which results in a Lorentzian broadening of the spectral line [1, 2]. This type of broadening depends on the gas temperature and the quantum number of the excited states [16]. In the work of Yubero et al [1], the van der Waals broadening is determined for emitting hydrogen particles in an atmospheric argon plasma for the first three lines of the hydrogen Balmer series. As the van der Waals broadening is proportional to the pressure, we can scale these expressions to a lower pressure. This gives the following expression for the half-width of the $H_\beta$ spectral line,

$$\Delta \lambda_W = \frac{5.521}{2 \times T_h^{1/10}} \times p,$$

where $\Delta \lambda_W$ is the van der Waals half-width expressed in nm and $p$ the pressure in bar. This broadening term depends solely on the gas temperature and gas pressure.

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For typical conditions, $p \sim 10^{-2}$ bar and $T_h \sim 1000$ K, a half-width of 0.4 pm is obtained. We will correct for this type of pressure broadening by subtracting the $\Delta W$ value from the total Lorentzian half-width. This value is relatively small compared to the Stark width and the correction introduces only a minor decrease in the electron density.

4.3.3 Stark broadening

Stark broadening of spectral lines is caused by the interaction of the radiating atom with the electric field of neighboring charged particles like ions and electrons. The broadening of the Balmer $H_\beta$ line is used to determine the electron density because the Stark broadening effect is strong and practically independent of ion dynamics [2]. The theory of Kepple and Griem [9] can be used to find a relationship between the line-width and the electron density [9]. This theory is based on a quasi-static approximation, which assumes that the collisions occur instantaneously and that radiation is not emitted during these events. Perturbation terms are added to describe correlation effects between the particles. This theory does not include the effect of the ion dynamics on the broadening of spectral lines [2], [4]. The width of the spectral lines is generally expressed in terms of the fractional semi-half-width $\alpha_{1/2}$, which is defined by $\alpha_{1/2} \equiv \Delta \lambda_S / F_0$, with $F_0 = 1.23 \times 10^{-14} n_e^{2/3}$ the Holtsmark normal field and $\Delta \lambda_S$ the Stark half-width. Therefore, according to this so-called Kepple and Griem (KG) theory, the Stark half-width $\Delta \lambda_S$ can be found using

$$\Delta \lambda_S = 1.23 \times 10^{-14} \alpha_{1/2} n_e^{2/3}. \quad (4.5)$$

The $\alpha_{1/2}$-values, presented in [9] as function of $n_e$ and $T_e$, are shown in figure 4.4 as a function of the electron density for $T_e = 15000$ K.

![Figure 4.4: Semi-half-width values $\alpha_{1/2}$ as function of the electron density for $T_e = 15000$ K extrapolated to lower $n_e$-values for the $H_\beta$ line.](image-url)
Unfortunately, the $\alpha_{1/2}$-values for the $KG$ models of $H\beta$ are only presented for values of $n_e$ of $10^{20}\text{ m}^{-3}$ and higher [9]. Therefore, we had to extrapolate these $\alpha_{1/2}$-values to $n_e$-values below $10^{20}\text{ m}^{-3}$. The extrapolated values of $\alpha_{1/2}$ for $T_e = 15000\text{ K}$ as function of $\log n_e$ are also shown in figure 4.4. At an electron temperature of 15000 K, the relationship between $\log n_e$ and $\alpha_{1/2}$ is almost linear and using a linear fit we obtain $\alpha_{1/2} = 0.00238 + 0.00375 \log n_e$. For $n_e = 10^{19}\text{ m}^{-3}$, this results in $\alpha_{1/2} = 7.36 \times 10^{-2}$. Using $T_e = 10000\text{ K}$ and $n_e = 1 \times 10^{19}\text{ m}^{-3}$ gives $\alpha_{1/2} = 7.4 \times 10^{-2}$, which is more or less equal to the value obtained at $T_e = 15000\text{ K}$. Therefore, the $\alpha_{1/2}$-values for $H\beta$ only weakly depend on $T_e$.

A numerical model which includes the ion dynamic effects has been developed by Gigosos and Cardenoso [10, 17]. This new theory, referred to as the $GC$ theory, was applied to the $H\beta$ and $H\alpha$ line in order to determine the electron density from the Stark broadening and to compare these results with $n_e$-values obtained with the $KG$ theories [2]. For $H\beta$, the results obtained with both theories were in good agreement with each other, this was not the case for $H\alpha$ for which the electron density obtained with the $KG$ was much larger. The $GC$ theory is used in the work of [3, 4] to determine the electron density and electron temperature from the Stark broadenings of the $H\beta$ and $H\alpha$ lines simultaneously.

Using the $GC$ model for the Balmer $H\beta$ line, the full width at half maximum (FWHM) or $2\Delta\lambda_S$ is given in terms of electron temperature, electron density and reduced mass $\mu$ of the colliding system. For an argon plasma with a small amount of hydrogen, the reduced mass is approximately equal to unity. For $T_e = 15000\text{ K}$ the $GC$ tables [10, 17] give a linear relationship between the logarithm of the FWHM and the logarithm of $n_e$ (cf. figure 4.5).

**Figure 4.5:** The logarithm of the FWHM $2\Delta\lambda_S$ in pm of the Balmer $H\beta$ line as function of $n_e$ for $T_e = 15000\text{ K}$ and a reduced mass $\mu = 1$ for the argon-hydrogen system as obtained from the $GC$ model.
With the use of the linear fits for the KG and GC models for $H_\beta$ at $T_e = 15000$ K and equation 4.5, we can compare the obtained results, i.e. the FWHM as function of $\log n_e$, with each other. Figure 4.6 shows that both theories are in a very good agreement. This is also found in [2], where Stark broadening results obtained with both theories for $H_\beta$ are similar for electron densities around $10^{20}$ m$^{-3}$. Note that this was not the case for $H_\alpha$ broadening, where using the KG theories resulted in much larger $n_e$-values compared to the $n_e$-values obtained with the more sophisticated GC model.

![Figure 4.6](image.png)

**Figure 4.6**: Comparison of the logarithm of the FWHM $2\Delta\lambda_S$ in pm of the Balmer $H_\beta$ line as function of $n_e$ at $T_e = 15000$ K for both the GC and KG theory. In the GC theory we use a reduced mass $\mu = 1$ for the Ar-H system.

It can be concluded that both the KG and GC can be used to determine the electron density from the Stark width of the $H_\beta$ line. Because the extrapolation of the GC tables is less straightforward than the extrapolation of $\alpha_{1/2}$, we will hereafter use the KG models. For this purpose, we use equation 4.5 combined with the linear fit $\alpha_{1/2} = 0.00238 + 0.00375 \log n_e$ to determine $n_e$ from the Stark width of $H_\beta$. This will be done in an iterative way. First $n_e$ is determined using a begin value for $\alpha_{1/2}$, then $\alpha_{1/2}$ is calculated using the equation for the linear fit. This procedure is repeated until convergence for $n_e$-value is reached.

In chapter 6, this Stark broadening technique is applied to a low pressure surfatron induced argon plasma and the obtained results are compared with the simultaneously obtained Thomson scattering results [11, 12]. The Stark half-width was equal to 5.4 pm and the Thomson Scattering result for $n_e$ was found to be $(3.9 \pm 0.4) \times 10^{19}$ m$^{-3}$. Inserting these values into equation 4.5 results in $\alpha_{TS} = 0.0765 \pm 0.006$. Inserting $n_e = (3.9 \pm 0.4) \times 10^{19}$ m$^{-3}$ into the linear fit of the KG theory, i.e. $\alpha_{1/2} = 0.00238 + 0.00375 \log n_e$, results in $\alpha = 0.0759 \pm 0.003$. This results in a systematic error in $\alpha$ of approximately 11%. Applying the KG theory to our typical plasma conditions results in $\alpha_{1/2} = 0.0736$ and a Stark half-width of $\Delta\lambda_S \sim 4$ pm.
4.3.4 Doppler broadening

Doppler broadening is caused by the velocity of the emitting particles relative to the observer. The intensity distribution of a Doppler broadened spectral line has a Gaussian shape of which the half-width $\Delta \lambda_D$ equals

$$\Delta \lambda_D = \lambda_0 \sqrt{\ln 2 \left( \frac{2k_B T_h}{M_a c^2} \right)^{1/2}},$$

with $k_B$ the Boltzmann constant and $M_a$ the atomic mass. Numerically, this leads to

$$\Delta \lambda_D = 7.16 \times 10^{-7} \lambda_0 \sqrt{T_h / A},$$

where $A$ is the atomic mass of the emitter in amu. Using this formula, a Doppler temperature can be obtained from the Gaussian part of a spectral line.

Inserting the typical atom temperature of $\sim 1000$ K into equation 4.7 results in a Doppler half-width of $\Delta \lambda_D = 11$ pm.

4.3.5 Instrumental broadening

The optical system used to record the spectrum causes an extra broadening of spectral lines. This type of broadening is called instrumental broadening and is independent of the plasma properties. It is determined by parameters of the spectrometer like the width of the entrance slit, the type of grating and focal length. In the ideal case, the instrumental profile is obtained via a spectroscopic measurement of a monochromatic light source. In practice, light sources are not truly monochromatic. The most important aspect is that the FWHM of the applied light is small compared to the broadening of the spectrometer.

The FWHM of the DEMON is specified to be 6.1 pm at a wavelength of 486 nm [14]. Therefore, a good candidate is the argon spectral line at a wavelength of 470.23 nm. Using equation 4.7 with $A = 40$, $T_h = 300$ K and $\lambda_0 = 470.23$ nm results in $\Delta \lambda_D = 0.9$ pm. The FWHM of this argon line is approximately 2 pm, which is about 30% of the specified FWHM of the instrumental profile. Therefore, the broadening of this argon line at room temperature is small compared to the specified FWHM and will be used to determine the instrumental profile.

For the measurement of this argon line, an argon plasma was made at low pressure ($p = 0.5$ mbar) and low power ($\approx 150$ W) conditions and the measurement was made far away from the launching gap. In this way the gas temperature remained low. This resulted in a Gaussian profile with a FWHM of 5.2 pm, which is somewhat smaller than the specified value. However, it is clear that a correction for the instrumental broadening has to be performed.

4.3.6 Fine structure of $H_\beta$.

The $H_\beta$ spectral line is based on a transition from the upper level with main quantum number $n = 4$ to the lower level with $n = 2$. The upper level $n = 4$ has the following sub-shells $s$, $p$, $d$, $f$, which correspond with the angular momentum $l = 0, 1, 2, 3$. The spin of one electron equals $|s| = 1/2$. With the possible values of $l$ and $s$ the total angular momentum $j$ lies in the
range \( j = |l + s|, |l + s| - 1, \ldots, |l - s| \). Here, the notation \( ^{2S+1}L_J \) is used, where the capitals refer to the total spin and angular momentums of all electrons in the atom. For hydrogen, only one electron is present. Therefore, we obtain: \( S = s, L = l \) and \( J = j \). The upper level \( n = 4 \) has the components \( ^2S_{1/2}, ^2P_{1/2}, ^2P_{3/2}, ^2D_{3/2}, ^2D_{5/2}, ^2F_{5/2} \), and \( ^2F_{7/2} \). Applying this notation to the lower level \( n = 2 \) with shells \( S \) and \( P \) results in the components \( ^2S_{1/2}, ^2P_{1/2}, ^2P_{3/2} \). Using the selection rules \( \Delta L = \pm 1, \Delta J = 0, \pm 1 \), the transitions shown in table 4.1 can be observed [19]. The relative intensities are determined using \( g_j A_j / \sum g_i A_i \), where \( g_j \) is the statistical weight of level \( j \) and \( A_j \) the transition probability. The \( H_\beta \) spectral line corresponds to a series of transitions positioned at small distances from each other (see table 4.1). The wavelength distance between the first and last peak is 9.6 pm, which is significant in relation to the broadening mechanism of the line.

<table>
<thead>
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<th>( n )</th>
<th>( n )</th>
<th>( \lambda ) (nm)</th>
<th>( A_j ) (s(^{-1}))</th>
<th>( g_j )</th>
<th>( g_j A_j / \sum g_i A_i )</th>
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<td>2</td>
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</tr>
</tbody>
</table>

### 4.4 Fitting procedure

The \( H_\beta \) line at \( \lambda = 486.133 \) nm will now be used to determine the electron density and hydrogen temperature. The temperature of the hydrogen atoms can be determined from the Gaussian part and the electron density is related to the Lorentzian part of the \( H_\beta \) line. However, for the low pressures in this work, the broadening is relatively small and an accurate fitting procedure is required in order to derive the Gaussian and Lorentzian width from the measured line. In addition, the broadening of the line due to the instrumental profile of the spectrometer and the fine structure has to be taken into account. To determine the combined effect of the individual line broadening mechanisms, we use the convolution product. The convolution of two functions \( f(t) \) and \( g(t) \) is denoted by \( (f * g)(t) \) and is analytical representation is defined by

\[
h(t) = (f * g)(t) = \int_0^\infty f(\tau)g(t - \tau) d\tau,
\]

The fitting procedure starts with a convolution of the instrumental profile and the fine structure (cf. 4.4.1). The resulting profile is independent of the plasma conditions. This profile is convoluted with a Voigt profile (4.4.2) and the obtained profile is compared with the measured \( H_\beta \) line (see 4.4.3). The Gaussian and Lorentzian half-widths are varied until a best fit is obtained. The resulting half-widths are related to the Doppler temperature and
electron density, respectively.

The entire fitting procedure is based on model steps which have a size of 0.1 times the size of a CCD pixel. The Lorentzian and Stark half-widths are obtained in terms of CCD pixel number and are converted from pixel to nm using the specified dispersion at the centre wavelength of $H_\beta$, where one CCD pixel corresponds with 2.1 pm.

### 4.4.1 Instrumental profile and fine structure

First, the instrumental profile was determined from a measured argon transition in the same wavelength range under low pressure and low power conditions. For this purpose, the Ar line at 470 nm was measured. To correct for the influence of the fine structure, which was presented in table 4.1, a convolution of the Gaussian instrumental profile with the fine structure has to be performed. However, the convolution product defined in equation 4.8 can only be used for analytical functions while our measured line profiles are 1-dimensional arrays. These can be seen as discrete vectors. The convolution of two discrete vectors $u$ and $v$ with lengths of $m$ and $n$, respectively, results in a new vector $w$ of length $m + n - 1$ whose $k$th element is

$$w(k) = \sum_j u(j)v(k + 1 - j). \quad (4.9)$$

When $m = n$, the vector $w$ has a length of $2n - 1$.

A Gaussian fit of the instrumental profile, obtained with a model step size $j$ which is 0.1 times the measured step size of 1 CCD pixel, was made in Origin and serves as the input for the fit procedure. This fit of the instrumental profile is shown on the left-hand side of figure 4.7, where the horizontal axis is in terms of CCD pixels. Note that in the presented figures 1 CCD pixel, that corresponds to 2.1 pm, contains 10 model steps. The fine structure of $H_\beta$, is shown in the second graph of this figure. The figure on the right-hand side, referred to as basic-line-profile, is the result of the convolution product of the instrumental profile and the fine structure. This basic line-profile is independent of the plasma properties.

![Figure 4.7](image-url)  
**Figure 4.7:** The left figure represents the Gaussian fit of the instrumental profile, the figure in the middle the fine structure and the right figure the convolution product of the instrumental profile and fine structure called the basic-line-profile.
The one dimensional arrays representing the instrumental profile and the fine structure have the same length \( n \). When \( X_{\text{max}} \) is the pixel number which corresponds with the maximum intensity of the instrumental profile, the basic-line-profile has to be shifted \( 2n - 1 \) steps in order to put the maximums at the same pixel position.

### 4.4.2 Voigt profile

The second step is to calculate a Voigt profile, thus a convolution of a Gaussian and Lorentzian profile for specific Gaussian and Lorentzian half-widths and peak position. The Gaussian intensity distribution \( I_G(\lambda) \) is described by

\[
I_G(\lambda) = \frac{2\sqrt{\ln 2}}{\Delta \lambda_{1/2} \sqrt{\pi}} \exp \left[ -4 \ln 2 \left( \frac{\lambda - \lambda_0}{\Delta \lambda_{1/2}} \right)^2 \right],
\]

in which \( \lambda \) is the wavelength, \( \lambda_0 \) the central wavelength and \( \Delta \lambda^G_{1/2} \) the Gaussian half-width.

The Lorentzian intensity distribution \( I_L(\lambda) \) is equal to

\[
I_L(\lambda) = I_0 \frac{\Delta \lambda_{1/2} / 2\pi}{(\lambda - \lambda_0)^2 + (\Delta \lambda_{1/2}/2)^2},
\]

with \( \Delta \lambda^L_{1/2} \) the Lorentzian half-width.

The total profile is obtained via a convolution of the Lorentzian with a Gaussian intensity distribution and results in a so-called Voigt profile:

\[
I_V(\lambda) = (I_G * I_L)(\lambda).
\]

To obtain adequate starting conditions for the fit procedure, the Lorentzian and Gaussian half-widths are determined with estimations of \( n_e \) and \( T_h \). These half-widths are then used to calculate the Lorentzian and Gaussian intensity distribution functions. Using the discrete convolution product (cf. equation 4.9), we can now determine the Voigt profile. The last step is to divide the theoretical profile by its maximum intensity in order to obtain a normalized Voigt profile. This theoretical Voigt profile is shown in figure 4.8.

Because the theoretical profile has to be compared with the measured profile, the influence of the corrected instrumental profile has to be taken into account. Therefore, the theoretical Voigt profile is convoluted with the basic-line-profile. This is also included in figure 4.8, which clearly shows that including the basic-line-profile results in an asymmetrical line. Since the instrumental profile is symmetric, this asymmetry is the result of the fine structure.

### 4.4.3 Measured profile

The theoretical Voigt profile convoluted with the instrumental profile and fine structure can now be compared with the measured \( H_\beta \) line profile. The measured and calculated \( H_\beta \) profiles are normalized and converted to a finer grid using interpolation. In this way, the same step-size as the instrumental profile is obtained. Using a least square fitting procedure in Matlab, the Gaussian and Lorentzian half-widths are varied until the best fit is obtained.
The measurement, the theoretical fit and the difference are shown in figure 4.9. Since the half-widths are in terms of pixels, the dispersion of the DEMON at the centre wavelength is used to convert the results from pixel to nm.

**Figure 4.8:** Example of a theoretical Voigt profile (dashed line) and of the Voigt profile convoluted with the basic-line-profile (solid line). The asymmetry of the convoluted Voigt is caused by the fine structure which is included in the basic-line-profile.

**Figure 4.9:** The sub-figure on the top shows the measured $H\beta$ profile (dashed line) and modeled $H\beta$ profile (solid line). Because both profiles are almost indistinguishable from each other, the difference between the measured and modelled profile is enlarged by a factor of 10 and presented in the sub-figure at the bottom.
4.5 Results

Line broadening measurements were made for two different plasma conditions at different axial positions. In both cases, the input power was equal to 600 W, the argon flow was set to 300 sccm and the hydrogen flow to 1.5 sccm. The first plasma had a pressure of 9 mbar and a total plasma length $L$ of 63 cm. The second plasma had a total pressure of 18 mbar and a length $L$ of 50 cm. To determine the van der Waals broadening, the gas temperature was assumed to be around 1000 K in all cases. This resulted in half widths of $\Delta \lambda_W = 0.2$ pm and $\Delta \lambda_W = 0.4$ pm for 9 and 18 mbar, respectively.

The electron densities obtained from the Stark broadening and equation 4.5 are shown in figure 4.10. The temperatures obtained from the Doppler broadening are presented in figure 4.10. The error bars are determined using the absolute random errors of 0.3 pm for the Gaussian and 0.1 pm for the Lorentzian half-width. These random errors are estimated by successively measuring the $H_\beta$ line three times for identical plasma conditions and positions. The relative random error in the electron density is then equal to $\frac{\Delta n_e}{n_e} = 0.15/\Delta \lambda_S$. For the Doppler temperature, the relative error is determined using $\frac{\Delta T_h}{T_h} = 0.3/\Delta \lambda_G$. The systematic error in the $\alpha$ value of 12% introduces an extra uncertainty in the electron density, given by $\frac{\Delta n_e}{n_e} = 0.75\Delta \alpha/\alpha = 8\%$. Note that systematic errors are not included in the error bars of figure 4.10 and figure 4.11.

The axial density of the argon 4p-level was determined via a radially integrated absolute line intensity (ALI) measurement at a wavelength of 811 nm. Via a collisional radiative (CR) model for argon [20, 21] and the measured 4p-density, the electron temperature was determined [5]. Axial profiles of the electron temperature are shown in figure 4.11, where also the axial wall temperature profiles measured with a thermocouple are presented. The wall temperature close to the plasma launcher is lower as a result of the air cooling of the tube.
4.6 Discussion

4.6.1 Observed trends

For the 9 mbar plasma, the electron density has a maximum close to the launching gap \((z = 0)\) and decreases along the plasma column. The microwave power decreases along the tube so less energy is available for the creation of new electrons. For 18 mbar, only a minor decrease is observed. In both cases, the electron density at the column end is higher than the critical electron density \(n_c\) \[^{[22]}\]

\[
n_c = 3.14 \times 10^{-4} \omega^2 (1 + \varepsilon_g),
\]

with \(\omega\) the radial frequency of the microwaves and \(\varepsilon_g\) the discharge tube relative permittivity. For the microwave frequency of 2.45 GHz and \(\varepsilon_g = 4.3\) for a quartz tube, the value of \(n_c\) equals \(3.9 \times 10^{17} \text{m}^{-3}\). This is more than a factor 10 smaller than the observed \(n_e\)-values at the end of the plasma column. The condition that \(n_e\) must be larger than the critical electron density \(n_c\) is often found in literature. So apparently this condition is not sufficient for our plasma conditions. The same axial behaviour was observed with the use of absolute continuum measurements in a surfatron induced argon plasma \[^{[23]}\].

The hydrogen temperature of the 18 mbar plasma is a little higher than for 9 mbar. The gas temperature has a maximum value close to the launcher and decreases towards the column end for the 18 mbar plasma. The 9 mbar plasma also has a maximum temperature close to the launcher, is constant in between and decreases towards the column end. This behaviour is also observed in \[^{[24]}\]. The gas temperature is influenced by the air cooling of the gap, which results in a lower wall temperature close to the gap as can be seen in figure 4.11.

4.6.2 Comparison of the results with a global plasma model

The measured electron density \(n_e\) and heavy particle temperature \(T_h\) can be compared with the results of a zero dimensional global plasma model \[^{[25]}\], where the main plasma param-
eters are related to control parameters like the input power, plasma size, pressure and wall temperature [26]. The electron energy balance gives an expression for \( n_e \), whereas the heavy particle energy balance results in \( T_a \). For the input parameters, we use \( n_{Ar} = 5 \times 10^{22} \text{m}^{-3}, \) \( T_w = 320 \text{K}, \) \( P_{in} = 600 \text{W} \) and \( L = 63 \text{cm} \) (cf. section 4.2). The electron temperature is not determined with modelling; instead a measured value of \( T_e = 1 \text{eV} \) is used.

The power balance of the low pressure microwave induced argon plasma can schematically be expressed as,

\[
\text{EM} \Rightarrow \{e\} \Rightarrow \{h\} \Rightarrow \{\text{wall}\} \Rightarrow \text{surroundings}
\]

which states that the electrons \( \{e\} \) absorb energy from the electromagnetic (EM) field and loose part of this energy to the heavy particles \( \{h\} \) by elastic collisions. The heavy particles are cooled by radial heat conduction to the wall. Some part of the EM field is not absorbed by the plasma but transferred to the surroundings. We estimate that 500 W is truly absorbed by the plasma.

The electron energy balance can be cast in the following form,

\[
\epsilon = n_e \left( \theta^\text{el}(\text{Ar}) + \theta^\text{in}(\text{Ar}) \right), \quad (4.14)
\]

where \( \epsilon \) is the microwave power per unit volume absorbed by the electrons from the electromagnetic field. The parameter \( \theta^\text{el}(\text{Ar}) \) describes elastic electron energy losses to the argon atoms per electron and \( \theta^\text{in}(\text{Ar}) \) the inelastic electron energy losses like excitation and ionization processes per electron. The energy balance for the argon atoms is given by

\[
n_e \theta^\text{el}(\text{Ar}) = \frac{\lambda_H}{\lambda_D} (T_h - T_w), \quad (4.15)
\]
in which \( \lambda_H \) stands for the heat conductivity of argon, \( T_w \) is the wall temperature while the heat diffusion length \( \lambda_D \) is of the same order as the tube radius. The term on the left-hand side describes heating of the argon atoms due to elastic electron-atom collisions; it is the same as the first term on the right-hand side of equation 4.14.

We assume that all the heavy particles (ions, argon atoms, hydrogen atoms) have the same temperature \( T_h \) and that the ion density \( n_{Ar^+} \) equals the electron density \( n_e \). The elastic and inelastic electron energy losses per electron are equal to

\[
\theta^\text{el}(\text{Ar}) = n_{Ar} k^\text{heat}_{\text{Ar}} k_B (T_e - T_h), \quad (4.16)
\]

\[
\theta^\text{in}(\text{Ar}) = n_{Ar} k_{\text{ion}} \left( E_{\text{ion}} + \frac{3}{2} k_B T_e \right), \quad (4.17)
\]

where \( k^\text{heat}_{\text{Ar}} \) is the electron argon heat transfer coefficient, \( k_{\text{ion}} \) the effective ionization rate and \( E_{\text{ion}} \) the energy difference between the ground state atom and ground state ion.

The electron argon heat transfer \( k^\text{heat}_{\text{Ar}} \) is given by

\[
k^\text{heat}_{\text{Ar}} = \frac{3 m_e}{m_{Ar}} k^\text{mom}_{\text{Ar}} = \frac{3 m_e}{m_e} \sigma_{\text{mom}}^{\text{Ar}} \sqrt{\frac{8 k_B T_e}{\pi m_e}}, \quad (4.18)
\]
where $\sigma_{\text{mom}}^{e\text{Ar}}$ is the electron-atom cross section for momentum transfer in m$^2$, for which the following expression is used [27]:

$$
\sigma_{\text{mom}}^{e\text{Ar}} = \frac{5 \times 10^{-20}}{(1.0 + 1.7 \times 10^{-3} \cdot T_e)} - 3 \times 10^{-21} + 2.8 \times 10^{-24} \cdot T_e - 4.1 \times 10^{-34} \cdot T_e^3. \quad (4.19)
$$

For the thermal conductivity coefficient $\lambda_H$ of the argon gas (cf. equation 4.15), we use

$$
\lambda_H = \sqrt{\frac{2 k_B}{\sigma_{\text{aa}}} \sqrt{\frac{8 k_B T_h}{\pi m_{\text{Ar}}}}}, \quad (4.20)
$$

with $\sigma_{\text{aa}} = 1.884 \times 10^{-19} (T_h/11604.6)^{-0.31}$ m$^2$. The heat diffusion length $\Lambda_D$ is determined using $\Lambda_D = a/2.405$ where $a = 5.8 \times 10^{-3}$ m is the inner radius of the tube.

The effective ionization rate $k_{\text{ion}}$ equals [28],

$$
k_{\text{ion}} = 6.8 \times 10^{-17} \sqrt{T_e} \exp \left(-12.06/\hat{T}_e\right), \quad (4.21)
$$

where $T_e$ is the electron temperature in K and $\hat{T}_e$ the electron temperature in eV.

The coefficients $k_{\text{heat}}^{e\text{Ar}}$ and $\lambda_H$ are weakly dependent on the plasma conditions. Therefore, a procedure is required where we use adequate starting values and iteratively determine the coefficients and solve the energy balance equations. The value of $k_{\text{ion}}$ is treated as a constant based on the experimentally determined value $T_e = 1$ eV. Solving this system for the defined control parameters yield: $n_e = 1.1 \times 10^{20}$ m$^{-3}$ and $T_h = 900$ K. Compared to the axially averaged experimental results, i.e. $n_e \sim 10^{19}$ m$^{-3}$ and $T_h \sim 1700$ K, it is clear that the electron density obtained from these equations is too high and the gas temperature much too low. Therefore, it can be concluded that the argon plasma in which 0.5 % of hydrogen is added can not be described with a global plasma model for pure argon. The influence of hydrogen on the argon plasma can not be neglected and has to be included in the model. The influence of a small amount of hydrogen on the argon plasma is investigated in chapter 5.

### 4.7 Summary and conclusions

The broadening of the $H_\beta$ spectral line has been used to determine the electron density and gas temperature of a low pressure ($\sim 10$ mbar) surface wave sustained argon plasma. The Stark broadening is related to the electron density while the gas temperature is determined by the gas temperature. For the observed electron density values $\sim 10^{19}$ m$^{-3}$, the Stark broadening is relatively small ($\sim 5$ pm). Therefore, a high resolution spectrometer, called the DEMON, was used to measure the $H_\beta$ line profile with high resolution. The FWHM of the DEMON around 486 nm was measured to be 5.2 pm.

For typical plasma conditions of the microwave induced argon plasma, $n_e \sim 10^{19}$ m$^{-3}$ and $T_h \sim 1000$ K, natural and resonance broadening are found to be negligible. The van der Waals broadening is $\sim 0.4$ pm and the Doppler broadening is typically $\sim 15$ pm. Also the fine structure of the $H_\beta$ line is important because the distance between the first and last peak is around 10 pm, which is not negligible compared to the other broadening mechanism. These
numbers show that a sophisticated fitting procedure is required to de-convolute the measured Voigt profile. We employed a fitting procedure where the measured instrumental profile is convoluted with a theoretical profile of $H_\beta$ including the fine structure, and compared the resulting profile with the measured profile. A least squares fitting method is applied to find the best fit. The derived Gaussian part is used to determine the temperature of the hydrogen atoms and the Lorentzian part is, after a small correction for the van der Waals broadening, used to obtain the electron density.

After the Stark broadening is obtained from the measured $H_\beta$ line shape, we have to know the relationship between the Stark width and the electron density. In most theories for $H_\beta$, values are only given for electron densities of $10^{20}$ m$^{-3}$ and higher. Therefore, an important aspect of this study was to extrapolate the tables of Kepple and Griem [9] and Gigosos [10] which relate the Stark width to lower electron density. Both theories were found to be in a good agreement with each other. The Kepple and Griem theory has been used because the extrapolation of these tables is more straightforward. To validate the fitting procedure and the employed extrapolation method, the Stark broadening technique and Thomson scattering have been applied simultaneously to a low pressure argon plasma [11, 12]. The Stark broadening results for the electron density were found to be in a good agreement with the simultaneously obtained Thomson scattering results. The plasma conditions of the waveguide surfatron plasma employed in this study are comparable to conditions of the conventional surfatron plasma which validates the use of this method.

For 9 mbar, an axially averaged electron temperature of 11600 K, a gas temperature of 1700 K and an electron density of around $10^{19}$ m$^{-3}$ were found. The electron density and gas temperature both have a maximum close to the plasma launcher and decreases along the column. The axial profile of the electron temperature was more or less constant with a decrease at the end of the plasma. The measured electron density values at the end of the column were found to be higher than the calculated critical electron density. This is a subject for future work.

The experimental results for the electron density and gas temperature were compared with a global zero dimensional plasma model for argon where the electron temperature was used as an input parameter. For this purpose, the electron temperature was determined from an ALI measurement of the 811 nm argon line and a CR-model. The global model results were found to be too high for the electron density and too low for the gas temperature. This can be caused by the hydrogen addition (0.5 %) which was required in order to measure the $H_\beta$ line with a sufficiently high intensity. It seems that the influence of hydrogen on the argon plasma can not be neglected and has to be included in the global model. The influence of a small amount of hydrogen on the argon plasma is investigated in the subsequent chapter.

Bibliography

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Abstract. The influence of hydrogen on a low pressure argon plasma is examined using a global plasma model. The motivation for this study is that the experimental results for the electron density and heavy particle temperature of a low pressure (10 mbar) argon plasma with a minor amount of hydrogen (< 0.5%) could not be explained with a global model for pure argon. The presence of hydrogen significantly alters the energy balances compared to pure argon because a large number of reactions is now possible. The experimental results determined from the Stark and Doppler broadening of the $H\beta$ line for the electron density and heavy particle temperature are $n_e = 1.0 \times 10^{19} \text{m}^{-3}$ and $T_h = 1700 \text{K}$. The global model for argon-hydrogen is used with and without vibrational excitations. The results of the global model without the vibrational term are: $n_e = 1.5 \times 10^{19} \text{m}^{-3}$ and $T_h = 1100 \text{K}$. Including this term gives $n_e = 1.2 \times 10^{19} \text{m}^{-3}$ and $T_h = 1200 \text{K}$. Both global model results for the electron density show a good agreement with the experimental results for $n_e$. The heavy particle temperature determined with the argon-hydrogen global model is still somewhat lower than the experimental value. Because the pure argon global model resulted in values of $n_e = 1.1 \times 10^{20} \text{m}^{-3}$ and $T_h = 900 \text{K}$, it is clear that the results obtained with the extended global model for argon-hydrogen are in a better agreement with the experimental results than the results of the pure argon global model.
5.1 Introduction

The broadening of the $H_\beta$ spectral line can be used to determine the electron density and the gas temperature in a plasma. The Stark broadening and the Doppler broadening of $H_\beta$ are related to the electron density and the gas temperature, respectively. For non-hydrogen plasmas, it is often required to add a small amount of hydrogen to the plasma in order to measure the broadening of the $H_\beta$ spectral line. However, the results of the previous chapter suggests that even a very small amount of hydrogen in a low pressure argon plasma can alter the plasma properties drastically.

In the previous chapter, the electron density and electron temperature of a microwave induced argon plasma with 0.5% of hydrogen were determined from the Stark and Doppler broadening of the $H_\beta$ line. The electron temperature was determined from an absolute line intensity measurement of the 811 nm argon line using a collisional radiative model. For a 9 mbar argon plasma, an axially averaged electron temperature of 11600 K, a hydrogen temperature of 1700 K and an electron density of around $10^{19} \text{m}^{-3}$ were found. To validate the experimental results for $n_e$ and $T_h$ a global model for argon was used with the electron temperature as an input parameter. However, the obtained model results where about one order too high for $n_e$ and 800 K too low for $T_h$. Therefore, it was concluded that a low pressure argon plasma which contains only 0.5% of hydrogen can not be described with a global plasma model for pure argon. Apparently, the influence of hydrogen on the argon plasma can not be neglected and more reaction processes have to be included in the model.

The aim of this work is to determine how the electron density and heavy particle temperature are affected by the introduction of the hydrogen gas to the argon plasma. The electron energy and heavy particle balances are extended in order to include the extra reaction processes in the Ar/H$_2$ plasma compared to the pure argon plasma. In order to solve these balances, knowledge of the atomic and molecular densities is required. These are obtained by solving the particle balances of the individual species [1]. To solve this set of equations, the measured electron temperature value was used as a fixed input parameter. The particle and energy balances are solved in Matlab using an iterative procedure. The results obtained using this global plasma model for Ar/H$_2$ are compared with the experimental results for a 9 mbar argon plasma with 0.5% of hydrogen as given in chapter 4.

This chapter starts with a description of the Ar/H$_2$ plasma in section 5.2, where the most important species and reaction processes are given. The particle balances for the atomic and molecular ions, as well as the electron and heavy particle energy balances, are presented in section 5.3. The employed iterative procedure to solve the particle and energy balances is briefly discussed in section 5.4. Results are given in section 5.5 and conclusions in section 5.6.

5.2 Plasma properties of hydrogen-argon plasma

The addition of a small amount of hydrogen to an argon plasma can alter the plasma properties drastically. The hydrogen particles in the argon plasma are responsible for extra reaction processes hereby changing the electron energy and heavy particle balances. In order to understand the effect of hydrogen we start this section with the energy balance equations for a
pure atomic Ar plasma, followed by the energy balances for an Ar/H₂ mixture. Furthermore, the Ar/H₂ system and reactions will be discussed.

5.2.1 Introduction

The electron energy balance of the pure Ar plasma can be cast in the following form,

\[ \epsilon = n_e \left[ \theta_{el}^{el}(Ar) + \theta_{el}^{in}(Ar) \right], \]  

where \( \epsilon \) is the microwave power per unit volume absorbed by the electrons from the electromagnetic field. The parameter \( \theta_\text{e} \) describes the energy losses per electron per second, where \( \theta_{el}^{el}(Ar) \) is equal to the elastic electron energy losses to the argon atoms per electron and \( \theta_{el}^{in}(Ar) \) to the inelastic electron energy losses per electron per second. In an atomic plasma, these inelastic losses are caused by electron impact excitation and ionization processes (see subsection 4.6.2). The elastic and inelastic electron energy losses per electron are equal to

\[ \theta_{el}^{el}(Ar) = n_{Ar} k_{\text{heat}}^{Ar} k_B (T_e - T_h), \]  
\[ \theta_{el}^{in}(Ar) = n_{Ar} k_{\text{ion}} (E_{\text{ion}} + 3/2 k_B T_e), \]  

where \( k_{\text{heat}}^{Ar} \) is the electron argon heat transfer coefficient, \( k_{\text{ion}} \) the effective ionization rate and \( E_{\text{ion}} \) the energy difference between the ground state atom and ground state ion. These expressions are based on the assumption that all the heavy particles (ions and argon atoms) have the same temperature \( T_h \) and that the argon ion density \( n_{Ar^+} \) equals the electron density \( n_e \).

The energy balance for the heavy particles is given by

\[ n_e \theta_{el}^{el}(Ar) = \frac{\lambda_h}{\Lambda_D} (T_h - T_w), \]  

in which \( \lambda_h \) stands for the heat conductivity of the heavy particles (in this case mostly Ar atoms), \( T_w \) for the wall temperature while \( \Lambda_D \) is the heat diffusion length which is of the same order as the radius of the tube. The term on the left-hand side describes heating of the argon atoms due to elastic electron-atom collisions and it is the same as the first term on the right-hand side of 5.1. Note that these inelastic electron energy losses do not heat the heavy particles.

The introduction of hydrogen into the argon plasma significantly alters the energy balances. The elastic term \( \theta_{el}^{el} \) increases due to the presence of light hydrogen atoms and molecules. Due to hydrogen related dissociation and recombination processes, the inelastic electron energy losses are enhanced. Also electron induced vibrational excitations lead to more electron energy losses. For an Ar/H₂ plasma, the electron energy balance can be expressed as,

\[ \epsilon = n_e \left[ \theta_{el}^{el}(Ar/H_2) + \theta_{el}^{in}(Ar/H_2) + \theta_{el}^{vib}(Ar/H_2) \right], \]  

where the first term on the right-hand side describes elastic, the second inelastic and the third vibrational electron energy losses.
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The elastic electron energy losses, $\theta_{e}^{el}(\text{Ar/H}_2)$, are determined by the total heat transfer from the electrons to the heavy particles. This elastic term is now not only determined by the heat transfer from the electrons $\{e\}$ to the argon atoms $\{\text{Ar}\}$ but also by heat transfer from the electrons $\{e\}$ to hydrogen atoms $\{\text{H}\}$ and hydrogen molecules $\{\text{H}_2\}$. For the simplicity of the employed expressions it is assumed that the temperatures of these particles are equal. In this case the elastic electron energy losses can be expressed as

$$\theta_{e}^{el}(\text{Ar/H}_2) = k_B \left( T_e - T_h \right) \left( n_{\text{Ar}} k_{\text{heat}}^{e\text{Ar}} + n_{\text{H}_2} k_{\text{heat}}^{e\text{H}_2} + n_{\text{H}} k_{\text{heat}}^{e\text{H}} \right),$$

where $k_{\text{heat}}^{eX}$, the heat transfer coefficient for the interaction between an electron and a particle $X$, is related to the momentum transfer coefficient $k_{\text{mom}}^{eX}$ via $k_{\text{heat}}^{eX} = \frac{3 m_X}{m_e} k_{\text{mom}}^{eX}$. For $T_e = 1 \text{ eV}$, the following values: $k_{\text{mom}}^{e\text{Ar}} = 2.1 \times 10^{-14} \text{ m}^3\text{s}^{-1}$, $k_{\text{mom}}^{e\text{H}_2} = 2.0 \times 10^{-13} \text{ m}^3\text{s}^{-1}$ and $k_{\text{mom}}^{e\text{H}} = 2.0 \times 10^{-13} \text{ m}^3\text{s}^{-1}$ [2] are used.

The second electron energy loss term $\theta_{e}^{in}(\text{Ar/H}_2)$ contains inelastic collisions and is the sum of a number of processes. The most important ones are:

- Ionization of argon atoms.
- Ionization of hydrogen atoms. For hydrogen, the ionization potential is lower than for argon atoms. This results in a larger ionization rate of hydrogen atoms compared to argon atoms and thus a more effective energy transfer.
- Dissociative recombination reactions of molecular ions like $\text{H}_2^+$, $\text{H}_3^+$ and $\text{ArH}^+$ with electrons [4]. These electron energy loss channels are much more efficient than two-electron recombination.

To determine the losses caused by the recombination processes, knowledge of the density of the hydrogen-related ions (i.e. the species $\text{H}^+$, $\text{H}_2^+$, $\text{H}_3^+$ and $\text{ArH}^+$) is required. These densities can be obtained from the particle balances of the individual species $\text{H}^+$, $\text{H}_2^+$, $\text{H}_3^+$ and $\text{ArH}^+$. These particle balances are formulated in section 5.1.

The third term $\theta_{e}^{vib}(\text{Ar/H}_2)$ describes electron energy losses of electron induced molecular vibrational excitations. Although these processes are also inelastic in nature, they are not incorporated in $\theta_{e}^{in}$ but treated independently and denoted by $\theta_{e}^{vib}$.

The energy balance for the heavy particles in the $\text{Ar/H}_2$ mixture is given by

$$n_e \left[ \theta_{e}^{el}(\text{Ar/H}_2) + \theta_{h}^{in}(\text{Ar/H}_2) + \theta_{e}^{vib}(\text{Ar/H}_2) \right] = \frac{\lambda_h}{\Lambda^2_D} \left( T_h - T_w \right),$$

where the elastic electron energy losses $\theta_{e}^{el}(\text{Ar/H}_2)$ are absorbed by the heavy particles in the plasma. The term $\theta_{e}^{el}(\text{Ar/H}_2)$ is not the same as $\theta_{e}^{el}(\text{Ar})$ because the elastic collisions do not only occur via electron-argon collisions but also by interactions between electrons and hydrogen atoms and molecules. In contrast to the atomic argon plasma, where $\theta_{h}^{in}$ is absent, we have to include the term $\theta_{h}^{in}(\text{Ar/H}_2)$. The reason is that the heavy particles are also heated by inelastic processes like the dissociative recombination reactions. Also, the electron energy losses caused by molecular vibrations provide an extra heating term for the heavy particles.
For a complete description of the inelastic and vibrational energy loss terms $\theta_{\text{in}}^e(\text{Ar}/\text{H}_2)$, $\theta_{\text{in}}^h(\text{Ar}/\text{H}_2)$ and $\theta_{\text{vib}}^e(\text{Ar}/\text{H}_2)$, all reactions by which the electrons and heavy particles gain or lose energy have to be taken into account. The involved species and reactions are discussed in subsection 5.2.2. Hereafter, a more precise formulation of the electron and heavy particle energy balances is presented in section 5.3.

5.2.2 Species and reactions

The discussion of the role of the various species and reactions will be guided by figure 5.1. It shows a part of the species ordered in three systems; the molecular H$_2$ system and the atomic systems of H and Ar. The reactions that will be discussed are presented in table 5.1 and are accompanied with their rate coefficients. Apart from transitions in the systems, such as $k_1$ (H $\rightarrow$ H$^+$) and $k_2$ (Ar $\rightarrow$ Ar$^+$), also transitions between the systems are relevant such as $k_3$ (dissociation of H$_2$). Not all related species that can be found in the systems are given in figure 5.1, so for instance H$_3^+$ and ArH$^+$ are missing.

![Figure 5.1: Schematic presentation of some of the energy levels for atomic hydrogen H, atomic argon Ar and molecular hydrogen H$_2$. Energy levels for the hydrogen ion H$^+$, argon ion Ar$^+$ and the molecular hydrogen ion H$_2^+$ are included as well.](image-url)
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Table 5.1: List of reactions. When expressions for the rate coefficients are not presented, the values are based on $T_e = 1$ eV for the electron induced collisions and $T_h = 0.2$ eV for heavy particle kinetics. In this table, $T_e$ refers to the electron temperature in K and $T_h$ to the electron temperature in eV. All rate coefficients are given in $\text{m}^3/\text{s}$.

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate coefficients</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e + H$ → $e + H^+ + e$</td>
<td>$k_1 = 1.9 \times 10^{-14} T_e^{0.738} \exp\left(-9.556/T_e\right)$</td>
<td>[2]</td>
</tr>
<tr>
<td>$e + Ar$ → $e + Ar^+ + e$</td>
<td>$k_2 = 6.8 \times 10^{-17} \sqrt{T_e} \exp\left(-12.06/T_e\right)$</td>
<td>[3]</td>
</tr>
<tr>
<td>$e + H_2$ → $e + H + H$</td>
<td>$k_3 = 1.0 \times 10^{-16}$</td>
<td>[2]</td>
</tr>
<tr>
<td>$e + H_2(\nu = 0)$ → $e + H_2(\nu = 1)$</td>
<td>$k_4 = 1.0 \times 10^{-15}$</td>
<td>[2]</td>
</tr>
<tr>
<td>$e + H_2(\nu = 0)$ → $e + H_2(\nu = 2)$</td>
<td>$k_5 = 1.0 \times 10^{-16}$</td>
<td>[2]</td>
</tr>
<tr>
<td>$e + H_2$ → $e + H_2^+ + e$</td>
<td>$k_6 = 1.0 \times 10^{-20}$</td>
<td>[2]</td>
</tr>
<tr>
<td>$e + H_3^+$ → $H^+ + H$</td>
<td>$k_7 = 6.0 \times 10^{-14}$</td>
<td>[2]</td>
</tr>
<tr>
<td>$e + H_3^+$ → $H^+ + H + e$</td>
<td>$k_8 = 2.0 \times 10^{-14}$</td>
<td>[2]</td>
</tr>
<tr>
<td>$H_2(\nu = 4) + H^+$ → $H_2^+ + H$</td>
<td>$k_9 = 2.5 \times 10^{-15}$</td>
<td>[6]</td>
</tr>
<tr>
<td>$H_2^+ + H_2$ → $H_3^+ + H$</td>
<td>$k_{10} = 2.0 \times 10^{-15}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$e + H_3^+$ → $H + H + H$</td>
<td>$k_{11} = 6.0 \times 10^{-14}$</td>
<td>[2]</td>
</tr>
<tr>
<td>$Ar^+ + H_2$ → $Ar + H_2^+$</td>
<td>$k_{12} = 8.0 \times 10^{-17}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$Ar + H_3^+$ → $ArH^+ + H$</td>
<td>$k_{13} = 1.7 \times 10^{-15}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$Ar + H_4^+$ → $Ar^+ + H_2$</td>
<td>$k_{14} = 2.2 \times 10^{-16}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$Ar^+ + H_2$ → $ArH^+ + H$</td>
<td>$k_{15} = 6.0 \times 10^{-16}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$ArH^+ + H_2$ → $Ar + H_3^+$</td>
<td>$k_{16} = 1.5 \times 10^{-15}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$Ar + H_3^+$ → $H^+ + H_2 + Ar$</td>
<td>$k_{17} = 1.3 \times 10^{-19}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$e + ArH^+$ → $Ar + H$</td>
<td>$k_{18} = 1.7 \times 10^{-13}$</td>
<td>[4]</td>
</tr>
</tbody>
</table>

5.2.3 The atomic hydrogen and argon systems

The ionization of hydrogen and argon is schematically given by:

$$e + H + \Delta E_{\text{ion}}^H \rightarrow e + H^+ + e ; \quad k_1 ; \quad \Delta E_{\text{ion}}^H = 13.61 \text{ eV}, \quad (5.8)$$

$$e + Ar + \Delta E_{\text{ion}}^{Ar} \rightarrow e + Ar^+ + e ; \quad k_2 ; \quad \Delta E_{\text{ion}}^{Ar} = 15.76 \text{ eV}, \quad (5.9)$$

where $k_1$ and $k_2$ are the ionization rate coefficients and $\Delta E_{\text{ion}}^H$ and $\Delta E_{\text{ion}}^{Ar}$ are the ionization potentials of hydrogen and argon, respectively. This way of presenting relevant features of reactions will be employed for the other reactions as well. The reaction equation is followed by the symbol of the rate coefficients $k$ (cf. Table 5.1) and the energy $\Delta E$ needed for the reaction. Note that most reactions are endothermic ($\Delta E > 0$). The contribution of the ionization reactions to the electron energy balance is given by

$$\theta_e^{in}(\text{Ar/H}_2) = n_H k_1 \Delta E_{\text{ion}}^H + n_{Ar} k_2 \Delta E_{\text{ion}}^{Ar}. \quad (5.10)$$

For the observed electron densities $\sim 10^{19} \text{ m}^{-3}$, most ionization processes occur via electron induced stepwise excitation processes which means that ground state excitation to the first excited state $1 \rightarrow 2$ is followed by the excitations $2 \rightarrow 3, 3 \rightarrow 4$ etc. Due to this ladder-like ionization, the threshold for effective ionization is reduced to a value around the energy level of the first excited state; that is 9.6 eV instead of 13.6 eV for $H$ and 12.06 eV instead of...
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15.7 eV for Ar. These values can be found in the exponents \( \exp \left( \frac{-\Delta E_{\text{eff}}}{k_B T_e} \right) \) in the rate coefficients for H and Ar. In both cases, the reverse reactions of two electron recombination are negligible compared to the forward reactions¹ and are therefore not taken into account.

Dissociation of the hydrogen molecules

The dissociation of hydrogen molecules in the ground state by electrons is expressed as

\[
e + \text{H}_2 + \Delta E_{\text{dis}}^H \rightarrow e + \text{H} + \text{H} ; \quad k_3 ; \quad \Delta E_{\text{dis}}^H = 4.5 \text{ eV},
\]

with a rate coefficient of \( k_3 = 1.0 \times 10^{-16} \text{ m}^3\text{s}^{-1} \) for \( T_e = 1 \text{ eV} \). This reaction is endothermic and a minimum electron energy of 4.5 eV is required. Inelastic electron energy losses \( \theta_{\text{e}}^{\text{dis}} \) due to dissociation of hydrogen molecules are equal to

\[
\theta_{\text{e}}^{\text{dis}} (\text{Ar}/\text{H}_2) = n_{\text{H}_2} k_3 \Delta E_{\text{dis}}^H.
\]

The reverse reaction, called electron assisted association, is not taken into account. Dissociation of hydrogen molecules can also occur by heavy particle assisted dissociation, where a hydrogen atom or hydrogen molecule is involved in the reaction. Because these heavy particle reactions do not change the electron energy, they will not be considered.

Ionization of the hydrogen molecule

The ionization of ground state molecules to molecular ions is given by

\[
e + \text{H}_2 + \Delta E_{\text{ion}}^\text{M} \rightarrow e + \text{H}_2^+ + e ; \quad k_6 ; \quad \Delta E_{\text{ion}}^\text{M} = 15.4 \text{ eV}.
\]

This leads to an inelastic energy loss of

\[
\theta_{\text{e}}^{\text{ionM}} (\text{Ar}/\text{H}_2) = n_{\text{H}_2} k_6 \Delta E_{\text{ion}}^\text{M}.
\]

Vibrational molecular system of hydrogen

For the vibrational transitions only the excitations to the first and second vibrational states are taken into account [5],

\[
e + \text{H}_2(\nu = 0) + \Delta E_{01}^{\text{vib}} \rightarrow e + \text{H}_2(\nu = 1) ; \quad k_4 ; \quad \Delta E_{01}^{\text{vib}} = 0.5457 \text{ eV},
\]

\[
e + \text{H}_2(\nu = 0) + \Delta E_{02}^{\text{vib}} \rightarrow e + \text{H}_2(\nu = 2) ; \quad k_5 ; \quad \Delta E_{02}^{\text{vib}} = 1.0914 \text{ eV}.
\]

Electron energy losses caused by the vibrational excitation to the first and second vibrational states \( \theta_{\text{e}}^{\text{vib}} \) are equal to

\[
\theta_{\text{e}}^{\text{vib}} (\text{Ar}/\text{H}_2) = n_{\text{H}_2} \left( k_4 \Delta E_{01}^{\text{vib}} + k_5 \Delta E_{02}^{\text{vib}} \right).
\]

It is assumed that this vibrational energy is converted into kinetic energy of the heavy particles and the molecules so that the \( \theta_{\text{e}}^{\text{vib}} \) term leads to heating of the heavy particles.

¹This is shown in subsection 7.3.1 for an argon plasma at comparable plasma conditions.
5.2.4 The electronic molecular hydrogen system

The molecular ion H$_2^+$ can be destroyed via dissociative recombination,

\[ e + H_2^+ \rightarrow H + H^* ; \quad k_7 ; \quad \Delta E_{\text{dis}} = 5.2 \text{ eV}, \quad (5.18) \]

and this results in excited hydrogen atoms H$^*$ with quantum-number $p = 2$ (10.2 eV cf. figure 5.1). It depends on the plasma conditions whether this reaction is followed by either an ionization or by a radiative transition of the excited hydrogen atom H$^*$,

\[ H + H^* \Rightarrow H + H + h\nu \chi, \quad (5.19) \]
\[ H + H^* \Rightarrow H + H^+ + e \quad 1 - \chi, \quad (5.20) \]

where the parameter $\chi$ gives the fraction of the reactions that result in two ground state atoms and an emitted photon (equation 5.19) and figure 5.1. As a consequence, the value $1 - \chi$ is the fraction of reactions that results in a H$^+$ particle (equation 5.20). This is schematically shown in figure 5.1. The value of $\chi$ can be determined using the expression

\[ \chi = \frac{A_{21} A_{21}}{n_e k_2 + A_{21} A_{21}}. \quad (5.21) \]

where $A_{21}$ is the escape factor for the optical transition 2 $\rightarrow$ 1, $A_{21}$ the corresponding transition probability and $k_2$ the effective rate coefficient of the $p = 2$ level. For the latter it is assumed that it equals the stepwise excitation rate to level 3 that corresponds to

\[ k_2 = k_23 \approx 1.724 \times 10^{-13} \hat{T}_e^{0.39} \exp\left(-1.84/\hat{T}_e\right). \quad (5.22) \]

Inserting $n_e = 1 \times 10^{19}$, $\hat{T}_e = 1 \text{ eV}$, $A_{21} = 10^{-4}$ [2] and $A_{21} = 4.699 \times 10^8 \text{s}^{-1}$ into equation 5.21 results in $\chi = 0.14$. Therefore, the dissociative recombination reaction results most of the times in the combination of a hydrogen atom and atomic hydrogen ion.

For the radiative branch ($\chi = 0.14$), the electrons lose an energy of

\[ \theta_{e}^{\text{DR}} = \chi n_{H^+} k_7 \frac{3}{2} k_B T_e, \quad (5.23) \]

while the heavy particles gain

\[ \theta_{h}^{\text{DR}} = \chi n_{H^+} k_7 \left(\Delta E_\chi + \frac{3}{2} k_B T_e\right), \quad (5.24) \]

where $\frac{3}{2} k_B T_e$ is the thermal energy of the colliding electron and $\Delta E_\chi = 0.746 \text{ eV}$ is the difference between $E_{H^+}$ and $E_{H^*}$. Since the electron is now part of the (excited) atom, the elastic energy of the hydrogen atoms is increased. In the last step of the process, a photon with an energy of 10.2 eV is emitted. As shown in table 5.1, these radiative losses are not included.

The ionizing branch has a different energy distribution. The energy of the heavy particles $\{h\}$ is not affected, while the electrons $\{e\}$ lose an energy of

\[ \theta_{e}^{\text{DR}} = (1 - \chi) n_{H^+} k_7 \Delta E_{1-\chi}, \quad (5.25) \]
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with $\Delta E_{1-4} = 2.649 \text{ eV}$ the energy difference between $E_{H_2^+}$ and $E_{H^+}$.

Dissociation of molecular ions also occurs by electron impact,

$$e + H_2^+ + \Delta E^{\text{dei}} \rightarrow H^+ + H + e ; \quad k_8 ; \quad \Delta E^{\text{dei}} = 2.649 \text{ eV},$$

(5.26)

where the electron energy loss is given by

$$\theta^{\text{dei}}_e = n_{H_2^+} k_8 \Delta E^{\text{dei}}.$$

(5.27)

The molecular ion $H_2^+$ can also be created or destroyed via heavy particle kinetics. An important population process is the collision between a vibrational excited molecule $H_2(\nu = 4)$ and an atomic hydrogen ion [6, 7],

$$H_2(\nu = 4) + H^+ \rightarrow H_2^+ + H.$$

(5.28)

that is charge transfer between $H_2(\nu = 4)$ and $H_2^+$. The energy difference between the molecular and atomic ion is 1.827 eV, which is the minimum energy of the vibrational excited hydrogen molecule to let this reaction occur. Because the energy differences between two excited states equals 0.5457 eV, this reaction can occur for excited molecules in the vibrational states ($\nu \geq 4$). This reaction is most likely to occur when the energy of the vibrationally excited state is close to the energy difference between the molecular and atomic ion (1.827 eV). Therefore, this reaction takes place via $H_2(\nu = 4)$ at 2.18 eV. The excess energy is absorbed as kinetic energy by the heavy particles,

$$\theta_h = n_{H_2^+} k_9 \Delta E ; \quad \Delta E = 1.827 \text{ eV}$$

(5.29)

Molecular ions can be destroyed via reactions with hydrogen molecules in the ground state, and result in the production of another type of molecular ion [4], namely $H_3^+$,

$$H_2^+ + H_2 \rightarrow H_3^+ + H ; \quad k_{10} ; \quad \Delta E^{\text{vib}}_{92} = 1.0914 \text{ eV}.$$  

(5.30)

This reaction is followed by a recombination reaction,

$$e + H_3^+ \rightarrow H + H + H.$$  

(5.31)

In this reaction process, the electrons lose an energy of

$$\theta_e = n_{H_3^+} k_{11} \frac{3}{2} k_B T_e,$$

(5.32)

which is absorbed by the heavy particles in the plasma.

5.2.5 Hydrogen-argon coupling

Recombination of $ArH^+$ molecular ions occurs via the reaction,

$$e + ArH^+ \rightarrow Ar + H,$$  

(5.33)

where the energy of the electrons is

$$\theta_e = n_{ArH^+} k_{18} \frac{3}{2} k_B T_e,$$

(5.34)

which is equal to the energy absorbed by the Ar and H atoms.
5.3 Particle and energy balances

In the previous sections we have seen that the ions \( \text{H}^+ \), \( \text{H}_2^+ \), \( \text{H}_3^+ \) and \( \text{ArH}^+ \) play an important role in the inelastic energy loss channels of the electrons. That means that the densities of these species have to be known. These can be obtained by solving the particle balances of the individual species. In table 5.2, the particle balances for the intermediate species are formulated under the assumption that the transport of these species can be neglected. In this way, the atomic and molecular ion densities are coupled to the atomic hydrogen, atomic argon and molecular hydrogen densities. These particle balances will be solved in an iterative way using fixed values for the electron temperature \( T_e \) and the densities \( n_e, n_{\text{Ar}}, n_{\text{H}} \) and \( n_{\text{H}_2} \). It was found that the total density of H-related ions is less than 10% of that of \( \text{Ar}^+ \).

\[
\begin{align*}
\text{H}^+ & \quad 0 = n_e n_{\text{H}} k_1 + (1 - \chi) n_e n_{\text{H}}^+ k_7 + n_e n_{\text{H}}^{\text{H}_2} k_8 - n_{\text{H}} n_{\text{H}}^{\text{H}_2} k_9 \\
\text{H}_2^+ & \quad 0 = n_e n_{\text{H}_2} k_6 + n_{\text{H}}^{\text{H}_2} n_{\text{H}}^{\text{H}_2} k_9 + n_{\text{Ar}} + n_{\text{H}}^{\text{H}_2} k_{12} + n_{\text{H}}^{\text{H}_2} (n_e k_7 + n_e k_8 + n_{\text{H}}^{\text{H}_2} k_{10} + n_{\text{Ar}} k_{13} + n_{\text{Ar}} k_{14}) \\
\text{H}_3^+ & \quad 0 = n_{\text{H}}^{\text{H}_2} n_{\text{H}}^{\text{H}_2} k_{10} + n_{\text{ArH}}^{\text{H}_2} n_{\text{H}}^{\text{H}_2} k_{16} - n_{\text{H}}^{\text{H}_3} (n_e k_{11} + n_{\text{Ar}} k_{17}) \\
\text{ArH}^+ & \quad 0 = n_{\text{Ar}} n_{\text{H}}^{\text{H}_2} k_{13} + n_{\text{Ar}} n_{\text{H}}^{\text{H}_2} k_{15} - n_{\text{ArH}}^{\text{H}_2} (n_{\text{H}}^{\text{H}_2} k_{16} + n_e k_{18}) 
\end{align*}
\]

With the known densities of the hydrogen related ions (\( \text{H}^+ \), \( \text{H}_2^+ \), \( \text{H}_3^+ \) and \( \text{ArH}^+ \)) the energy balances of the electrons and heavy particles, respectively defined by the equations 5.5 and 5.7, can be solved. Here, these balances are reproduced for convenience, while the missing terms in the expressions of \( \theta^\text{in}_{\text{e}}(\text{Ar}/\text{H}_2) \), \( \theta^\text{in}_{\text{e}} \) and \( \theta^\text{vib}_{\text{e}}(\text{Ar}/\text{H}_2) \) are implemented. The electron energy balance for \( \text{Ar}/\text{H}_2 \) reads

\[
\epsilon = n_e \left[ \theta^\text{cl}_{\text{e}}(\text{Ar}/\text{H}_2) + \theta^\text{in}_{\text{e}}(\text{Ar}/\text{H}_2) + \theta^\text{vib}_{\text{e}}(\text{Ar}/\text{H}_2) \right]. \tag{5.35}
\]

Here,

\[
\theta^\text{cl}_{\text{e}}(\text{Ar}/\text{H}_2) = k_B (T_e - T_b) \left( n_{\text{Ar}} k^\text{heat}_{\text{eAr}} + n_{\text{H}}^{\text{H}_2} k^\text{heat}_{\text{eH}_2} + n_{\text{H}}^{\text{H}_3} k^\text{heat}_{\text{eH}_3} \right), \tag{5.36}
\]

\[
\theta^\text{in}_{\text{e}}(\text{Ar}/\text{H}_2) = n_{\text{H}}^{\text{H}_2} k_6 \Delta E_{\text{ionM}}^{\text{H}_2} + n_{\text{H}}^{\text{H}_2} \Delta E_{1-\chi}^{\text{H}_2} [(1 - \chi) k_7 + k_8] + n_{\text{H}}^{\text{H}_2} k_6 \Delta E_{\text{ionM}}^{\text{H}_3} + n_{\text{H}}^{\text{H}_2} \Delta E_{1-\chi}^{\text{H}_3} [(1 - \chi) k_7 + k_8] + (\chi n_{\text{H}}^{\text{H}_2} k_7 + n_{\text{H}}^{\text{H}_3} k_{11} + n_{\text{ArH}}^{\text{H}_2} k_{18}) 3/2 k_B T_e, \tag{5.37}
\]

\[
\theta^\text{vib}_{\text{e}}(\text{Ar}/\text{H}_2) = n_{\text{H}}^{\text{H}_2} k_4 \Delta E_{01}^{\text{vib}} + k_5 \Delta E_{02}^{\text{vib}}. \tag{5.38}
\]
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The heavy particle energy balance

\[ n_e \theta_e^{el}(\text{Ar/H}_2) + n_e \theta_h^{in}(\text{Ar/H}_2) + n_e \theta_h^{vib}(\text{Ar/H}_2) = \frac{\lambda_h}{\Lambda_D} (T_a - T_w), \]  

(5.39)

uses for \( \theta_e^{el} \) and \( \theta_h^{vib} \) the expressions 5.36 and 5.38 while the inelastic heating term equals

\[ \theta_h^{in} = (\chi n_{\text{H}_2} + k_7 + n_{\text{H}_3} k_{11} + n_{\text{ArH}^+} k_{19}) \times \frac{3}{2} k_B T_e + \chi n_{\text{H}_2} + \frac{7}{2} \Delta E_{\chi}. \]  

(5.40)

5.4 Method

In the global model, the main plasma parameters are determined for a specific set of experimentally determined control parameters. Here, the following control parameters are required: the microwave power, pressure, argon-hydrogen flow ratio, plasma volume and wall temperature. The following procedure is followed to determine the electron density, heavy particle density and hydrogen related ions for the defined control parameters. For the electron temperature the measured value of \( T_e = 1 \text{ eV} \) (cf. chapter 4) is used. The vibrational temperature \( T_v \) is set to 5000 K and initial values of \( T_h = 1500 \text{ K} \) and \( n_e = 10^{19} \text{ m}^{-3} \) are used. Using these (initial) values and the defined control parameters, the following steps are made:

- The atomic argon density is determined via the measured pressure, the value for \( T_h \) and the ideal gas law. The density of the argon ions is determined using \( n_{\text{Ar}^+} = n_e \). This is allowed because the hydrogen related ion density is at least one order smaller than the electron density. The molecular hydrogen density just before the plasma entrance is determined via the fraction of molecular hydrogen derived via the flow ratios, i.e.

\[ \chi_{\text{H}_2} = \frac{Q_{\text{H}_2}}{Q_{\text{Ar}} + Q_{\text{H}_2}}, \]  

(5.41)

with \( Q_{\text{Ar}} \) and \( Q_{\text{H}_2} \) the measured mass flows of Ar and \( \text{H}_2 \), respectively. The atomic hydrogen density \( n_{\text{H}} \) is estimated assuming that the dissociation ratio is around 10% [2, 8].

- The density of hydrogen molecules in the vibrational state \( \nu = 4 \), is determined using \( n_{\text{H}_2(\nu=4)} = f_4 n_{\text{H}_2} \), with

\[ f_4 = \left[ 1 - \exp\left( \frac{h \nu_c c}{k T_v} \right) \right] \exp\left( \frac{4h \nu_c c}{k T_v} \right). \]  

(5.42)

The vibrational frequency \( \nu_c \) is equal to 4401.21 cm\(^{-1}\) and \( c = 2.998 \times 10^8 \text{ m/s} \). Using \( T_v = 5000 \text{ K} \), the following relation is obtained: \( n_{\text{H}_2(\nu=4)} = 0.0045 \times n_{\text{H}_2} \). As a result, the \( n_{\text{H}_2(\nu=4)} \) value depends on the molecular ground state density \( n_{\text{H}_2} \).

- The particle balances for \( \text{H}^+, \text{H}_2^+, \text{H}_3^+ \) and \( \text{ArH}^+ \) (cf. table 5.2) can now be solved for the determined input parameters \( T_e, n_{\text{H}}, n_{\text{Ar}}, n_{\text{H}_2}, n_{\text{H}_2(\nu=4)} \). For the electron density \( n_e \), a reasonable starting value is used and it is assumed that \( n_{\text{Ar}^+} = n_e \).

- The electron energy balance (equation 5.35–5.38) can be solved for \( n_e \) using the measured power density \( \epsilon \), the fixed input parameters \( T_e, n_{\text{H}}, n_{\text{Ar}}, n_{\text{H}_2}, n_{\text{H}_2(\nu=4)} \) and the (molecular) ion densities that followed from the particle balances.
Finally, the heavy particle balance (equation 5.39) is solved for the heavy particle temperature $T_H$. For this purpose, the measured wall temperature, the electron density and the other input parameters are required.

These steps are repeated in an iterative way until convergence for the results of $n_e$ and $T_h$ is reached. This is necessary because the particle balances depend on $n_e$ and the energy balances are related to the ion densities determined from the particle balances. Moreover, the coefficients $L_{\text{heat}}^{e\text{Ar}}$ and $\lambda_h$ are weakly dependent on the plasma conditions.

### 5.5 Results of the Ar/H$_2$ global model

For the control parameters, the experimental plasma conditions as defined in chapter 4 are used. The pressure $p$ is 9 mbar, the absorbed microwave power $P_{\text{in}} = 500$ W, the plasma length $L = 63$ cm and $T_w = 320$ K. The argon flow was set at 300 sccm and the hydrogen flow at 1.5 sccm, resulting in a molecular hydrogen concentration of $n_{\text{H}_2} = 0.005 \times n_{\text{Ar}}$. As discussed in chapter 4, the experimental results for this 9 mbar plasma are $T_e \sim 1$ eV, $n_e \sim 10^{19}$ m$^{-3}$ and $T_h = 1700$ K.

The global model for Ar/H$_2$, as described in the previous section, is now used to determine the electron density and heavy particle temperature. Also information of the ion density is obtained. These results are presented in table 5.3 where two cases are distinguished; in case A all electron energy losses are taken into account, thus elastic, inelastic and vibrational. Case B only deals with elastic and inelastic electron energy losses. In this way, the effect of vibrational excitations can be examined.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_{\text{Ar}}$</td>
<td>$5.6 \times 10^{22}$</td>
<td>$5.9 \times 10^{22}$</td>
</tr>
<tr>
<td>$n_{\text{H}}$</td>
<td>$2.8 \times 10^{19}$</td>
<td>$2.9 \times 10^{19}$</td>
</tr>
<tr>
<td>$n_{\text{H}_2}$</td>
<td>$2.8 \times 10^{20}$</td>
<td>$2.8 \times 10^{20}$</td>
</tr>
<tr>
<td>$n_{\text{H}_2}(\nu=4)$</td>
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<td>$1.3 \times 10^{18}$</td>
</tr>
<tr>
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</tr>
<tr>
<td>$n_e$</td>
<td>$1.2 \times 10^{19}$</td>
<td>$1.5 \times 10^{19}$</td>
</tr>
<tr>
<td>$T_h$</td>
<td>$1.2 \times 10^{3}$ K</td>
<td>$1.1 \times 10^{3}$ K</td>
</tr>
</tbody>
</table>

Comparing the experimental results for the electron density ($n_e \sim 10^{19}$ m$^{-3}$) with the $n_e$ values obtained using the global shows a good agreement. The experimental value for the heavy particle temperature $T_h = 1700$ K is higher than obtained from the Ar/H$_2$ model.
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Including the molecular term increases the temperature with 100 K, which is not enough to explain the difference between the experimental and modelled value. The individual contributions to the heating of heavy particles are respectively given by \( n_e \theta_{h}^{\text{el}} = 1.8 \times 10^5 \text{Wm}^{-3} \), \( n_e \theta_{h}^{\text{in}} = 5.4 \times 10^5 \text{Wm}^{-3} \) and \( n_e \theta_{h}^{\text{vib}} = 3.5 \times 10^5 \text{Wm}^{-3} \). This shows that the inelastic heating term is the most important heating process, followed by the heating caused by vibrational transitions.

As discussed in chapter 4, the pure argon global model yielded \( n_e = 1.1 \times 10^{20} \text{m}^{-3} \) and \( T_h = 900 \text{K} \) for the same control parameters. When these values are compared with the results of the Ar/H\(_2\) model (\( n_e = 1.2 \times 10^{19} \text{m}^{-3} \), \( T_h = 1200 \text{K} \)), it can be seen that the electron density is significantly decreased and the heavy particle temperature is increased. With the Ar/H\(_2\) model, a much better correspondence with the experimental results for the electron density is obtained, while the heavy particle temperature determined using the Ar/H\(_2\) model is still too low.

5.6 Discussion and conclusions

The influence of hydrogen on the argon plasma has been examined. The reason for this study was that experimental results for the electron density and electron temperature of a low pressure argon plasma with a minor amount of hydrogen (< 0.5%) can not be explained with a global model for pure argon (cf. chapter 4). The hydrogen was added to the argon plasma in order to measure the \( H_\beta \) line with a sufficient signal to noise ratio.

The global plasma model employed in this work is based on the electron energy and heavy particle energy equations for the argon-hydrogen plasma. The presence of hydrogen significantly alters these balances compared to pure argon because a large number of reactions is now possible. Molecular ions can be formed during collisions with electrons and hydrogen molecules but also by collisions between hydrogen molecules and argon atoms and ions. Recombination of these molecular ions with electrons is very effective and introduces a major loss term for the electron energy. This energy is absorbed by the heavy particles in the plasma. Also, the elastic electron energy losses are enhanced because the electrons can collide with atomic and molecular hydrogen particles. Vibrational excitations provide an effective electron energy loss term. The effect of vibrational excitations on the rate coefficients is not investigated in this work.

In order to determine the density of the different ionic species, the particle balances for each species were solved in an iterative way. The electron temperature is a fixed input parameter based on an experimental value. The obtained ion densities are inserted into the electron energy balance and heavy particle energy balance in order to determine the electron density and heavy particle temperature, respectively.

The experimental results determined from the Stark and Doppler broadening of the \( H_\beta \) line for the electron density and heavy particle temperature are \( n_e = 1.0 \times 10^{19} \text{m}^{-3} \) and \( T_h = 1700 \text{K} \). The results of the global model have been determined with and without the vibrational term. Without the vibrational term, the following values are obtained: \( n_e = 1.5 \times 10^{19} \text{m}^{-3} \) and \( T_h = 1100 \text{K} \). Including this term gives \( n_e = 1.2 \times 10^{19} \text{m}^{-3} \).
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and $T_h = 1200 K$. Both global model results show a good agreement with the experimental results for $n_e$. The heavy particle temperature is too low compared to the experimental values.

The results obtained with the extended global model for argon-hydrogen are in a better agreement with the experimental results than the results of the pure argon global model, although the experimental value of the heavy particle temperature is still higher than obtained from the Ar/H$_2$ model. It should be realised that the employed Ar/H$_2$ model is based on a large number of assumptions:

- The electron temperature is set equal to the measured value obtained using absolute line intensity measurements and the collisional radiative model.
- For the dissociation ratio H/H$_2$ an estimated value of 10\% is used.
- Diffusion of hydrogen related particles and wall interactions are neglected.
- Backward reactions are not included.
- The vibrational temperature is set to 5000 K; somewhere in between the electron and heavy particle temperature.
- Only direct vibrational excitations from the molecular ground state to the first and second vibrationally excited state are taken into account.
- All the particles have the same temperature.

These items require further investigations. It would be more accurate to determine the electron temperature from the electron particle balance. Also, the dissociation can be calculated, although this requires more knowledge of backward reactions like electron and heavy particle assisted association, diffusion and wall interactions. The influence of rotational and vibrational kinetics can also be improved. First, the vibrational temperature has to be determined, whereas also the stepwise vibrational excitations and backward processes can be important. Also rotational terms might be important. To take all these contributions into account, it is recommended to develop a grand model in Plasimo [9] where also the effects of the gas flow and spatial profiles can be included.

It is also possible that the experimentally determined gas temperature is too high. In the previous chapter, the gas temperature was determined from the Doppler broadening of the $H_\beta$ line. The derived temperature is equal to the temperature of the emitting hydrogen atoms. When these excited hydrogen atoms have a higher temperature than the argon atoms, the Doppler temperature is higher than the argon temperature. Therefore, it is recommended to determine experimentally whether the Doppler temperature is equal to the argon temperature. This can for example be done via a spectroscopic measurement of the Fulcher band. A second possibility is to use the surfatron setup and compare the Doppler temperature with the gas temperature determined from Rayleigh scattering. These aspects are left for future work.

To conclude, the study performed in this chapter shows that the influence of a very small amount of hydrogen in a low pressure (10 mbar) argon plasma significantly alters the plasma properties. The employed global model for Ar/H$_2$ is based on a number of assumptions that
Influence of a small amount of hydrogen on the argon plasma requires further investigations. Therefore, this work should be seen as a first step towards a more detailed grand plasma model for the Ar/H$_2$ mixture. This grand model can then be used to determine the maximum amount of hydrogen that can safely be added to the argon plasma without changing the plasma properties.

Bibliography


Polydiagnostic calibration performed on a low pressure surface wave sustained argon plasma

Abstract. The electron density and electron temperature of a low pressure surface wave sustained argon plasma have been determined using passive and active (laser) spectroscopic methods simultaneously. In this way the validity of the various techniques is established while the plasma properties are determined more precisely. The electron density, \( n_e \), is determined with Thomson Scattering (TS), absolute continuum measurements, Stark broadening and an extrapolation of the atomic state distribution function (ASDF). The electron temperature, \( T_e \), is obtained using TS and absolute line intensity (ALI) measurements combined with a collisional radiative (CR) model for argon. At an argon pressure of 15 mbar, the \( n_e \)-values obtained with TS and Stark broadening agree with each other within the error bars and are equal to \((4 \pm 0.5) \times 10^{19} \text{ m}^{-3}\), whereas the \( n_e \)-value obtained from the continuum is with \((2 \pm 0.5) \times 10^{19} \text{ m}^{-3}\) about 30% lower. This suggests that the used formula and cross-section values for the continuum method have to be reconsidered. The electron density determined by means of extrapolation of the ASDF to the continuum is too high (\( \sim 10^{20} \text{ m}^{-3}\)). This is most probably related to the fact that the plasma is strongly ionizing so that the extrapolation method is not justified. At 15 mbar, the \( T_e \)-values obtained with TS are equal to \( \sim 13400 \pm 1100 \text{K}\) while the ALI/CR-model yields an electron temperature that is about 10% lower. It can be concluded that the passive results are in good or fair agreement with the active results. Therefore, the calibrated passive methods can be applied to other plasmas in a similar regime for which active diagnostic techniques can not be used.
Chapter 6.

6.1 Introduction

Surface wave sustained (SWS) discharges are stable and reproducible under a wide range of working conditions and can be used for a number of applications like material processing (deposition, oxidation, etching), light creation and spectrochemical analysis [1, 2]. The electromagnetic waves propagate along the interface between the plasma column and the quartz tube [3–7]. The coupling of surface waves into a dielectric tube can be realized by using a surface wave launching device like the ro-box, the surfatron, the waveguide surfatron or the surfaguide. Knowledge of the main plasma parameters is essential in order to improve the technological applications and has been obtained via plasma modelling [5–11], probe measurements [12, 13] and optical diagnostics [14–16].

In the past, SWS argon plasmas have been investigated with several distinct diagnostic techniques [17–19]. However, a comparison of the results is not possible since the experimental conditions under which the measurements were made are not exactly identical. This is a major difficulty in working with SWS plasmas. Even an accurate measurement of the incident and reflected microwave power does not give an unambiguous value of the power absorbed by the plasma. This last quantity is important since it is strongly related to the electron density. For an accurate comparison of different diagnostics, it is essential that all methods are applied to the same plasma controlled by the same plasma settings. This is only possible when all diagnostic techniques are applied simultaneously to the same plasma and to the same plasma position.

In this article we present a comparative diagnostic study performed on SWS argon plasmas in the intermediate pressure range $\sim 10\text{ mbar}$ generated inside a quartz tube using a surfatron. Several diagnostic methods have been applied simultaneously. In this way, two main parameters, namely the electron density $n_e$ and electron temperature $T_e$, are determined. The techniques can be divided into active and passive methods. In general, the active techniques are experimentally demanding but the interpretation of the experimental data is straightforward, whereas for passive techniques the experimental part is relatively easy, but the interpretation of the data often not straightforward. Therefore, the active techniques can be used to validate the passive techniques. The passive methods can then be applied to (industrial) plasmas with comparable plasma conditions for which active methods are too difficult to be applied.

We use one active method, Thomson Scattering (TS) [20, 21], and several passive methods, namely $H_\beta$-line broadening [22], absolute line intensity (ALI) measurements [17] and absolute continuum measurements [18]. Using TS, it is possible to measure $n_e$ and $T_e$ simultaneously at one plasma location [19]. ALI measurements yield an excitation temperature that can be converted to the electron temperature with the use of a collisional radiative (CR) model [17, 23–25]. The ALI measurements also yield an estimate of $n_e$. Both $H_\beta$-line broadening and absolute continuum measurements give $n_e$.

This article starts with a description of the microwave setup and the plasma conditions in section 6.2. In section 6.3, the applied diagnostic methods are presented. This is followed by results and discussion (section 6.4), where the results obtained with the different methods are compared. Section 6.5 contains the discussion and conclusions.
6.2 Microwave setup and plasma conditions

In this article, only a short description of the microwave setup is given (see figure 6.1). For a more detailed description, we refer to our previous articles [17, 18]. Electromagnetic waves with a frequency $f$ of about 2.46 GHz generated in a Muegge magnetron are transported by coaxial cables to the surfatron launcher. To measure the incident and reflected power, a bidirectional coupler, two power sensors and a power meter are used. A triple stub tuner is used to optimize the impedance matching. The electromagnetic waves are coupled into a quartz tube with an inner radius of 3 mm via the launching gap of the surfatron and can travel in both axial directions in the interface between the plasma and the tube. The main part of the waves is launched in a preferred axial direction in front of the surfatron (positive axial direction). In order to apply TS measurements, Brewster windows are attached to the vacuum equipment on both sides.

![Figure 6.1: Schematic representation of the surfatron induced plasma and the total microwave setup.](image)

An overview of the studied plasma conditions is shown in table 6.1, where $L_A$ refers to the plasma length in the preferred direction and $L_B$ to the length in the opposite direction. In all cases, the argon flow was set at a constant value of 50 sccm. A very small amount of hydrogen was introduced into the discharge via water vapour which was present in the gas pipelines. The measured incident power was 40 W while the reflected power was below 1 W. The gas pressure was equal to 10, 15 and 20 mbar, which resulted in variations of the plasma length $L_A$ between 36 – 42 cm. The wall temperature $T_w$ at the axial position $z = 16$ mm was estimated using a Fluke infrared thermometer. Values of the central gas temperature $T_a$ are determined using a global plasma model which relates the control parameters like the wall temperature, pressure and microwave absorbed power to the main plasma parameters [26].
The atom densities $n_a$ are determined via the measured argon pressures and the ideal gas law using the values of $T_a$.

Table 6.1: Overview of the plasma conditions studied in this work.

<table>
<thead>
<tr>
<th>pressure nbar</th>
<th>$P_{in}$ W</th>
<th>$L_A$ cm</th>
<th>$L_B$ cm</th>
<th>$T_w$ K</th>
<th>$T_a$ K</th>
<th>$n_a$ m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>40</td>
<td>42.0</td>
<td>6.5</td>
<td>400</td>
<td>510</td>
<td>$1.4 \times 10^{23}$</td>
</tr>
<tr>
<td>15</td>
<td>40</td>
<td>40.8</td>
<td>6.2</td>
<td>400</td>
<td>560</td>
<td>$1.9 \times 10^{23}$</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td>36.2</td>
<td>3.5</td>
<td>400</td>
<td>590</td>
<td>$2.5 \times 10^{23}$</td>
</tr>
</tbody>
</table>

6.3 Applied diagnostic methods

The experimental setup was organized such that three different types of diagnostics could be applied to the same plasma condition and position. All techniques were applied to the plasma within one day. A schematic overview of the applied techniques is shown in figure 6.2. The laser, microwave setup, triple grating spectrometer (TGS) and the high resolution double Echelle monochromator (DEMOn) [27] have a fixed position. The plasma light is focussed into the DEMOn using a small lens and an optical fibre. This optical system is placed on an optical rail in front of the plasma and can easily be removed and restored at the same position.

Figure 6.2: Total setup used for active and passive spectroscopic measurements on the surfatron plasma.
The procedure is as follows; first we remove the optical fibre and fill the quartz tube with nitrogen in order to perform a Raman calibration measurement. The tube is pumped to vacuum, refilled with argon and a microwave induced plasma is created using the surfatron launcher. Now, we perform a TS measurement. After a TS and dark measurement, the optical fibre and lens are repositioned. The position of this optical system corresponds to the focal position of the laser focusing lens, which is 16 mm in front of the surfatron (cf. figure 6.1). Subsequently, the high resolution spectrometer is used to measure line intensities of argon excited states, the $H_\beta$ spectral line shape and the continuum at a wavelength interval of 2 nm around $\lambda = 648$ nm. Finally, a tungsten ribbon lamp is used to perform an absolute calibration of the continuum and line intensities. In this section, a short overview of the applied diagnostic methods is given. More information of ALI, continuum and TS measurements can be found in earlier publications [17–19], whereas the $H_\beta$ broadening of a low pressure argon plasma will be discussed in more details in a subsequent article.

6.3.1 Thomson Scattering

Thomson Scattering is based on the scattering of (laser) photons on the free electrons in a plasma. If the scattering is incoherent, which employs that the electrons do not respond collectively to the laser interaction, the TS spectrum will have a Gaussian profile. The width is related to the electron temperature and the area to the electron density. The setup that was used for TS experiments can be divided into three parts: the optical path of the laser, the microwave setup and the spectrometer including an iCCD (cf. figure 6.2). A frequency doubled Nd:YAG laser produces a horizontally polarized laser beam at a wavelength of 532 nm with a maximum energy of approximately 115 mJ per pulse [28]. To obtain a vertical polarization, the beam is guided two times through a quarter wave plate, after which it is focussed into the plasma by a plano-convex lens with a focal length of 1 m [19]. The radiation scattered by the electrons in the plasma is imaged onto the entrance slit of a triple grating spectrograph (TGS) using two lenses. The combination of the first and second spectrometer of the TGS operates as a notch filter for the rejection of stray light in the centre of the spectrum. A third spectrograph is used for dispersion and focusses the signal onto a two-dimensional iCCD detector that is used to record the spectrum. A more detailed description of the TGS can be found in [29].

The electron density can be obtained from the Thomson Scattered power $P_T$ using,

$$n_e = n_{N_2} \cdot \frac{P_T}{P_{Rm}} \cdot \Gamma_{RmN_2},$$

with $P_{Rm}$ the Raman scattered power in pure nitrogen and $\Gamma_{RmN_2} = 8.15 \times 10^{-5}$ for the experimental configurations [30]. The electron temperature is determined using the relation

$$T_e = 5238 \times \Delta \lambda_{1/e}^2,$$

with $\Delta \lambda_{1/e}$ the half $1/e$ width of a Gaussian profile. The uncertainty of the $n_e$ determination is estimated to be 11 % and the $T_e$-values have an error of 8 % [19].

6.3.2 Emission spectroscopy

The emitted plasma light is focussed by a small lens into an optical fibre, by which the light is guided to the entrance slit of a spectrometer. A high resolution spectrometer called the Double Echelle MONochromator, abbreviated to DEMON, was used to measure the line
shapes with high resolution. The DEMON consists of an Echelle spectrometer in sequence with a prism pre-monochromator which serves for the selection of the inspection range. The Echelle monochromator is the actual high resolution component of the spectrometer. An Andor DV434 CCD is used to record the spectrum. The 1024 × 1024 array consists of pixels with a size of 13×13 µm. The width of the entrance slit of the DEMON was set equal to the horizontal size of a CCD pixel (13 µm) and the FWHM at a wavelength of 486 nm is specified to be 6.1 pm [27].

**Absolute line intensity measurements**

Absolute line intensity (ALI) measurements are used to determine densities of atomic states \( n_p \) from the absolutely measured transition integrated intensities \( I_{pq} \) of optical thin lines. If the plasma is optically thin for the transition \( p \rightarrow q \), the radiation escapes from the plasma and absorption can be neglected. The population density \( n_p \) of level \( p \) can be found using

\[
 n_p = j_{pq} \frac{4\pi}{A(p, q) E_{qp}},
\]

where \( j_{pq} \) is the transition integrated emission coefficient, \( E_{qp} = E_p - E_q = h \nu_{pq} \) the energy of the photon and \( A(p, q) \) the transition probability. The \( j_{pq} \) values are determined experimentally using an absolute measurement of the emitted line radiation divided by the plasma length in the line of sight \( L \), thus \( j_{pq} = I_{pq}/L \). By applying this procedure to various transitions, the atomic state distribution function (ASDF) can be constructed by plotting the natural logarithm of \( \eta_p = n_p/g_p \) as a function of the energy of the upper level of the transition, \( E_p \). A measured ASDF for the 10 mbar Ar plasma is shown in figure 6.3.

![Figure 6.3: Measured ASDF of an argon plasma at 10 mbar.](image-url)
Polydiagnostic calibration performed on a low pressure argon plasma

For the non-LTE plasma conditions in this work, the relation between the ASDF and the electron temperature is not straightforward. The lower part of the ASDF is used as input of a collisional radiative (CR) model. The electron temperature can then be determined using

\[
k_B T_e = E_{13} \left[ \ln \left( \frac{\eta_1 r_3^1}{\eta_3} \right) \right]^{-1},
\]

where "3" refers to the 4p-levels and "1" to the atomic ground state. The population densities \( \eta_3 \) and \( \eta_1 \) are determined experimentally and \( r_3^1 \) follows from the CR-model [17]. This coefficient is defined by \( r_3^1 = \eta_p / \eta_p^B \), and thus presents the ratio between the measured population and the value given by the Boltzmann distribution law [23]. For this purpose, a CR-model of argon developed by [24, 25] is used to convert the excitation temperature into the electron temperature.

The upper part of the ASDF is used to estimate the \( \eta_\infty \) value, from which the electron density can be obtained. If we assume that levels high in the atomic system are in partial local Saha equilibrium (pLSE), then \( \eta_\infty \) can be obtained by extrapolating the upper part of the measured ASDF to the continuum. For argon this corresponds with \( E_p = 15.76 \text{ eV} \). The electron density can be determined using

\[
\eta_\infty = \eta_e \eta_i \left( \frac{\hbar^2}{2\pi m_e k_B T_e} \right)^{3/2}.
\]

Because \( \eta_\infty \) is obtained via an extrapolation and based on the pLSE assumption, the \( n_e \)-values obtained by this method are sensitive to the degree of equilibrium departure. However, they can be used as input for the CR-model to determine \( T_e \) when it is not possible to apply alternative methods [17].

Deviations from a Maxwellian electron energy distribution function (EEDF) can influence the \( T_e \)-values determined using the ALI/CR-model method. An excitation of an atom by an electron reduces the energy of that electron, which is thus migrated from the high energy to the low energy range. This tends to deplete the high energy part of the EEDF which can, in principle, be restored by electron-electron collisions. However, in low temperature atomic plasmas with a low ionization degree, the frequency of these electron-electron collisions might not be large enough to restore the equilibrium state of the EEDF [23]. This may result in a depletion of the high energy part (tail) of the EEDF. As discussed in [31, 32], the EEDF can be divided into two parts: a bulk and a tail. The boundary between the parts is equal to the first inelastic excitation threshold, i.e. the energy level of the first excited state \( \epsilon_{12} \). When the electron temperature is low compared to the energy of the first excited state, i.e. \( k_B T_e \ll \epsilon_{12} \), the bulk electrons are not involved in excitation reactions. The electron temperature is approximately equal to the bulk temperature and the tail temperature is lower than the bulk temperature. With the TS technique, we measure the bulk temperature. On the other hand, the ALI method gives a value that is in between the bulk and tail temperature. Therefore, the ALI/CR-model values for \( T_e \) might be somewhat lower than the values obtained by TS.
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Absolute continuum measurements

Continuum radiation can be created by Brehmsstrahlung or recombination processes. Brehmsstrahlung is created by elastic collisions between electrons (e) and other particles like atoms (a) or ions (i). During the interaction, the electron is slowed down and a photon is emitted. Since transitions occur between two free electron states, this type of radiation is denoted by free-free (ff) radiation. Two types of Brehmsstrahlung processes are considered, collisions between electrons and atom (e−a) and between electrons and ions (e−i). Continuum radiation is also created in the process in which a free electron is captured by an ion A⁺; a process that leads to recombination. The emitted radiation is called free-bound (fb) radiation. An absolute measurement of the continuum radiation allows the determination of the electron density [18].

The total emission coefficient for continuum radiation can be found by the summation

\[ j = j_{ff}^{e-a} + j_{ff}^{e-i} + j_{fb}^{e-i} \]

In [18], it was shown that the contribution of electron-ion collisions can be neglected for ionization degrees observed in low pressure SWS argon plasmas. Using \( j = j_{ff}^{e-a} \), the following expression was obtained to determine the electron density [18],

\[ n_e = \frac{j}{g(\lambda, T_e) n_a}, \]  

(6.5)

where \( n_a \) is the atom density, \( T_e \) the electron temperature and \( g(\lambda, T_e) \) a function defined by

\[ g(\lambda, T_e) = \frac{c_2}{\lambda^2 T_e^{3/2}} Q^{Ar}(T_e) \left[ 1 + \left( 1 + \frac{hc}{\lambda k_B T_e} \right)^2 \right] \times \exp \left( -\frac{hc}{\lambda k_B T_e} \right), \]  

(6.6)

with

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

(6.7)

and \( Q^{Ar}(T_e) \) the cross-section for momentum transfer of electrons with argon atoms.

Examples of the measured continuum spectra around \( \lambda = 648 \text{ nm} \) for argon plasmas at pressures of 10, 15 and 20 mbar are shown in figure 6.4. The corresponding integration times of these spectra are 60 s and the average of 5 repeated measurements was taken. An atomic argon line at \( \lambda = 648.11 \text{ nm} \) is present with a transition probability of \( A = 9.4 \times 10^4 \text{s}^{-1} \). Some small peaks most probably related to impurities in the argon gas can also be observed. To obtain the emitted continuum intensity, base line values of the spectra were used. The absolute value of the emission coefficient \( j \) is obtained after an intensity calibration of the optical equipment by means of a tungsten ribbon lamp. The random error due to these fluctuations is determined by calculating \( n_e \) for a minimum and a maximum intensity value, as shown in figure 6.4 for the pressure of 10 mbar. This resulted in a random error of \( \sim 20 \% \).

Hβ line broadening

The Stark broadening of the \( H_\beta \) spectral line is used to determine the electron density in the plasma. The measured line shape is a convolution of a Lorentzian and Gaussian profile caused by Stark and Doppler broadening, respectively. Also, the instrumental profile of the spectrometer, the Van der Waals broadening and the fine structure can result in an extra broadening.
Polydiagnostic calibration performed on a low pressure argon plasma

Figure 6.4: Measured intensities divided by the exposure time and corrected for the dark current for three different argon pressures.

of the spectral line. For the experimental conditions in this study, the Stark broadening is relatively small and an accurate fitting procedure is required in order to obtain the Lorentzian and Gaussian width of the hydrogen line. In addition, the measured instrumental profile and fine structure are included in the fitting routine. The Van der Waals broadening was found to be very small compared to the Stark broadening and was therefore neglected. Here, a short summary of the experimental and fitting procedure is presented. A more detailed discussion is given in chapter 4.

The instrumental profile of the DEMON is determined by means of a measurement of an argon spectral line at a wavelength of 470.23 nm. For the measurement of this argon line, an argon plasma was made at low pressure (\( p = 0.5 \) mbar) and low power (\( \sim 15 \) W) conditions and the measurement was made far away from the launching gap. In this way the gas temperature remained low, i.e. around 300 K. This resulted in a Gaussian profile with a full width half maximum (FWHM) of 5.2 pm, which is somewhat smaller than the specified value of the DEMON being 6.2 pm. This value is substantially smaller than the FWHM of the
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$H_\beta$-line, which is about 32 pm. However, a correction for the instrumental broadening has to be performed in view of the accuracy we are aiming for. Secondly, the $H_\beta$ spectral line corresponds to a series of transitions positioned at small distances from each other [33]. The wavelength distance between the first and last peak is 9.6 pm, which is significant in relation with the broadening mechanism of the line. Therefore, the contribution of fine structure to the broadening of the line has to be taken into account.

The fitting procedure starts with the convolution of the instrumental profile and the fine structure. The result, the so-called "basic line profile", is independent of the plasma conditions. The next step is to construct a theoretical Voigt profile for begin values of the Lorentzian and Gaussian broadening. The theoretical Voigt is convoluted with the basic line profile and compared with the measured $H_\beta$ spectral line profile. Using a fitting routine programmed in Matlab, the Gaussian and Lorentzian half-widths and the position of the maximum are varied until the best fit is obtained.

Figure 6.5 shows normalized measured profiles of $H_\beta$ for argon plasmas of 10, 15 and 20 mbar. The hydrogen lines could be measured with a sufficient signal/noise ratio because a very small amount of hydrogen came into the discharge via water vapour which was present in the gas pipelines.

![Figure 6.5:Measured line shapes of the $H_\beta$ Balmer line.](image)

For the argon plasma at 15 mbar, the Lorentzian width was found to be 12.1 pm and the Gaussian width was 19.7 pm. As the influence of the van der Waals broadening is negligible, the Stark width is equal to the Lorentzian width and related to the electron density. The random error in $n_e$ is determined by three successive measurements of the $H_\beta$ line on the same plasma condition and position and was found to be around 2%.
According to the Kepple and Griem (KG) theory, the electron density $n_e$ can be obtained from the FWHM of the Stark broadening, i.e. $2\Delta\lambda_S$, using

$$n_e = 10^6 \times \left( \frac{2\Delta\lambda_S}{2.5\alpha_{1/2}} \right)^{3/2}$$

where $n_e$ is in m$^{-3}$, $\Delta\lambda_S$ in nm and $\alpha_{1/2}$ is the fractional semi-half width and is denoted in [22] as function of $n_e$ and $T_e$. The $\alpha_{1/2}$ values are only determined for electron densities of $10^{20}$ m$^{-3}$ and higher. Therefore, we had to extrapolate these values to electron density values of $10^{19}$ m$^{-3}$. At an electron temperature of 15000 K, the relationship between $\log n_e$ and $\alpha_{1/2}$ is found to be almost linear and we obtained $\alpha_{1/2} = 7.42 \times 10^{-2}$ for $n_e = 1 \times 10^{19}$ m$^{-3}$ and $\alpha_{1/2} = 7.66 \times 10^{-2}$ for $n_e = 5 \times 10^{19}$ m$^{-3}$. For the $H_\beta$ line, results obtained with the KG theory are in good agreement with the results of a newer computational model referred to as GC theory [34, 35]. This theory includes the ion dynamic effects [36, 37].

The electron densities obtained from the $H_\beta$ line using the fitting procedure and the extrapolation of the GC theory are compared with the results of TS scattering in subsection 6.4.1.

6.4 Results and discussion

The passive spectroscopic techniques yield the electron density and electron temperature in an indirect way. Hence, for the processing of the experimental data a model is needed. In the case of the continuum it is the function given in equation 6.6, in the case of ALI the CR-model. On the other hand, with TS we directly measure properties of the free electrons. The only assumption is that the bulk of the electrons has a Maxwellian electron energy distribution function. The electron densities obtained with the different techniques are compared with each other. For the electron temperature, only two techniques are applied, namely TS and ALI measurements. The TS results are obtained in the centre of the tube ($r = 0$), whereas the passive results are determined via lateral measurements integrated along the line of sight. The electron density has a maximum value in the centre, whereas the electron temperature is expected to be constant as a function of radial position. Therefore, the TS results for $n_e$ can be somewhat higher then the passive results. Note that the error bars for the TS results include both the random and systematic errors, while for the other methods only the random errors are presented.

6.4.1 Comparison of electron densities

Results for $n_e$ are presented in figure 6.6, which shows that the $n_e$-values obtained from the Stark broadening are in good agreement with the TS results. The values obtained from the continuum are systematically lower whereas the $n_e$ results from the ASDF extrapolation are higher. However, the latter values are obtained assuming the presence of pLSE for the highest observable levels, an assumption that might be invalid.

The $n_e$-values obtained from the absolute continuum measurement are obtained by line of sight integration along the tube diameter and therefore represent averaged values. The relationship between the averaged value of $n_e$ and the value of $n_e$ at the centre of the tube
Figure 6.6: Electron densities obtained with several diagnostic techniques. Due to the size of the data points, the small error bars for TS and Stark broadening are not visible.

\[ n_e(r = 0) \text{ depends on the spatial distribution. If we assume that the radial electron density profile is a zero order Bessel function [38],} \]

\[ n_e(r) = n_e(r = 0) J_0 \left( x_0 r / R \right) \]  \hspace{1cm} (6.9)

with \( r \) the radial position and \( R \) the inner radius of the tube. For \( 0 \leq r \leq R \), we can use the approximation \( J_0 \left( x_0 r / R \right) \approx f \), with

\[ f(r) = \cos \left( \frac{r \pi}{R/2} \right). \]  \hspace{1cm} (6.10)

This function is unity in the centre \( r = 0 \) and zero in \( r = R \). The averaged value can be obtained using the following expression,

\[ \langle f(r) \rangle = 1/R \int_0^R f(r) \, dr, \]  \hspace{1cm} (6.11)

and equals \( 2/\pi \) so that the central value of the electron density \( n_e(r = 0) \) can be derived from the averaged value, \( \langle n_e \rangle \) using

\[ n_e(r = 0) = 1.57 \langle n_e \rangle. \]  \hspace{1cm} (6.12)

It is more appropriate to compare \( n_e(r = 0) \) with the TS results. At 15 mbar, \( \langle n_e \rangle = (2.1 \pm 0.5) \times 10^{19} \text{ m}^{-3} \), which corresponds to a central value of \( n_e(r = 0) = (3.3 \pm 0.7) \times 10^{19} \text{ m}^{-3} \). This value is closer to the TS value of \( n_e = 4.4 \times 10^{19} \text{ m}^{-3} \) but still 30% lower.

The central value of \( n_e \) as determined by Stark broadening cannot be corrected in the same way. The reason is that the line broadening is not an additive quantity so that equation 6.12 is not applicable.
6.4.2 Comparison of electron temperatures

The electron temperature is obtained using one active (TS) and one passive (ALI) method. These results are presented in figure 6.7. The $T_e$-values are in good agreement with each other, although the TS-results are somewhat higher than the passive results. As a consequence, it can be stated that the depletion of the high energy tail of the EEDF is not so prominent. Possibly multi-step electron excitation processes are dominating, bringing the discharge closer to a Maxwell equilibrium.

![Figure 6.7: Electron temperatures obtained with two diagnostic techniques.](image)

The electron temperature also depends on the radial position of the tube. In [11], the radial variation of the electric field is calculated for the surface wave sustained plasma. This radial electric field has a minimum in the centre, increases until a maximum value is reached and then decreases towards the wall. However, the electron temperature does not depend on the electric field solely but is also determined by the electron heat conductivity. As a result, it is expected that the radial profile of the electron temperature is more or less flat or shows a small increase close to the wall.

6.4.3 The influence of radial dependencies

An important issue in the comparison of the results of TS with those of passive spectroscopy is the spatial resolution. The passive methods give information of the intersection of the line-of-sight of the plasma whereas the information of TS comes from the small volume formed by the intersection of the laser beam, directed along the axis, and the line-of-sight. As a result, it can be stated that TS gives spatially resolved results for $r = 0$ whereas passive spectroscopic methods give averaged values along the tube diameter. For an accurate comparison, the line-of-sight results has to be transformed into spatially resolved information for the plasma centre.
In the reasoning given in the previous section a Bessel-like profile of the radial electron density profile was assumed. For this profile, it was found that the central value of the electron density $n_e(r = 0)$ is about 1.6 larger than the mean value $\langle n_e \rangle$. However, for a proper treatment Abel-inversion has to be applied to the laterally obtained continuum intensity in order to deduce the radial profile of the continuum and thus $n_e(r = 0)$. In principle, the same holds for the ALI/CR-model method. The 4p-line radiation should first be solved radially after which the excitation temperature and, deduced from this, the electron temperature could be obtained for each location (including $r = 0$). The method to obtain a spatially resolved electron density via the $H_\beta$ broadening is even more complicated. The best approach in that case is to divide the spectral line in wavelength intervals, to perform Abel inversion for all these intervals independently, and to construct from the obtained set of radial resolved profiles spectral line-profiles for each location of interest. The spectral line form for $r = 0$ can then be used for comparison with the results of TS.

These improvements are left for future studies and we assume in the current study that the spatial profile of the continuum is a Bessel-like, which leads to a correction of the factor 1.6 mentioned above. For $H_\beta$ and the ALI-CR-model method it is expected that the $r = 0$ properties are close to the line-of-sight averaged value. The reasoning behind the last assumption is that most radiation comes from the centre so that in the contribution of the intensities the features of the centre (broadening and 4p emission) are most important.

6.5 Conclusions

A surface wave sustained argon plasma has been studied using both active and passive diagnostic methods. The spectroscopic methods have been performed at three different argon pressures, 10, 15 and 20 mbar, with an incident power of about 40 W and a reflected power below 1 W resulting in a plasma length of around 40 cm. To make an accurate comparison of the diagnostic results, the methods were applied simultaneously to the same plasma and to the same plasma position. Because TS is an active method, i.e. the results for $n_e$ and $T_e$ follow directly from the measured TS spectrum, these results are most reliable.

The electron temperature was determined with ALI-measurements combined with a CR-model (passive) and TS (active). For all pressures, the $T_e$-values obtained with the passive method are about 10% lower than the TS results for $T_e$. This difference is within the error bars of both methods. Therefore, the passive method can be applied to microwave plasmas with comparable plasma conditions for which the application of TS is not an option.

The electron density has been determined with one active method, namely TS, and three passive methods: Stark broadening of the $H_\beta$ spectral line, absolute continuum measurements and extrapolation of the measured ASDF. The $n_e$-results obtained from the ASDF are considerably higher than the TS-results. This method is not very accurate because the $n_e$-values are based on the assumption that the measured top of the ASDF is in pLSE. The $n_e$-values obtained from the continuum were about 30% lower than those obtained with TS. Therefore, the formula values and input data (cross sections) used in the continuum method have to be reconsidered in a future study. The electron densities obtained with Stark broadening are in good agreement with the TS results. Therefore, it can be concluded that the
extrapolation of the Kepple and Griem theory to lower electron densities and the used fitting routine are correct. This implies that the Stark broadening technique can be applied to other low pressure ($\sim 10$ mbar) argon plasmas with $n_e$-values of about $10^{19}$ m$^{-3}$.

Bibliography

[33] http://physics.nist.gov/cgi-bin/ASD/lines1.pl
Comparative study of microwave induced argon plasmas

Abstract. A comparative study between three different microwave induced argon plasmas is presented. The surfatron, waveguide surfatron and resonator plasma are studied with the results obtained from spectroscopic techniques and a global plasma model. In addition, the global plasma model is used to relate the results obtained at different experimental configurations with each other. The global model overestimates the electron density compared to the experimental results. This indicates that the real microwave power absorbed by the plasma is lower than the measured value and that radiative and coupling losses occur. The global model yields much lower electron temperatures than the experimental results for the surfatron induced plasmas, whereas for the waveguide surfatron and resonator plasmas a reasonable agreement is found. This points toward extra energy loss processes which are not included in the model, for example recombination of molecular ions.
Chapter 7.

7.1 Introduction

At the company Draka, a process called plasma activated chemical vapor deposition (PCVD) is used for the production of optical fibres [1–4]. A gas mixture of SiCl$_4$, O$_2$ and GeCl$_4$ is set at the inlet side of a quartz tube. The tube is partially surrounded by a moving microwave cavity, also called resonator, which couples the microwave energy directly to the plasma inside the tube. Due to molecular reactions in the plasma, a thin layer of glass is deposited on the inner wall of the tube. The resonator traverses along the tube, and during each pass a layer of glass is deposited. The complete system is placed inside an oven, so that the temperature of the substrate tube is at a constant high temperature during the deposition process. The cavity operates at the microwave frequency of about 2.46 GHz and high powers (200 – 6000 W). A pressure between 10 – 20 mbar is maintained inside the tube by means of a downstream pumping system.

This PCVD plasma, from now on referred to as resonator induced plasma, is not easily accessible for optical diagnostic techniques. Therefore, we have built two alternative microwave induced plasmas which are closely related to the resonator plasma but more suitable for the application of active and passive diagnostic techniques. These alternative sources are the surfatron and the waveguide surfatron [5–8]. As a first step to a better understanding of these microwave induced plasmas, we study atomic microwave induced argon plasmas. This enables the development and validation of spectroscopic techniques [9] and the comparison with plasma modelling [10].

To obtain more insight in the resonator induced plasma, it is useful to relate results obtained on the (waveguide) surfatron induced plasmas [11–13] to the results obtained on the resonator plasma [14–16]. For this purpose, it is useful to study the differences and similarities between the sources. A global plasma model has been used to examine the effect of control parameters, like absorbed power, pressure or tube radius, on the most important plasma properties. It has also been used to relate experimental results, obtained at different conditions, to each other. In addition, experimental and global modelling results for the surfatron, waveguide surfatron and resonator plasma will be compared among each other.

This chapter is organized as follows: in section 7.2, experimental settings and typical plasma parameters of the surfatron, waveguide surfatron and resonator induced plasmas are given. This is followed by a description of the global plasma model which is based on particle and energy conservation equations (section 7.3), whereas a trend-study performed with this global model is presented in section 7.4. Section 7.5 summarizes diagnostic results obtained from the three different microwave induced argon plasmas, and these results are also compared and explained with results of the global plasma model. Conclusions and recommendations are given in section 7.6.

7.2 Experimental configurations

This work is focussed on the microwaves plasmas created by the surfatron, waveguide surfatron and resonator. We will refer to these as surfatron, waveguide surfatron and resonator (induced plasma). These plasmas are generated at the microwave frequency of about 2.46 GHz inside
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Argon is flowing through the tube at a specific flow rate and the setups are designed to operate in a pressure range around 10 mbar. Typical control parameters for the three plasmas are presented in Table 7.1. The diameter of the quartz tube, applied microwave power and the flow rate are much larger for the waveguide surfatron and resonator plasma than for the surfatron. The resonator plasma is placed inside an oven which results in a higher wall temperature. The wall temperature of the waveguide surfatron is slightly lower than the wall temperature of the surfatron. This can partly be explained by the fact that it was required to cool the waveguide surfatron tube using air.

Table 7.1: Representative control parameters of the microwave induced plasma sources discussed in this work.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Dimension</th>
<th>Suratron</th>
<th>Waveguide Suratron</th>
<th>Resonator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbed power</td>
<td>$P$</td>
<td>W</td>
<td>30</td>
<td>400</td>
<td>500</td>
</tr>
<tr>
<td>Pressure</td>
<td>$p$</td>
<td>mbar</td>
<td>10</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>Plasma length</td>
<td>$l$</td>
<td>cm</td>
<td>50</td>
<td>102</td>
<td>25</td>
</tr>
<tr>
<td>Inner tube radius</td>
<td>$a$</td>
<td>mm</td>
<td>3.0</td>
<td>13.5</td>
<td>13.5</td>
</tr>
<tr>
<td>Gas flow</td>
<td>$q$</td>
<td>sccm</td>
<td>50</td>
<td>300</td>
<td>1000</td>
</tr>
<tr>
<td>Wall temperature</td>
<td>$T_w$</td>
<td>K</td>
<td>400</td>
<td>350</td>
<td>1200</td>
</tr>
<tr>
<td>Power density</td>
<td>$\epsilon$</td>
<td>W cm$^{-3}$</td>
<td>2.1</td>
<td>6.8</td>
<td>3.5</td>
</tr>
<tr>
<td>Flow velocity</td>
<td>$v$</td>
<td>cm s$^{-1}$</td>
<td>5.9</td>
<td>1.8</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Because we deal with surface wave induced plasmas, an increase in microwave power results in longer plasma lengths, and not directly in higher power densities. This is especially the case for the (waveguide) surfatron plasmas because these are not confined within a limited axial range. Therefore, instead of comparing input powers, it is more appropriate to compare the absorbed power densities $\epsilon$. The power density of the surfatron and resonator plasma are more or less comparable, whether the power density of the waveguide surfatron is much lower.

Due to the difference in tube radius, it is more useful to compare axial flow velocities instead of mass flows. The flow velocity is determined using

$$v_z(r) = \frac{2q}{\pi r_0^2} \left[ 1 - \left( \frac{r}{r_0} \right)^2 \right].$$

(7.1)

At the center of the tube, the flow velocity equals $v_z(r) = \frac{2q}{\pi r_0^2}$, with $q$ the value of the mass flow in sccm (standard cubic centimeter per minute). According to the results presented in Table 7.1, the axial velocity ($v_z(r)$) of the gas in the surfatron and resonator plasma are comparable. The gas flow in the waveguide surfatron is lower.

Typical plasma parameters for the control parameters presented in Table 7.1 are presented in Table 7.2. These results are based on experimental results; for the surfatron results are used from [13], for the resonator from [16] and the waveguide surfatron values are new results.
Table 7.2: Typical electron gas properties for the surfatron, waveguide surfatron and resonator induced plasmas for the control parameters defined in table 7.1. The electron and atom temperature are in K, the densities in $m^{-3}$.

<table>
<thead>
<tr>
<th>parameter</th>
<th>symbol</th>
<th>surfatron</th>
<th>waveguide surfatron</th>
<th>resonator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron temperature</td>
<td>$T_e$</td>
<td>14100</td>
<td>10700</td>
<td>11400</td>
</tr>
<tr>
<td>Atom temperature</td>
<td>$T_a$</td>
<td>500 K</td>
<td>1000 K</td>
<td>2600 K</td>
</tr>
<tr>
<td>Electron density</td>
<td>$n_e$</td>
<td>$3.0 \times 10^{19}$</td>
<td>$1.9 \times 10^{19}$</td>
<td>$4.0 \times 10^{19}$</td>
</tr>
<tr>
<td>Atom density</td>
<td>$n_a$</td>
<td>$1.4 \times 10^{23}$</td>
<td>$6.9 \times 10^{22}$</td>
<td>$4.2 \times 10^{22}$</td>
</tr>
</tbody>
</table>

7.3 Description of a global plasma model

A global plasma model has been used to obtain a relationship between the control parameters and the mean plasma properties. To obtain a more accurate description of the plasma, a grand model should be used. The model applied in this work is zero-dimensional and based on the balance equations for the electron particles, electron energies and heavy particle energies [17, 18]. In this global plasma model, these balance equations are solved in an iterative way.

The model assumes steady-state conditions and charge neutrality, thus the ion density is in all cases equal to the electron density. Also, it assumes that the ion temperature is equal to the temperature of the atoms and that the efflux of electrons and ions is caused by ambipolar diffusion. Interactions between heavy particle collisions are not considered in the model. Also molecular species like $Ar^+_2$ are not taken into account.

7.3.1 Electron particle balance

Derivation

In steady-state conditions, $\frac{\partial}{\partial t} = 0$, the electrons are produced during electron-atom collisions and removed by recombination with ions or by ambipolar diffusion (c.f. appendix 7.7). This means that the efflux due to ambipolar diffusion has to be balanced by a nett ionization rate, thus the ionization rate minus recombination,

$$\frac{D_a n_e}{\Lambda^{2}_{n_e}} = n_e n_a k_{ion} - n_e^2 n_+ \alpha_{rec}. \quad (7.2)$$

In this balance, $D_a$ represents the ambipolar diffusion coefficient, $\Lambda_{n_e}$ the effective electron diffusion length, $k_{ion}$ the effective ionization rate, $n_+$ the ion density, $n_e$ the electron density, $n_a$ the atom density and $\alpha_{rec}$ the two electron recombination rates. For atomic plasmas in which stepwise ionization is the most important ionization process an effective ionization rate can be defined

$$k_{ion} = k_{rate} T_e^q \exp \left( \frac{-I^*}{k_B T_e} \right), \quad (7.3)$$

where $k_{rate}$, the exponent $q$ and the effective ionization potential $I^*$ depend on the gas and the ionization mechanism. These factors can be determined using a collisional radiative model. For an argon plasma, the factors in equation 7.3 are equal to $k_{rate} = 6.8 \times 10^{-17} \text{ m}^3/\text{s}$, $q = 0.5$
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and \( I^* = 12.06 \text{ eV} \) [19]. The validity of these values for a lower electron density range, i.e. \( 10^{18} \text{ m}^{-3} \leq n_e \leq 10^{20} \text{ m}^{-3} \), is checked with the use of a collisional radiative model for argon (c.f. appendix 7.8).

The three particle recombination rate, \( \alpha_{\text{rec}} \), can be obtained from the ionization rate using the principle of detailed balancing [20, 21]

\[
\alpha_{\text{rec}} = \frac{k_{\text{ion}}}{2g_\text{a}g_+/(\pi m_e k_B T_e)^{3/2}} \exp \left( \frac{E_{\text{ion}}}{k_B T_e} \right),
\]

in which \( g_\text{a}, g_e \) and \( g_+ \) are the statistical weights of the atom, electron and ion, respectively.

The ambipolar diffusion coefficient reads [21]

\[
D_a = D_l \left( 1 + \frac{T_e}{T_l} \right) = \frac{2}{3 n_a \sigma_{ia}} \sqrt{\frac{k_B T_a}{\pi M}} \left( 1 + \frac{T_e}{T_a} \right),
\]

with \( \sigma_{ia} \) the ion-atom collision cross-section and \( M \) the mass of the argon atom. The cross section is a function of the atom temperature and for argon equal to [22]

\[
T_a < 2000 K : \quad \sigma_{ia} = 1 \cdot 10^{-18} + 1.5 \cdot 10^{-15} \times (\ln T_a)^{-3.9} \text{ m}^2
\]

\[
T_a \geq 2000 K : \quad \sigma_{ia} = 3.17 \cdot 10^{-19} + 3.9 \cdot 10^{-17} \times (\ln T_a)^{-1.7} \text{ m}^2
\]

The diffusion length for a cylindrical tube of length \( l \) and radius \( a \) equals [3, 23]

\[
1/\Lambda_d^2 = \left( \frac{2.405}{a} \right)^2 + \left( \frac{\pi}{l} \right)^2,
\]

which simplifies to \( R^* = a/2.405 \) for long cylinders where \( l^2 \gg a^2 \). This expression is only valid when the radial profile is described by a perfect Bessel function. In surface wave sustained plasmas, the diffusion length can be smaller due to the skin effect. The diffusion length is denoted by \( R^* \). This distance will be used for both the electron diffusion coefficient \( \Lambda_d \) and the heat diffusion coefficient \( \Lambda_h \) (see subsection 7.3.3). Therefore, it is assumed that \( R^* = \Lambda_d = \Lambda_h \).

Discussion

Using the resonator plasma parameters given in table 7.2, it can be shown that three particle recombination, \( \alpha_{\text{rec}} n_a^2 n_+ = 2 \times 10^{19} \text{ m}^3 \text{s}^{-1} \), is negligible compared to electron impact ionization \( k_{\text{ion}} n_a n_e = 4.5 \times 10^{23} \text{ m}^3 \text{s}^{-1} \). It is convenient to introduce an effective ambipolar diffusion coefficient \( D'_a \equiv D_a n_a \). According to equation 7.5, this parameter is independent of the ground state density \( n_a \). Neglecting recombination and inserting equation 7.3 into the electron particle balance, equation 7.2, yields

\[
k_{\text{ion}}(T_e) = \frac{D'_a}{(n_a R^*)^2}.
\]

Because \( D'_a \) is only weakly dependent on the plasma parameters and \( k_{\text{ion}} \) strongly dependent on \( T_e \) (c.f. equation 7.3), equation 7.9 gives an expression to determine the electron temperature. The effective ambipolar diffusion coefficient \( D'_a \) is mainly determined by the
atom temperature $T_a$. The atom density is related to the pressure and the atom temperature via the ideal gas law, $n_a = p_a/(k_B T_a)$. The diffusion length only depends on the inner radius of the tube $a$. Because $T_e$ depends on the product of $n_a$ and $R^s$, which is proportional to the product of pressure $p$ times tube radius $a$, it is for a constant $T_a$ useful to investigate the influence of $p \times a$ instead of determining the influence of the separate contributions [24], [25]. At a constant gas temperature, it can be concluded that an increase in pressure or tube radius results in a lower electron temperature.

Table 7.3: Transport parameters and related terms of the surfatron and resonator plasma.

<table>
<thead>
<tr>
<th>parameter</th>
<th>surfatron</th>
<th>waveguide surfatron</th>
<th>resonator</th>
<th>dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{ia}$</td>
<td>$2.2 \times 10^{-18}$</td>
<td>$1.8 \times 10^{-18}$</td>
<td>$1.5 \times 10^{-15}$</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$D'_a$</td>
<td>$1.6 \times 10^{21}$</td>
<td>$9.1 \times 10^{20}$</td>
<td>$1.0 \times 10^{21}$</td>
<td>m$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>$D_a$</td>
<td>$1.2 \times 10^{-2}$</td>
<td>$1.3 \times 10^{-2}$</td>
<td>$2.4 \times 10^{-2}$</td>
<td>m$^2$s$^{-1}$</td>
</tr>
<tr>
<td>$R^s$</td>
<td>$1.2 \times 10^{-3}$</td>
<td>$5.6 \times 10^{-3}$</td>
<td>$5.6 \times 10^{-3}$</td>
<td>m</td>
</tr>
<tr>
<td>efflux</td>
<td>$2.2 \times 10^{23}$</td>
<td>$1.4 \times 10^{22}$</td>
<td>$3.0 \times 10^{22}$</td>
<td>m$^{-3}$s$^{-1}$</td>
</tr>
</tbody>
</table>

The larger tube radius of the waveguide surfatron and resonator plasma is expected to result in a lower electron temperatures than inside the surfatron plasma. This effect will be tempered because the larger radius results in higher gas temperature inside the resonator, as discussed in subsection 7.3.3. This higher $T_a$ value enhances the effective ambipolar diffusion coefficient $D'_a$ and, according to the ideal gas law, results in a lower atom density. Using the parameters defined in table 7.3, it can be shown that the efflux due to diffusion is about one order higher for the surfatron plasma compared to the waveguide surfatron and resonator plasma.

7.3.2 Electron energy balance

Derivation

The electron energy balance can be expressed as

$$\epsilon = n_e n_a k_{ea} k_B (T_e - T_a) + n_e n_i k_{ei} k_B (T_e - T_i) + (n_e n_a k_{ion} - n_e^2 n_i k_{rec}) E_{ion} \quad (7.10)$$

The first term $\epsilon$ describes the input power per unit volume supplied to the electron gas. Electrons can lose their energy due to elastic and inelastic collisions with the heavy particles in the plasma. The first two terms on the right hand side describe elastic collisions of electrons with respectively atoms and ions which results in the heating of the heavy particles. The third term describes inelastic electron collisions which result in an effective ionization of atoms or recombination of ions. Assuming charge neutrality, $n_e = n_i$, neglecting recombination and setting the ion temperature equal to the gas temperature, i.e. $T_i = T_a$, equation 7.10 turns into

$$\epsilon = n_e n_a k_{ea} k_B (T_e - T_a) + n_e^2 k_{ei} k_B (T_e - T_a) + n_e n_a k_{ion} E_{ion}. \quad (7.11)$$

The power density $\epsilon$ is equal to the total power absorbed in the plasma ($P$) divided by the plasma volume ($V$). The electron-atom and electron-ion heat transfer coefficients $k_{ea}$ and $k_{ei}$
Comparative study of microwave induced argon plasmas

are defined as

\[ k_{ea} = \frac{3\sigma_{ea}}{M} \sqrt{\frac{8k_BT_e m_e}{\pi}}, \quad k_{ei} = \frac{3\sigma_{ei}}{M} \sqrt{\frac{8k_BT_e m_e}{\pi}}, \]  

respectively. Temperature dependent electron-atom cross-sections for momentum transfer \(\sigma_{ea}\) in m\(^2\) are based on data of Milloy [26], whereas the electron-ion cross section \(\sigma_{ei}\) in m\(^2\) is based on the Coulomb interaction,

\[ \sigma_{ea} = \frac{5 \times 10^{-20}}{(1.0 + 1.7 \times 10^{-3} \cdot T_e)} - 3 \times 10^{-21} + 2.8 \times 10^{-24} \cdot T_e - 4.1 \times 10^{-34} \cdot T_e^3 \]
\[ \sigma_{ei} = 5.8 \times 10^{-10} \cdot T_e^{-2} \cdot \ln \Lambda_C, \]

where \(\ln \Lambda_C\) is the so called Coulomb logarithm. Introducing a total heat transfer coefficient

\[ k_{heat} = k_{ea} + \frac{n_e}{n_a} k_{ei}, \]  

reduces equation 7.11 into

\[ \epsilon = n_e n_a k_B k_{heat} (T_e - T_a) + n_e n_a k_{ion} E_{ion}. \]  

Inserting the electron particle balance 7.2 into equation 7.14 leads to

\[ n_e = \frac{\epsilon}{n_a k_{heat} k_B (T_e - T_a) + \frac{D_{ion} E_{ion}}{n_a R^*^2}}. \]  

Discussion

In order to find the dependence of the electron density on the control parameters equation 7.14 can be written as

\[ \epsilon = \epsilon_{elas} + \epsilon_{in}. \]  

The elastic contribution leads to heating of the atoms, the inelastic term describes creation of new species (excited states or ions). For constant \(T_e\) and \(T_a\) values, the elastic and inelastic contributions of the electron energy lead to the following proportionality

\[ \epsilon_{elas} = n_e n_a k_{heat} k_B (T_e - T_a), \quad n_e \propto \frac{\epsilon_{elas}}{n_a} \]
\[ \epsilon_{in} = n_e n_a k_{ion} E_{ion} = \frac{n_e D_{ion}}{n_a R^*^2} E_{ion}, \quad n_e \propto \frac{\epsilon_{in}}{n_a R^*^2}. \]

The electron density is in all cases proportional to the dissipated power density \(\epsilon\). For the dependence on the atom density and diffusion length (radius), two situations can be distinguished. If the elastic collisions are the most important, the electron density is found to be inversely proportional to the atom density and independent of the tube radius. If the inelastic term dominates we find that the electron density is proportional to the atom density and strongly depends on the inner radius of the tube.

The fraction of the inelastic energy losses can be expressed by the creation efficiency \(\varsigma\) [27],

\[ \varsigma = \frac{\epsilon_{in}}{\epsilon_{in} + \epsilon_{elas}}. \]  

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Using equation 7.9, the variable $\varsigma$ can be written as

$$\varsigma = \frac{1}{C(n_a R^*)^2 + 1}.$$  \hfill (7.18)

The parameter $C = k_B k_{\text{heat}}(T_e - T_a)/(D_{\text{ne}}E_{\text{ion}})$ is mainly determined by $T_e$ and $T_a$, and therefore independent of $n_e$. This expression shows that the creation efficiency is related to the product $n_a R^*$ and decreases with an increasing diffusion length $R^*$ and increasing atom density $n_a$. The values of and the parameters related to the creation efficiency are presented in table 7.4.

<table>
<thead>
<tr>
<th>parameter</th>
<th>surfatron</th>
<th>waveguide surfatron</th>
<th>resonator</th>
<th>dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{ea}$</td>
<td>$3.7 \times 10^{-20}$</td>
<td>$2.9 \times 10^{-20}$</td>
<td>$3.1 \times 10^{-20}$</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$\sigma_{ei}$</td>
<td>$2.4 \times 10^{-17}$</td>
<td>$4.2 \times 10^{-17}$</td>
<td>$3.5 \times 10^{-17}$</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$k_{\text{heat}}$</td>
<td>$1.3 \times 10^{-18}$</td>
<td>$1.1 \times 10^{-19}$</td>
<td>$1.8 \times 10^{-18}$</td>
<td></td>
</tr>
<tr>
<td>$C$</td>
<td>$6.0 \times 10^{-41}$</td>
<td>$6.3 \times 10^{-41}$</td>
<td>$8.4 \times 10^{-41}$</td>
<td></td>
</tr>
<tr>
<td>$n_a R^*$</td>
<td>$1.7 \times 10^{20}$</td>
<td>$3.9 \times 10^{20}$</td>
<td>$2.4 \times 10^{20}$</td>
<td>m$^{-2}$</td>
</tr>
<tr>
<td>$\varsigma$</td>
<td>$35%$</td>
<td>$10%$</td>
<td>$18%$</td>
<td>-</td>
</tr>
</tbody>
</table>

The results presented in this table show that the creation efficiency $\varsigma$ is larger for the surfatron plasma than for the waveguide surfatron and resonator plasma. This is mainly the result of the smaller diffusion length (i.e. a larger efflux).

### 7.3.3 Thermal energy balance of the argon particles

The stationary thermal balance for heavy particles is given by,

$$Q_{\text{en}} = -\nabla \cdot (\lambda_h \nabla T_a)$$  \hfill (7.19)

where $Q_{\text{en}}$ is the gas heating term and $\lambda_h$ the thermal conductivity. The stationary thermal balance for heavy particles can be expressed as,

$$n_e n_a k_{\text{heat}} k_B (T_e - T_a) = \frac{\lambda_h}{\Lambda_h^2} (T_a - T_w).$$  \hfill (7.20)

Here, we inserted the elastic energy loss term for $Q_{\text{en}}$ which is equal to the first term on the right-hand side of equation 7.14). Also, the approximation $\nabla \cdot (\lambda_h \nabla T_a) \approx \lambda_h (T_a - T_w)/\Lambda_h^2$ is used. As discussed in subsection 7.3.1, we use the approximation $\Lambda_h = R^*$. The thermal conductivity can be determined using,

$$\lambda_h = \frac{\sqrt{2} k_B}{\sigma_{aa} + \frac{n_e}{n_a} \sigma_{ai}} \times \sqrt{\frac{8 k_B T_a}{\pi M_a}}.$$ \hfill (7.21)

The first term of expression 7.20 describes the total elastic energy transferred from the electrons to the heavy particles. This is equal to the energy gained by the heavy particles
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during elastic collisions with electrons. The right part describes the cooling term for the heavy particles. For the microwave induced plasmas studied in this work, a gas temperature gradient is only present in the radial and not in the axial direction. Therefore, the radial heat conduction is the most important cooling mechanism; the heavy particles lose their energy by heat conduction to the wall.

The temperature of the heavy particles (i.e. the atoms and ions) can be expressed in terms of the electron and wall temperature. For this purpose, we introduce the parameters $\nu_t \equiv \lambda_h R^* z_e^{-2}$, $\nu_b \equiv k_{\text{heat}} n_e n_a$, and the ratio of these parameters as $\gamma$. Using the coefficient $\gamma$, equation 7.20 can be written as,

$$T_a = \frac{T_e + \gamma T_w}{1 + \gamma}. \quad (7.22)$$

This equation shows that the temperature of the heavy particles (i.e. the atoms and ions), is a weighted average between the temperature of the electrons and the temperature of the wall. The exact value is determined by the coefficient $\gamma$. In the limit $\gamma \to 0$, the atom temperature reaches the electron temperature ($T_a \to T_e$) and does not depend on the wall temperature. This is caused by either an increased number of electron-atom interactions or by a larger diffusion length. A gas temperature close to the electron temperature is expected for a high pressure ($\propto n_a$), a high input power ($\propto n_e$) or a large inner tube radius ($\propto R^*$).

The left part of the heavy particle balance is equal to the elastic energy loss of the electrons. Therefore, the heavy particle balance can be coupled to the electron energy balance. Inserting the heavy particle balance into the electron energy balance (7.15) and rewriting yields

$$n_e = \frac{\epsilon R^* z_e^2}{\lambda_h (T_a - T_w) + \frac{D_a E_{\text{ion}}}{n_a}}, \quad (7.23)$$

which shows that the electron density is proportional to power per unit length. Using $\epsilon = \epsilon_{\text{in}} / \zeta$, equation 7.23 can be expressed as

$$\zeta = \frac{1}{1 + \frac{\epsilon_{\text{in}}}{D_a E_{\text{ion}} \lambda_h (T_a - T_w)}}. \quad (7.24)$$

For higher atom densities the creation efficiency decreases. Thus, for higher pressures a larger part of the absorbed power is used for heating of the gas particles.

7.3.4 Summary of the global plasma model

The global plasma model calculates axially averaged plasma parameters at the centre of the discharge ($r = 0$) for specific plasma configurations. The model is based on the electron particle, electron energy and heavy particle energy balance.

First, the electron particle balance yields the electron temperature

$$k_{\text{ion}}(T_e) = \frac{D_a}{n_a \Lambda^2} + \frac{n_a^3 \alpha_{\text{rec}}}{n_a}. \quad (7.25)$$
The electron energy balance gives the electron density

\[ n_e = \frac{\epsilon}{n_a k_{\text{heat}} k_B (T_e - T_a) + \frac{D_{\text{v}} E_{\text{ion}}}{n_a k_B}}, \]  

(7.26)

and the heavy particle temperature is determined from the heavy particle balance

\[ T_a = \frac{T_e + \gamma T_w}{1 + \gamma} \]  

(7.27)

where,

\[ \gamma = \frac{\lambda_h R_s^2}{k_{\text{heat}} n_e n_a k_B}. \]  

(7.28)

These balances are iteratively solved using the coefficients which have been defined in the previous section. Since these coefficients are also functions of the plasma parameters, they are recalculated during each iteration. A schematic scheme of the model is shown in figure 7.1. First, the electron particle balance is solved in order to obtain a good initial value of the temperature. This value is used as an accurate starting condition for the second stage of the model, where the electron temperature, atom temperature and electron density are determined. A more detailed description of the model can be found in [17].

![Figure 7.1: Flow chart of the algorithm used to solve the equations for the electron temperature, electron density and atom temperature.](image)

### 7.3.5 Discussion of the control parameters

The global plasma model determines plasma parameters for a specific set of control parameters, which is shown in table 7.5. However, it is questionable whether this set represents the true control parameters. The adjustable experimental parameters are the absorbed power, tube radius and the gas pressure. In surface wave sustained plasmas, the plasma length depends on the microwave power, the gas temperature and the pressure. Therefore, it is not straightforward to maintain a constant power density, which is the most important property.
for the electron density. The diffusion length is related to the tube radius, but is in practice determined by the radial electron density distribution. The ground state density depends via the ideal gas law on the pressure and the atom temperature. However, this temperature is determined by the plasma conditions via equation 7.20 and can thus not be controlled directly. Therefore, we used the global plasma model to determine the gas temperature for an estimate of the ground state density. Then the $n_a$-value was determined with the new gas temperature etc.

<table>
<thead>
<tr>
<th>Input</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbed power</td>
<td>Electron density</td>
</tr>
<tr>
<td>Plasma length</td>
<td>Heavy particle temperature</td>
</tr>
<tr>
<td>Inner tube Radius</td>
<td>Electron temperature</td>
</tr>
<tr>
<td>Diffusion length</td>
<td></td>
</tr>
<tr>
<td>Ground state density</td>
<td></td>
</tr>
<tr>
<td>Wall temperature</td>
<td></td>
</tr>
</tbody>
</table>

### 7.3.6 Validation of global model results

The results of the global model results can be validated with the results of a grand model constructed in Plasimo. For this we use the results as published in [28]. Typical values used in this grand model are based on old conditions of the resonator plasma and are as follows: the pressure in the tube is 10 mbar at the pump side (gas outlet) and a total power of 400 W is supplied to the plasma. The quartz inner tube radius is 7.5 mm and the plasma length is 30 cm. The wall temperature is fixed at 500 K. Axially averaged results at the centre of the discharge, i.e. $r = 0$, are $n_e = 3 \times 10^{20} \text{ m}^{-3}$, $T_e = 11000 \text{ K}$ and $T_a = 2200 \text{ K}$.

To validate our global model, we use an atom density of $n_a = 5 \times 10^{22} \text{ m}^{-3}$. The other control parameters, i.e. the power, tube radius, plasma length and wall temperature have the same value as the grand model. Using the global model, we find $n_e = 2.0 \times 10^{20} \text{ m}^{-3}$, $T_e = 11700 \text{ K}$ and $T_a = 1700 \text{ K}$. The obtained electron density is in a good agreement with the Plasimo results, the electron temperature is 700 K higher and the gas temperature 500 K lower. The difference is only 6% for the electron temperature and 23% for the gas temperature. Therefore, we may state that the results for $n_e$ and $T_e$ are in a good agreement. The results for $T_a$ are considerably lower than the grand model results.

### 7.4 Study of trends using the global plasma model

The global plasma model has been used to determine the influence of the external settings and to study trends. Four parameters have been studied: the atom density, input power, inner tube radius and wall temperature. This has been done by computing the electron density, electron temperature and gas temperature as a function of one input parameter and keeping the other input parameters constant. For the reference, the atom density, tube
radius, plasma length, wall temperature and power were set equal to \( n_a = 7 \times 10^{22} \text{m}^{-3} \), \( a = 13.0 \text{mm} \), \( L = 30.0 \text{cm} \), \( T_w = 1000 \text{K} \), and \( P = 500 \text{W} \), respectively. These values correspond to the experimental configuration of the resonator plasma and will be referred to as standard conditions. The found trends can be used to compare experimental results obtained under different experimental conditions.

7.4.1 Gas pressure

The influence of the atom density on the plasma properties has been tested by varying the value \( n_a \). Figure 7.2 shows that in the studied range, \( T_e \) decreases and \( T_a \) increases slightly with increasing \( n_a \). The electron density \( n_e \) as a function of \( n_a \) is shown in figure 7.3. For relatively low \( n_a \) values, \( n_e \) increases with \( n_a \). From \( n_a \approx 5 \times 10^{23} \text{m}^{-3} \), \( n_e \) no longer increases as a function of \( n_a \). This point corresponds to a transition from the regime dominated by inelastic collisions to that ruled by elastic collisions, as described in the previous section.

![Figure 7.2: Computed electron (squares) and gas (circles) temperature as a function of the atom density and standard resonator conditions (\( a = 13 \text{mm} \), \( L = 30 \text{cm} \), \( T_w = 1000 \text{K} \) and \( P = 500 \text{W} \))(left). Figure 7.3: Computed electron density as a function of the atom density. The input parameters are as in figure 7.2.](image)

7.4.2 Input power

The effect of the input power on the plasma properties is investigated using the global model. The results are shown in figure 7.4 for \( T_e \), \( T_a \) and in figure 7.5 for \( n_e \). These figures show that \( T_e \) is almost constant, while \( T_a \) and \( n_e \) increase with increasing power. The increase in \( n_e \) is easily explained by equation 7.11.

7.4.3 Inner tube radius

The electron density, electron and gas temperature have been determined for several tube diameters. The diffusion length was calculated for each radius and \( n_a \) was equal to a constant value of \( 7 \times 10^{22} \text{m}^{-3} \). To obtain the same power density in all cases, the input power was scaled for each setting. Results are shown in the figures 7.6 and 7.7.
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Figure 7.4: $T_e$ (squares) and $T_a$ as function of the input power $P$ at standard resonator conditions.

Figure 7.5: $n_e$ as function of the input power $P$. The input parameters are as in figure 7.4.

Figure 7.6: Plot of $T_e$ and $T_a$ in the centre of the discharge as a function of the tube radius and standard resonator conditions.

Figure 7.7: Plot of $n_e$ as a function of the tube radius.

7.4.4 Wall temperature

Varying $T_w$ between 300 K and 1200 K shows a minor decrease in $T_e$ and a minor increase of $n_e$. As expected $T_a$ increases: from 1900 K at $T_w = 300$ K to 2500 K at $T_w = 1200$ K.

7.4.5 Summary of the trends

The influences of the various control parameters on the plasma properties are summarized in table 7.6. In this table, the term 'constant' means that variations in the studied parameter range are less than 10%. A single arrow represents a small variation, a double arrow denotes a strong dependence on the control parameter.
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Table 7.6: Summary of the observed trends.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>( T_e )</th>
<th>( T_a )</th>
<th>( n_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom density</td>
<td>( n_a )</td>
<td>↑</td>
<td>↓</td>
<td>const</td>
</tr>
<tr>
<td>Power density</td>
<td>( \varepsilon )</td>
<td>↑</td>
<td>const</td>
<td>↑</td>
</tr>
<tr>
<td>Radius</td>
<td>( a )</td>
<td>↑</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td>Wall temperature</td>
<td>( T_w )</td>
<td>↑</td>
<td>const</td>
<td>↑</td>
</tr>
</tbody>
</table>

7.5 Comparative study of surfatron, waveguide surfatron and resonator

The observed trends in section 7.4 are used to compare the experimental results of the surfatron, waveguide surfatron and resonator. The settings are summarized in table 7.7.

Table 7.7: Experimental settings and dimensions of the surfatron and resonator plasma.

<table>
<thead>
<tr>
<th>Type</th>
<th>Launcher</th>
<th>Pressure nbar</th>
<th>Power W</th>
<th>Radius mm</th>
<th>Length cm</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Surfatron</td>
<td>10</td>
<td>30</td>
<td>3</td>
<td>51</td>
<td>[13]</td>
</tr>
<tr>
<td>b</td>
<td>Surfatron</td>
<td>15</td>
<td>30</td>
<td>3</td>
<td>43</td>
<td>[13]</td>
</tr>
<tr>
<td>c</td>
<td>Waveguide Surfatron</td>
<td>9</td>
<td>400</td>
<td>13.5</td>
<td>102</td>
<td>This work</td>
</tr>
<tr>
<td>d</td>
<td>Waveguide Surfatron</td>
<td>19</td>
<td>600</td>
<td>13.5</td>
<td>93</td>
<td>This work</td>
</tr>
<tr>
<td>e</td>
<td>Resonator</td>
<td>10-15</td>
<td>500</td>
<td>13.5</td>
<td>25</td>
<td>[16]</td>
</tr>
</tbody>
</table>

For the surfatron and resonator plasma, the microwave power corresponds to measured values, as discussed in [11, 16]. In the case of the waveguide surfatron plasma, the denoted power is equal to the value on the microwave power supply, and therefore the real value might be lower. Even with a measurement of the incident and reflected microwave power, it is difficult to determine how much microwave energy is truly absorbed by the plasma. Losses can occur in the coupling between the launcher and the plasma and the microwaves can radiate into the open air.

7.5.1 Global model results

The global plasma model is applied to the settings of the surfatron, waveguide surfatron and resonator plasma. The control parameters, i.e. the input power, tube radius and ambipolar diffusion length, correspond with the experimental configurations presented in table 7.7. As discussed in table 7.6, the power density and diffusion length are the most important control parameters for the electron density. The \( n_e \)-values increase strongly with increasing power density and diffusion length. This explains the \( n_e \)-values of the plasmas a−d, for the plasmas c,d the power density is lower and the diffusion length is larger than for the plasmas a,b. Due to the combined effect of these control parameters, the obtained electron densities are of the same order. The higher \( n_e \)-values of plasma b compared to a (or d versus c) is explained by the increase of power density. Plasma e has the largest power density and a large diffusion.
length compared to a,b and this results in high values of $n_e$.

The electron temperature is strongly related to the atom density and the diffusion length. An increase in atom density or diffusion length results in a decrease of the electron temperature. The lower diffusion length of the plasmas c–e compared to the surfatron plasmas a,b explains the lower electron temperatures of the waveguide surfatron and resonator plasma. However, the lower atom densities of the plasmas c–e partly compensate for this effect since the lower atom densities increase the $T_e$-values.

The atom temperature increases with wall temperature, diffusion length and power density. The small diffusion length of the surfatron plasmas a,b explains the low atom temperatures compared to the waveguide surfatron and resonator plasma. The higher power density and wall temperature of plasma e compared to the plasmas c,d results in higher atom temperatures. The atom temperature increases with wall temperature, diffusion length and power density. The small diffusion length of the surfatron plasmas a,b explains the low atom temperatures compared to the waveguide surfatron and resonator plasma. The higher power density and wall temperature of plasma e compared to the plasmas c,d results in higher atom temperatures.

<table>
<thead>
<tr>
<th>Type</th>
<th>$T_w$ (K)</th>
<th>$n_a$ (m$^{-3}$)</th>
<th>$R^*$ (mm)</th>
<th>$\varepsilon$ (Wm$^{-3}$)</th>
<th>$n_e$ (m$^{-3}$)</th>
<th>$T_e$ (K)</th>
<th>$T_a$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>400</td>
<td>$1.4 \times 10^{23}$</td>
<td>1.3</td>
<td>$2.1 \times 10^6$</td>
<td>$5.3 \times 10^{19}$</td>
<td>11500</td>
<td>520</td>
</tr>
<tr>
<td>b</td>
<td>400</td>
<td>$1.9 \times 10^{23}$</td>
<td>1.3</td>
<td>$2.5 \times 10^6$</td>
<td>$6.2 \times 10^{19}$</td>
<td>10900</td>
<td>560</td>
</tr>
<tr>
<td>c</td>
<td>350</td>
<td>$7.0 \times 10^{22}$</td>
<td>5.6</td>
<td>$6.8 \times 10^5$</td>
<td>$4.8 \times 10^{19}$</td>
<td>10100</td>
<td>960</td>
</tr>
<tr>
<td>d</td>
<td>350</td>
<td>$1.1 \times 10^{23}$</td>
<td>5.6</td>
<td>$1.1 \times 10^6$</td>
<td>$6.4 \times 10^{19}$</td>
<td>9500</td>
<td>1200</td>
</tr>
<tr>
<td>e</td>
<td>1200</td>
<td>$4.2 \times 10^{22}$</td>
<td>5.6</td>
<td>$3.5 \times 10^6$</td>
<td>$1.5 \times 10^{20}$</td>
<td>10900</td>
<td>2600</td>
</tr>
</tbody>
</table>

7.5.2 Diagnostics results

Spectroscopic measurements have been made in surface wave sustained argon plasmas under variable experimental conditions which were presented in table 7.7. In the past, the argon surfatron induced plasma was studied with absolute line intensity (ALI) measurements (chapter 2 or [11]), absolute continuum measurements (chapter 6 and [12]), Stark broadening [9] (chapter 4 and 6) and Thomson Scattering (TS) (chapter 3, 6 and [13]). The waveguide surfatron was investigated with ALI measurements, continuum measurements and Stark and Doppler broadening. The resonator plasma was poorly accessible for optical diagnostics and is only examined with axially integrated ALI measurements [16]. These ALI measurements enable the construction of the atomic state distribution function (ASDF). The ASDF and a collisional radiative model [29] can be used to obtain an estimate for $n_e$ and to determine $T_e$.

In this work we use the most recent diagnostic results, which are TS results for the surfatron plasmas a, b, ALI and absolute continuum results for the waveguide surfatron plasmas...
c, d and ALI measurements for the resonator plasma e. Table 7.9 shows a summary of the employed methods and results.

The TS results are obtained in the centre of the discharge, \( r = 0 \), close to the launching gap. The results of the waveguide surfatron are radially integrated and obtained close to the launching gap, whereas the resonator results are axially and radially integrated. In the radial direction, the electron density is assumed to have a parabolic profile with a maximum in the centre of the tube, whereas a small decrease in the electron density with increasing axial distance relative to the launching gap is observed. For the resonator plasma, due to the axial integration over the plasma length, part of the emitted photons can be re-absorbed. This measurement might slightly underestimate the population densities of the argon states and can result in lower electron temperatures and lower electron densities.

<table>
<thead>
<tr>
<th>Type</th>
<th>( n_e )-method</th>
<th>( n_e ) ( \text{m}^{-3} )</th>
<th>( T_e )-method</th>
<th>( T_e ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>TS</td>
<td>3.0 ( \times ) 10^{19}</td>
<td>TS</td>
<td>14100</td>
</tr>
<tr>
<td>b</td>
<td>TS</td>
<td>3.2 ( \times ) 10^{19}</td>
<td>TS</td>
<td>13600</td>
</tr>
<tr>
<td>c</td>
<td>Abs. Con.</td>
<td>1.9 ( \times ) 10^{19}</td>
<td>ALI+CRM</td>
<td>10700</td>
</tr>
<tr>
<td>d</td>
<td>Abs. Con.</td>
<td>2.0 ( \times ) 10^{19}</td>
<td>ALI+CRM</td>
<td>10400</td>
</tr>
<tr>
<td>e</td>
<td>ALI-ASDF</td>
<td>4.0 ( \times ) 10^{19}</td>
<td>ALI+CRM</td>
<td>11400</td>
</tr>
</tbody>
</table>

### 7.5.3 Comparing experimental and global model results

The results obtained with the global plasma model are compared with the experimental results in table 7.10. For the surfatron induced plasmas a and b, both diagnostic (Thomson Scattering) and global model results correspond with values determined at the centre of the discharge \( r = 0 \). The \( n_e \)-values obtained with the global model are somewhat higher compared to the experimental results whereas the \( T_e \)-values are too low. Experimental results of the waveguide surfatron induced plasmas c and d correspond with radially integrated results. The radial profile of the electron density is assumed to be parabolic with a maximum in the centre whereas the radial electron temperature distribution is more or less constant or shows a minor increase towards the wall (see chapter 6). For these two plasmas, the global model results for \( n_e \) are higher and the \( T_e \)-values are lower than the experimental results. However, the difference in the electron temperatures is much smaller than for the surfatron plasmas and are in agreement with each other when an experimental error of 10% is taken into account. For the resonator plasma, the experimental \( n_e \) values are too low and the \( T_e \)-values are in a reasonable agreement with each other.

The larger \( n_e \)-values of the global model compared to the experimental results can be caused by an incorrectly determined control parameter like the power density or diffusion length. Although the absorbed power has been measured in most cases (a, b, e), it is difficult to determine how much microwave energy is not coupled to the plasma but radiated away. Therefore, the real absorbed power can be lower than the measured values which are inserted.
into the global model. This might explain the lower experimental \( n_e \)-values. Another control parameter which might be overestimated in the global model is the diffusion length. The used value is based on a parabolic electron density profile. However, in case of plasma \( e \) the real plasma might stick to the quartz surface (donut shape) \[15\] and the true diffusion length can be much smaller than the used approximation of \( R^* = a/2.4 \). Using a lower value of the diffusion length in the global model results in a lower electron density and higher electron temperature according to respectively the equations 7.15 and 7.9.

The uncertainty in the control parameters might result in differences between the experimental and global model results. For plasma \( a \) (surfatron plasma), we investigate the influence of deviations in the control parameters on the global model results for \( n_e \) and \( T_e \). First, the measured absorbed power was 30 W. However, radiative and cable losses were not taken into account. For a true absorbed power of 20 W, the global model results in \( n_e = 3.7 \times 10^{19} \text{ m}^{-3} \) and \( T_e = 11500 \text{ K} \). Compared to the 30 W results, this is a decrease in \( n_e \) of 30 %. The \( T_e \) value is not affected.

Moreover, the atom density is determined via the gas pressure and a gas temperature of 500 K. When the real gas temperature is 700 K, the atom density is equal to \( 1.4 \times 10^{23} \text{ m}^{-3} \). Using this value and the other control parameters of plasma \( a \) results in \( n_e = 5.1 \times 10^{19} \text{ m}^{-3} \) and \( T_e = 12000 \text{ K} \). Therefore, using \( T_a = 700 \text{ K} \) instead of \( T_a = 500 \text{ K} \) results in a decrease in \( n_e \) of 3.9 % and in an increase in \( T_e \) of 4.6 %.

The third parameter is the diffusion length. Using half of the original values for the diffusion length, i.e. \( R^* = 0.7 \text{ mm} \), yields: \( n_e = 2.6 \times 10^{19} \text{ m}^{-3} \) and \( T_e = 12900 \text{ K} \). This is a decrease in \( n_e \) of 57 % and in an increase in \( T_e \) of 12 %. Taking these uncertainties in the control parameters into account, a reasonable agreement between the global model and experimental results is found for most plasmas.

However, the discrepancies between experimental and global model \( T_e \)-values of the surfatron plasmas \( a \) and \( b \) can not be explained by overestimated values for the diffusion length alone. The large difference indicates that an extra loss term might be present which is not included in the global model, for example recombination processes of molecular argon ions, by which the electron temperature is enhanced \[30\]. This can also be caused by deviations from a Maxwellian distribution function. A collisional excitation of an atom by an electron reduces the energy of an electron, which is thus migrated from the high energy to the low energy
range. This energy is restored by electron-electron collisions. However, in low temperature atomic plasmas with a low ionization degree, the frequency at which these electron-electron collisions occur is too small to restore the energy loss of the electrons due to electron-atom excitations. This may result in a depletion of the high energy part (tail) of the electron energy distribution (EEDF) function (c.f. chapter 6). To obtain the same ionization rate for a non-Maxwellian distribution function compared to a Maxwellian distribution function, a higher electron temperature is required [31].

7.6 Conclusions and Recommendations

In this work the influence of the experimental configuration on the plasma has been investigated. The tube radius was found to be an important parameter in a direct and indirect way. The electron temperature decreases for larger diffusion lengths. Also, it increases the gas temperature which influences the ambipolar diffusion. The power density was also found to be an important parameter since it mainly determines the electron density. Experimental results obtained for different configurations have been compared among each other. The measured \( n_e \) and \( T_e \) values can be explained using the trends obtained with the global plasma model.

For all plasma conditions, the electron densities obtained with the global model are lower than the experimentally determined \( n_e \)-values. A possible explanation for this is that the real absorbed microwave power, which is an important parameter for the electron density, is lower than the measured values.

Another control parameter which might be too large in the global plasma model is the diffusion length. The global model results are then too large for the electron density, too low for the electron temperature and too high for the atom temperature. For surface wave sustained plasmas, the assumption that the radial electron density profile is a perfect Bessel function might not be justified. This is especially the case for the resonator plasma which can have a doughnut like plasma shape, and thus a smaller diffusion length.

For both surfatron plasmas, large discrepancies between experimental and global model results for the electron temperature have been found. The experimentally obtained \( T_e \)-values were much higher. The difference can not be explained by a too large diffusion length. For very small diffusion lengths, the global model result for the electron temperature remained too low. The electron temperature is possibly increased by recombination processes which are not included in the global plasma model. Also deviations from a Maxwellian distribution function, for example a depletion of the high energy tail, results in a higher electron temperature.

Recommendations for the experimental setups and diagnostic techniques are:

- Surfatron plasma: measure the power as close to the launcher as possible and minimize the length of the coaxial cables.
- Waveguide surfatron plasma: implement power meters.
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- Resonator and waveguide surfatron plasma: measure the radial profile of the plasma. This can be done by measuring the intensity of the plasma light emitted in the axial direction (along the tube) using two pinholes and a detector (photomultiplier).

- Resonator plasma: measure in the radial direction in order to avoid self-absorption. In addition, choose lines which are less sensitive for self absorption (lower transition probability).

The global model can be improved when the accuracy of the control parameters is improved or when the model itself is adapted:

- Use values for the diffusion length that are more appropriate for surface wave sustained plasmas. The radial electron density profiles for different tube radii obtained with the grand Plasimo model can be used to find improved expressions for the diffusion length.

- Extra particles like the molecular ion can be added to the chemistry. However, this requires a rewriting of the code of the global plasma model.

- The effective ionization coefficients can be determined with a two temperature collisional radiative model where one temperature refers to the bulk and the other to the tail temperature [29].

7.7 Appendix: Continuity equation of the electrons

The particle balance for the electrons can be obtained by integrating the Boltzmann transport equation over the velocity space. This results in,

\[
\frac{\partial n_e}{\partial t} + \nabla n_e w_e = \left( \frac{\partial n_e}{\partial t} \right)_{\text{in}} \tag{7.29}
\]

with \( w_e \) the mean velocity vector of the electrons and \( n_e \) the particle density of the electrons. The second term of this expression describes the change in \( n_e \) due to transport of the electrons. The right-hand side is the source term \( S_e = (\frac{\partial n_e}{\partial t})_{\text{in}} \) and presents the net production rate of electrons due to inelastic collisions.

The second term can be written in a more usable from. First, using the following expression for the efflux of the electrons,

\[
n_e w_e = -D_\alpha \nabla n_e + \frac{j_e}{e}, \tag{7.30}
\]

in which \( D_\alpha \) is the ambipolar diffusion coefficient and \( j_e = e n_e \mu_e E \) is the electron current density, the following relation is obtained

\[
\nabla \cdot \cdot n_e w_e = \nabla \cdot (-D_\alpha \nabla n_e) + \nabla \cdot \frac{j_e}{e}. \tag{7.31}
\]

The first term on the right represents the outward transport due to ambipolar diffusion, while the second term represents the outward transport due to the divergence of the current density. Neglecting convection and the divergence in the current density gives

\[
\nabla \cdot n_e w_e = -\nabla \cdot (D_\alpha \nabla n_e) \approx \frac{D_\alpha n_e}{\Lambda^2 n_e}, \tag{7.32}
\]

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The last step has been made by writing the diffusion term \( \nabla \cdot (D_a \nabla n_e) \) in terms of the gradient length of the electron density \( \Lambda_{n_e} \),

\[
\frac{1}{\Lambda_{n_e}^2} = \left| \left( \nabla^2 n_e \right) \right|.
\]  

(7.33)

In this way, equation 7.29 is reduced to,

\[
\frac{\partial n_e}{\partial t} + \frac{D_a n_e}{\Lambda_{n_e}^2} = S_e.
\]  

(7.34)

For stationary plasmas, \( \frac{\partial n_e}{\partial t} = 0 \), it states that the loss of electrons due to ambipolar diffusion equals the net production rate of electrons.

7.8 Appendix: Arrhenius rate

A collisional radiative model for argon has been used to validate the use of equation 7.3 and to calculate the total ionization rate as a function of the temperature at a certain electron density value. Using the package Origin 7.0, these results were fitted with equation 7.3, in which only the \( q \) factor was allowed to vary. The CRM results and the fit result for the ionization rate \( (S_{\text{ion}}) \) are shown in figure 7.8. In the applied parameter range, the ionization rate did not depend on \( n_e \). In figure 7.9, \( S_{\text{ion}} \) is compared with the expression used in this work \((k_{\text{ion}})\). A good agreement between these results is found.

![Figure 7.8: CR-model results; \( S_{\text{ion}} = 6.8 \times 10^{-17} T_e^{0.44} \exp \left(-\frac{12.06}{k_B T_e}\right) \)](image)

![Figure 7.9: \( S_{\text{ion}} \) and \( k_{\text{ion}} \); \( k_{\text{rate}} = 6.8 \times 10^{-17}, q = 0.5, I^* = 12.06 \text{ eV} \).](image)

Bibliography


Comparative study of microwave induced argon plasmas

Abstract. A low pressure microwave induced argon plasma with a small amount of molecular oxygen (5\%) is investigated using active and passive spectroscopic methods and the obtained results are compared with the results of a pure argon plasma. The applied diagnostics are Thomson Scattering, Stark broadening and absolute line intensity measurements. These methods were successfully applied to a pure argon plasma. In this work it is examined whether these methods can also be applied to a molecular argon-oxygen plasma. In the argon plasma, with a pressure of 10 mbar and an absorbed power of 40 W, the electron density obtained with Thomson Scattering was approximately equal to $4 \times 10^{19}$ m$^{-3}$ and the electron temperature to $T_e \approx 1.2$ eV. In the argon-oxygen plasma, with a pressure of 10 mbar and an absorbed power of 65 W, the electron density is found to be $1 \times 10^{19}$ m$^{-3}$ and the electron temperature $T_e \approx 1.4$ eV. The differences in the electron gas properties can be explained by extra electron energy losses in the argon-oxygen plasma, for example molecular dissociation or vibrational and rotational excitations.
8.1 Introduction

Low pressure molecular plasmas play an important role in plasma processing and new material technologies. The plasma-application that attracts our attention is the microwave induced molecular deposition plasma used in the production process of optical fibres [1–3]. The deposition technique is called Plasma-activated Chemical Vapour Deposition, abbreviated to PCVD. The oxygen gas is a major component of the deposition plasma which is generated inside a quartz tube located inside a cylindrical microwave resonator [4].

As a first step to a better understanding of the deposition plasma and the PCVD process, an atomic microwave induced argon plasma sustained in a quartz tube at comparable operational conditions was studied using active and passive spectroscopic methods. The introduction of molecules to the resonator plasma can significantly alter the plasma behaviour. The logical next step is to determine the plasma properties of a microwave induced molecular plasmas with the use of the same spectroscopic methods. However, it is not guaranteed that the passive diagnostic techniques that have successfully been applied to an atomic argon plasma [5] are applicable to a molecular argon-oxygen plasma.

An important aspect of this study is to determine whether the passive diagnostics applied to the atomic argon plasma are also applicable to molecular plasmas. Because oxygen is an important component of the deposition plasma used at Draka, a low pressure argon-oxygen molecular plasma is studied in this work. The active diagnostic Thomson Scattering (TS) is only applicable to plasmas with a sufficiently high electron density \( n_e \gg 10^{18} \text{ m}^{-3} \) and the oxygen strongly reduces the electron density. Therefore, only a limited amount of oxygen gas was introduced into the argon gas. This enabled the application of both active and passive diagnostics to the low pressure surface wave sustained argon-oxygen plasma.

The second aim of this work is to make a comparison between the electron gas properties of the atomic argon plasma and the molecular argon-oxygen plasma. The TS results shows that the introduction of oxygen results in a significant decrease in the electron density and an increase in the electron temperature. This can be explained using the electron particle and electron energy balances. From the electron particle balance it follows that the electron temperature is higher in a molecular plasma in order to compensate for extra ionization processes. The electron energy balance shows that the electron loses more energy than in an atomic plasma due to the electron-oxygen interactions. Hereby, the energy available for the creation of electrons and ions is reduced and as a result the electron density is lower in the argon-oxygen plasma compared to the argon plasma.

The plasma conditions are shown in section 8.2 while the methods and results are presented in section 8.3. For an overview of the employed setup and diagnostic methods we refer to previous chapters of this thesis. A polydiagnostic study of the molecular argon-oxygen plasma is described in section 8.4. The influence of oxygen on the plasma characteristics is discussed in section 8.5 and concluding remarks are given in section 8.6.
8.2 Plasma conditions

In this work a pure argon surfatron induced plasma is compared with an argon/oxygen mixture. The employed plasma conditions are presented in table 8.1. A major difference between the plasma types is the plasma length, which is significantly decreased when a small amount of oxygen is added. As a result, the power density $\varepsilon_{in}$ is much higher for the argon/oxygen plasma.

<table>
<thead>
<tr>
<th>type</th>
<th>$Q_{Ar}$ sccm</th>
<th>$Q_{O_2}$ sccm</th>
<th>$P_{in}$ W</th>
<th>$L$ cm</th>
<th>$\varepsilon_{in}$ W m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>50</td>
<td>0</td>
<td>40</td>
<td>52.5</td>
<td>$2.7 \times 10^6$</td>
</tr>
<tr>
<td>Ar/O$_2$</td>
<td>45</td>
<td>5</td>
<td>65</td>
<td>13.5</td>
<td>$1.7 \times 10^7$</td>
</tr>
</tbody>
</table>

The setup employed in this study is based on three major components:

- Surfatron setup
- Laser Thomson scattering setup
- Optical setup for high resolution emission spectroscopy.

The surfatron and laser TS setup are extensively discussed in chapter 3, while the optical setup is described in chapter 5. For the experimental setup we refer to these chapters.

8.3 Methods and results

In this section, diagnostic results of a pure argon plasma are compared with those of an argon-oxygen plasma at the same pressure and approximately the same power. Both plasmas have been studied with the following diagnostics:

- Absolute line intensity (ALI) measurements
- Thomson Scattering
- Stark broadening of the $H_\beta$ spectral line.

ALI measurements yield the electron temperature, Stark broadening the electron density and TS gives both the electron density and electron temperature. For a detailed description of these methods, we refer to chapter two (ALI), chapter three (TS) and chapter four ($H_\beta$ broadening). In order to obtain an accurate comparison between the results of the different diagnostics, it is important to apply all techniques to the same plasma condition and location. The measuring procedure is the same as described in chapter 6 and [6], were also an overview of the applied diagnostics is given. This section continues with results of TS, $H_\beta$ broadening and ALI-measurements for both the argon and argon/oxygen plasmas.
8.3.1 Thomson Scattering

Laser TS is an active spectroscopic method which gives direct information of both the electron density and electron temperature. TS measurements are made around an axial position of \( \sim 15 \text{ mm} \) from the launching gap of the surfatron. Results for the electron density and electron temperature are shown in figure 8.1. Due to the addition of \( \text{O}_2 \), the electron density decreases from about \( 4 \times 10^{19} \text{ m}^{-3} \) to \( 1 \times 10^{19} \text{ m}^{-3} \) and the electron temperature increases from approximately 14000 K to 16000 K.

\[
\Delta \lambda_S = 1.23 \times 10^{14} \alpha_{1/2} n_e^{2/3}, \quad \text{with} \quad \alpha_{1/2} \text{ the fractional semi-half width.}
\]

For the \( \text{Ar} \) plasma, we used \( \alpha_{1/2} = 0.0766 \), which is the extrapolated value for \( n_e = 5 \times 10^{19} \text{ m}^{-3} \) and \( T_e = 15000 \text{ K} \) while for \( \text{Ar}/\text{O}_2 \) we used \( \alpha_{1/2} = 0.0725 \), which is determined at \( n_e = 5 \times 10^{18} \text{ m}^{-3} \) and \( T_e = 15000 \text{ K} \). The Stark half-widths \( \Delta \lambda_S \) and the corresponding electron density values are presented in table 8.2 for both the \( \text{Ar} \) and \( \text{Ar}/\text{O}_2 \) plasma. The Gaussian (Doppler) half-widths are equal to 18.6 pm (\( \text{Ar} \) plasma) and 15.8 pm (\( \text{Ar}/\text{O}_2 \) plasma). As can be seen, the Stark width of \( \text{H}_\beta \) emitted by the \( \text{Ar}/\text{O}_2 \) mixture is much smaller than in pure \( \text{Ar} \). This is also observed in figure 8.2. For the \( \text{Ar}/\text{O}_2 \) plasma, the Gaussian half-width is almost five times larger than the Stark half-width. This can decrease the accuracy of the \( n_e \) determination. The Doppler temperature, related to the Gaussian half width of the \( \text{H}_\beta \) line, is not used in this chapter. The reason for this is that it is still not verified whether this Doppler temperature represents the gas temperature (chapter 5 and [8]).

Figure 8.1: TS results of a single CCD frame for \( n_e \) (left) and \( T_e \) (right) for a pure \( \text{Ar} \) and an \( \text{Ar}/\text{O}_2 \) plasma. The axial position is relative to the surfatron launcher.

8.3.2 Stark broadening of \( \text{H}_\beta \)

Emission spectroscopic measurements of the \( \text{H}_\beta \) spectral line obtained at an axial position of \( z = 15 \text{ mm} \) from the launcher are presented in figure 8.2. This figure shows that the width of the \( \text{H}_\beta \) line in the \( \text{Ar}/\text{O}_2 \) plasma is significantly smaller than for pure \( \text{Ar} \).

To obtain the Stark broadening from the total profile, we used the same fitting routine as described in chapter four. The theory of Kepple and Griem [7] is employed to determine the electron density from the Stark half width. In this theory, the Stark half-width is determined using the formula \( \Delta \lambda_S = 1.23 \times 10^{14} \alpha_{1/2} n_e^{2/3} \), with \( \alpha_{1/2} \) the fractional semi-half width. For the \( \text{Ar} \) plasma, we used \( \alpha_{1/2} = 0.0766 \), which is the extrapolated value for \( n_e = 5 \times 10^{19} \text{ m}^{-3} \) and \( T_e = 15000 \text{ K} \) while for \( \text{Ar}/\text{O}_2 \) we used \( \alpha_{1/2} = 0.0725 \), which is determined at \( n_e = 5 \times 10^{18} \text{ m}^{-3} \) and \( T_e = 15000 \text{ K} \). The Stark half-widths \( \Delta \lambda_S \) and the corresponding electron density values are presented in table 8.2 for both the \( \text{Ar} \) and \( \text{Ar}/\text{O}_2 \) plasma. The Gaussian (Doppler) half-widths are equal to 18.6 pm (\( \text{Ar} \) plasma) and 15.8 pm (\( \text{Ar}/\text{O}_2 \) plasma). As can be seen, the Stark width of \( \text{H}_\beta \) emitted by the \( \text{Ar}/\text{O}_2 \) mixture is much smaller than in pure \( \text{Ar} \). This is also observed in figure 8.2. For the \( \text{Ar}/\text{O}_2 \) plasma, the Gaussian half-width is almost five times larger than the Stark half-width. This can decrease the accuracy of the \( n_e \) determination. The Doppler temperature, related to the Gaussian half width of the \( \text{H}_\beta \) line, is not used in this chapter. The reason for this is that it is still not verified whether this Doppler temperature represents the gas temperature (chapter 5 and [8]).
Diagnostic study of argon-oxygen plasmas

Figure 8.2: Spectroscopic measurements of Hβ for a pure argon plasma and an Ar/O₂ mixture. The central wavelength in Ar/O₂ is shifted by approximately 4 pm compared to Ar. This absolute shift can be caused by the changed plasma properties or by slightly different settings of the spectrometer.

Table 8.2: Stark half-widths $\Delta \lambda$ and $n_e$-values of Hβ

<table>
<thead>
<tr>
<th>Type</th>
<th>$\Delta \lambda$</th>
<th>$n_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>10.8 pm</td>
<td>$3.6 \times 10^{19}$ m⁻³</td>
</tr>
<tr>
<td>Ar/O</td>
<td>3.3 pm</td>
<td>$6.9 \times 10^{18}$ m⁻³</td>
</tr>
</tbody>
</table>

8.3.3 Absolute line intensity measurements

ALI measurements of a number of spectral lines enables the construction of the Atomic State Distribution function (ASDF). In an ASDF, the population density of excited states is plotted as a function of the energy of the excited state. Here, we use the lower part of the ASDF to determine the electron temperature and the high energy part to estimate the electron density. Both methods are discussed in detail in chapter 2 and [5].

For pure argon, the population density of the argon 4p-level denoted by $\eta_{4p}$, is determined via an absolute measurement of the 801.48 nm or the 811.53 nm spectral line. The atom density $n_a$ is determined by inserting the measured pressure and an estimated value for the atom temperature into the ideal gas law. In the ASDF, the slope between these two points gives the excitation temperature $T_{13}$. Via a collisional radiative (CR) model for argon, this excitation temperature $T_{13}$ is converted into the electron temperature $T_e$.

In the presence of partial local Saha equilibrium (pLSE), an estimation of the electron density can be obtained by extrapolating the ASDF to the ion state $E_{ion}$. For pLSE, the Saha balance has to be valid which states that the rate of electron induced ionization processes
Chapter 8.

equals that of two electron recombination,

\[ A + e \leftrightarrow e + A^+ + e. \] (8.1)

The population density at the ionic ground state is denoted by \( \eta_\infty \) and equals

\[ \eta_\infty \equiv \eta_e \left( \frac{\hbar^2}{2\pi m_e k_B T_e} \right)^{3/2}. \] (8.2)

Since \( n_e = 2 \eta_e \), this gives an expression for \( n_e \) provided that the ion density \( n_i = 2 \eta_i \) is equal to the electron density \( n_e \). An estimation of the electron density can be obtained by extrapolating the ASDF to the ion state \( E_{\text{ion}} \), assuming that the ion density is equal to the electron density and that the levels high in the atomic system are in pLSE.

For the Ar-plasma, the Ar-ASDF is measured and for the argon/oxygen mixture the ASDF of both argon and O are obtained. The measured argon lines are shown in table 8.3, the oxygen lines in table 8.4.

### Table 8.3: Overview of the transitions in argon.

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>( A_{jk} ) (s(^{-1}))</th>
<th>( j )</th>
<th>( E_j ) (eV)</th>
<th>( k )</th>
<th>( E_k ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>518.77</td>
<td>( 1.38 \times 10^9 )</td>
<td>4p</td>
<td>12.907</td>
<td>5d</td>
<td>15.296</td>
</tr>
<tr>
<td>522.13</td>
<td>( 8.80 \times 10^5 )</td>
<td>4p</td>
<td>13.076</td>
<td>7d</td>
<td>15.450</td>
</tr>
<tr>
<td>545.17</td>
<td>( 4.70 \times 10^5 )</td>
<td>4p</td>
<td>12.907</td>
<td>7s</td>
<td>15.181</td>
</tr>
<tr>
<td>549.59</td>
<td>( 1.69 \times 10^6 )</td>
<td>4p</td>
<td>13.076</td>
<td>6d</td>
<td>15.331</td>
</tr>
<tr>
<td>555.87</td>
<td>( 1.42 \times 10^6 )</td>
<td>4p</td>
<td>12.907</td>
<td>5d</td>
<td>15.137</td>
</tr>
<tr>
<td>560.67</td>
<td>( 2.20 \times 10^6 )</td>
<td>4p</td>
<td>12.907</td>
<td>5d</td>
<td>15.118</td>
</tr>
<tr>
<td>588.26</td>
<td>( 1.23 \times 10^6 )</td>
<td>4p</td>
<td>12.907</td>
<td>6s</td>
<td>15.014</td>
</tr>
<tr>
<td>603.21</td>
<td>( 2.46 \times 10^6 )</td>
<td>4p</td>
<td>13.076</td>
<td>5d</td>
<td>15.131</td>
</tr>
<tr>
<td>696.54</td>
<td>( 6.39 \times 10^6 )</td>
<td>4s</td>
<td>11.548</td>
<td>4p</td>
<td>13.328</td>
</tr>
<tr>
<td>801.48</td>
<td>( 9.28 \times 10^6 )</td>
<td>4s</td>
<td>11.548</td>
<td>4p</td>
<td>13.095</td>
</tr>
<tr>
<td>811.53</td>
<td>( 3.31 \times 10^7 )</td>
<td>4s</td>
<td>11.548</td>
<td>4p</td>
<td>13.076</td>
</tr>
</tbody>
</table>

### Table 8.4: Overview of the transitions in atomic oxygen.

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>( A_{jk} ) (s(^{-1}))</th>
<th>( j )</th>
<th>( E_j ) (eV)</th>
<th>( k )</th>
<th>( E_k ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>615.7</td>
<td>( 1.91 \times 10^8 )</td>
<td>3p</td>
<td>10.74</td>
<td>4d</td>
<td>12.75</td>
</tr>
<tr>
<td>645.5</td>
<td>( 4.13 \times 10^7 )</td>
<td>3p</td>
<td>10.74</td>
<td>5s</td>
<td>12.66</td>
</tr>
<tr>
<td>700.2</td>
<td>( 5.30 \times 10^7 )</td>
<td>3p</td>
<td>10.99</td>
<td>4d</td>
<td>12.76</td>
</tr>
<tr>
<td>822.2</td>
<td>( 2.28 \times 10^8 )</td>
<td>3p</td>
<td>12.54</td>
<td>3s*</td>
<td>14.05</td>
</tr>
<tr>
<td>926.3</td>
<td>( 1.11 \times 10^9 )</td>
<td>3p</td>
<td>10.74</td>
<td>3d</td>
<td>12.08</td>
</tr>
</tbody>
</table>
The measured Ar-ASDF is shown in figure 8.3 for both pure Ar and the Ar/O₂ mixture. It is remarkable that the density of the lowest observable argon states is the same for both plasmas whereas the densities of high energy argon states are slightly higher for the Ar/O₂ mixture than for the pure Ar plasma.

![Figure 8.3: ASDF of Ar in a pure argon and Ar/O₂ mixture. In both cases, the pressure is equal to 10 mbar.](image)

For pure argon, the population density $\eta_{4p}$ of the argon 4p-level is determined via an absolute measurement of the 801.48 nm spectral transition and has a density of $9.4 \times 10^{14}$ m$^{-3}$. Inserting $\eta_{4p}$, the ground state density $n_a = 1.4 \times 10^{23}$ m$^{-3}$ and the TS result $n_e = 4.0 \times 10^{19}$ m$^{-3}$ into the CR-model results in $T_e = 13000$ K. Assuming pLSE, inserting the $T_e$-value obtained by TS, the extrapolated $\eta_\infty = 3.2 \times 10^{11}$ m$^{-3}$ and $E_{\text{ion(Ar)}} = 15.76$ eV into equation 8.2 yields $n_e = 1.2 \times 10^{20}$ m$^{-3}$. The $T_e$-value obtained from the passive method is in good agreement with the TS result for $T_e$, whereas the $n_e$-value derived from the ASDF is a factor 3 larger than the TS-value. This suggests that pLSE is not present and that the extrapolation is not accurate.

For the Ar/O₂ plasma, the 801.48 nm transition results in a population density of $8.4 \times 10^{14}$ m$^{-3}$. Inserting $n_a = 7.2 \times 10^{23}$ m$^{-3}$ ($p = 10$ mbar, $T_h \sim 1500$ K) and the TS result for $n_e = 1.0 \times 10^{19}$ m$^{-3}$ in the CR argon model results in $T_e = 14300$ K. Because the $\eta_{4p}$-values are comparable for the Ar and Ar/O₂ plasma, the higher electron temperature for Ar/O₂ is caused by the lower input values of the CR-model for both the electron and argon density. Extrapolating the argon ASDF to the ion state gives $\eta_\infty = 3.2 \times 10^{11}$ m$^{-3}$, which results in $n_e = 1.2 \times 10^{20}$ m$^{-3}$. Thus the extrapolation of the Ar and Ar/O₂-ASDF results in the same value for the electron density. Compared to the pure argon plasma, the difference between the $n_e$-values obtained via the ASDF extrapolation and TS is even larger.
The O-ASDF is shown in figure 8.4. Interpolation of the O-ASDF to $E_{\text{ion}}(O) = 13.6 \text{ eV}$ results in $\eta_{\infty} = 2.5 \times 10^{12} \text{ m}^{-3}$. Inserting $T_e = 15000 \text{ K}$ in the expression for $\eta_{\infty}$ and assuming that $n_e = n_+(O)$ results in $n_e = 2.3 \times 10^{20} \text{ m}^{-3}$.

Figure 8.4: ASDF of atomic oxygen in an Ar/O$_2$ mixture.

We want to emphasize an important difference between the Ar and O systems. For O, transitions of double excited atoms with energies above the ionization energy of oxygen are measurable. Therefore, the $\eta_{\infty}$-value is obtained via an interpolation of the O-ASDF. Using an interpolation rather than an extrapolation suggests that the result is more accurate. However, the electron density value obtained using the O-ASDF is significantly larger than the TS-value. This indicates that the high energy states are not in pLSE or that the ion density is not equal to the electron density or a combination of both.

8.4 The validity of passive spectroscopic methods in an Ar/O$_2$ mixture

8.4.1 Comparison of electron temperatures

The $T_e$-values are obtained with active (TS) and passive (ALI and CR-model) diagnostics for both the Ar and Ar/O$_2$ plasma and the results are presented in table 8.5. A good agreement of the results is found for pure Ar. For Ar/O$_2$, the passive method gives a lower $T_e$-value than TS.

Table 8.5: Comparison of $T_e$-values obtained with active and passive diagnostic methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>TS ($\text{K}$)</th>
<th>ALI/CR-model ($\text{K}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_e$ (Ar)</td>
<td>$13600 \pm 1100$</td>
<td>$13000 \pm 900$</td>
</tr>
<tr>
<td>$T_e$ (Ar/O$_2$)</td>
<td>$16300 \pm 1300$</td>
<td>$14300 \pm 800$</td>
</tr>
</tbody>
</table>
The lower values of the electron temperature obtained from the Ar-ASDF in Ar/O₂ indicates that the Ar-ASDF is disturbed by the addition of oxygen. In [9], it is stated that the introduction of a small amount of oxygen (≤ 5%) in a low pressure argon plasma decreases the Ar metastable density by about one order of magnitude. Indirectly, this also results in lower densities of the Ar(4p)-levels as stepwise excitations are dominant for our plasma conditions. This depopulation of the Ar metastable and Ar(4p)-levels due to quenching by oxygen atoms and molecules is not included in the CR-model. Therefore, using the pure atomic CR-model for argon to determine the electron temperature from the absolutely measured 4p-density in an Ar/O₂ plasma results in an underestimated value for the electron temperatures. The involved quenching reactions are discussed in more detail in section 8.5.1.

8.4.2 Comparison of electron densities

The \( n_e \)-values obtained with active (TS) and passive (Stark, ASDF) diagnostics are shown in table 8.6 for both the Ar and Ar/O₂ plasma. Note that the TS error margins include systematic and random errors while the Stark broadening only contains the random error. This random error bar is estimated from three successive measurements of the \( H_β \) line of a comparable argon plasma (see chapter 4). Error bars for the ASDF-method are not presented. The systematic TS error is caused by the uncertainty in the Raman cross section employed for the calibration [10].

<table>
<thead>
<tr>
<th>Method</th>
<th>TS</th>
<th>H₇-broadening</th>
<th>Ar-ASDF</th>
<th>O-ASDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_e ) (Ar)</td>
<td>3.9 ± 0.5 \times 10^{19}</td>
<td>3.6 ± 0.1 \times 10^{19}</td>
<td>1.2 \times 10^{20}</td>
<td>-</td>
</tr>
<tr>
<td>( n_e ) (Ar/O₂)</td>
<td>1.0 ± 0.1 \times 10^{19}</td>
<td>6.9 ± 0.4 \times 10^{18}</td>
<td>1.2 \times 10^{20}</td>
<td>2.3 \times 10^{20}</td>
</tr>
</tbody>
</table>

For pure argon, the \( n_e \)-values obtained from the Stark broadening of the \( H_β \) line are in a good agreement with the TS results. For the argon-oxygen mixture, the Stark broadening results for \( n_e \) are about 30% lower than the TS-results and the error bars of the TS-and \( H_β \) method do not overlap.

In case of Ar/O₂, the Stark broadening is very small, the FWHM is about \( \sim 6 \) pm. For the error bar associated with the \( H_β \) method we used the value of the pure argon plasma, where the FWHM was approximately 11 pm. Due to the relatively large difference in the spectral width of the \( H_β \) line, it is expected that the random error in case of Ar/O₂ is larger than for pure argon. Also, the systematic error is expected to be larger for the lower electron densities observed for the Ar/O₂ plasma. The relation between \( n_e \) and the Stark half width depends on the fractional half width \( \alpha_{1/2} \). The \( \alpha_{1/2} \)-values for the Kepple and Griem models of \( H_β \) are only presented for values of \( n_e \) of \( 1 \times 10^{20} \text{ m}^{-3} \) and higher [7]. The pure argon results show that the extrapolation for \( \alpha_{1/2} \) is correct for \( n_e \)-values around \( 10^{19} \text{ m}^{-3} \). However, for Ar/O₂ the electron density is even lower and the used value for \( \alpha_{1/2} \) is expected to have a larger systematic error.
Chapter 8.

The extrapolated Ar-ASDF for both the Ar and Ar/O\textsubscript{2} plasma results in \( n_e \)-values which are 3 to 12 times higher than the results of TS and H\textsubscript{β}-broadening. Moreover, the Ar-ASDF in Ar and Ar/O\textsubscript{2} gives the same \( n_e \)-value, although from TS and Stark we observe a decrease in \( n_e \) when oxygen is added to the Ar discharge. We expected that the O-ASDF would result in more accurate \( n_e \)-values because this method is based on an interpolation of the ASDF instead of an extrapolation, as is the case for Ar. However, the O-ASDF gives an even higher value for \( n_e \). Apparently, this method of \( n_e \)-determination is not accurate. This suggests that the high energy states are not in pLSE. In addition, an underlying assumption of this method is that the electron density is equal to positive atomic ion density. Due to the presence of oxygen molecules in the argon plasma it is not sure whether this is the case for the Ar/O\textsubscript{2} plasma. It will be shown that this effect even increases the discrepancy between the obtained results for the electron density. Both assumptions are discussed below in more detail.

Atomic ion density

The difference between the \( \eta_\infty \)-value in an Ar-plasma and in the Ar/O\textsubscript{2} mixture can be shown as follows. For convenience, the \( \eta_\infty \) is expressed as

\[
\eta_\infty \equiv \eta_e \eta_i \cdot v, \tag{8.3}
\]

with \( v = [\hbar^2/(2\pi m_e k_B T_e)]^{3/2} \). In an atomic argon plasma, the ion density is equal to the electron density (\( n_i = n_e \)). Inserting \( \eta_i = \eta_e \cdot g_e/g_i \) and rewriting expression 8.3 yields

\[
\eta_e^* = \sqrt{\eta_\infty g_i/g_e v}. \tag{8.4}
\]

The symbol * is used to show that this expression is only valid for \( n_e = n_+ \). When molecular oxygen is introduced into the argon plasma, three types of ions can be present, namely Ar\textsuperscript{+}, O\textsuperscript{+} and O\textsuperscript{2+}. As a result, the argon or oxygen atomic ion density is smaller than the electron density which means that both for Ar\textsuperscript{+} and O\textsuperscript{+}, \( \eta_i < \eta_e \cdot g_e/g_i \). This can be expressed as

\[
\eta_i = \eta_e \cdot g_e/g_i \times \xi, \quad \text{with } \xi < 1.
\]

Therefore,

\[
\eta_e = \sqrt{\eta_\infty g_i/g_e v} \times \xi^{-1/2} = \eta_e^* \times \xi^{-1/2}, \quad \xi < 1. \tag{8.5}
\]

Comparing this expression with equation 8.4 shows that \( \eta_e > \eta_e^* \). According to this result, it can be stated that the \( n_e \)-value obtained using \( n_i = n_e \) is an underestimation. However, the electron densities obtained from this extrapolation method using this assumption were already larger than the TS results. This means that the discrepancy will increase even further when \( n_+ < n_e \) is taken into account. As a result, it can be concluded that the interpolation or extrapolation method based on the assumption of pLSE is not working. This strongly indicates that the levels used to determine \( \eta_\infty \) are not in pLSE.

The pLSE assumption

In the following, the ASDF of an ionizing plasma and the pLSE assumption are discussed in more detail. For this purpose, the general form of the ASDF of an ionizing plasma is shown in figure 8.5. Three regions can be distinguished. In the first region the low lying levels are populated by electron impact excitation and depopulated by radiative transitions
or de-excitation by electron impact. In the second region, the Excitation Saturation Balance (ESB) is valid, where the levels are populated by electron impact excitations and depopulated by excitations to the adjacent higher level. As both excitation and de-excitation occur by electron impact collisions, the density of these levels is only weakly dependent of the electron density. Levels close to the continuum are in pLSE. In this region the Saha balance is valid, i.e. the rate at which ionization reactions occur is equal to that of two-electron recombination.

Figure 8.5: Typical shape of the ASDF for an ionising plasma. Figure taken from [11].

In the above discussion, it was initially assumed that the levels used for the extrapolation are in or close to pLSE. From the fact that the \( n_e \)-value obtained in this way is too large we had to conclude that this proposition is not correct. Figure 8.5 shows that these levels are most probably in ESB. The population and depopulation of levels in ESB is determined by the electron temperature and the atom density. This means that the density of these levels is almost independent of the electron density and can therefore not be used to obtain the \( \eta_\infty \) value. This corresponds to our experimental results, where the extrapolation of the Ar-ASDF of both the Ar and the Ar/O\(_2\) plasma resulted in the same \( \eta_\infty \)-value while the TS results show that the \( n_e \)-value of the Ar-plasma is significantly higher than the \( n_e \)-value obtained in the Ar/O\(_2\) plasma.

8.5 Influence of oxygen addition to the argon plasma

8.5.1 Argon-oxygen interaction

The effect of minor additions of oxygen on the argon metastable density of low pressure RF argon plasmas was determined with laser-induced fluorescence imaging by [9] and by means of two dimensional computer simulations in [9, 12]. It was found that the addition of oxygen
results in a decrease of the argon metastable density by approximately one order of magnitude. However, the oxygen addition also results in an increase in argon $5p \rightarrow 4s$ emission, which indicates that the metastable argon production is increased. This was explained by an increase of the reduced electric field $E/N$, and therefore also of $T_e$, required to sustain the plasma. In the same article [9], it was concluded that the decrease of the metastable argon density is the result of quenching by the added molecules. As discussed in [13], these reactions occur with oxygen molecules or oxygen atoms and lead to argon atoms in the ground state $\text{Ar}(1)$ and (excited) oxygen atoms, where $\text{O}(1)$ refers to the atomic ground state and $\text{O}(^1\text{D})$ to the first excited state of oxygen. The 4p-argon levels and argon ions can also be affected by quenching with oxygen atoms or molecules [13]. Interaction between the argon and oxygen systems can also occur via reactions between argon ions and oxygen atoms or molecules. These reactions are presented in table 8.7.

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ar}(4s) + \text{O}(1)$ → $\text{Ar}(1) + \text{O}(1)$</td>
<td>$4.1 \times 10^{-17}$ m$^3$s$^{-1}$</td>
</tr>
<tr>
<td>$\text{Ar}(4s) + \text{O}_2$ → $\text{Ar}(1) + \text{O}(1) + \text{O}(1)$</td>
<td>$1.0 \times 10^{-16}$ m$^3$s$^{-1}$</td>
</tr>
<tr>
<td>$\text{Ar}(4s) + \text{O}_2$ → $\text{Ar}(1) + \text{O}(^1\text{D}) + \text{O}(1)$</td>
<td>$1.1 \times 10^{-16}$ m$^3$s$^{-1}$</td>
</tr>
<tr>
<td>$\text{Ar}(4p) + \text{O}_2$ → $\text{Ar}(1) + \text{O}(1) + \text{O}(1)$</td>
<td>$3.0 \times 10^{-16}$ m$^3$s$^{-1}$</td>
</tr>
<tr>
<td>$\text{Ar}(4p) + \text{O}_2$ → $\text{Ar}(1) + \text{O}(^1\text{D}) + \text{O}(1)$</td>
<td>$3.3 \times 10^{-16}$ m$^3$s$^{-1}$</td>
</tr>
<tr>
<td>$\text{Ar}^+ + \text{O}$ → $\text{Ar}(1) + \text{O}^+$</td>
<td>$1.4 \times 10^{-17}$ m$^3$s$^{-1}$</td>
</tr>
<tr>
<td>$\text{Ar}^+ + \text{O}_2$ → $\text{Ar}(1) + \text{O}_2^+$</td>
<td>$6.4 \times 10^{-18}$ m$^3$s$^{-1}$</td>
</tr>
</tbody>
</table>

For the experimental conditions of the Ar-plasma, the results of the CR-model show that the $\text{Ar}(4p)$-level is mainly populated by excitation from the metastable $\text{Ar}(4s)$-levels and depopulated by excitation to higher levels. For the $\text{Ar}/\text{O}_2$ mixture, the population is also via the metastable Ar-levels and depopulation occurs via excitation to higher energy levels and quenching by oxygen molecules. However, the population term via the metastable levels is smaller because this level is depopulated by the quenching reactions. Because we observe that the measured $\text{Ar}(4p)$-densities have similar values for the Ar and the $\text{Ar}/\text{O}_2$ mixture (cf. figure 8.3), the population rate of the $\text{Ar}(4p)$ has to be larger in case of the $\text{Ar}/\text{O}_2$ mixture. As these rate coefficients depend on the electron temperature, this means that the electron temperature in the $\text{Ar}/\text{O}_2$ plasma has to be higher in order to explain the fact that the (4p)-densities have similar values for the Ar and the $\text{Ar}/\text{O}_2$ mixture. This is also observed with TS. To obtain accurate electron temperatures using the method of ALI and a CR-model, it is required to make the CR-model more complete by adding various oxygen related reactions.

The processes described in table 8.7 lead to an extra depopulation of the atomic argon ion density and to an enhanced population of atomic oxygen ions compared to respectively pure atomic argon and oxygen plasmas. It also shows that the molecular oxygen ion dissociates via electron impact processes and results in a ground state oxygen atom and an oxygen atom in an excited state. However, this difference can not be observed in the measured ASDF. The obtained $\eta_\infty$-values are not affected by these extra population or depopulation processes. The
densities of these high energy levels used for this extrapolation were found to be in ESB and are therefore not coupled with the ion ground state density.

8.5.2 Influence of oxygen on the electron gas properties

According to the TS results, the electron temperature is $\sim 3000\text{K}$ higher and the electron density $\sim 3 \times 10^{19}\text{m}^{-3}$ lower in the Ar/O$_2$ mixture compared to the pure argon plasma. In this subsection, a qualitative approach is used in order to explain the effect of molecular oxygen on the argon plasma. First, the electron particle and electron energy balances for the argon plasma are briefly discussed. Then the balances for the Ar/O$_2$ are examined.

Electron temperature

As discussed in [10, 14], the electron temperature follows from the electron particle balance while the electron density is determined by the electron energy balance. In steady state, the particle balance for electrons equals

$$ n_e \frac{D_a}{\Lambda^2} + \nabla \cdot n_e \mathbf{w_e} = P_e, \quad (8.6) $$

where the first term on the left hand side describes the destruction of electrons in electron induced reactions, the second term is the reduction of the electron density due to transport and the term on the right hand side describes the total production term.

For an atomic argon plasma, electrons are produced by ionization of argon atoms and removed by ambipolar diffusion. The destruction term, two electron recombination, is negligible (cf. chapter 7). The electron particle balance can then be expressed as

$$ \frac{n_e D_a}{\Lambda^2} = n_e n_{\text{Ar}} k_1(T_e), \quad (8.7) $$

where $D_a$ is the ambipolar diffusion coefficient, $\Lambda$ the diffusion length which is proportional to the inner radius of the tube, $n_{\text{Ar}}$ the argon density and $k_1(T_e)$ a temperature dependent effective ionization rate of which an approximation is given in table 8.8.

For the Ar/O$_2$ plasma, electrons are still produced by electron-argon collisions and also removed from the discharge by ambipolar diffusion. However, destruction of electrons by chemical reactions can now be important. For example, the formation of a molecular ion O$_2^+$ produced by argon-oxygen reactions, is followed by the following recombination reaction,

$$ e + O_2^+ \rightarrow O + O(1^D), \quad (8.8) $$

with a rate of $2.2 \times 10^{-14}\text{m}^3\text{s}^{-1}$. As a result of these fast recombination reactions, the chemical destruction losses are important and the population of electrons has to be increased. This can only be accomplished by an increase in the electron temperature.

Electron density

The electron energy balance for a pure argon plasma is given by (chapter 4),

$$ \frac{\varepsilon}{n_e} = \theta^{\text{el}}(\text{Ar}) + \theta^{\text{in}}(\text{Ar}) \quad (8.9) $$

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with $\varepsilon$ the absorbed microwave power per unit volume, $\theta_{el}$ the elastic and $\theta_{in}$ the inelastic electron energy transfer:

$$\theta_{el}(Ar) = n_{Ar} k_{eAr}^e k_B (T_e - T_h), \quad (8.10)$$

$$\theta_{in}(Ar) = n_{Ar} k_1 \left( \Delta E_1 + \frac{3}{2} k_B T_e \right). \quad (8.11)$$

Here, $k_{eAr}$ is the electron argon energy transfer, $T_h$ the heavy particle temperature and $\Delta E_1$ the ionization energy of the first reaction process in table 8.8. The electron particle and electron energy balance for the Ar/O$_2$ mixture has to include electron-oxygen reactions as well. According to [15], the complex oxygen chemistry can be reduced to the reactions presented in table 8.8.

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate coefficient m$^3$s$^{-1}$</th>
<th>Energy eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>e + Ar $\rightarrow$ e + Ar$^+$ + e</td>
<td>$k_1 = 6.8 \times 10^{-17} (T_e K)^{0.5} \exp(-12.06/T_e)$</td>
<td>$\Delta E_1 = 15.76$</td>
</tr>
<tr>
<td>e + O $\rightarrow$ e + O$^+$ + e</td>
<td>$k_2 = 9.0 \times 10^{-15} T_e^{0.7} \exp(-13.61/T_e)$</td>
<td>$\Delta E_2 = 13.61$</td>
</tr>
<tr>
<td>e + O$_2$ $\rightarrow$ e + O + O</td>
<td>$k_3 = 7.1 \times 10^{-15} \exp(-8.6/T_e)$</td>
<td>$\Delta E_3 = 5.62$</td>
</tr>
<tr>
<td>e + O$_2$ $\rightarrow$ 2e + O + O$^+$</td>
<td>$k_4 = 1.7 \times 10^{-15} \exp(-3.1/T_e)$</td>
<td>$\Delta E_4 = 1.43$</td>
</tr>
<tr>
<td>e + O$_2$ $\rightarrow$ e + O$_2^+$</td>
<td>$k_5 = 5.3 \times 10^{-16} T_e^{0.9} \exp(-20.0/T_e)$</td>
<td>$\Delta E_5 = 19.23$</td>
</tr>
<tr>
<td>e + O$_2^+$ $\rightarrow$ e + O$_2$</td>
<td>$k_6 = 5.6 \times 10^{-15} \exp(-2.2/T_e)$</td>
<td>$\Delta E_6 = -1.43$</td>
</tr>
<tr>
<td>e + O$_2^+$ $\rightarrow$ e + O + O</td>
<td>$k_7 = 4.2 \times 10^{-15} \exp(-4.6/T_e)$</td>
<td>$\Delta E_7 = 4.19$</td>
</tr>
</tbody>
</table>

The elastic $\theta_{el}$ and inelastic $\theta_{in}$ terms in the electron energy equation of the Ar/O$_2$ mixture both contain extra contributions. The elastic term is now given by

$$\theta_{el} = \left( n_{Ar} k_{eAr}^e k_B + n_O k_{eO}^e k_B + n_{O_2} k_{eO_2}^e k_B \right) k_B (T_e - T_h), \quad (8.12)$$

where it is assumed that the all heavy particles have the same temperature. The inelastic term is now expressed as,

$$\theta_{in} = n_{Ar} k_1 \left( \Delta E_1 + \frac{3}{2} k_B T_e \right) + n_O k_2 \left( \Delta E_2 + \frac{3}{2} k_B T_e \right) +$$

$$n_{O_2} \left[ k_3 \Delta E_3 + k_4 \Delta E_4 + k_5 \Delta E_5 + \frac{3}{2} k_B T_e \right] + n_{O_2} \left( k_6 \Delta E_6 + k_7 \Delta E_7 \right). \quad (8.13)$$

Electron impact collisions with molecular oxygen molecules can also result in rotational and vibrational excitation of the molecule [16]. Therefore, an extra electron energy loss term $\theta_{e^{ro/vib}}$ has to be added to the electron energy balance. According to the relation

$$n_e = \frac{\varepsilon}{\theta_{el} + \theta_{in} + \theta_{e^{ro/vib}}}, \quad (8.14)$$

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the extra contributions due to the electron-oxygen interaction enhance the total energy loss per electron ($\theta_{\text{tot}}^{\text{el}} = \theta_{\text{el}} + \theta_{\text{in}} + \theta_{\text{ro/vib}}$). As a result, the energy per electron required to sustain the plasma is much higher in the molecular argon-oxygen plasma. This is also observed in our experimental results. The Ar/O$_2$ plasma is shorter than the pure argon plasma and therefore has a higher power density, approximately 1 order higher than the pure argon plasma. The electron density in the Ar-plasma is a factor 4 higher than the electron density in the Ar/O$_2$ plasma. Concluding, when the applied power density is comparable, the electron density is significantly smaller in an argon/oxygen plasma.

8.6 Concluding remarks

In this chapter, the effect of the addition of a minor amount of molecular oxygen on the electron density and electron temperature has been investigated. For this purpose, several passive and active diagnostic methods were applied to a pure argon and an Ar/O$_2$ plasma. This allowed us to determine whether the passive spectroscopic methods, which we employed to determine the electron gas properties from emission spectroscopy in an atomic argon plasma, can also be applied to a molecular plasma.

The electron density in the pure argon plasma was obtained using TS, Stark broadening and from the extrapolation of the argon ASDF. The $n_e$-results obtained with TS and Stark broadening were in good agreement with each other, while the $n_e$-values determined from the Ar-ASDF were too high. As discussed before, the ASDF extrapolation method is not very accurate. In the Ar/O$_2$ mixture, the $n_e$-values were determined using TS, Stark broadening, and from the argon and oxygen ASDF. As the oxygen ASDF is based on an interpolation instead of an extrapolation, we expected that this would be more accurate than the argon ASDF. This was not the case because the $n_e$-values obtained from both the argon and oxygen ASDF were much larger than from TS. As a result, we conclude that the used argon and oxygen levels are not in pLSE but in excitation saturation balance. In this regime the level densities are more or less independent of the electron density and therefore not applicable for the $n_e$-determination. The Stark broadening results for $n_e$ in the Ar/O$_2$ mixture were about 30% lower than the TS values. For the Ar/O$_2$ plasma, the Stark broadening of the line is close to the limit of the equipment and therefore less accurate.

The electron temperature was obtained using TS and ALI measurements where a CR-model for argon has been used for the interpretation of the experimental data. For the argon plasma, the $T_e$-values obtained from both methods were in a good agreement. For the Ar/O$_2$ mixture, the ALI-method resulted in lower $T_e$-values compared to the TS results. A possible explanation is the quenching of metastable, 4s, and 4p-argon levels by oxygen atoms and molecules. Therefore, these argon-oxygen quenching reactions have to be taken into account in the CR-model.

Due to the addition of a small amount of oxygen ($\leq 5\%$) to the argon plasma, the plasma length decreases from about 50 cm to 10 cm. In order to sustain the plasma, it was required to increase the microwave power from 40 W to 65 W. As a result, the power density in the Ar/O plasma is a factor of 10 higher than in the argon plasma. The TS results in argon are: $T_e = 13600 \pm 1100$ K and $n_e = 3 \pm 0.5 \times 10^{19}$ m$^{-3}$. In Ar/O$_2$, the TS results are
$T_e = 16300 \pm 1300 \text{ K}$ and $n_e = 1 \pm 0.1 \times 10^{19} \text{ m}^{-3}$. This means that the electron temperature is 17% higher and the electron density 33% lower in the Ar/O$_2$ mixture compared to the argon plasma. These differences can be understood in a qualitative way when oxygen reactions are added to the electron particle and electron energy balance.

**Bibliography**


Rotational temperature measurements in a low pressure oxygen plasma with a small amount of argon

**Abstract.** Emission spectroscopic measurements of the so-called atmospheric band transition in oxygen $O_2(b^1Σ_g^+, ν = 0) \rightarrow O_2(X^3Σ_g^-, ν = 0)$ have been made of a microwave induced plasma. The plasma was created using a surfatron and sustained inside a quartz tube filled with oxygen and a small amount of argon. Emission spectroscopic measurements have been performed for gas pressures between 4 and 10 mbar. The rotational temperature is deduced from a molecular Boltzmann plot. Due to the long life time of the metastable state ($b^1Σ_g^+, ν = 0$), enough collisions occur in order to reach an equilibrium between the rotational and gas temperature. As a result, the rotational temperature is close to the gas temperature. Depending on the pressure, the obtained temperatures vary between 600 and 800 K. The kinetic reactions involved in the population of the $O_2(b^1Σ_g^+, ν = 0)$ state are discussed and the shape of the rotational spectrum of the atmospheric A-band transition is explained.
Chapter 9.

9.1 Introduction

In low-pressure molecular plasmas the gas temperature is one of the most important parameters. Knowledge of this parameter is essential in order to obtain accurate reaction rates [1]. In addition, it enables an accurate determination of the neutral density concentration via the ideal gas law, which gives insight in the ionization ratio.

Touzeau et al [2] determined rotational temperatures and the gas temperature in the positive column of a low pressure oxygen discharge \((0.7 \text{ -- } 6.7 \text{ mbar})\) via optical emission spectroscopy, coherent anti-Stokes Raman spectroscopy and vacuum ultraviolet (VUV) absorption spectroscopy. They found that the rotational temperature deduced from emission spectroscopic measurements of the atmospheric A-band transition \(\text{O}_2(b^1\Sigma_g^+, \nu = 0) \rightarrow \text{O}_2(X^3\Sigma_g^-, \nu = 0)\) and a classical Boltzmann plot [3] was equal to the temperatures of the singlet \(\text{O}_2(a^1\Sigma_g^+)\) state and the molecular ground state \(\text{O}_2(X^3\Sigma_g^-)\) as obtained from coherent anti-Stokes Raman spectroscopy. These rotational temperatures were found to be equal to the gas temperature that was deduced from concentration measurements by VUV absorption spectroscopy. Therefore, they concluded that the rotational temperature of the \(\text{O}_2(b^1\Sigma_g^+)\) state is a good measure for the gas temperature. Time resolved spectroscopic measurements of the atmospheric A-band transition in a low pressure pulsed oxygen discharge were performed by Macko et al [4]. They concluded that the gas temperature and the density of the \(\text{O}_2(b^1\Sigma_g^+, \nu = 0)\) state could be obtained via a comparison of the measured and simulated spectra. To conclude, it can be stated that emission spectroscopy of the transition \(\text{O}_2(b^1\Sigma_g^+, \nu = 0) \rightarrow \text{O}_2(X^3\Sigma_g^-, \nu = 0)\) is a suitable and validated method to determine the gas temperature for oxygen plasmas at pressures of 1 mbar and higher.

The aim of this study is to determine the gas temperature of a low pressure \((4 \text{ -- } 10 \text{ mbar})\) surface wave sustained plasma in oxygen. For this purpose, the rotational spectrum of the \(\text{O}_2(b^1\Sigma_g^+, \nu = 0) \rightarrow \text{O}_2(X^3\Sigma_g^-, \nu = 0)\) transition at 760 nm was measured using emission spectroscopy. A small amount of argon was added to the oxygen discharge in order to determine the dissociation degree using actinometry (cf. chapter 10). However, due to the presence of an intense argon transition at 763.51 nm, only the intensities of rotational lines of the \(\text{R}_R(759.5 \text{ nm} < \lambda < 761.6 \text{ nm})\) and \(\text{R}_Q(759.4 \text{ nm} < \lambda < 761.5 \text{ nm})\) branch could be measured in an absolute way. The rotational temperature was deduced from a molecular Boltzmann plot. The atmospheric A-band transition is electronically forbidden, which results in a long life time (metastable) of the upper state \(b^1\Sigma_g^+, \nu = 0\) and a low intensity of the rotational transition. This is a disadvantage of this method. On the other hand, due to the relatively long life time of this upper state, the collisional frequency is high enough to obtain an equilibrium between the rotational and gas temperature. Therefore, the rotational temperature of \(b^1\Sigma_g^+, \nu = 0\) is close to the gas temperature.

This chapter starts with a global description of the theory of the rotational spectrum of diatomic molecules in section 9.2. In section 9.3, a diagnostic method to determine the rotational temperature from a measured atmospheric A-band is presented. The setup and experimental results are given in section 9.4. A discussion of the results, more specifically the intensities and rotational temperatures as function of pressure, is given in section 9.5. Conclusions are presented in section 9.6.
9.2 Rotational spectra

The rotational spectra are often measured in molecular plasmas using emission spectroscopy in order to derive the gas temperature [2, 5]. However, the interpretation of a rotational spectrum is not straightforward. Even for relatively simple diatomic molecules like oxygen or nitrogen, deviations from a pure rotational spectrum are present. It is the aim of this section to analyse on the shape of rotational emission spectra of a diatomic gas.

This section starts with a description of a pure rotational transition, followed by a rovibronic transition, where apart from the rotational also an electronic and/or vibrational transition takes place. After that, a short summary of the electronic motion and the coupling between the electronic and rotational motion. Also, expressions for the intensities of rotational lines in emission are presented.

9.2.1 Rotational transition

To a first approximation, the rotational spectrum of a diatomic molecule can be described in terms of a rigid rotator. The two masses rotate about their centre of mass and using classical mechanics, it can easily be shown that the moment of inertia \( I \) is given by
\[
I = \mu R^2,
\]
where \( \mu \) is the reduced mass and \( R \) the distance between the two masses [6]. In classical mechanics, the energy \( E \) of the rotation of a rigid body is
\[
E = \frac{1}{2} I \omega^2,
\]
with \( \omega \) the angular velocity about the principle axis. Using the classical angular momentum, \( J_{cl} = I \omega \), the rotational energy can be expressed as
\[
E = \frac{J_{cl}^2}{2I}.
\]
In quantum mechanics, the energy eigenvalues are obtained by solving the Schrödinger equation for rotational motion of the rigid rotator. It can be shown that the quantum mechanical expression is obtained when \( J_{cl} \) is replaced by
\[
J = J(J+1)\hbar^2,
\]
where \( J \) is the angular momentum quantum number [3]. The corresponding energy eigenvalues are now given by
\[
E_r = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, 2, ... \quad M = -J, -J+1, 0, J,
\]
(9.1)
where the quantum number \( M \) defines the component of the angular momentum on the principle axis. Because the energy of the rotational levels is independent of \( M \), the degeneracy of the rotator is: \( 2J + 1 \). During a rotational transition, the angular momentum has to be conserved. This introduces the following selection rules for a rigid rotator:
\[
\Delta J = \pm 1 \quad \Delta M_J = 0, \pm 1.
\]
(9.2)

In a rotational transition from a higher to a lower energy level, a photon is emitted with a wave number,
\[
\nu_r = \frac{E_r'}{\hbar c} - \frac{E_r''}{\hbar c} = F(J') - F(J''),
\]
(9.3)
with \( E_r' \) and \( E_r'' \) the rotational energies in the upper \( J' \) and lower \( J'' \) states and \( F(J) \) the so-called rotational term having a dimension of cm\(^{-1}\). This term can thus be expressed as
\[
F(J) = \frac{E_r'}{\hbar c} = \frac{\hbar}{8\pi^2cI} J(J+1) = BJ(J+1),
\]
(9.4)
with \( B \equiv \hbar / (8\pi^2cI) \) the rotational constant. When \( J' > J'' \) (emission), only transitions for which \( \Delta J = +1 \), the so-called \( R \) branch, have to be considered. Using the rotational term,
the wave number of such a transitions is

\[ \nu_r = F(J'' + 1) - F(J'') = 2B(J'' + 1). \]  

(9.5)

The rotational emission spectrum of a rigid rotator is a series of equidistant lines separated at a distance \(2B\).

In a molecule, also vibrations due to centrifugal forces in the line joining the two nuclei occur. Therefore, a model of non-rigid rotator should also include the vibrational motion. In this model the two nuclei are connected by a massless string instead of a massless rigid bar. This can be corrected for by adding an extra term to equation 9.4 [7],

\[ F(J) = BJ(J + 1) - DJ^2(J + 1)^2, \]  

(9.6)

where \(D\) is a centrifugal distortion constant defined by \(D = 4B^3/\omega^2\) in which \(\omega\) is the equilibrium vibrational frequency. Since \(\omega \gg B\), the constant \(D\) is much smaller than \(B\). The selection rules are the same as for the rigid rotator. Therefore, the wave numbers of the emission lines can be expressed as

\[ \nu_r = F(J + 1) - F(J) = 2B(J + 1) - 4D(J + 1)^3 \quad J = 0, 1, 2, 3, ... \]  

(9.7)

As a result, the separation between the lines decreases slightly with increasing \(J\). The lines are no longer equidistant, as is the case for the rigid rotator.

### 9.2.2 Rovibronic transition

A rotational transition is often accompanied with an electronic and vibrational transition. Such a transition is referred to as a rovibronic. The total energy difference \(\Delta E\) between two states is given by

\[ \Delta E = E_e + E_v + E_r = \hbar c (\nu_e + \nu_v + \nu_r), \]  

(9.8)

with \(E_e\) and \(E_v\) the energy differences between the electronic and vibrational states. Hence, the total wavenumber can be expressed as

\[ \nu = \nu_e + \nu_v + \nu_r \equiv \nu_0 + \nu_r, \]  

(9.9)

where \(\nu_e\) and \(\nu_v\) correspond to the wavenumber of the electronic and vibrational transition, respectively. Since the upper and lower state are not part of the same vibrational or electronic state, the rotational constant \(B\) and thus the term \(F\) are not the same for the upper and lower level. Using equation 9.5 for the rotational frequency \(\nu_r\), the total wavenumber can be written as

\[ \nu = \nu_0 + F'(J') - F''(J''), \]  

(9.10)

with \(\nu_0\) the so-called wavenumber of the band origin. The terms of the upper and lower levels are respectively defined by \(F'(J') = B'J'(J' + 1)\) and \(F''(J'') = B''J''(J'' + 1)\). Here, the influences of the centrifugal distortion terms are neglected. The selection rules for rovibronic transitions are now given by

\[ \Delta J = 0, \pm 1 \quad \Delta J = J' - J''. \]  

(9.11)
Rotational temperature measurements

In addition to the R branch ($\Delta J = +1$) and the P branch ($\Delta J = -1$), the transition $\Delta J = 0$ results in a third band called the Q branch. Neglecting the centrifugal distortion, the following expressions are obtained.

R branch: $\nu = \nu_0 + 2B' + (3B' - B'')J'' + (B' - B'')J''^2$ \hspace{1cm} (9.12)

Q branch: $\nu = \nu_0 + (B' - B'')J'' + (B' - B'')J''^2$ \hspace{1cm} (9.13)

P branch: $\nu = \nu_0 - (B' + B'')J'' + (B' - B'')J''^2$ \hspace{1cm} (9.14)

Generally, the $B$-value of the upper level ($B'$) is slightly smaller than the $B$-value of the lower level ($B''$), thus $B' - B'' < 0$. Therefore, while moving away from the band centre, the lines of the R branch converge slightly and the lines of the P branch diverge. The lines present in the Q branch are spaced closely together.

9.2.3 Electronic motion

In this subsection a short summary of electronic states and motion is presented [3]. Analogous to the atomic case, the total motion of the electrons is the result of the coupling between the orbital motion and electron spin.

The electronic orbital angular momentum is denoted by $-\vec{L}$. A precession of $-\vec{L}$ occurs around the internuclear axis with a constant component $M_L \hbar$. The component $M_L$ can be equal to $M_L = L, L - 1, L - 2, ..., -L$. Reversing the direction of motion of all electrons changes the sign of $M_L$. For diatomic molecules, the energy remains unaltered. The vector $\Lambda$ represents the component of the electronic orbital angular momentum along the internuclear axis. The absolute value of $M_L$ is per definition equal to the quantum number $\Lambda$:

$$\Lambda = |M_L|, \quad \Lambda = 0, 1, 2, ..., L.$$ \hspace{1cm} (9.15)

Generally, the term symbols for $\Lambda = 0, 1, 2, ...$ are denoted by the Greek letters $\Sigma, \Pi, \Delta, ...$. These states $\Pi, \Delta, ..$ are double degenerate since $M_L$ can be positive $+\Lambda$ or negative $-\Lambda$.

The total spin of the electrons is defined by the vector $-\vec{S}$. If $\Lambda \neq 0$, an internal magnetic field is present in the direction of the internuclear axis resulting from the orbital motion of electrons. This field causes a precession of $-\vec{S}$ around the internuclear axis with a constant component $M_S \hbar$. The component $M_S$ is denoted by the quantum number $\Sigma$ and can take the following values $\Sigma = S, S - 1, S - 2, ..., -S$, thus $2S + 1$ different states are possible. The quantum number $\Sigma$ is not defined for $\Lambda = 0$ states.

The total angular momentum of electrons, $-\vec{J}_e$ is obtained by adding $-\vec{L}$ and $-\vec{S}$. The component of $-\vec{J}_e$ along the internuclear axis is denoted by $-\vec{\Omega}$. The absolute value of this vector, $\Omega$, can be found using an algebraic addition of the quantum numbers $\Lambda$ and $\Sigma$, thus $\Omega = |\Lambda + \Sigma|$. This is allowed because both vectors are oriented in the direction of the internuclear axis, i.e. the line joining both nuclei. The value $2S + 1$ is called the multiplicity of a state and the electronic term with $\Lambda \neq 0$ splits into a multiplet of $2S + 1$.

9.2.4 Coupling of electronic and rotational motion

The rotation of the molecule takes place simultaneously with the motions of the electrons. For an accurate description of the rotational spectrum, it is required to determine the influence of
rotational and electronic motion on each other. These are described by Hund’s coupling cases.

In all cases, the vector \( \vec{J} \) is used to describe the total angular momentum. The vector \( \vec{N} \), called the angular momentum of nuclear rotation, is per definition equal to the component of the total angular momentum \( \vec{J} \) perpendicular to the internuclear axis. The magnitude of this vector is determined by \( \vec{\Omega} \) and \( \vec{J} \).

The motion of the simple rotator corresponds to \( \vec{J} = \vec{N} \), thus the total angular momentum is equal to the angular momentum of nuclear rotation. This correspond to a zero total electron spin \( (S = 0) \) and orbital momentum \( (\Lambda = 0) \), thus to a \( ^1\Sigma \) state. If these quantum numbers are not equal to zero, the coupling cases as described by Hund have to be used. Here, only a short discussion of Hund’s case (a) and Hund’s case (b) is given. A more detailed description can be found in [3].

In case (a), it is assumed that the influence of nuclear rotation on the orbital motion of the electrons is very weak. As a result, the electronic motion is strongly coupled to the internuclear axis. Therefore,

\[
\vec{J} = \vec{\Omega} + \vec{N} \quad (9.16)
\]
\[
J = \Omega, \Omega + 1, \Omega + 2, \ldots \quad (9.17)
\]

Hund’s case (b) occurs when the spin vector \( \vec{S} \) is not or weakly coupled to the internuclear axis. For states with \( \Lambda = 0, S \neq 0 \), the vector \( \vec{\Omega} \) is not defined and the spin is thus not coupled to the axis. The weak coupling occurs in light molecules and also for states with \( \Lambda \neq 0, S \neq 0 \). The coupling is described by a new vector \( \vec{K} \) and corresponding quantum number \( K \), which describes the total angular momentum apart from spin,

\[
\vec{K} = \vec{\Lambda} + \vec{N} \quad (9.18)
\]
\[
K = \Lambda, \Lambda + 1, \Lambda + 2, \ldots \quad (9.19)
\]

and the total momentum \( J \) including spin equals

\[
\vec{J} = \vec{K} + \vec{S} \quad (9.20)
\]
\[
J = K + S, K + S - 1, K + S - 2, \ldots, |K - S|. \quad (9.21)
\]

A level with quantum number \( K \) consists of \( 2S + 1 \) states. The selection rules for \( K \) are

\[
\Delta K = 0, \pm 1 \quad (9.22)
\]
\[
\Delta K = 0 \text{ forbidden for } \Sigma \rightarrow \Sigma \text{ transitions.} \quad (9.23)
\]

For Hund’s case (a) and case (b) some general selection rules are

- \( \Delta J = 0, \pm 1 \), forbidden is \( J = 0 \rightarrow J = 0 \)
- \( \Lambda = 0, \pm 1 \)
- \( \Delta S = 0 \), upper and lower states have the same multiplicity (spin)
- Only positive term – negative term transitions, thus \( + \leftrightarrow - \)
- Even electronic states \( g \) combine with odd \( u \), thus \( g \leftrightarrow u \).
9.2.5 Emission spectrum

The thermal distribution of the rotational levels can be found using the Boltzmann exponent multiplied with the statistical weights. Assuming that only the $v = 0$ vibrational state is populated, the fraction of molecules in a rotational energy level $J$ is given by

$$f_J = \frac{N_J}{N} = \frac{g_J \exp \left(-\epsilon_J/kT\right)}{Q_r}, \quad (9.24)$$

with $Q_r = \sum g_J \exp \epsilon_J/kT$. The summation runs over the rotational states. Ignoring the centrifugal distortion term, using $g_J = 2J + 1$, $\epsilon_J = F(J)hc = hcBJ(J+1)$ and the approximation $Q_r \approx kT/hcB$ [3], this equation can be expressed as

$$f_J = \frac{hcB}{kT} (2J + 1) \exp \left(-hcBJ(J+1)/kT\right). \quad (9.25)$$

For the upper state of the atmospheric band transition, $O_2(b^1\Sigma_g^+, v = 0)$ ($B = 1.39138$), the (relative) population as function of the rotational level is shown in figure 9.1 for different rotational temperatures. For a constant temperature and increasing $J$, the population of the rotational levels first goes to a maximum, then decreases with increasing $J$. The position of the maximum shifts to higher $J$ values with increasing temperature and the maximum population decreases with increasing temperature.

![Figure 9.1](image)

**Figure 9.1:** Fraction of oxygen molecules, $N_J/N$, as function of the rotational level $J$. It is assumed that only the $v = 0$ vibrational state is populated and the energy levels are derived using the model of the rigid rotator.

The line integrated emission coefficient, $e_{nm}$, of a rotational line\(^1\) is defined by

$$e_{nm} = N_nhc\nu_{nm} A_{nm}/(4\pi), \quad (9.26)$$

\(^1\)In the other chapters of this thesis, the symbol $j$ is used to denote the line integrated emission coefficient. Because this symbol can easily be confused with $J$, the symbol $\epsilon$ is used instead.
where \( N_n \) is the number density of molecules in the initial rotational energy state \( n \), \( \nu_{nm} \) the frequency of a photon emitted in the transition from \( n \) to the lower rotational state \( m \) and \( A_{nm} \) is the Einstein transition probability. For a transition between two non-degenerate levels of degeneracy \( g_n \) and \( g_m \), the transition probability is [3]

\[
A_{nm} = \frac{64\pi \nu_{nm}^3}{3\hbar} \sum \frac{|R_n^{mk}|^2}{g_n},
\]

(9.27)
in which \( i \) and \( k \) are the indices to label the sub-levels of the states \( n \) and \( m \). The vector quantity \( R_n^{mk} \) represents the matrix elements of the electric dipole moment of the radiating system. For the upper rotational level \( n \), the degeneracy was given by \( g_n = 2J' + 1 \).

Equation 9.26 can be expressed as

\[
N_n = \frac{N g_n}{Q_r} \exp\left(-\frac{B'J'(J'+1)hc}{kT}\right).
\]

(9.28)

Inserting equation 9.27 and equation 9.28 into equation 9.26 yields

\[
\epsilon_{nm} = \frac{64\pi \nu_{nm}^4}{34\pi Q_r} \frac{C}{4\pi} \left( \sum |R_n^{mk}|^2 \right) \exp\left(-\frac{B'J'(J'+1)hc}{kT}\right).
\]

(9.29)

It is common to write equation 9.29 as

\[
\epsilon_{nm} = \frac{2C \nu_{nm}^4}{Q_r} S_J \exp\left(-\frac{F'(J' + 1)hc}{kT}\right),
\]

(9.30)

where \( C \) is a constant depending on \( N \) and \( S_J \) the so-called line strength, also referred to as Hön-London factors. The line strength is obtained via the square of the magnitude of the matrix elements \( R_n^{mk} \). In the simple case of a rotator, the following series of line strengths are found,

\[
\Delta J = +1 : \quad S_J = J + 1 \quad (R \text{ branch}),
\]

\[
\Delta J = -1 : \quad S_J = J \quad (P \text{ branch}).
\]

(9.31)

(9.32)

As a result, the intensity distribution depends on \( \Delta J \). This simplified expression is only valid for a pure rotational transition, where the coupling to electronic motions is negligible.

Equation 9.30 can be generalized by replacing \( B'J'(J'+1) \) with \( F'(J') \) and \( S_J \) by \( S_{J'} \). The Hön-London factors depend on the rotational constants of the upper and lower rotational levels. From now on, the line integrated emission coefficient \( \epsilon_{nm} \) of a rotational line with upper level \( J' \) and lower level \( J'' \) is expressed as

\[
\epsilon_{J'J''} = \frac{2\nu_{nm}^4 C}{4\pi Q_r} S_{J'} \exp\left(-\frac{F'(J')hc}{k_B T}\right).
\]

(9.33)

This expression can be used to determine the intensity of a rotational transition in which the electronic or vibrational state of the upper and lower level is different. The factor \( 2\nu_{nm}^4 C/(4\pi Q_r) \) is nearly constant for a given rotational band at a specific temperature. Therefore, equation 9.33 can be written as

\[
\epsilon_{J''} = A S_{J''} \exp\left(-\frac{F'(J')hc}{k_B T}\right),
\]

(9.34)
where $A$ is a constant and $F'(J')$ equal to the term of the upper level (equation 9.6)

$$F'(J') = B'J'(J + 1) - D'J'^2(J' + 1)^2.$$  \hspace{1cm} (9.35)

For $B'$ and $D'$, values of the vibrational state corresponding to the upper rotational level $J'$ have to be used. Equation 9.35 can be expressed as

$$\ln \left( \frac{e^{J'}}{S_{yy}^{J'}} \right) = \ln (A) - \frac{F'(J')hc}{kT_r}.$$  \hspace{1cm} (9.36)

The emission coefficients of the rotational transitions can be obtained using emission spectroscopy and the values for the H"onl-London factors are reported in literature. According to equation 9.36, the rotational temperature can be determined from the slope of a Boltzmann plot, with the $F'(J')$ value on the x-axis and the value $\ln \left( \frac{e^{J'}}{S_{yy}^{J'}} \right)$ on the y-axis.

### 9.3 Rotational temperature of $(b^1\Sigma_g^+, \nu = 0) \rightarrow (X^3\Sigma_g^-, \nu = 0)$

A rotational temperature was deduced from emission spectroscopic measurements of the atmospheric A-band of molecular oxygen. The oxygen molecule $O_2$ is a diatomic molecule with axial symmetry around the internuclear axis. The total number of electrons of $O_2$ is even, which means that the total spin is an integer. Using the general theory of the previous section, it is now possible to analyze the rotational spectrum of the transition $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$. Since $\Lambda = 0$ for the upper and lower state, the rotational and electronic coupling is described by Hund’s coupling case b and the appropriate quantum numbers are $J$, $K$ and $S$. This transition violates a number of selection rules like spin $\Delta S = 1$ (singlet – triplet) and parity (even – even parity $(g \leftrightarrow g$). The $g \leftrightarrow g$ transition only occurs as magnetic dipole radiation. As a result, $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ is a magnetic dipole transition with a low intensity of the emitted radiation.

The upper level $b^1\Sigma_g^+$ is a state with $\Lambda = 0$. Therefore, the quantum number $K$ can be equal to $K = 0, 1, 2, 3...$ Since $S = 0$ this is a singlet state and $J = K$. The lower level $X^3\Sigma_g^-$ also has $\Lambda = 0$ and the same values for $K$. In this case $S = 1$ and $J = K + 1, K, K - 1$. Thus for each $K$ value, three different values for $J$ are possible.

Since this is a $\Sigma - \Sigma$ transition, $\Delta K = 0$ is not allowed and only $\Delta K = \pm 1$ transitions have to be considered. Without the coupling between rotational and electronic motion, three rotational branches are present, namely the R branch ($\Delta J = +1$), P branch ($\Delta J = -1$) and Q branch ($\Delta J = 0$). The quantum number $\Delta K = \pm 1$ results in an extra branch. Using a superscript for the $\Delta K$-values, the following branches with corresponding H"onl-London factors are observed for the $(b^1\Sigma_g^+, \nu = 0) \rightarrow (X^3\Sigma_g^-, \nu = 0)$ transition:

- **R**R branch: $\Delta K = +1 \land \Delta J = 1$ \hspace{1cm} $S_{yy}^{J''} = 1/2J''$
- **R**Q branch: $\Delta K = +1 \land \Delta J = 0$ \hspace{1cm} $S_{yy}^{J''} = 1/2(J'' + 0.25)$
- **P**P branch: $\Delta K = -1 \land \Delta J = -1$ \hspace{1cm} $S_{yy}^{J''} = 1/2(J'' + 0.75)$
- **P**Q branch: $\Delta K = -1 \land \Delta J = 0$ \hspace{1cm} $S_{yy}^{J''} = 1/2(J'' + 1)$.
The rotational constant of the upper level in the vibrational ground state \( b^1\Sigma^+_g, \nu = 0 \) is equal to \( B' = 1.39138 \text{ cm}^{-1} \). For the lower level in the vibrational ground state \( X^3\Sigma^-_g, \nu = 0 \) this value equals \( B'' = 1.44566 \text{ cm}^{-1} \). Because \( B' - B'' < 0 \), the lines of the R branch (equation 9.12) converge slightly and the lines of the P branch diverge (see equation 9.13). The lines present in the Q branch are spaced closely together (cf. equation 9.14). The band origin is at a wavelength of 761.9 nm.

For the level \( O_2(b^1\Sigma^+_g, \nu = 0) \), values for \( B' \) and \( D' \) of the vibrational ground state corresponding to the upper rotational level \( J' \) have to be used. The \( B' \)-value is defined earlier in the text, while \( D' = 5.486 \times 10^{-6} \text{ cm}^{-1} \). Inserting these values into the term \( F'(J') \) in equation 9.36, it is possible to determine the rotational temperature from the slope of a Boltzmann plot when the intensities of the rotational transitions are measured using emission spectroscopy.

### 9.4 Experiments and results

A surfatron launcher was used to create a microwave induced oxygen plasma inside a quartz tube. The tube had an inner radius of 3 mm and was cooled using air. To estimate the dissociation degree using actinometry (chapter 10), a small amount of argon was added to the discharge. In all cases, 50 sccm of oxygen and 2 sccm of argon was used. The total pressure was varied between 4 mbar and 10 mbar and the incident power was held to a constant value of approximately 45 W. The frequency of the microwaves is fixed at 2.46 GHz. The emitted plasma light of the atmospheric band is focussed by a small lens into an optical fibre, which transports the light to the entrance slit of a 1 meter monochromator. A high pass filter was placed in between the plasma and the optical fibre in order to block the low wavelength part of the spectrum. In this way, it is prevented that higher orders interact with the true spectrum. A CCD camera was used to record the spectra.

The atmospheric band is a magnetic dipole transition with a low transition probability estimated to be around \( 0.1 \text{s}^{-1} \). Therefore, long exposure times (7 minutes) were required in order to obtain a sufficient signal to noise ratio. Moreover, an intense argon line is present and saturates the CCD at these long exposure times, hereby destroying the rotational spectrum. The argon line is a \( 4p - 4s \) transition at 763.51 nm with \( A \approx 10^7 \text{s}^{-1} \). As a consequence, it was not possible to record the \( ^3P \) (762.1 nm < \( \lambda < 776.9 \text{ nm} \)) and \( ^3Q \) (762.3 nm < \( \lambda < 776.7 \text{ nm} \)) branch. Therefore, only the measured intensities of rotational lines of the \( ^3R \) (759.5 nm < \( \lambda < 761.6 \text{ nm} \)) and \( ^3Q \) (759.4 nm < \( \lambda < 761.5 \text{ nm} \)) branch are used. It was shown that the lines of the \( R \) branch converge slightly and that the rotational lines of the \( Q \) branch are spaced closely together. Therefore, only lines which could be resolved with our spectroscopic system are used in the Boltzmann plot.

Figure 9.2 shows a CCD image and the corresponding spectrum of a rotational band measurement. This transition is characterized by a head line at 759.4 nm and an origin line at 761.9 nm. The bright line on the right side of the CCD image is caused by the argon line and is positioned at a wavelength of 763.51 nm. Figure 9.3 shows Boltzmann plots for pressures of 4 mbar, 6 mbar and 10 mbar with corresponding plasma lengths of respectively 3.0 cm, 2.8 cm and 2.3 cm. The error bar in the measured line intensity was mainly caused by the inaccuracy
of the line area and was estimated to be 3%. This figure also shows that the intensity of the rotational lines increases with increasing pressure in the studied pressure range. Since the radiative transition probability does not depend on the plasma conditions, this means that the population of this level increases with pressure.

Figure 9.2: CCD image (left) and rotational spectrum (right) of the atmospheric band measured in a 4 mbar oxygen/argon plasma. The bright line on the right side of the CCD image is caused by the Ar line and is positioned at a wavelength of 763.51 nm. The Ar line, the head line of the A-band at 759.4 nm and its origin line at 761.9 nm are clearly visible in the spectrum.

Figure 9.3: Molecular Boltzmann plot for the $^{R}Q$ branch (left) and the $^{R}R$ branch (right) of the rotational spectrum.
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The rotational temperatures derived from the $^RQ$ and the $^R\!R$ branch as function of the pressure are shown in figure 9.4. For the $^RQ$ branch, the lower $J'$ values deviate from the linear relation and are therefore not used. The error bars in the $^RQ$ and $^R\!R$ branch are mainly determined by the inaccuracies of the linear fits and are equal to 70 K and 50 K, respectively. The figure shows that the results obtained from both branches are, within error bars, in agreement with each other. The experimental results also show that the rotational temperature increases with increasing pressure.

![Figure 9.4: Rotational temperatures as function of the pressure. The error bars are mainly caused by inaccuracies of the linear fits.](image)

9.5 Discussion

9.5.1 Pressure dependance of the $O_2(b^1\Sigma_g^+)$ density

The experimental results shows that the population of the $O_2(b^1\Sigma_g^+)$ state increases with increasing pressure. The population of the $O_2(b^1\Sigma_g^+)$ level, denoted by $[O_2(b^1\Sigma_g^+)]$, is obtained using

$$[O_2(b^1\Sigma_g^+)] = \frac{P(b^1\Sigma_g^+)}{D(b^1\Sigma_g^+)}, \quad (9.37)$$

with $P$ the population term

$$P(b^1\Sigma_g^+) = [O_2(X^3\Sigma)][n_e k_1 + [O_2(a^1\Delta)] n_e k_2 + [O_2(X^3\Sigma)] [O(^1D)] k_3], \quad (9.38)$$

and $D$ the depopulation term

$$D(b^1\Sigma_g^+) = [O(^3P)] d_1 + d_2 + n_e \sum_{i=3}^{8} d_i. \quad (9.39)$$

The $k$'s and $d$'s refer to reactions that lead to population and depopulation of $O_2(b^1\Sigma_g^+)$, respectively. The list of reactions and coefficients can be found in table 9.1.
Expression. For an electron temperature of 20000 K and $T_s = 800$ K. Reaction coefficient $d_2$ is expressed in $s^{-1}$, the other coefficients in $m^3 s^{-1}$.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction rate</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2(X^3\Sigma_g^-) + e \rightarrow O_2(b^1\Sigma_g^+) + e$</td>
<td>$k_1 = 3.2410^{-16} \times \exp(-2.218/T_e)$</td>
<td>$9.0 \times 10^{-17}$</td>
</tr>
<tr>
<td>$O_2(a^1\Sigma_u^-) + e \rightarrow O_2(b^1\Sigma_g^+) + e$</td>
<td>$k_2 = 3.2410^{-16} \times \exp(-1.218/T_e)$</td>
<td>$1.6 \times 10^{-16}$</td>
</tr>
<tr>
<td>$O_2(X^3\Sigma_g^-) + O(^1D) \rightarrow O_2(b^1\Sigma_g^+) + O(^1D)$</td>
<td>$k_3 = 2.5610^{-11} \times \exp(67/T_e)$</td>
<td>$2.8 \times 10^{-17}$</td>
</tr>
<tr>
<td>$O_2(b^1\Sigma_g^+) + O(3P) \rightarrow O_2(a^1\Sigma_g^-) + O(3P)$</td>
<td>$d_1 = 8.1 \times 10^{-20}$</td>
<td>$8.1 \times 10^{-20}$</td>
</tr>
<tr>
<td>$O_2(b^1\Sigma_g^+) + \text{wall} \rightarrow O_2(X^3\Sigma_g^-) + e$</td>
<td>$d_2 = 400 \times \sqrt{T_e/300}$</td>
<td>653.2</td>
</tr>
<tr>
<td>$O_2(b^1\Sigma_g^+) + e \rightarrow O_2(X^3\Sigma_g^-) + e$</td>
<td>$d_3 = 5.6 \times 10^{-15} \exp(-2.2/T_e)$</td>
<td>$1.6 \times 10^{-15}$</td>
</tr>
<tr>
<td>$O_2(b^1\Sigma_g^+) + e \rightarrow O_2(a^1\Sigma_u^-) + e$</td>
<td>$d_4 = 5.6 \times 10^{-15} \exp(-2.2/T_e)$</td>
<td>$1.6 \times 10^{-15}$</td>
</tr>
<tr>
<td>$O_2(b^1\Sigma_g^+) + e \rightarrow O + O^+$</td>
<td>$d_5 = 7.1 \times 10^{-15} \exp(-10.23/T_e)$</td>
<td>$1.9 \times 10^{-17}$</td>
</tr>
<tr>
<td>$O_2(b^1\Sigma_g^+) + e \rightarrow O + O(^1D) + e$</td>
<td>$d_6 = 1.810^{-13} \exp(-19.96/T_e)$</td>
<td>$1.7 \times 10^{-19}$</td>
</tr>
<tr>
<td>$O_2(b^1\Sigma_g^+) + e \rightarrow O^+ + 2e$</td>
<td>$d_7 = 9.010^{-16} \exp(-14.23/T_e)$</td>
<td>$2.3 \times 10^{-19}$</td>
</tr>
<tr>
<td>$O_2(b^1\Sigma_g^+) + e \rightarrow O + O^+ + 2e$</td>
<td>$d_8 = 5.310^{-16} T_e^{0.9} \exp(-21.62/T_e)$</td>
<td>$3.1 \times 10^{-21}$</td>
</tr>
</tbody>
</table>

Because the energy difference between the first excited O($^1D$) and the atomic ground state O($^3P$) as well as the energy difference between the first molecular excited state O$_2$(a$^1\Delta$) and the molecular ground state O$_2$(a$^1\Lambda$) are small, it is expected that these excited levels are in a Boltzmann/Saha equilibrium with the atomic and molecular ground states. Therefore, these densities can be expressed as

$$[O(^1D)] = [O(^3P)] \times \frac{g_{1D}}{g_{3P}} \exp\left(\frac{-(E_{1D} - E_{3P})}{k_B T_e}\right) \equiv [O(^3P)] C_{BA},$$

(9.40)

$$[O_2(a^1\Delta)] = [O_2(X^3\Sigma)] \times \frac{g_{a1\Delta}}{g_{X^3\Sigma}} \exp\left(\frac{-(E_{a1\Delta} - E_X)}{k_B T_e}\right) \equiv [O_2(X^3\Sigma)] C_{BM},$$

(9.41)

where $C_{BA}$ and $C_{BM}$ depend on the electron temperature and follow from the Boltzmann expression. For an electron temperature of $T_e = 20000$ K, we obtain $C_{BA} = 0.18$ and $C_{BM} = 0.19$. The population of O$_2$(b$^1\Sigma_g^+$) can be written in terms of [O$_2$(X$^3\Sigma$)]:

$$P(O_2(b^1\Sigma_g^+)) = [O_2(X^3\Sigma)] \times (n_e k_1 + n_e C_{BM} k_2) + [O(^3P)] C_{BA} k_3.$$  

(9.42)

For an electron density $n_e \sim 10^{18}$ m$^{-3}$ and a dissociation ratio $[O]/[O_2(X^3\Sigma)]$ of 10%, it can easily be shown that the third term on the right hand side that describes the quenching reactions is negligible compared to electron induced excitations (first and second term). Using the same values, it can be shown that depopulation mainly occurs via electron impact deexcitation towards lower molecular states. The wall reactions and quenching reactions are too slow to be of importance. Equation 9.37 reduces to:

$$[O_2(b^1\Sigma_g^+)] = \frac{k_1 + C_{BM} k_2}{d_3 + d_4}.$$  

(9.43)

Therefore, this level is mainly populated by collisions of electrons with ground state molecules and collisions between electrons and metastable molecules. Depopulation also
occurs via electron impact de-excitation. As a result, the population of \( [O_2(b^1\Sigma^+_g)] \) is independent of the electron density and proportional to the molecular ground state density. Because an increase in the pressure directly results in a higher number of oxygen molecules in the ground state, the population of \( O_2(b^1\Sigma^+_g) \) increases with pressure.

At 10 mbar, the gas temperature was found to be 900 K. Using the ideal gas law, this results in \( [O_2(X^3\Sigma^-_g)] \approx 10^{23} \text{ m}^{-3} \). Inserting this density and the values presented in table 9.1 into equation 9.43 yields \( [O_2(b^1\Sigma^+_g)] \approx 3 \times 10^{21} \text{ m}^{-3} \).

The radiative lifetime of the \( O_2(b^1\Sigma^+_g) \) level is around 10 s which results in a transition probability of only 0.1 s\(^{-1}\). As the integration time was equal to 420 s, about \( 10^{23} \text{ m}^{-3} \) events occur. A typical Ar(4p \( - 4s \)) transition has a 4p density of \( 4 \times 10^{15} \text{ m}^{-3} \), a transition probability of \( 10^7 \text{ s}^{-1} \) and an integration time of 1 s (cf. chapter 2), which results in \( 4 \times 10^{22} \) emission events per unit of volume. This value is comparable to that of the A-band. As a result, it can be concluded that the high population density of the \( O_2(b^1\Sigma^+_g) \) level enabled the intensity measurement of the very weak A-band transition.

9.5.2 Pressure dependance of the gas temperature

The second experimental observation is that the gas temperature increases with pressure. According to [10], the stationary gas thermal balance can be expressed as

\[
\frac{8\lambda(T_g)}{R^2}(T_g - T_w) = Q_{in}, \tag{9.44}
\]

where \( R \) is the inner radius of the tube, \( \lambda \) the thermal conductivity, \( T_w \) the wall temperature and \( Q_{in} \) the net power transfer per unit volume from different heat sources. In this one dimensional expression, only radial heat conduction is taken into account as a cooling mechanism. Axial heat transport is not important because the gas temperature is more or less homogenous along the axis. In molecular plasmas, dissociation of molecules is an important heat source. Also, wall reactions can be important. According to [11], the following dissociation reactions,

\[
\begin{align*}
O_2(X^3\Sigma) + e &\rightarrow O(^3P) + O(^1D) + e; \quad K_a \quad \Delta E_a = 1.3 \text{ eV} \tag{9.45} \\
O_2(X^3\Sigma) + e &\rightarrow O(^3P) + O(^3P) + e \quad K_b \quad \Delta E_b = 0.9 \text{ eV} \tag{9.46}
\end{align*}
\]

can lead to gas heating via the creation of hot atoms. The heating term due to dissociative excitation can be expressed as

\[
Q_{in} = n_e[O_2(X^3\Sigma)](K_a\Delta E_a + K_b\Delta E_b). \tag{9.47}
\]

An increase in pressure leads to more oxygen molecules in the ground state which results in more heating via the dissociative term. It is also suggested that exothermic wall reactions involving O(^3P) or O\(_2(b^1\Sigma)\) are an important heating source. Due to the higher density of the \( O_2(b^1\Sigma) \) state at higher pressures, also the heating due to exothermic wall reactions is enhanced. Both terms result in a higher heating source and therefore in a higher gas temperature. This corresponds to our experimental results, where the measured rotational temperature values are higher for higher pressures.
9.6 Conclusion

The aim of the study described in this chapter was to determine the gas temperature of a surfatron induced oxygen plasma using emission spectroscopy. The rotational spectrum of the atmospheric A band transition \((b^1\Sigma^+_g, \nu = 0) \rightarrow (X^3\Sigma^-_g, \nu = 0)\) has been measured in a low pressure \((4 - 10 \text{ mbar})\) oxygen discharge in which a small amount of argon was added. The rotational temperature was derived from the spectrum using a molecular Boltzmann plot. In the work of [2], it was experimentally validated that the rotational temperature of \(O_2(b^1\Sigma)\) of a low pressure oxygen plasma is equal to the gas temperature. Thus enough collisions occur before the \(O_2(b^1\Sigma)\) level is de-excited to a lower state. These collisions lead to an equilibrium between the rotational and kinetic temperature.

In this chapter, a short summary of the general theory of the rotational spectrum and molecular emission spectroscopy has been given. This theory has been used to describe the shape of rotational spectrum of the transition \(b^1\Sigma^+_g \rightarrow X^3\Sigma^-_g\). For this transition, the coupling between rotational and electronic motion is described by Hund’s coupling case \(b\). The rotational spectrum consists of four branches, namely \(R R\), \(R Q\), \(P P\) and \(P Q\). The lines of the \(R\) branch converge slightly, the lines of the \(P\) branch diverge whereas lines present in the \(Q\) branch are spaced closely together. The band origin is at a wavelength of 761.9 nm. Due to the presence of an intense argon line at 763.51 nm it was not possible to measure the \(P P\) \((762.1 \text{ nm} < \lambda < 776.9 \text{ nm})\) and \(P Q\) \((762.3 \text{ nm} < \lambda < 776.7 \text{ nm})\) branch. Therefore, only the intensities of rotational lines of the \(R R\) \((759.5 \text{ nm} < \lambda < 761.6 \text{ nm})\) and \(R Q\) \((759.4 \text{ nm} < \lambda < 761.5 \text{ nm})\) branch were used. Depending on the pressure, the gas temperatures derived from separate Boltzmann plots of the \(R R\) and \(R Q\) branches are in a good or reasonable agreement with each other.

The experimental results show that both the intensity of the measured rotational lines and the gas temperature increase with pressure. Because the intensity is related to the population density of \(b^1\Sigma^+_g\), also the population density of this level increases. This level is effectively populated by collisions with electrons and the oxygen molecules \(O_2(X^3\Sigma^-_g)\) and \(O_2(a^1\Sigma^-_g)\). Depopulation reactions of this level are ineffective. Therefore, as the densities of the molecules \(O_2(X^3\Sigma^-_g)\) and \(O_2(a^1\Sigma^-_g)\) increase with pressure, also the population of the emitting \(b^1\Sigma^+_g\) state is increased. Due to the higher molecular densities and exothermic wall reactions involving \(b^1\Sigma^+_g\), the gas temperature is increased.

Bibliography


Application of actinometry to a microwave induced oxygen plasma at low and intermediate pressures

Abstract. Actinometry is a method that aims to determine the dissociation degree of molecular plasmas. In this work, actinometry is applied to an oxygen discharge in which a small amount of argon is added. The method is based on the ratio of line intensities between selected atomic oxygen and argon lines. A diagnostic validation is performed to test whether this method could be applied to a larger pressure range. Via a diagnostic verification, it is found that the argon strongly influences the plasma at pressures higher than 10 mbar. Line intensities are obtained in an absolute way and rotational band measurements have been made to determine the gas temperature. The actinometry method is applied to two argon/oxygen line pairs, namely O[844.6]/Ar[811.5] and O[777.3]/Ar[750.4]. Using a classical expression, the atomic ground state density of oxygen can directly be determined from this ratio. However, also other reaction processes can populate and depopulate the actinometry levels. These different processes are included in the general expression which makes it possible to determine the dissociation ratio and ground state density in an iterative way. Dissociation ratios derived from the line intensity ratio O[844.6]/Ar[811.5] are more or less as expected, results deduced from O[777.3]/Ar[750.4] are too high. To explain the differences between results found for both line pair ratios and to improve the accuracy of the expressions, the influence of deviations from a Maxwellian distribution function is investigated. It is found that using a non-Maxwellian distribution function to calculate rate coefficients decreases the dissociation ratio and reduces the influence of the molecular population term. The differences between both line pairs cannot be explained by deviations from Maxwell. A possible explanation might be that O[777.3] is strongly populated by dissociative excitation of metastable oxygen levels.
Chapter 10.

10.1 Introduction

Microwave induced oxygen plasmas are often used in industry. At very low pressures of about $10^{-3}$ mbar, oxygen based plasmas are for example used for the etching of polymer films [1]. Another example of an industrial oxygen based plasma at higher pressures is the so-called Plasma activated Chemical Vapour deposition (PCVD) process [2] used in the production process of optical fibres. Here, a plasma in the intermediate pressure range (in between 5 and 20 mbar) is used. Due to the high microwave powers these industrial plasmas are often shielded. Therefore, it is difficult to apply laser aided diagnostics such as (two photon) laser induced fluorescence (LIF) or Thomson scattering. These methods are generally used to determine important plasma parameters such as the electron density, electron temperature and dissociation degree. Especially the dissociation degree is an important parameter in molecular plasmas. A possible method that can be applied under industrial conditions is actinometry. It is a technique that can be used to monitor the oxygen atom concentration by a simple intensity measurement of the 844.6 nm or 777.3 nm line emitted by excited oxygen atoms and the 811.5 nm or 750.4 nm line emitted by argon that is introduced into the discharge as the actinometer. In most cases, it was assumed that the levels of interest are ruled by the corona balance, thus that these levels are populated by Maxwellian electron excitation of atoms in the ground level and depopulated by radiative decay. Hereafter, this will be referred to as classical actinometry.

In the past, the validity of the actinometry technique was investigated and compared with other techniques by several groups. Booth [1], compared actinometry with resonance absorption measurements in a low pressure ($(1-8) \times 10^{-3}$ mbar) electron cyclotron resonance plasmas. In that study it was found that the classical method fails because the 844.6 nm emitting oxygen level is strongly populated by molecular dissociation. Also, the rate coefficients strongly depend on the electron distribution function. In such a situation, the actinometry signal is not only related to the atomic but also to the molecular oxygen density. In the work of Katsch [3], a good agreement between results based on actinometry of the O[844.6] line and TALIF measurements was observed for a pressure of around 0.2 mbar. In that study, a model of the discharge was employed to determine the electron energy distribution function. Granier [4] studied a microwave induced O$_2$ surfatron plasma at a pressure of 1.3 mbar and compared the actinometry results with VUV absorption measurements. Compared to the classical case, excitation rates were determined with a modelled electron energy distribution function (EEDF) while quenching processes were included. A good agreement with the VUV results was obtained when the oxygen 844.6 nm and the argon 750.4 nm line were used. Pagnon [5] investigated current driven molecular oxygen plasmas inside a Pyrex tube in the pressure range 0.5 to 2.6 mbar, and also compared results with VUV absorption measurements. A good agreement was found when quenching and molecular dissociation processes were included. To conclude, the actinometry method has been applied to various oxygen plasmas in a pressure range from $\sim 10^{-3}$ to 3 mbar. Around the maximum pressure of 3 mbar, reasonable results are only obtained when correction terms for dissociative excitation and quenching are included.

The aim of this study is to investigate whether actinometry can be applied to a microwave induced oxygen plasma in the pressure range between 5 and 20 mbar. This means that the pressure range to which actinometry is generally applied has to be extended. This will be done
using two different methods: an experimental and a theoretical one. After that the theoretical method will be used to determine the dissociation ratio of a surfatron induced oxygen plasma.

A diagnostic validation was performed to test whether the pressure range could be extended to a larger pressure range. The intensities of the argon and oxygen actinometry levels were measured for different oxygen argon flow ratios. It was directly clear that the method becomes very inaccurate at pressures of 15 and 20 mbar because the argon addition significantly enhanced the intensity of the oxygen line emission.

In this chapter, it is shown that deviations from the classical expression can be included in coefficients. In this way, it is relatively easy to add extra contributions like the collisional radiative (CR) model correction, a term which describes all atomic population and depopulation processes. It is expected that this term is increasingly important for pressures higher than ∼ 1 mbar for which the corona balance breaks down and much more population and depopulation processes of the actinometry levels become relevant. Especially at higher electron densities, ladder-like excitation processes enhance the effective excitation rate. Correction terms for quenching, molecular dissociation and atomic collisional radiative processes are constructed.

The constructed theoretical expressions are applied in an iterative way in order to determine the atomic oxygen ground state density and dissociation ratio from the experimental results. The experimental results are the absolutely measured intensities of the O[844.6]/Ar[811.5] and O[777.3]/Ar[750.4] line pairs, the gas temperature and the total pressure. The gas temperature was obtained via a measurement of the rotational spectrum of the atmospheric oxygen band (cf. chapter 9) and the pressure was measured on both sides of the tube. The total particle density was obtained via the pressure and the gas temperature. The influence of deviations from a Maxwellian distribution function was discussed separately. It was found that using a non-Maxwellian distribution to calculate rate coefficients decreases the dissociation ratio and reduces the influence of the molecular population term. The atomic oxygen density derived from the O[777.3]/Ar[750.4] line pair was larger than from the O[844.6]/Ar[811.5] line ratio. Using the CR-model correction or the modelled EEDF did not bring the results closer together. Following the results of previous studies [1, 4], the O[844.6]/Ar[811.5] line pair ratio is expected to give the most accurate result since the results of this line pair corresponded with those of active spectroscopy.

This article starts with a description of the experimental setup and diagnostic methods in section 10.2, followed by the diagnostic validation in section 10.3. In section 10.4 and 10.5, the classical and generalized actinometry methods are discussed. The actinometry systems are shown in section 10.6, results are presented in section 10.7. In section 10.8, the influence of the electron energy distribution on the actinometry results is presented, followed by the discussion and conclusions in section 10.9.
10.2 Experimental configuration

10.2.1 Experimental setup

A surfatron launcher was used to create a microwave induced oxygen plasma inside a quartz tube. The tube has an inner radius of 3 mm and was cooled using air. To estimate the dissociation degree using actinometry, a small amount of argon was added to the discharge. In all cases, we used 50 sccm of oxygen and 2 sccm of argon. The total pressure was varied between 4 mbar and 10 mbar and the input power had a constant value of approximately 45 W. The frequency of the microwaves is fixed at 2.46 GHz. The emitted plasma light is focussed by a small lens into an optical fibre, which transports the light to the entrance slit of a 1 meter monochromator equipped with a grating of 1200 lines/mm. A CCD camera with a horizontal pixel width of 7 µm is attached to the monochromator and has been used to record the spectra. This setup, described in detail in chapter 2, enabled us to measure the emitted plasma light along a radial line of sight at a specific axial position.

10.2.2 Absolute line intensity measurements

Absolute measurements of optically thin spectral lines can be used to determine densities of excited states in a plasma. The measured intensities of spectral lines have to be calibrated with a light source of which the intensity is accurately known. A tungsten ribbon lamp operated at an accurately known electric current can be used for this purpose. The obtained emission coefficient \( j(p, q) \) in Wm\(^{-3}\)nm\(^{-1}\)sr\(^{-1}\) for a transition from an upper level \( p \) to a lower level \( q \) is related to the density of the upper level \( n(p) \) via

\[
j(p, q) = n(p)A(p, q)E(p, q)/(4\pi),
\]

where \( n(p) \) is the population density of level \( p \), \( A(p, q) \) the transition probability and \( E(p, q) = E(p) - E(q) = h\nu(p, q) \). As the plasma is optically open for the radiation, the density of the level is proportional to the transition integrated intensity

\[
I(p, q) = \int_0^L j(p, q)dl = j(p, q)L = n(p)A(p, q)E(p, q)L/(4\pi)
\]

with \( L \) the plasma depth. In the second step it is assumed that the plasma is homogenous along the line of sight. This severe constraint can be relaxed in reality. For actinometry, it is sufficient if the spatial profiles of the relevant Ar and O lines are the same.

The experimental actinometry ratio, \( J^* \), is equal to the measured intensity ratio of the argon and oxygen actinometry lines:

\[
J^* = \frac{I^O(3, 2)}{I^{Ar}(3, 2)} = \frac{n^O(3)A^O(3, 2)E^O(3, 2)L^O/(4\pi)}{n^{Ar}(3)A^{Ar}(3, 2)E^{Ar}(3, 2)L^{Ar}/(4\pi)}.
\]

Since \( L^O = L^{Ar} = L \), the measured actinometry ratio \( J^* \) can be expressed as,

\[
J^* = \frac{j^O(3, 2)}{j^{Ar}(3, 2)} = \frac{n^O(3)A^O(3, 2)E^O(3, 2)}{n^{Ar}(3)A^{Ar}(3, 2)E^{Ar}(3, 2)}.
\]
not required. However, it is still important to determine whether the sensitivity of the spectrometer is the same for the selected wavelengths. In this study a relatively high resolution monochromator was used so that the actinometry lines could not be measured during one single measurement. Therefore, these lines were measured in an absolute way.

The aim of actinometry is to determine the ground state density ratio \( n_O(1)/ n_{Ar}(1) \) from the measured actinometry signal \( J^* \). Therefore, theoretical expressions are required to relate \( n_O(3)/ n_{Ar}(3) \) to \( n_O(1)/ n_{Ar}(1) \). Because \( n_{Ar}(1) \) can be determined experimentally, it is possible to deduce the atomic oxygen ground state density \( n_O(1) \). This is the subject of the sections 10.4 and 10.5.

10.2.3 Rotational band measurements

An important parameter needed in this study is the gas temperature. Inserting the measured pressure and the gas temperature into the ideal gas law yields the total particle density. In the previous chapter, it was shown that the gas temperature can be determined from molecular emission spectroscopy. An emission spectroscopic measurement of the atmospheric A-band transition \( (b^1 \Sigma_g^+ \rightarrow X^3 \Sigma_g^-) \) of molecular oxygen \((O_2)\) yields a molecular Boltzmann plot from which the rotational temperature can be deduced. As discussed in the previous chapter and in the work of [6, 7], it is likely that the measured rotational temperature is close to the gas temperature. Therefore, this temperature will be used in order to determine the total number of particles in the plasma.

10.3 Diagnostic validation

Actinometry can only be used when the addition of argon does not influence the oxygen plasma. Thus when the intensity of an oxygen line changes by adding argon to the plasma, an obvious interaction between the argon and oxygen system is present and the actinometry method is not applicable. This is the subject of this section, in which we report the intensity measurements of the actinometry lines for increasing argon flows \( Q_{Ar} \) at a constant oxygen flow \( Q_{O_2} \) and microwave power. The argon concentration is defined by \( Q_{Ar}/( Q_{Ar} + 2 Q_{O_2}) \).

Results for 5 mbar and 10 mbar are shown in figure 10.1 and for 15 mbar and 20 mbar in figure 10.2. Figure 10.1 shows that the absolute intensities of the oxygen lines are more or less constant up to the addition of 5% Ar. Over the total range, the intensity of the argon lines increases with increasing argon concentrations. It means that it is not likely that important plasma parameters like the electron temperature and electron density will change due to the argon addition.

The behaviour of the oxygen lines at pressures higher than 10 mbar is different. Here, the intensity of the oxygen lines already increases for low amounts of added argon (1%). According to these diagnostic results, it can be concluded that the actinometry method can not be applied to the pressure range in between 15 mbar and 20 mbar without changing the plasma properties. For pressures of 10 mbar and lower it is required that the argon concentration is below 5%.
Figure 10.1: Measured absolute line intensities for increasing argon concentrations. The oxygen flow is 50 sccm, the argon flow is increased from 1.1 sccm to 20 sccm. The total pressure is 5 mbar (left) and 10 mbar (right) and the absorbed power equals 38 W.

Figure 10.2: Measured absolute line intensities for increasing argon concentrations at pressures of 15 mbar (left) and 20 mbar (right). The symbols are the same as used in figure 10.1.

10.4 Classical actinometry: the Maxwellian corona balance

Actinometry is a method that aims to determine the dissociation degree and atomic state density of molecular plasmas; for instance an oxygen plasma. To that end, a small amount of argon is added to an oxygen discharge. The method is based on the ratio of line intensities between selected atomic oxygen and argon lines.

The interpretation is usually based on the assumption that radiation is emitted by levels that are ruled by the corona balance (CB). In the corona balance, the upper states are populated by direct excitation from the atomic ground state and depopulated by radiative
Actinometry applied to a low pressure oxygen plasma
decay. The emission radiated away during this decay is the so-called actinometry signal. It is assumed that no other processes of the upper level are relevant. This situation is shown in figure 10.3 and will be referred to as classical actinometry. The ground level is denoted by "1", the upper level by "3" and the lower level of the radiative transition is denoted by "2".

$$E_1 \longrightarrow \text{Level "3"}$$
$$A_32$$
$$E_2 \longrightarrow \text{Level "2"}$$
$$k_1 (1,3)$$
$$E_i = 0 \longrightarrow \text{Level "1"}$$

Figure 10.3: Representation of the corona balance.

In classical actinometry, the relevant levels are ruled by the corona balance, which means that the particle balance for level "3" can be expressed as

$$n_e n(1) k_e (1,3) = n(3) A(3, 2), \quad (10.5)$$

where the term on the left-hand side describes the population of level "3" which occurs by electron collisions with ground state atoms and the term on the right-hand side describes depopulation due to radiative decay. This production/destruction balance for level "3" gives the following relation between the density of this level and the corresponding ground state:

$$n(3) = n(1) n_e k_e (1,3)/A(3, 2). \quad (10.6)$$

Substituting of this expression for O and Ar into equation 10.4 gives the following theoretical expression for the actinometry ratio

$$J_{\text{CL}} = \frac{k_e^O (1,3) n_O}{k_e^{\text{Ar}} (1,3) n_{\text{Ar}}} \frac{E^O (3, 2)}{E^{\text{Ar}} (3, 2)}. \quad (10.7)$$

For brevity the ground state densities of argon $n_{\text{Ar}} (1)$ and oxygen $n_O (1)$ are denoted by $n_{\text{Ar}}$ and $n_O$ respectively, while the subscript CL indicates that this is the actinometric ratio as predicted by classical actinometry. Note that a distinction is made between the notation of the measured actinometry ratio $J^*$ and the theoretical expression of this ratio $J$. In this case $J_{\text{CL}}$ is the theoretical expression as obtained by classical actinometry. If the conditions of classical actinometry are satisfied and thus $J^* = J_{\text{CL}}$ the atomic ground state density of oxygen can be obtained using

$$n_O = n_{\text{Ar}} J^* \times \frac{k_e^{\text{Ar}} (1,3)}{k_e^O (1,3)} \times \frac{E^{\text{Ar}} (3, 2)}{E^O (3, 2)}. \quad (10.8)$$
Chapter 10.

The derivation given above shows that the expression of $J_{CL}$ is based on the following assumptions:

1. There is no interaction between the argon and oxygen systems.
2. The population via other (metastable) atomic levels is negligible compared to direct electron impact excitation from the ground state.
3. Population of excited levels via molecular dissociation routes is not included.
4. Depopulation takes place via one radiative decay channel creating the actinometry signal, thus de-excitation to higher or lower states caused by electron impact or quenching is not allowed.

Hereafter, the actinometry problem will be approached as general as possible in order to determine correction factors that relate the general actinometry ratio to the classical case. An extra assumption for the classical actinometry case is that the excitation impact excitation rates are determined using a Maxwellian EEDF. The influence of a non-Maxwellian EEDF on the actinometry signal is investigated separately from the other contributions in section 10.8.

10.5 Generalization of the actinometry method

In the general case, the levels are not ruled by the corona balance. A CR-model has to be constructed that consists of a set of balance equations. For an atomic state $p$, the particle balance is given by

$$\left( \frac{\partial n_p}{\partial t} \right)_{CR} = \frac{\partial n_p}{\partial t} + \nabla \cdot n_p w_p,$$

in which $n_p$ is the number density of state $p$ and $w_p$ is the velocity of this state. This equation expresses how local collisional radiative (CR) processes lead to accumulation $\partial n_p/\partial t$ or efflux $\nabla \cdot n_p w_p$ of the particles. Typical time scales for transport related processes are in most cases larger than $10^{-4}$s. This is much larger than time scales for CR processes of excited atoms and molecules, which are in the order of $10^{-7}$ s. This means that for these species the local production processes are balanced with the local destruction processes so that transport can be neglected. This simplifies equation (10.9) into

$$\left( \frac{\partial n_p}{\partial t} \right)_{CR} = 0$$

This is called the Quasi Steady State Solution (QSSS). For the plasmas under study, it is assumed that it can be applied to all excited levels.

By applying the QSSS to level "3", the density of this level can be expressed as the ratio between the production term and destruction factor,

$$n(3) = P(3)/D(3),$$

with

$$P(3) = \sum_{j \neq 3} n_j D(j, 3),$$

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Actinometry applied to a low pressure oxygen plasma

Describing all processes that results in population and depopulation being the total depopulation or destruction-factor of level "3". Here, $D(j, i)$ stands for the frequency of the destruction of level "j" that leads to a population of the level "i". In general, it reads

$$D(j, i) = A(j, i) + n_e k_e(j, i) + n_Y k_Y(j, i)$$

and consist of the transitions due to radiative decay, electron impact and impact by the particle $Y$ which can be an atom, ion, molecule or molecular ion.

Substituting equation 10.11 into equation 10.4 yields the following general theoretical expression,

$$J = \frac{P^O(3)}{P^A(3)} \frac{A^O(3, 2) E^O(3, 2)}{A^A(3, 2) E^A(3, 2)}$$

Before dealing with the general case, it will be confirmed that the equations 10.11-10.14 include the classical actinometry expression. In the corona limit, level "3" is populated by direct electron impact excitation, $P(3) = n_e n(1) k_e(1, 3)$ and depopulated by radiative transitions to level "2", $D(3) = A(3, 2)$. Inserting these terms into equation 10.11 gives $n(3) = n_e n(1) k_e(1, 3) / A(3, 2)$. Substituting this expression of $n(3)$ for both oxygen and argon into 10.15 results in the classical actinometry signal (cf. equation 10.8) as obtained in the previous section.

The departure from classical actinometry can now be cast in the following equation

$$J = C_P C_Q C_{CRM} J_{CL},$$

where the correction factors take other effects into account. The first factor $C_P$ refers to additional population channels, $C_Q$ to quenching and $C_{CRM}$ to the CR-model correction. Hereafter, the various factors will be discussed guided by table 10.1 where the first line refers to classical population and depopulation contribution. Moving downwards more population and depopulation contributions are taken into account. Besides the molecular terms, the processes that lead to population and depopulation of the argon level "3", Ar(3), are the same as for O(3). This corresponds to the expressions in table 10.1 that are related to the correction factors $C_{CL}$ and $C_{CRM}$.

10.5.1 Population

In this subsection, an expression for the first correction factor $C_P$, referring to the additional population channels, is derived. Various reaction channels via big density reservoirs can lead to the population of the radiating actinometry levels. In general, this can be expressed as

$$J = C_P J_{CL},$$

with

$$C_P = \frac{1 + \left( \sum_{\alpha \neq 1} n_\alpha^O D^O(\alpha, 3) \right) / \left( n_e n_O(1) k_e^O(1, 3) \right)}{1 + \left( \sum_{\alpha \neq 1} n_\alpha^A D^A(\alpha, 3) \right) / \left( n_e n_A(1) k_e^A(1, 3) \right)}.$$
### Chapter 10.

#### Table 10.1: Important population and depopulation processes of the oxygen level ”3”

<table>
<thead>
<tr>
<th>Population</th>
<th>Depopulation</th>
<th>Depopulation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron excitations</td>
<td>Radiative decay</td>
<td></td>
</tr>
<tr>
<td>$e + O(1) \rightarrow e + O(3)$</td>
<td>$O(3) \rightarrow O(2) + h \nu_{32}$</td>
<td>$C_{CL}$</td>
</tr>
<tr>
<td>Step excitation</td>
<td>Step de-excitation</td>
<td></td>
</tr>
<tr>
<td>$e + O(2) \rightarrow e + O(3)$</td>
<td>$e + O(3) \rightarrow e + O(2)$</td>
<td>$C_{CRM}$</td>
</tr>
<tr>
<td>Electron de-excitation ($i &gt; 3$)</td>
<td>Electron de-excitation ($i &gt; 3$)</td>
<td></td>
</tr>
<tr>
<td>$e + O(i) \rightarrow e + O(3)$</td>
<td>$e + O(3) \rightarrow e + O(i)$</td>
<td>$C_{CRM}$</td>
</tr>
<tr>
<td>Radiative cascade</td>
<td></td>
<td>$C_{CRM}$</td>
</tr>
<tr>
<td>$O(4) \rightarrow O(3) + h \nu_{43}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Two electron recombination</td>
<td></td>
<td>$C_{CRM}$</td>
</tr>
<tr>
<td>$e + e + O(+) \rightarrow e + O(3)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radiative recombination</td>
<td></td>
<td>$C_{CRM}$</td>
</tr>
<tr>
<td>$e + O(+) \rightarrow O(3) + h \nu$</td>
<td></td>
<td>$C_{CRM}$</td>
</tr>
</tbody>
</table>
| Dissociative excitation | | $C_{P}$
| $e + O_2 \rightarrow e + O(3) + O(1)$ | Quenching | $C_{Q}$
| | $O(3) + O_2 \rightarrow O(j) + O_2$ | |
| | Quenching | $O(3) + O_2 \rightarrow O(1) + O_2$ | $C_{Q}$ |

where $D(\alpha, 3)$ stands for the destruction frequency of species $\alpha$ that leads to a population of the level ”3”. The denotation $\alpha$ refers to big particle reservoirs such as the molecular, atomic or ionic ground state. Generally, the roman letters $i, j, ..$ refers to excited atomic states. In this subsection, the following main density reservoirs are considered.

- The ground state of the atomic systems.
- The ionic ground state.
- The molecular ground state.

#### The atomic ground state

The ground state of the atomic systems is denoted by $\alpha = ”1”$ and the atomic ground state density by $n(1)$. Electron impact collisions with atoms in the ground state lead to the production term $n_e n(1) k_e(1, 3)$. This is the classical production and, as can be seen in equation 10.18, will serve as a normalization.

#### The ionic ground state

The ionic ground state is given by $\alpha = +$ and the corresponding density $n_\alpha = n(+)$. Level ”3” can now be populated by means of recombination,

$$n_\alpha D(\alpha, 3) = n(+) \left( n_e^2 k_e^3 (+, 3) + n_e^2 k_e^3 (+, 3) \right).$$

(10.19)
Due to the relatively low electron and atomic ion densities, this contribution is negligible compared to the other population terms. This is related to the fact that the plasma under study is strongly ionizing.

**The molecular ground state**

In this case the role of $\alpha$ is played by $O_2$, thus $\alpha = O_2$ and the corresponding density $n_\alpha = n_{O_2}$. Due to molecular dissociation by electron impact, i.e. $e + O_2 \rightarrow e + O(3) + O$, the radiating actinometry level is populated with a contribution equal to

$$n_\alpha D(\alpha, 3) = n_e n_{O_2} k_{de}^O,$$

(10.20)

where $k_{de}$ is the dissociative excitation rate. It is obvious that this dissociation route is not present for argon levels so that the denominator of equation 10.18 equals unity. Inserting equation 10.20 into equation 10.18 results in:

$$C_P = 1 + \frac{n_{O_2} k_{de}^O}{n_O k_e^O(1, 3)}.$$

(10.21)

With this expression a boundary criterion can be formulated. The contribution of dissociation reactions to the actinometry signal is negligible provided

$$\frac{n_{O_2} k_{de}^O}{n_O k_e^O(1, 3)} << 1.$$

(10.22)

Setting the boundary at 0.1 leads to the following critical value for the dissociation ratio:

$$\alpha_{\text{dis}} > \alpha_{\text{crit}} \text{ dis} \quad \text{with} \quad \alpha_{\text{crit}} \text{ dis} = 10 \frac{k_{de}^O}{k_e^O(1, 3)},$$

(10.23)

where $\alpha_{\text{dis}}$ is the atom to molecule ratio:

$$\alpha_{\text{dis}} = \frac{n_O}{n_{O_2}}.$$

(10.24)

In section 10.6, numerical values of $\alpha_{\text{crit}} \text{ dis}$ will be determined for the actinometry systems under study.

**10.5.2 Depopulation and quenching**

Various quenching and radiative processes can lead to the depopulation of the radiating actinometry level "3". In general, this can be expressed as

$$J = J_{\text{CL}} C_Q,$$

(10.25)

with

$$C_Q = \frac{A^O(3)/D^O(3)}{A^A(3)/D^A(3)}.$$

(10.26)

where $D(3)$ stands for the total destruction frequency of level "3". This frequency is obtained when the equations 10.13 and 10.14 are applied to level "3"
\[ D(3) = \sum_{i<3} A(3, i) + n_e \sum_{i \neq 3} k_e(3, i) + n_y k_y n_{O_2} k_Q. \] (10.27)

For the moment, we confine ourselves to the last term and take the colliding particle \( y = O_2 \) as a collision partner so that equation 10.26 can be expressed as

\[ C_Q = \frac{A^O(3, 2)}{A^A(3, 2)} \frac{A^A(3, 2)}{A^O(3, 2) + n_{O_2} k_Q^O} = \frac{1}{1 + n_{O_2} k_Q^O / A^O(3, 2)}. \] (10.28)

The classical expression is obtained when \( C_Q \) reaches unity, thus when

\[ \frac{n_{O_2} k_Q^O}{A^O(3, 2)} << 1. \] (10.29)

In analogy with the dissociation (cf. equation 10.23), we can now define a boundary condition. For

\[ n_{O_2} << n_{O_2}^{\text{crit}} \text{ with } n_{O_2}^{\text{crit}} = 0.1 \frac{A^O(3, 2)}{k_Q^O}, \] (10.30)

the effect of quenching can be neglected.

In section 10.6, numerical values of \( n_{O_2}^{\text{crit}} \) will be determined for the actinometry systems under study. Other depopulation mechanisms of level "3" that are not included in the actinometric transition with frequency \( A(3, 2) \) can, as demonstrated by equation 10.27, be radiative in nature and electron induced. These processes are dealt with in the CR-model correction.

10.5.3 The CR-model correction

In the classical expression it is assumed that the actinometry levels are populated by electron excitations from the ground state and depopulated by radiative decay transitions. At higher electron densities, levels can be populated by stepwise excitation processes, for instance via \( 1 \rightarrow 2 \rightarrow 3 \). Therefore, the method can be improved when a CR-model is used to relate the intensity ratios with the atomic ground state densities. These CR-models are based on atomic transitions only, so quenching and molecular processes are not included. In the framework of atomic CR-models, the density \( n_p \) of an exited level \( p \) can be seen as composed out of two contributions, one from the atomic \( n_1^p \) and the other from the ionic ground level \( n_p^+ \):

\[ n_p = n_p^+ + n_1^p. \] (10.31)

Here, \( n_p^+ \) corresponds to the CR-model solution for the case that the atom ground level density is put equal to zero, and \( n_1^p \) with the solution for the case that the ion ground levels are set to zero [8].

These contributions can be related by their equilibrium quantities [9]. The \( n_1^p \) value can be related to the Boltzmann population density and \( n_p^+ \) to the Saha population density via

\[ n_1^p = r_1^p n_p^B \] (10.32)

and

\[ n_p^+ = r_p^+ n_p^S. \] (10.33)
The dimensionless quantities $r_p^+$ and $r_p^1$ are known as the relative population coefficients. In a strongly ionizing plasma the ion contribution can be neglected for lower excited states so that $n_p^+ \ll n_p^1$. Therefore, the density of level "$3$" can be written as

$$n(3) = r^1(3) n^B(3).$$  \hspace{1cm} (10.34)

The actinometry signal can be expressed as

$$J = C_{CRM} J_{CL},$$  \hspace{1cm} (10.35)

with $C_{CRM}$ the CR-model correction factor, defined by

$$C_{CRM} = \frac{r^1(O)/r^1_{CB}(O)}{r^1(Ar)/r^1_{CB}(Ar)}.$$  \hspace{1cm} (10.36)

where the $r^1$ coefficients can be determined using CR-models (cf. chapter 2 or [10]). The $r^1_{CB}$ coefficients correspond to the situation in which the level occupation is ruled by the corona balance. Expressions for the corona $r^1$ coefficients are given in subsection 10.6.4.

10.6 The actinometry systems

The transitions that are usually studied in literature for actinometry on oxygen are summarized in table 10.2. In most cases, the line pair ratios O[844.6]/Ar[811.5] and O[777.2]/Ar[750.4] are employed. Among others, the table shows that the assumption $A(3,2) \approx \sum_{q<p} A(p, q)$, is not valid for the argon transitions. The deviations of this near equality are automatically dealt with in the CR-model.

**Table 10.2: Overview of the actinometry transitions.**

<table>
<thead>
<tr>
<th>Level</th>
<th>$\sum_{q&lt;p} A(p, q)$</th>
<th>$A(p, q)$</th>
<th>Wavelength</th>
<th>$E_{qp}$</th>
<th>$E_{1p}$</th>
<th>$g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(3P)</td>
<td>$3.22 \times 10^7$</td>
<td>$3.05 \times 10^7$</td>
<td>844.6 nm</td>
<td>1.47</td>
<td>10.99</td>
<td>9</td>
</tr>
<tr>
<td>O(5P)</td>
<td>$3.69 \times 10^7$</td>
<td>$3.50 \times 10^7$</td>
<td>777.2 nm</td>
<td>1.59</td>
<td>10.74</td>
<td>15</td>
</tr>
<tr>
<td>Ar(4P)</td>
<td>$4.44 \times 10^7$</td>
<td>$3.31 \times 10^7$</td>
<td>811.5 nm</td>
<td>1.53</td>
<td>13.08</td>
<td>3</td>
</tr>
<tr>
<td>Ar(4P)</td>
<td>$6.83 \times 10^7$</td>
<td>$4.45 \times 10^7$</td>
<td>750.4 nm</td>
<td>1.65</td>
<td>13.48</td>
<td>1</td>
</tr>
</tbody>
</table>

To study the excitation of these levels cross-section values are required in order to determine the excitation rates. Excitation and dissociation cross-sections for oxygen as given by Katsch [3] are employed in this study. Recent cross sections for the argon transitions are found in the work of Yanguas-Gil [11]. These cross-sections are presented in figure 10.4. Using these cross-sections and a Maxwellian EEDF, excitation rates are obtained as a function of the mean energy and shown in figure 10.5.
Figure 10.4: Cross-section values as function of the electron energy $u$. The letter 'e' is used to denote electron impact excitation and 'de' refers to dissociative excitation.

Figure 10.5: Excitation rates as a function of the electron temperature $T_e$. The $T_e$ value for the plasmas under study is about 20000 K.

10.6.1 Classical actinometry

The classical actinometry ratio, $J_{CL}$, given by equation 10.7, is calculated as a function of the oxygen atom density. The excitation rates, shown in figure 10.5, are determined at an electron temperature of $T_e = 20000$ K. This temperature is determined using Thomson Scattering measurements on surfatron induced argon plasmas with increasing amounts of oxygen.
Actinometry applied to a low pressure oxygen plasma

Calculated classical actinometry results for both line pair ratios are shown in figure 10.6. The figure shows that for the same atomic oxygen density, the actinometry signal of the line pair \( \text{O}[844.6]/\text{Ar}[811.5] \) is larger than the signal of \( \text{O}[777.2]/\text{Ar}[750.4] \). The electron impact excitation rates for both argon levels are the same. Therefore, the larger actinometry signal is the result of the larger value for \( k_e^O \) of the level \( \text{O}[844.6] \) compared to that of \( \text{O}[777.2] \). It can be concluded that the classical actinometry method is most sensitive for the line pair ratio \( \text{O}[844.6]/\text{Ar}[811.5] \).

![Figure 10.6: Calculated 'classical' actinometry signal as function of the oxygen atom density. The excitation rates were calculated using a Maxwellian EEDF for an electron temperature of 20000 K. The argon density was set equal to \( n_{\text{Ar}} = 1.6 \times 10^{21} \text{m}^{-3} \).](image)

**10.6.2 Molecular dissociation**

According to equation 10.23, dissociation of molecules by electron impact can be neglected when the atom to molecule ratio \( \alpha_{\text{dis}} = \frac{n_O}{n_{\text{Ar}}} \) is higher than a boundary value \( \alpha_{\text{dis}} > \alpha_{\text{dis}}^{\text{crit}} \), with

\[
\alpha_{\text{dis}}^{\text{crit}} = 10(\frac{k_{\text{de}}}{k_{e}(1, 3)})^O.
\] (10.37)

In figure 10.7, values for \( \alpha_{\text{dis}}^{\text{crit}} \) are shown as a function of the electron temperature for both the 777 nm and 844 nm transitions. At an electron temperature of 20000 K, this figure shows that the boundaries are equal to \( \alpha_{\text{dis}}^{\text{crit}} = 0.31 \) and \( \alpha_{\text{dis}}^{\text{crit}} = 0.05 \) for the \( \text{O}[777.3] \) and \( \text{O}[844.6] \) level, respectively. As a result, the molecular contribution can be neglected for dissociation ratios larger than 5 % when the line pair \( \text{O}[844.6]/\text{Ar}[811] \) is used. The line pair \( \text{O}[777.3]/\text{Ar}[750.4] \) is much more sensitive for molecular contributions. In this case, molecular processes can only be neglected when the dissociation ratio is at least 30 %.

In figure 10.8, results are shown for both the theoretical value of the classical actinometry signal, \( J_{\text{CL}} \), and the actinometry signal corrected for molecular dissociation, \( J = C_p J_{\text{CL}} \). For the oxygen atom densities expected in the surfatron plasma \( 10^{21} \text{m}^{-3} < n_O < 10^{22} \text{m}^{-3} \),
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the results clearly show that the line pair ratio O[777.2]/Ar[750.4] is largely influenced by dissociative excitation. Below \( n_O = 2 \times 10^{21} \, \text{m}^{-3} \), which corresponds to \( \alpha = 4.4\% \), the curve is flat, the theoretical \( J \) value \( (J = J_{\text{CL}} \, C_p) \) saturates so that a measured value of \( J^* = 4 \) does not provide an unique value of \( n_O \). To determine oxygen atom densities, the ratio O[844.6]/Ar[811.5] again looks more suitable.

\[ \text{Figure 10.7: Values of } \alpha_{\text{crit}} \text{ as function of the electron temperature.} \]

\[ \text{Figure 10.8: The theoretical } J \text{-value as a function of the oxygen atom density for the line pairs O[844.6]/Ar[811.5] (left) and O[777.2]/Ar[750.4] (right) for two cases: the classical case } J_{\text{CL}} \text{ and the case for which the correction due to dissociative excitation is taken into account } J = J_{\text{CL}} \, C_p. \text{ Results are determined for } T_e = 20000 \, \text{K}, \, n_Ar = 1.6 \times 10^{21} \, \text{m}^{-3} \text{ and } n_{O_2} = 4.5 \times 10^{22} \, \text{m}^{-3}. \text{ Especially the O[777.2]/Ar[750.4]} \text{ ratio saturates between } 1 \times 10^{20} \leq n_O \leq 2 \times 10^{21} \, \text{m}^{-3} \text{ meaning that the values around } J^* = 4 \text{ can not be used to determine the atomic oxygen density.} \]
10.6.3 Correction for quenching

The term $k_Q$ describes quenching of the excited argon or oxygen states by oxygen molecules. Pagnon [5] found expressions for pressures below 3 mbar, namely

$$k_Q^{3P}(844.6) = 7.8 \times 10^{-16} \text{m}^3\text{s}^{-1},$$  

(10.38)

$$k_Q^{3P}(777.2) = 10.8 \times 10^{-16} \text{m}^3\text{s}^{-1}.$$  

(10.39)

These values will be used in this work.

Inserting these values into the expression for the critical molecular oxygen density $n_{O_2}^{\text{crit}}$ (cf. equation 10.30) results in $n_{O_2}^{\text{crit}} = 3.2 \times 10^{21} \text{m}^{-3}$ and $n_{O_2}^{\text{crit}} = 3.9 \times 10^{21} \text{m}^{-3}$ for the line pair O[777.2]/Ar[750.4] and O[844.6]/Ar[811.5], respectively. The molecular oxygen density observed for our experimental conditions is higher than the critical density of both line pair ratios. Therefore, a correction for quenching processes has to be made in all cases.

The correction term for quenching processes is included in the parameter $C_Q$. An expression to calculate this value is given in equation 10.28 and calculated results for typical $n_{O_2}$ densities are shown in table 10.3.

**Table 10.3:** Correction term for quenching for different molecular oxygen densities.

<table>
<thead>
<tr>
<th>$n_{O_2}$ / $C$</th>
<th>$1 \times 10^{22}$</th>
<th>$2 \times 10^{22}$</th>
<th>$4 \times 10^{22}$</th>
<th>$5 \times 10^{22}$</th>
<th>$6 \times 10^{22}$</th>
<th>$8 \times 10^{22}$</th>
<th>$1 \times 10^{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(844.6 nm)</td>
<td>0.80</td>
<td>0.66</td>
<td>0.49</td>
<td>0.44</td>
<td>0.39</td>
<td>0.33</td>
<td>0.28</td>
</tr>
<tr>
<td>C(777.2 nm)</td>
<td>0.76</td>
<td>0.62</td>
<td>0.45</td>
<td>0.39</td>
<td>0.35</td>
<td>0.29</td>
<td>0.24</td>
</tr>
</tbody>
</table>

10.6.4 Collisional radiative models

**CR-model argon**

An existing CR-model for atomic argon is used. The pure argon model is presented in [12] and the general CR-modelling code of Hartgers [8] is used. The $r^1$-coefficients of a surfatron induced pure argon plasma are discussed in [10]. For the experimental conditions encountered in this study, typical values for the $r^1$-coefficients are around $10^{-4}$ (cf. table 10.6).

**CR-model oxygen**

The collisional radiative model for atomic oxygen is largely based on the work of Soon [13]. Again the general CR-modelling code of Hartgers [8] is used. Compared to [13], the negative ion O$^-$ and the $|\Delta S| = 2$ transitions are not included. Atomic energy levels and terms are shown in table 10.4.

The escape factors for the optically allowed radiative transitions to the ground state are estimated using the formulae of Fujimoto [9, 14, 15] for a plasma length of 3 mm and an atomic oxygen density of $10^{21} \text{m}^{-3}$ (see table 10.5). The escape factors for all other radiative transitions, landing on excited states, are set to unity.
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Table 10.4: Energy levels of atomic oxygen.

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>Statistical weight $g_i$</th>
<th>Principal quantum number</th>
<th>Term</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>eV</td>
<td>$i$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>9</td>
<td>2</td>
<td>$^3$P</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2p$^4$</td>
</tr>
<tr>
<td>1.97</td>
<td>2</td>
<td>5</td>
<td>2</td>
<td>$^1$D</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2p$^4$</td>
</tr>
<tr>
<td>4.19</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>$^1$S</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2p$^4$</td>
</tr>
<tr>
<td>9.15</td>
<td>4</td>
<td>5</td>
<td>3</td>
<td>$^5$S</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3s</td>
</tr>
<tr>
<td>9.52</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>$^3$S</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3s</td>
</tr>
<tr>
<td>10.74</td>
<td>6</td>
<td>15</td>
<td>3</td>
<td>$^5$P</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3p</td>
</tr>
<tr>
<td>10.99</td>
<td>7</td>
<td>9</td>
<td>3</td>
<td>$^3$P</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3p</td>
</tr>
<tr>
<td>11.84</td>
<td>8</td>
<td>5</td>
<td>4</td>
<td>$^5$S</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4s</td>
</tr>
<tr>
<td>11.93</td>
<td>9</td>
<td>3</td>
<td>4</td>
<td>$^3$S</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4s</td>
</tr>
<tr>
<td>13.62</td>
<td>ion</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 10.5: Escape factors for oxygen transitions to the ground state.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$n_O$</th>
<th>$1.0 \times 10^{21}$ m$^{-3}$</th>
<th>$5.0 \times 10^{21}$ m$^{-3}$</th>
<th>$1.0 \times 10^{22}$ m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 – 1</td>
<td>0.065</td>
<td>0.010</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>9 – 1</td>
<td>0.387</td>
<td>0.092</td>
<td>0.044</td>
<td></td>
</tr>
</tbody>
</table>

$r^1$-coefficients CR-model

Using the CR-models of atomic oxygen and argon, the $r^1$-coefficients for the actinometry levels are determined as function of the electron density and electron temperature and are presented in table 10.6. This method is explained in detail in chapter 2 or [10]. With the employed CR-model for argon, $r^1$(Ar 750)-coefficients can not be determined separately since all 4p-levels are lumped together. Therefore, the values of the $r^1$(Ar 750)-coefficients are set equal to the $r^1$(Ar 811)-coefficients.

Table 10.6: The $r^1$-coefficients are determined for different electron densities at a constant electron temperature of 20000 K using a CR-model.

<table>
<thead>
<tr>
<th>$n_e$ in m$^{-3}$</th>
<th>$r^1$(O 844)</th>
<th>$r^1$(O 777)</th>
<th>$r^1$(Ar 811)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \times 10^{17}$</td>
<td>$7.0 \times 10^{-5}$</td>
<td>$4.6 \times 10^{-6}$</td>
<td>$2.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{18}$</td>
<td>$6.8 \times 10^{-4}$</td>
<td>$8.4 \times 10^{-5}$</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{19}$</td>
<td>$5.4 \times 10^{-3}$</td>
<td>$1.6 \times 10^{-3}$</td>
<td>$3.1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
r₁-coefficients corona balance

The formula of r₁_CBR coefficients can be derived directly using the equations 10.5 and 10.34. This gives the following expression

\[ r_{CB}^1 = \frac{n_e n_1 k_e(1, 3)/A(3, 2)}{n^B(3)}, \tag{10.40} \]

in which the Boltzmann density is given by

\[ n^B(3)/g_3 = n_1/g_1 \exp \left( -\frac{E_{13}}{k_B T_e} \right). \tag{10.41} \]

Combining 10.40 and 10.41 gives

\[ r_{CB}^1 = \frac{n_e k_e(1, 3) g_1}{A(3, 2)} g_3 \exp \left( \frac{E_{13}}{k_B T_e} \right). \tag{10.42} \]

These coefficients, determined for the argon and oxygen actinometry levels, are shown in table 10.7. Although the corona coefficients depend on the electron density, the ratio between the argon and oxygen is independent of \( n_e \).

Table 10.7: The corona r₁_CBR-coefficients are determined for different \( n_e \)-values and \( T_e = 20000 \) K.

<table>
<thead>
<tr>
<th>( n_e ) in m⁻³</th>
<th>( r_{CB}^1 ) (O844)</th>
<th>( r_{CB}^1 ) (O777)</th>
<th>( r_{CB}^1 ) (Ar811)</th>
<th>( r_{CB}^1 ) (Ar750)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.0 \times 10^{17} )</td>
<td>( 6.8 \times 10^{-6} )</td>
<td>( 1.4 \times 10^{-6} )</td>
<td>( 6.0 \times 10^{-7} )</td>
<td>( 1.7 \times 10^{-6} )</td>
</tr>
<tr>
<td>( 1.0 \times 10^{18} )</td>
<td>( 6.8 \times 10^{-5} )</td>
<td>( 1.4 \times 10^{-5} )</td>
<td>( 6.0 \times 10^{-6} )</td>
<td>( 1.8 \times 10^{-5} )</td>
</tr>
<tr>
<td>( 1.0 \times 10^{19} )</td>
<td>( 6.8 \times 10^{-4} )</td>
<td>( 1.4 \times 10^{-4} )</td>
<td>( 6.0 \times 10^{-5} )</td>
<td>( 1.8 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

The CR-model correction terms

Using \( n_e = 1.0 \times 10^{18} \) m⁻³ and \( T_e = 20000 \) K, the CR-model gives the following results. For O[844.6]/Ar[811.5], we obtain \( C_{CRM} = 0.33 \) and for O[777.2]/Ar[750.4] \( C_{CRM} = 0.60 \). For both line pair ratios, the CR-model correction results in higher ground state densities of atomic oxygen. This effect is more pronounced for the O[844.6]/Ar[811.5] line pair.

10.7 Results

The absolute intensities of the actinometry lines are obtained using ALI measurements and presented in table 10.8. All measurements were made at 2 cm relative to the plasma launcher (surfatron). The gas temperatures \( T_h \) were obtained from the rotational spectrum of the atmospheric oxygen band (cf. chapter 9). The total pressure and the gas temperature are used to obtain the total density \( N \) via the ideal gas law. As a first step, the argon density is derived using

\[ n_{Ar} = \frac{Q_{Ar}}{Q_{Ar} + 2Q_O} \times N \tag{10.43} \]
Table 10.8: Plasma conditions. In all cases, the absorbed microwave power was 45 W, the argon flow, \( Q_{\text{Ar}} \), 2 sccm and the oxygen flow, \( Q_{\text{O}} \), 50 sccm.

<table>
<thead>
<tr>
<th>Pressure mbar</th>
<th>( T_h ) K</th>
<th>Length cm</th>
<th>( j_O ) (844) Wm(^{-3})sr(^{-1})</th>
<th>( j_{\text{Ar}} ) (811) Wm(^{-3})sr(^{-1})</th>
<th>( j_O ) (777) Wm(^{-3})sr(^{-1})</th>
<th>( j_{\text{Ar}} ) (750) Wm(^{-3})sr(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>590</td>
<td>3.0</td>
<td>590</td>
<td>38</td>
<td>666</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>660</td>
<td>2.8</td>
<td>808</td>
<td>66</td>
<td>780</td>
<td>65</td>
</tr>
<tr>
<td>10</td>
<td>800</td>
<td>2.4</td>
<td>853</td>
<td>92</td>
<td>848</td>
<td>90</td>
</tr>
</tbody>
</table>

and the atomic density of oxygen is derived from

\[
J^* = J_{\text{CL}} = \frac{n_O}{n_{\text{Ar}}} \frac{k_e^O(1,3)}{k_e^\text{Ar}(1,3)} \frac{E^O(3,2)}{E^\text{Ar}(3,2)} = \frac{n_O}{n_{\text{Ar}}} C_{\text{cl}},
\]  

(10.44)

where \( C_{\text{cl}} \) is a constant that only depends on the properties of the argon and oxygen systems. The obtained values for \( n_O \) and \( n_{\text{Ar}} \) are used as starting values for the following iterative procedure:

1. Determine the molecular oxygen density \( n_{\text{O}_2} \) using \( n_{\text{O}_2} = N - n_O - n_{\text{Ar}} \).
2. Calculate the dissociation ration \( \alpha = n_O/n_{\text{O}_2} \).
3. Determine the ratio \( \varsigma = n_{\text{Ar}}/[(\alpha + 2) \times n_{\text{O}_2}] \).
4. Calculate the population \( C_P \) and quenching \( C_Q \) correction terms.
5. Obtain a new \( n_O \) density via the full expression: \( n_O = J^*/C_{\text{cl}} C_P C_Q \).
6. Determine a new \( n_{\text{Ar}} \) density: \( n_{\text{Ar}} = \varsigma \times (n_O/n_{\text{O}_2} + 2) \times n_{\text{O}_2} \).

The equations described in the steps 1–6 are solved in an iterative way until convergence is reached. Results of the line pair O[844.6]/Ar[811.5] are shown in table 10.9, for the line ratio O[777.2]/Ar[750.4] the results are presented in table 10.10. In both tables, atomic oxygen densities obtained using the classical actinometry expression, denoted by \( n_O^* \), are presented.

Table 10.9: Actinometry results of the line pair O[844.6]/Ar[811.5].

<table>
<thead>
<tr>
<th>Pressure mbar</th>
<th>( J^* ) m(^{-3})</th>
<th>( N ) m(^{-3})</th>
<th>( n_{\text{Ar}} ) m(^{-3})</th>
<th>( n_O^* ) m(^{-3})</th>
<th>( n_O ) m(^{-3})</th>
<th>( n_{\text{O}_2} ) m(^{-3})</th>
<th>( \alpha_{\text{dis}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>15.6</td>
<td>4.9 \times 10^{22}</td>
<td>1.0 \times 10^{21}</td>
<td>1.3 \times 10^{21}</td>
<td>8.5 \times 10^{21}</td>
<td>4.0 \times 10^{22}</td>
<td>0.22</td>
</tr>
<tr>
<td>6</td>
<td>12.3</td>
<td>6.6 \times 10^{22}</td>
<td>1.4 \times 10^{21}</td>
<td>1.4 \times 10^{21}</td>
<td>1.1 \times 10^{22}</td>
<td>5.4 \times 10^{22}</td>
<td>0.20</td>
</tr>
<tr>
<td>10</td>
<td>9.2</td>
<td>9.1 \times 10^{22}</td>
<td>1.9 \times 10^{21}</td>
<td>1.4 \times 10^{21}</td>
<td>1.3 \times 10^{22}</td>
<td>7.5 \times 10^{22}</td>
<td>0.17</td>
</tr>
</tbody>
</table>

The dissociation ratio \( \alpha_{\text{dis}} \) decreases with increasing pressure for both line pair ratios. The atomic oxygen density obtained from the classical expression, \( n_O^* \), is a factor 4 to 9 larger than the atomic ground state density \( n_O \) obtained from the total expression. This shows
Actinometry applied to a low pressure oxygen plasma

Table 10.10: Actinometry results of the line pair O[777.2]/Ar[750.4].

<table>
<thead>
<tr>
<th>Pressure mbar</th>
<th>J× N m⁻³</th>
<th>nAr m⁻³</th>
<th>nO n m⁻³</th>
<th>nO₂ m⁻³</th>
<th>αdis</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>17.7</td>
<td>4.9 × 10²²</td>
<td>1.1 × 10²¹</td>
<td>3.4 × 10²¹</td>
<td>5.6 × 10²²</td>
</tr>
<tr>
<td>6</td>
<td>12.1</td>
<td>6.6 × 10²²</td>
<td>1.4 × 10²¹</td>
<td>3.2 × 10²¹</td>
<td>5.1 × 10²²</td>
</tr>
<tr>
<td>10</td>
<td>9.4</td>
<td>9.1 × 10²²</td>
<td>1.9 × 10²¹</td>
<td>3.4 × 10²¹</td>
<td>7.1 × 10²²</td>
</tr>
</tbody>
</table>

the importance of the correction terms and the iterative procedure. The ratios obtained with the line pair O[777.2]/Ar[750.4] are a factor of 1.5 larger than ratios obtained with O[844.6]/Ar[811.5]. For reasons discussed in the next section, it is expected that the line pair O[844.6]/Ar[811.5] gives the most accurate results.

10.8 Influence of a non-Maxwellian electron energy distribution function

In this section, the influence of a non-Maxwellian EEDF on the actinometry signal is investigated. This EEDF has been calculated by Pinheiro [16] using a kinetic radial model for oxygen. The obtained EEDF will be used to determine the excitation and dissociation rates. It is assumed that introducing a small amount of argon in an oxygen plasma does not change the distribution function.

The kinetic radial model is based on the work of [17], [18] and [16] where the electron kinetics under the action of a high frequency field were studied in an oxygen discharge. The Boltzmann equation was used to derive electron transport coefficients (electron free diffusion coefficient, DC mobility, AC complex conductivity) from which rate coefficients were derived. These were coupled to the continuity and transport equations for the charged particles which can be solved to yield the field strength required to sustain a steady-state discharge. In [17], experimental values of the O₂(a¹Δ) and O(³P) populations and of the vibrational temperature were used to solve the Boltzmann equation. These values were based on the work of [4]. In [16], the kinetics of the atomic, molecular and excited oxygen species were added to this model. However, most calculations and experimental results were obtained for a frequency of 390 MHz. In this work, the latest model of [16] is used at the microwave frequency of 2.45 GHz.

The kinetic radial model has been applied for the experimental configurations of the surfatron plasma [10] under study, thus a frequency of 2.45 GHz an inner tube radius of 3 mm and gas densities in between 10²² ≤ N ≤ 10²³ m⁻³. The calculated EEDFs are shown in figure 10.9. In this study, EEDF 2 (N = 5 × 10²² m⁻³) is used to obtain non-Maxwellian rate coefficients. The corresponding mean electron temperature is equal to 2 eV. The excitation rates can be calculated using

\[ k = \int \sigma(u) \sqrt{\frac{2eu}{m}} f(u) \sqrt{u} du. \]  (10.45)

The cross sections presented in section 10.6 can now be combined with either a Maxwellian or the calculated distribution function to determine the excitation and dissociation rate coefficients. Rates obtained with a Maxwellian and non-Maxwellian distribution function (EEDF 2) are determined for a mean electron temperature of 2 eV and are presented in table 10.11.
Figure 10.9: Electron energy distribution functions $f(u)$ for three values of $N$, where $u = \frac{mv^2}{2e}$ equals the electron energy in eV and $f(u)$ is the energy distribution function in eV$^{-3/2}$. The first EEDF corresponds to $N = 1 \times 10^{22} \text{m}^{-3}$, EEDF 2 to $N = 5 \times 10^{22} \text{m}^{-3}$ and EEDF 3 to $N = 1 \times 10^{23} \text{m}^{-3}$. A frequency of 2.45 GHz and inner radius $R = 3 \text{mm}$ were used.

Table 10.11: Rate coefficients in $(\text{m}^3\text{s}^{-1})$ determined using a Maxwellian EEDF and EEDF 2 at $T_e = 2\text{ eV}$.

<table>
<thead>
<tr>
<th>Process</th>
<th>$k$ value Maxwell</th>
<th>$k$ value EEDF 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar$(^4\text{P})$ $k_{\text{Ar}}^e(811.5)$</td>
<td>$1.54 \times 10^{-18}$</td>
<td>$4.67 \times 10^{-19}$</td>
</tr>
<tr>
<td>Ar$(^4\text{P})$ $k_{\text{Ar}}^e(750.4)$</td>
<td>$1.55 \times 10^{-18}$</td>
<td>$4.73 \times 10^{-19}$</td>
</tr>
<tr>
<td>O$(^3\text{P})$ $k_{\text{O}}^e(844.6)$</td>
<td>$1.20 \times 10^{-17}$</td>
<td>$4.83 \times 10^{-18}$</td>
</tr>
<tr>
<td>O$(^3\text{P})$ $k_{\text{O}}^e(844.6)$</td>
<td>$9.88 \times 10^{-20}$</td>
<td>$1.39 \times 10^{-20}$</td>
</tr>
<tr>
<td>O$(^5\text{P})$ $k_{\text{O}}^e(777.2)$</td>
<td>$5.09 \times 10^{-18}$</td>
<td>$2.12 \times 10^{-18}$</td>
</tr>
<tr>
<td>O$(^5\text{P})$ $k_{\text{O}}^e(777.2)$</td>
<td>$2.56 \times 10^{-19}$</td>
<td>$2.72 \times 10^{-20}$</td>
</tr>
</tbody>
</table>

The results presented in this table show that the differences between the rate coefficients determined with a Maxwellian EEDF and EEDF 2 are equal to a factor of 2.5 for the argon electron impact excitation rates, a factor of 3.3 for the oxygen electron impact excitation rates, a factor of 7.1 for dissociative excitation of O$(^3\text{P})$ at 844.6 and a factor of 9.4 for dissociative excitation of O$(^5\text{P})$. These values can be explained by the shape and threshold of the cross sections (see figure 10.4). The rate coefficients of processes with a large threshold value, i.e. the dissociative excitation processes, are much more decreased as a result of deviations from a Maxwellian EEDF. Therefore, the influence of molecular processes is reduced when a calculated EEDF is used. Also, as all rate coefficients are smaller, the obtained atomic oxygen density and dissociation ratio will be decreased as well.
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The corona balance can be studied for both cases. When Maxwellian rate coefficients are used, we obtain the classical actinometry situation. Equation 10.46 shows the relationship between the actinometry signal and the atomic oxygen density of the O[844.6]/Ar[811.5] line pair ratio. Expressions for the line pair ratio are shown in equation 10.48 and 10.46. For these calculations, the excitation rates presented in table 10.11 were used.

\[
\text{Maxwell O}[844.6]/\text{Ar}[811.5] : \quad n_O = 0.13 \, n_{\text{Ar}} \frac{j_O}{j_{\text{Ar}}} \quad (10.46)
\]

\[
\text{EEDF 2 O}[844.6]/\text{Ar}[811.5] : \quad n_O = 0.10 \, n_{\text{Ar}} \frac{j_O}{j_{\text{Ar}}} \quad (10.47)
\]

\[
\text{Maxwell O}[777.2]/\text{Ar}[750.4] : \quad n_O = 0.32 \, n_{\text{Ar}} \frac{j_O}{j_{\text{Ar}}} \quad (10.48)
\]

\[
\text{EEDF 2 O}[777.2]/\text{Ar}[750.4] : \quad n_O = 0.23 \, n_{\text{Ar}} \frac{j_O}{j_{\text{Ar}}} \quad (10.49)
\]

According to these equations, using non-Maxwellian rates results in lower atomic oxygen densities than the Maxwellian ones. For O[844.6]/Ar[811.5], the non-Maxwellian density is 30% higher. For the line pair ratio O[777.2]/Ar[750.4], the non-Maxwellian atomic density is 37% lower. Therefore, using a Maxwellian EEDF overestimates the atomic ground state density values, and this effect is more pronounced for the O[777.2]/Ar[750.4] line pair ratio.

As discussed in subsection 10.6.2, dissociation of molecules by electron impact can be neglected when \( \alpha_{\text{dis}} > \alpha_{\text{dis}}^{\text{crit}} \),

\[
\alpha_{\text{dis}}^{\text{crit}} = 10 \times \frac{k_{\text{de}}}{k_{\text{el}}}, \quad (10.50)
\]

and \( \alpha_{\text{dis}} \) represents the dissociation ratio. Again using the rates of table 10.11, we obtain the following values for the dissociation boundaries (cf. table 10.12).

<table>
<thead>
<tr>
<th>Process</th>
<th>( \alpha_{\text{dis}}^{\text{crit}} ) (Maxwell)</th>
<th>( \alpha_{\text{dis}}^{\text{crit}} ) (EEDF 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(⁴P) 844.6</td>
<td>8.2 \times 10^{-2}</td>
<td>2.9 \times 10^{-2}</td>
</tr>
<tr>
<td>O(⁵P) 777.2</td>
<td>5.0 \times 10^{-1}</td>
<td>1.3 \times 10^{-1}</td>
</tr>
</tbody>
</table>

For both line pairs, the non-Maxwellian distribution function lowers the dissociation boundary. Therefore, the influence of molecular processes is expected to be lower when the correct distribution function is used. A higher dissociation ratio reduces the influence of the molecular population term. This can be observed in figure 10.10, where the actinometry signal \( J = J_{\text{cor}} \, C_P \) is compared with the classical signal, both calculated using EDF 2. For relatively low \( n_O \) values, the actinometry signal is greatly influenced by molecular processes. For the higher values, these are less dominant. The O[777.2]/Ar[750.4] line pair ratio is much more sensitive for molecular population, which is also the case for Maxwellian rate coefficients.
Figure 10.10: Calculated actinometry signal for the line pair ratios O\([777.2]\)/Ar\([750.4]\) (right) and O\([844.6]\)/Ar\([811.5]\) (left) as function of the oxygen atom density for the case that \(n_{Ar} = 1.6 \times 10^{21} \text{m}^{-3}\), \(n_{O_2} = 4.5 \times 10^{22} \text{m}^{-3}\), \(n_e = 1 \times 10^{18} \text{m}^{-3}\) and \(T_e = 2 \text{eV}\). The corona signals are presented by squares, the molecular ones by circles.

Using the same methods as discussed in section 10.7, we again determine the dissociation ratios. These results, presented in table 10.13, follow the same trends as before; the dissociation ratio decreases with pressure and the O\([777.2]\)/Ar\([750.4]\) line pair ratio gives higher dissociation values. Deviations from Maxwell decrease the dissociation ratios and reduce the influence of the molecular population term. However, the different results for both line pair ratios can not be explained by deviations from Maxwell. Note that the CR-model correction is not included in these calculations and that they are made at a slightly higher electron temperature. Therefore, these results can not be compared with those presented in table 10.10.

Table 10.13: Dissociation ratios \(\alpha_{\text{dis}} = n_O / n_{O_2}\) for \(T_e = 2 \text{eV}\). Note that the CRM correction is not included.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Maxwell(844)</th>
<th>EDF2(844)</th>
<th>Maxwell(777)</th>
<th>EDF2(777)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 mbar</td>
<td>0.097</td>
<td>0.071</td>
<td>0.28</td>
<td>0.22</td>
</tr>
<tr>
<td>6 mbar</td>
<td>0.090</td>
<td>0.066</td>
<td>0.21</td>
<td>0.17</td>
</tr>
<tr>
<td>10 mbar</td>
<td>0.082</td>
<td>0.060</td>
<td>0.20</td>
<td>0.17</td>
</tr>
</tbody>
</table>

10.9 Discussion and conclusions

The aim of the work described in this chapter was to extend the pressure range to which actinometry on oxygen plasmas is generally applied (\(\leq 3 \text{mbar}\)). This study can be split up into three different parts. First, a diagnostic validation has been performed to test whether
the actinometry method can be applied to higher pressures \((1 - 20 \text{ mbar})\). The second part is a theoretical study where it was shown that deviations from classical actinometry can be included in correction coefficients. The third part is the application of actinometry to surfatron induced oxygen plasmas to which a small amount of argon was added.

The diagnostic validations showed that at pressures higher than 10 mbar, the addition of a very small amount of argon significantly changes the behaviour of the oxygen lines. This limits the applicability of actinometry to pressures below 15 mbar.

In the theoretical study, deviations from classical actinometry were investigated. This was done via correction terms. In this way, it is relatively easy to add extra contributions like the CR-model correction, a term which describes all atomic population and depopulation processes. This term is increasingly important at higher pressures, where ladder-like excitation processes enhance the effective excitation rate. The influence of deviations from a Maxwellian distribution function was discussed in a separate section.

The actinometry method has been applied to surfatron induced oxygen plasmas at three different pressures, i.e. 4, 6 and 10 mbar. The line intensities of the actinometry levels were obtained in an absolute way and the rotational spectrum of molecular oxygen was measured to obtain the gas temperature. Using the ideal gas law, the measured pressure and gas temperature result in an accurate value of the total particle density. With the experimental data and the derived expressions, calculations have been made in an iterative way in order to obtain both the dissociation ratio and atomic oxygen density. The processes evaluated in this work are summarized in table 10.14. Including the molecular population correction \(C_P\) decreases the derived dissociation ratio, whereas taking the quenching and CR-model correction into account leads to a strong increase in the derived dissociation ratio.

\[
\text{Table 10.14: Processes evaluated in this work.}
\]

<table>
<thead>
<tr>
<th>Process</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classical actinometry</td>
<td>(J_{\text{CL}} = \frac{E^O n_O k_{\text{el}}^O}{E^A n_A k_{\text{el}}^A} J_{\text{CL}})</td>
</tr>
<tr>
<td>General actinometry</td>
<td>(J = C_P C_Q C_{\text{CRM}} J_{\text{CL}})</td>
</tr>
<tr>
<td>Molecular population</td>
<td>(C_P = 1 + \frac{n_O}{n_A} \frac{k_{\text{de}}^O}{k_{\text{el}}^O})</td>
</tr>
<tr>
<td>Quenching</td>
<td>(C_Q = \left[1 + n_{O_2} \frac{k_Q^O}{A^O(3, 2)}\right]^{-1})</td>
</tr>
<tr>
<td>CR-model correction</td>
<td>(C_{\text{CRM}} = \frac{r_1^O}{r_1^A} \frac{r_{\text{CRM}}^O}{r_{\text{CRM}}^A})</td>
</tr>
</tbody>
</table>

In order to explain the differences between results found for both line pair ratios and to improve the accuracy of the expressions, the influence of deviations from a Maxwellian distribution function has been investigated. It was found that using a non-Maxwellian distribution to calculate rate coefficients decreases the dissociation ratio and reduces the influence of the molecular population term. The differences between the line pairs could not be explained by deviations from Maxwell. In all cases, different results have been observed for both line pairs.
Including processes like molecular population and quenching did not make the differences smaller. The use of an atomic collisional radiative model increased the dissociation ratios in both cases. However, even with the CR-model correction, different dissociation ratios were observed.

Different results obtained for the two line pairs are also observed in other studies. In the work of Katsch [3], the behaviour of the O[844.6] and O[777.2] lines was studied using power interruption measurements. The different reactions to the power interruption were explained by the suggestion that the O[777.2] was strongly populated by an additional dissociative excitation channel via metastable molecules. In [5], the actinometry method was applied to an O₂ DC glow discharge and compared with VUV absorption measurements for pressures ranging from 0.5 to 2.6 mbar. To obtain a good agreement with the VUV absorption results, they had to include the dissociative excitation channel for the O[777.2] level. Results (atomic oxygen density) obtained with this correction for the O[777.2] level were still relatively high, although within error bars of both methods. In Granier [4], a microwave discharge in oxygen was studied using actinometry and VUV absorption measurements in the same way as in [5]. Results were obtained in the afterglow for a quartz tube of 16 mm, pressure of 1 mbar and a microwave frequency of 2.450 GHz. Actinometry results for the O[777.2] level were almost two times higher than densities obtained with the O[844.6] line and VUV.

Following the results of previous studies, the O[844.6]/Ar[811.5] line pair ratio gives the most accurate result since the results of this line corresponded with active spectroscopy. At a pressure of 10 mbar, the classical actinometry expression of the O[844.6]/Ar[811.5] line pair results in a dissociation degree (nₐ/nₒ₂) of 2% whereas the total expression (assuming a Maxwellian EEDF) yields 17%. This shows the importance of the corrections terms. At this pressure, the Maxwellian EEDF results in dissociation degrees that are a factor 1.3 larger than the non Maxwellian EEDF. Therefore, the dissociation degree of a 10 mbar surfatron induced oxygen plasma is in between 11% and 17%.

It can be concluded that the application of actinometry to plasmas at moderate pressure is complicated. For an accurate description of all the processes that lead to population and depopulation of the actinometry levels, a molecular collisional model is required wherein also the interaction between the argon and oxygen systems is taken into account. It would be useful to compare the actinometry results with results of active diagnostic techniques like laser induced fluorescence (LIF).

Acknowledgements

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Bibliography

Actinometry applied to a low pressure oxygen plasma

General conclusions and recommendations

The main aim of this thesis is to develop and validate optical spectroscopic methods that can be applied to microwave induced plasmas (MIPs) at low and moderate pressures. A second goal is to obtain more insight in the processes that occur in these plasmas via the use of global plasma models. These global models are used to support the interpretation of the trends in the experimental results and to relate the external control parameters to internal plasma properties. Apart from a global model for a pure atomic plasma, this model is extended for the addition of hydrogen molecules. In this concluding chapter, a summary of the most important conclusions of this thesis are given. Hereafter, recommended future experiments are described.

- Absolute line intensity (ALI) measurements were applied to a low pressure surfatron induced argon plasma in order to determine the excitation temperature. A collisional radiative (CR) model has been used to convert the excitation temperature into an electron temperature. Estimate values for the electron density and atom density were used as input parameters for the CR-model. At a pressure of 10 mbar, the electron temperature $T_e$ is found to be $1.1 \pm 0.1 \text{eV}$. The electron temperature is more or less constant along the tube and decreases with increasing pressures. (chapter 2)

- An existing Thomson Scattering (TS) setup was adapted so that TS could be applied on surfatron induced plasmas. This is experimentally difficult due to the large amount of stray-light and the relative low electron densities. TS measurements were made in a pressure range between 6 mbar and 20 mbar for different microwave powers in the range 25 – 65 W. For typical conditions, i.e. a pressure of 10 mbar and an absorbed microwave power of 50 W, the measured electron density equals $n_e \approx 4 \times 10^{19} \text{m}^{-3}$ and the electron temperature $T_e \approx 1.2 \text{eV}$. The TS results show that, for a constant absorbed microwave power density, $n_e$ increases with pressure in the range $6 \text{ mbar} \leq p \leq 10 \text{ mbar}$. Between 10 mbar and 20 mbar, these values are constant and the $T_e$ values decrease slightly with pressure. These results correspond to the trends obtained with the global plasma model. (chapter 3)

- With the use of a high resolution spectrometer, the DEMON, the broadening of the $H_\beta$ spectral line was measured. Via a sophisticated fitting routine, that takes the instrumental broadening and fine structure into account, the electron density was determined from the Stark broadening and the gas temperature from the Doppler broadening. For
the waveguide surfatron induced argon plasma at a pressure of \(~ 10\) mbar, the obtained electron densities are in the range of \(10^{19} \text{m}^{-3}\) and the gas temperatures are around \(0.14 \text{eV}\). (\textit{chapter 4})

- The addition of a small amount of hydrogen to an argon plasma for spectroscopic purposes drastically influences the argon plasma. Even a small fraction of \(0.5\%\) reduces the plasma length with \(40\%\). Moreover, it was found that the experimental results of the argon plasma with \(~ 0.5\%\) of hydrogen can not be understood using a global model for pure argon. When hydrogen related reactions are added to the global model, a reasonable agreement is found between the experimental and the global model results. (\textit{chapter 4} and \textit{chapter 5})

- The absorbed microwave power of a surface wave sustained plasma is difficult to measure. It is especially hard to determine how much microwave energy is radiated away. As the electron density is largely determined by the absorbed power, an accurate comparison of the different diagnostic methods is only possible when these methods are applied simultaneously to the same plasma location. (\textit{chapter 3} and \textit{chapter 7})

- In a poly-diagnostic study performed on an argon plasma, passive and active (laser) spectroscopic methods were simultaneously applied to the same plasma position. This enabled the validation of the various diagnostic techniques. The electron temperature has been obtained with two different methods, namely TS (active) and ALI measurements combined with a CR-model (passive). The ALI result at \(15\) mbar leads to \(T_e = (1.06 \pm 0.09) \text{eV}\) and is in reasonable agreement with the TS result \(T_e = (1.12 \pm 0.10) \text{eV}\). The slightly lower \(T_e\)-value obtained from the ALI/CR-model can be caused by deviations of the electron energy distribution from a Maxwellian distribution. The electron density is determined with four spectroscopic methods: TS, Stark broadening, absolute continuum measurements and from an extrapolation of the atomic state distribution function (ASDF). At \(15\) mbar, the \(n_e\)-values obtained with TS and Stark broadening are equal to \(4 \pm 0.5 \times 10^{19} \text{m}^{-3}\) whereas the continuum \(n_e\)-value is somewhat lower, i.e. equal to \((2 \pm 0.4) \times 10^{19} \text{m}^{-3}\). The \(n_e\)-value obtained from the ASDF is about one order higher than the TS value of \(n_e\). However, this method is not very accurate because it is based on the assumption that the measured top of the ASDF is in pLSE. This is probably not the case for our plasma conditions. It can be concluded that the passive techniques of Stark broadening and the ALI measurements combined with a CR-model are suitable to apply to other plasma sources that have approximately the same experimental conditions. (\textit{chapter 6})

- After validation, the spectroscopic methods were applied to three different argon MIPs, namely the surfatron, waveguide surfatron and microwave induced deposition plasma. The experimental results were compared with each other using a trend study performed with the global plasma model. The \(n_e\)-values obtained with the global model are somewhat higher than the experimental results. This can be explained by uncertainties in the measured control parameters. The most important factor is an overestimated value of the absorbed power. The measured electron temperatures for the surfatron plasma are substantially higher than the predictions of the global model. This indicates that extra loss terms are present which are not included in the global model. The most likely
candidate is recombination of molecular argon ions. A larger value for recombination or diffusion also results in lower electron densities. *(chapter 7)*

- The applicability of passive emission spectroscopic methods to an argon/oxygen plasma has been investigated. For this purpose, the optical diagnostics that were successfully applied to a pure argon plasma have also been applied to an argon/oxygen plasma. The electron density was determined with TS, Stark broadening and via the argon and oxygen ASDF. TS and Stark broadening results were found to be in a reasonable agreement, whereas both ASDF results are much too high. Therefore, it was concluded that the relevant excited states are not in partial Local Saha Equilibrium (pLSE). As a result, the ASDF method can not be employed for an accurate electron density determination. The electron temperature was obtained using TS and from the measured excited state densities of argon combined with the use of an argon CR-model. The second method resulted in lower $T_e$-values compared to the TS results. A possible explanation is the quenching of metastable 4s and 4p argon levels by oxygen atoms and molecules. These processes are not included in the CR-model. *(chapter 8)*

- The “rotational” temperature of a surfatron induced oxygen plasma with a minor amount of argon was determined using emission spectroscopic measurements of the atmospheric A-band transition $(b^1\Sigma_g^+, \nu = 0) \rightarrow (X^3\Sigma_g^-, \nu = 0)$. Via a molecular Boltzmann plot the rotational temperature was deduced. For the employed pressure range $4 \leq p \leq 10 \text{ mbar}$, the rotational temperature is close to the gas temperature. A major advantage of this method is that the gas temperature can be obtained from the oxygen plasma using emission spectroscopy without the addition of, for example, nitrogen. *(chapter 9)*

- Actinometry is a method that monitors the intensity ratio of spectral lines and can be used to determine the dissociation degree of molecular plasmas. As this method is experimentally easy, it is often applied to industrial plasmas. However, the employed equations to come from the line intensity ratio to the dissociation ratio are often based on too many simplifications. In this work, the actinometry method has been applied to an oxygen plasma with a small amount of argon added to the discharge. A theoretical discussion showed that the influence of molecular population, quenching and deviations from a Maxwellian distribution function can significantly alter the obtained dissociation ratio. *(chapter 10)*

Recommended future work:

- The TS setup can be used to measure the electron gas properties along the total column of the surfatron induced argon plasma. This gives more information about the end of the plasma column.

- The interpretation of experimental results obtained from molecular emission spectroscopy is extremely difficult. Therefore, it would be useful to apply TS to higher oxygen/argon ratios. The electron density, and thus the intensity of the TS signal, decreases when the oxygen/argon ratio increases. As a result, these TS measurements are only possible when a laser with a higher laser power is implemented in the setup.

- In this work, the gas temperature of an argon plasma was obtained from the Gaussian broadening of the $H\beta$ spectral line that is interpreted as a Doppler broadening. However,
it is not certain whether this interpretation is justified. In addition, the hydrogen that is sometimes added to the argon in order to measure the H$_{\beta}$ spectral line can alter the plasma properties significantly. As an alternative we suggest Rayleigh scattering. This is an active method that yields direct information about the gas temperature. These experiments can be performed using the same setup as used for TS, although stray-light due to the scattering of laser light on the quartz has to be minimized. This technique can be used to determine the gas temperature in a pure argon plasma and to validate the results obtained with Doppler broadening.

- The waveguide surfatron was especially designed for the application of high resolution emission spectroscopy to pure molecular plasmas. For the company Draka it is valuable that the current diagnostic study is continued to pure oxygen and Ar/SiH$_4$ plasmas.

- Industrial plasmas like the microwave induced deposition plasma at Draka can be investigated with emission spectroscopy. In molecular oxygen plasmas, actinometry can be used to estimate the dissociation ratio. The gas temperature and total particle density can be obtained via a spectroscopic measurements of the transition (b$_1^1\Sigma^+_g, \nu = 0$) $\rightarrow$ (X$_3^3\Sigma^-_g, \nu = 0$).

- The obtained experimental results for argon and oxygen can be compared with results of the surfatron model that is designed with Plasimo. At this moment, further improvements are being made to this model.
Summary

Spectroscopic study of microwave induced plasmas
Exploration of active and passive methods

Microwave induced plasmas (MIPs) are used for a number of high-tech applications like material processing, light generation, gas cleaning and spectrochemical analysis. Especially the feature that MIPs can be operated remotely and that the propagation of the microwaves can be manipulated with slits, chokes and dielectra offers numerous technological opportunities.

This thesis concentrates on low-pressure MIPs as used for the production of optical fibers by the company Draka Communications in Eindhoven. To improve this fabrication process, more insight in the plasma is needed. The modeling of these low pressure plasmas is difficult, since they are far from local thermodynamical equilibrium (LTE). Therefore, an accurate description of transport, chemistry and electromagnetic power coupling is required. Experimental data are needed to validate the results of the plasma models.

This study describes the application of several spectroscopic techniques to low-pressure MIPs in pure argon and in mixtures of argon/hydrogen and argon/oxygen. These techniques can be divided in passive methods such as emission spectroscopy and active methods like Thomson scattering, absorption spectroscopy and laser induced fluorescence. Due to the non-LTE character of the plasma, the processing of experimental data obtained from the passive methods is not straightforward: plasma models are required to extract important plasma properties such as the electron density and electron temperature from the data. Therefore, the results have to be compared with the results of active spectroscopy. After validation, the passive methods can be applied to plasmas for which it is not possible to apply the experimentally difficult active techniques, such as in industrial situations.

Active spectroscopy can not be applied to the MIPs used at Draka Communications. These plasmas are not easily accessible with passive spectroscopy either since they are shielded from their environment. Therefore, at the TU/e, a microwave setup has been built which resembles the microwave plasmas used at Draka. A surfatron is used to launch electromagnetic surface waves into a small quartz tube filled with argon or oxygen gas. This surfatron setup is small and flexible and is therefore easy to investigate with both passive and laser aided diagnostics. The surfatron induced argon plasma was studied using a number of passive diagnostic methods like absolute line intensity measurements, continuum measurements and $H_{\beta}$-broadening.
These results were compared with the results of one active spectroscopic method, laser Thomson scattering. A good agreement between the results was obtained for atomic plasmas. For molecular plasmas, a number of discrepancies were found. These require further investigations.

Another aspect of this work is the application of global plasma models. This type of models relates external control parameters such as the microwave power, plasma length, tube radius and gas pressure to the electron density, electron temperature and gas temperature. Also, these models are used to explain the trends observed in experimental results. For atomic argon plasmas, a good agreement between the experimental and global model results was found. For molecular plasmas, it was found that molecule assisted recombination is the main loss process for the electron density instead of ambipolar diffusion, as is the case for atomic plasmas. This implies that an accurate description of the plasma chemistry and kinetic reactions is required.
Related publications


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