From temperature to reactivity: Optical diagnosis of high-density plasmas

PROEFSCHRIFT

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Corrigendum

The rate coefficients used in the 0-D chemical kinetics model of Subsection 2.2.3 were off by a factor of 1000 due to a mistake in units. The present erratum states the correct values and presents how this changes the calculation of equilibration and quenching. The publication based on Chapter 2 [den Harder et al. (2016), Homogeneous CO₂ conversion by microwave plasma: Wave propagation and diagnostics, Plasma Processes and Polymers, 10.1002/ppap.201600120] contains the correct data and proper interpretation.

The correct rate coefficients are given in Table 6.1, which should replace Table 2.1. All the pre-exponential factors should be a factor 10^3 smaller than in the original table.

Table 6.1: Reactions between CO₂, CO, O₂, and O, listed with pre-exponential factors and activation energies, which are both taken from Reference Butylkin et al. [1979]. Pre-exponential factors are given in m^3 s⁻¹ for bimolecular, and m^6 s⁻¹ for termolecular reactions.
Because of the detailed balancing procedure, the ratios between forward and backward pre-exponential factors were correct in the original table. Consequently, the comparison with the results from the CEA model presented in Figure 2.14a still holds, as shown in Figure 6.1a, which is calculated on basis of the new rates. However, because the prefactors are 3 orders of magnitude smaller, the chemistry takes place at a slower timescale, as shown in Figure 6.1b. As a result, the system of differential equations needs to be integrated for 2.5 seconds to reach the CEA equilibrium composition.

Figure 6.1: The overall behaviour of the system of equations matches the CEA equilibrium calculation. To illustrate the composition changes as the CO₂ mixture heats and cools, two different temperature evolutions are simulated.

Using the correct rates leads to longer CO equilibration times, and the cooling rates needed to preserve CO are slower, as shown in Figure 6.2. The equilibration times are calculated by fitting an exponential decay to the CO₂ concentration.

The efficiency of thermal CO production in the case of linear cooling rates, as shown in Figure 2.16, needs to be replaced by Figure 6.3. Lower cooling rates are needed to preserve the formed CO.
Figure 6.2: A CO₂ mixture reaches chemical equilibrium on a milliseconds timescale, thus, high cooling rates are needed to suppress CO loss. The increasing O radical concentration with temperature leads to a larger fractional CO loss.

Figure 6.3: The efficiency of thermal CO production in the case of linear cooling rates. Sufficiently high cooling rates on the order of 10⁶ K s⁻¹ inhibit back reactions, and energy efficiencies in excess of 40 % are reached.
The interpretation of the Rayleigh scattering measurements relies on the assumption of a thermal composition. When the equilibration times exceed the residence times, the mixture in the reactor might not be fully thermalized. The residence times in the experiment are calculated assuming plug flow, using a central density measurement. Because the density has a minimum in the middle of the reactor, the calculated residence times will be underestimated. Consequently, in the experiment the composition could be thermalized while the condition is not strictly met.

The Rayleigh signal decreases with increasing temperature, and also decreases with the thermal composition at higher temperatures. Because thermalization and heating lead to loss of signal, both effects do not cancel each other out. In all the on-axis measurements in the diffuse regime, where the temperatures are the lowest, the axial density profile is constant. This is a direct experimental indication that the composition and temperature are constant in the observation volume. Since there is approximately 1 cm distance from the start of the waveguide to the observation volume, thermalisation might happen in this plasma volume.

Based on afterglow measurements, cooling rates on the order of $10^6 \text{ K s}^{-1}$ were estimated. With the correct implementation of the 0-D model, these cooling rates are sufficient to prevent back reactions, i.e. efficiencies approaching the ideal-quenching efficiency are attainable. This strengthens the argumentation that the gas temperatures and CO production rates in the reactor are consistent with a thermal composition.

Niek den Harder
2017-01-24
To my parents
From temperature to reactivity:
Optical diagnosis of high-density plasmas

This thesis is centred around understanding of molecular processes (or chemical reactivity) in dense plasma environments on basis of insight in the thermal energy that is contained in the different degrees of freedom. Particularly emphasized is the non-thermal character of the systems under study: a different temperature is assigned to the electrons, ions, neutral gas and/or the vibrational and rotational degrees of freedom. Both active (laser scattering) and passive (emission spectroscopy) methods are used on a variety of plasmas, ranging from atmospheric carbon dioxide plasmas for generating solar fuels to the scrape-off layer of fusion reactors.

Plasma dissociation of CO$_2$: a first step towards solar fuel

Microwave plasmas can efficiently dissociate CO$_2$ into carbon monoxide and oxygen because of their non-equilibrium nature. Plasma electrons activate the carbon dioxide, while the gas temperature remains low, enabling energy efficiencies higher than thermolysis. The electron temperature is crucial to ensure maximum energy transfer to vibrational degrees of freedom, which directly leads to dissociation. A 2.45 GHz, 1 kW microwave plasma reactor is characterized with laser scattering (neutral density), FTIR (composition of exhaust), and optical emission (plasma size). CO production with high energy efficiency is demonstrated. The role of non-thermal processes is investigated on basis of modeling.

Fusion divertor grade plasma in linear machines

Linear plasma generators are an effective and flexible method to study Plasma Surface Interaction in divertor grade conditions. Reactive molecules, a by-product of the plasma source, lead to plasma loss via Molecular Activated Recombination. The rates depend steeply on the vibrational energy of the reacting molecules. In the linear machine Pilot-PSI, the vibrational temperature of the molecules was measured by spectroscopy on the Fulcher-$\alpha$ band, to establish the relative importance of the various MAR reactions. In addition, rotational and gas
temperatures were measured to establish relative densities. Molecules diffusing into the high-density plasma beam were found to rarefy due to fast heating.

Particle fluxes from plasma facing components are generally quantified with the $S/\chi_B$ method. It links photon fluxes to particle fluxes by assuming a local balance between ionization and excitation, set by the electron temperature. To extend this approach for tungsten to the low temperature range of $0.5$-2 eV, a controlled amount of W was introduced into the high density plasma ($1$-$6 \times 10^{20} \text{m}^{-3}$) of linear machine Pilot-PSI. Tungsten migration was studied with spectroscopy on the WI 400.9 nm line, and the total photon fluxes were used to calculate inverse photon efficiencies. The agreement is quantitative at the upper end of the studied temperature range. However, the measurements do not scale with the ionization and excitation rates at lower temperature. A simple model shows that escape of neutral tungsten from the plasma causes the measured "effective" $S/\chi_B$ to increase for decreasing temperature.

In-situ quantification of W sputtering in the JET tokamak

Tungsten erosion was quantified at the JET tokamak with optical emission spectroscopy. A novel cross-calibration procedure was developed to link slow high-resolution spectroscopy and fast PMT measurements to obtain the necessary time resolution to resolve the transient Edge Localized Modes. Tungsten erosion between ELMs was mainly caused by beryllium impurities, since the edge plasma temperature is below the sputter threshold of the fuel species. Sputtering during ELMs dominates the total W source, and this contribution varies independently from the inter-ELM erosion. The increased ion energy during ELMs causes fuel species also to sputter. The total W outer divertor source is found to linearly increase with the power crossing the separatrix, whilst excessive divertor fueling can break this trend. The influence of the W source rate on the tungsten content of the core plasma is investigated using the tungsten content as determined with Soft X-Ray emission.
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Chapter 1

Introduction

1.1 Energy in the 21st century: a changing landscape

Unsustainability of non-renewable sources

Growth in world population and energy consumption per capita are the main drivers of energy demand. Both trends have resulted in a tremendous increase in the world energy consumption over the 20th century, increasing from 0.40 exajoules in the year 1800, to 22 exajoules in 1900, to 363 exajoules in 2012 [Etemad et al., 1991; IEA, 2012]. Currently, we are heavily reliant on fossil fuels to meet the energy requirements. In 2010, more than 80 percent of the worldwide energy supply consisted of fossil fuels: natural gas, oil, and coal [IEA, 2012]. Our need for fossil fuels is undesirable for three main reasons: exhaustibility of fossil fuels, economic dependence on politically unstable regions, and the environmental impact of carbon dioxide emissions that are generated when burning fossil fuels.

As the 2015 Paris agreement illustrates, the environmental impact in the form of climate change is the main reason to transition to fully renewable energy generation in the next 50 years [UN, 2016]. However, the exhaustibility of fossil fuels also deserves some attention. Fossil fuels were formed by natural processes over millions of years, and we are currently burning fuels at a rate that will deplete reserves sometime in the near future. The moment at which the oil production rate is maximum, peak oil, will most probably be reached before 2030, after which the production rate will enter a terminal decline [Sorrell et al., 2010]. Estimating the peak in gas production is trickier because of uncertainties in the projected reserves and the demand-production models, but it is expected to be in the period 2025-2066 [Mohr and Evans, 2011]. The uncertainty on the world coal reserves is large, but scientific studies indicate that the world coal production will most probably peak within 50 years, even when using very optimistic estimates on recoverable
resources [Höök et al., 2010; Maggio and Cacciola, 2012; Mohr and Evans, 2009]. In conclusion, depletion of non-renewable sources will start playing a role sooner than commonly realized. Scarcity is already presently resulting in geopolitical friction [Klare; Randerson, 2009]. When these resources become scarcer, it is assumed that international relations become more strained. However, the main argument for a transition to renewables is the multitude of observations indicating the detrimental effect of an excess of atmospheric CO\(_2\) on ecosystem earth [IPCC, 2014c].

CO\(_2\) and climate change

This section about the role of CO\(_2\) in the earths climate system is based on the following IPCC reports: [IPCC, 2014a,b,c]. Numbers are taken from these reports unless stated otherwise.

The earth has a natural carbon cycle in which large amounts of CO\(_2\) move around. The oceans and land vegetation release and absorb over 200 billion tons of carbon into and out of the atmosphere each year. Since human activities account for approximately 7 billion tons of carbon release annually, the anthropogenic contribution to this cycle is relatively small. However, this contribution is enough to push the system out of balance. Only half of the human CO\(_2\) emission is absorbed by oceans and land vegetation, and the added carbon dioxide in the atmosphere is very persistent [Canadell et al., 2007; Solomon et al., 2009]. The effect of human activity on the atmospheric carbon dioxide concentration is undeniable. First measurements at the Mauna Loa observatory in 1958 reported atmospheric carbon dioxide concentrations of 313 ppm [Dlugokencky et al., 2014]. Since then, there has been an accelerating rise of atmospheric carbon dioxide, and the 400 ppm level was first exceeded in 2013, in the week of May 26th [Dlugokencky et al., 2014]. Ice core data, which is able to track the atmospheric CO\(_2\) content over longer timescales, indicates that for 650 thousand years, the CO\(_2\) concentration did not exceed 300 ppm [Petit et al., 1999].

The effect of the changing atmospheric composition on the heat balance of the earth is evaluated by considering the radiative forcing of the added carbon dioxide. Radiative forcing is defined as the difference of radiated and absorbed energy by the earth. The main contributions to the radiative balance are greenhouse gases and ozone, and their impact is well quantified. Smaller contributions are for example stratospheric water, albedo, aerosols and solar irradiance variations. As shown in Figure 1.1, the extra greenhouse gases added to the atmosphere by human activities contribute a large positive term to the radiative balance, resulting in net warming.
Figure 1.1: Global average radiative forcing in 2005 (best estimates and 5 to 95% uncertainty ranges) with respect to 1750 for CO₂, CH₄, N₂O, and other important agents and mechanisms [IPCC, 2007].

The causes and mechanisms of human induced global warming are well understood, and the effects of human induced global warming are confirmed by a variety of observations. Eleven of the twelve years from 1995 and 2006 rank among the twelve warmest years in the instrumental record of global surface temperature, which is kept since 1850 [IPCC, 2007]. The temperature increase is global, but is larger at higher northern latitudes. Warming is linked to changes in rainfall, such as a pattern of drying over much of the already dry subtropics [IPCC, 2007]. Heat waves have become more frequent over most land areas. Land regions have warmed faster than the oceans, although the oceans have been taking up over 80 percent of the added heat to the climate system. The combined effect of thermal expansion and melting land ice, has resulted in a global sea level rise of 0.19 meter. The sea level at the Dutch coast has risen by an average of 0.20 meter over the past century [Bresser et al., 2006]. This is of special interest since 26 percent of the land area of the Netherlands is below sea level, using Normaal Amsterdams Peil as the datum for sea level. Extrapolation of these trends is difficult given the large number of unknowns, but it is clear that climate change affects all regions around the world, mostly in a negative fashion.

The temperature increase caused by the extra atmospheric CO₂ is not expected to decrease significantly even if CO₂ emissions were to completely cease. Future and current emissions thus will lead to irreparable adverse changes in climate, irreversible on a time scale exceeding the end of the millennium in 3000 [Solomon et al., 2009]. To minimize the consequences, the carbon dioxide emissions need to
be reduced. In the Netherlands, the share of renewable energy in the total energy consumption increased from 1.4 percent in 2000 to 3.7 percent in 2010, while the absolute amount of energy from renewable sources almost tripled [van der Veen, 2012]. Still, there is a 96.3 percent gap to bridge, to fully transition to a renewable energy infrastructure.

Societal relevance of research

The use of energy has played a key role in the development of society. Our current fossil fuel use can be sustained for approximately one more century, and this will come at the price of far reaching environmental damage. Public awareness of these issues grows as people become more educated, and renewable sources are being implemented at an increasing rate [IEA, 2012; Lee et al., 2015].

A fully sustainable energy infrastructure does require several short-term and long-term technology solutions. There is a worldwide effort to develop and improve energy sources with minimal CO₂ emissions, such as fusion, fission, solar, and wind. Simultaneously, methods such as energy storage, smart grids, and dynamic pricing are explored to ready our energy infrastructure for the different demands of renewable sources. DIFFER, the Dutch Institute For Fundamental Energy Research, focuses on two energy related research themes: solar fuels and fusion. The solar fuels research theme addresses a critical issue for the implementation of renewables: intermittency. Storage of electrical energy in fuels is a method to mitigate fluctuations that renewable sources impart on the electricity grid. Solar fuels also contribute to sector integration, because renewable energy is then directly usable for e.g. transport. The fusion research theme is a longer running programme that aims at developing nuclear fusion as a renewable energy source. Both projects are listed as grand challenges of the 21st century by the National Academy of Engineering [Perry et al., 2008].

The two research themes will be introduced in more detail in the next sections. There will be special focus on the aspects that were researched in the context of this thesis. In the solar fuels chapter, the characterization of a microwave plasma is described, with emphasis on the non-equilibrium chemistry which enables high energy efficiencies. In the fusion chapters, tools to monitor tungsten erosion are benchmarked in linear machines and applied to fusion devices.
1.2 Solar fuels: energy storage in chemical bonds

Intermittency and storage of renewable sources

Renewable energy sources are naturally replenished on a human timescale, such as sunlight, wind, rain, tides, waves, and geothermal heat. Out of these sources, solar energy alone exceeds the current worldwide energy consumption by more than three orders of magnitude [Moriarty and Honnery, 2012]. Despite their abundance, most renewable sources can only supply energy locally and intermittently. Energy storage in fuels is a possible solution to both problems.

As of March 2012, more than 99 percent of the total installed grid energy storage is pumped-storage hydroelectricity, with about 130 gigawatt installed worldwide [economist, 2012]. The energy efficiency of this storage method is good, between 70 and 80 percent. However, since water needs to be stored at high altitudes, this method is only practical for a select group of countries. Also, this method stores electricity, whereas for some applications liquid fuels are preferred.

Unlike most energy storage methods, liquid fuels are very energy dense, in the gravimetric as well as the volumetric sense of the word. In addition, fuels can store energy for extended periods of time, and there is an existing infrastructure to transport fuels over global distances. Take for example the natural gas network extending through Germany. It is vast in terms of energy storage, it can store more than 200 terawatt hours, enough to satisfy demand for several months. This is in stark contrast with the combined pumped storage power plants, which only have a capacity of 0.04 terawatt hours. Additionally the transport of energy through a gas network is done with much less loss (<0.1%) than in a power network (8%). In conclusion, fuels are attractive as an energy storage and carrier medium, since fuels are stable, energy dense and easily transported. However, the practical application of liquid fuels as energy storage requires an energy efficient electricity to fuel conversion technique.

Fuels produced from renewable energy sources are called solar fuels. Possible feedstock materials include CO\textsubscript{2} and H\textsubscript{2}O. Using carbon dioxide as feedstock would allow to close the carbon cycle. Since atmospheric CO\textsubscript{2} is rather dilute, capture is key. Carbon capture projects are currently in development, but these techniques are not yet mature. Carbon capture is incentivized via e.g. carbon emission trading schemes. Notwithstanding the feedstock material, an efficient synthesis method for solar fuels is a prerequisite for the storage of large amounts of energy in fuel, which is needed when renewables are used for electricity generation.
Dissociation of CO$_2$: a first step towards fuel

In the conversion of carbon dioxide into fuels, an essential first step is to break up the CO$_2$ molecule. Different power to fuel and power to gas schemes are already available, and some approaches have been demonstrated at the megawatt scale [Fraunhofer-Gesellschaft, 2010]. However, processes based on electrolysis generally use scarce materials as catalysts and cannot be switched at short timescales. Schemes with carbon dioxide as feedstock in most cases use high pressures and temperatures to drive the chemical equilibrium in the direction of CO$_2$ splitting. This thermal approach has an inherent energy efficiency limit of 50 percent, because excess energy is spent in heating up the reactants and products.

To avoid these disadvantages, a different method is researched in the context of this thesis: dissociation of carbon dioxide in a microwave plasma. To connect with existing power to fuel methods such as electrolysis and thermolysis, this approach is dubbed plasmolysis. Plasmolysis of CO$_2$ has several advantages. It has low inertia, i.e. it can be switched on short timescales, which is ideal for grid balancing purposes. Since reactive species are generated in the plasma, no rare materials need to be used for catalysis. The high power density makes it scalable to high throughputs using only a small footprint. Microwave technology is relatively cheap, so that a significant amount of reactor downtime is not immediately prohibitive from a cost perspective.

The combination of these advantages make plasmolysis of carbon dioxide an attractive process to convert CO$_2$ into value-added chemicals. Still, some hurdles remain before this technique can be competitive with existing power to fuel schemes. The overall energy efficiency is an important parameter for a successful implementation of the process. Energy efficiencies of 80 percent have been demonstrated for dissociation of carbon dioxide in a microwave plasma [Rusanov et al., 1981]. These efficiencies were ascribed to the non-equilibrium nature of the plasma, where a large fraction of the microwave energy goes into vibrational excitation while the translational temperature stays low, which enhances the rate of the dissociation reactions. However, these high energy efficiencies were obtained at low conversion degrees, so that the output of the reactor still contained a large amount of CO$_2$. This is not ideal, and it is important to break this tradeoff. The first step towards improving these parameters is a fundamental understanding of the reactor chemistry and physics.

Microwave reactor and diagnostics

At DIFFER we constructed a pilot reactor to investigate various research questions: can we reproduce the high energy efficiencies, to what extent is the plasma in non-equilibrium, what is the physical mechanism is behind the obtained efficiencies,
Figure 1.2: A photograph of one of the reactors constructed at DIFFER. Carbon dioxide is injected from the top, the plasma is created in the waveguide.

and how to obtain high conversion degrees at high efficiencies.

A photograph of one of the reactors is shown in Figure 1.2. The heart of the reactor is a 1 kW microwave, which runs at 2.45 GHz, the same frequency and power output as a standard kitchen microwave. At 100 percent energy efficiency, this reactor could dissociates more than half a kg of carbon dioxide per hour. The microwaves are absorbed by a CO$_2$ plasma inside a quartz tube. At one side of the tube there is a gas inlet for various gases. The tube is pumped to reach reduced pressure conditions, the composition of the exhaust gas is monitored with Fourier Transform InfraRed absorption spectroscopy. The reactor performance is characterized on basis of the reaction products.

The pilot reactor is designed to provide good optical access for the laser scattering diagnostic which was constructed in the context of this thesis. With Rayleigh scattering, the neutral density is measured, which provides insights in microwave propagation behaviour and the local gas temperature. Measured quantities are used as input for plasma-chemical models to estimate the degree of non-equilibrium, and identify the physical mechanisms behind the observed reactor characteristics.
1.3 Fusion: abundant base-load electricity

Reactor concept: a star in a box

Fusion is a potential source of energy for future generations. The principle of fusion is that light nuclei fuse together and release energy because of the mass difference between reactants and products. The potential benefits of fusion are manifold: a virtually limitless supply of fuels located practically everywhere, low carbon dioxide emission, inherent safety, and no long-lived radioactive waste. However, there are also drawbacks. The 14.1 MeV neutrons created in D-T fusion reactions can activate materials [Glaser and Goldston, 2012; Zinkle and Busby, 2009]. Fusion power plants will require a high investment compared to conventional power plants. Electricity generation from fusion is yet unproven at a commercial scale. However, the potential benefits justify continued research and development effort.

The three prerequisites for fusion, fuel density \( n \), energy confinement time \( \tau_E \), and fuel temperature \( T \), are combined in the fusion triple product, \( n\tau_E T \), which is the figure of merit to judge fusion performance [Lawson, 1957]. We will limit ourselves here to tokamaks because these machines feature the highest triple product [Hawryluk, 1998]. In a tokamak, a hot plasma is confined in the shape of a torus with magnetic fields, as illustrated in Figure 1.3. From 1970 to 2000 the fusion triple product has doubled every 1.8 years [Ikeda, 2010]. As a result, confinement is no longer limiting in order to build a fusion power plant.

Technical challenges: wall materials

A working fusion reactor results in tremendous heat and particle fluxes to the wall, which is demanding on the wall material. Early tokamaks used limiters, which is a solid surface that sticks into the plasma, limiting the plasma edge. The main disadvantage of this approach is that impurities are introduced directly into the confined plasma. The use of a divertor is a way to overcome this problem. The divertor configuration is a modification to the magnetic field structure of the tokamak, so that the heat and particle exhaust takes place on the divertor plates, at a distance from the main plasma. The JET tokamak has been operated with both configurations, as illustrated in Figure 1.4 [Todd and Windsor, 1998]. Note that also in the diverted geometry, the heat and particle exhaust occurs on a surface area that is small compared to the total wall area. For a fusion reactor this results in stationary heat loads on the order of 10 MW per m\(^2\), with transient excursions to heat loads on the order of 10 GW per m\(^2\) during instabilities such as Edge-Localized Modes [ITER, 1999; Loarte et al., 2007]. For comparison, the heat load at the surface of the sun is 63 MW per m\(^2\) [Grayzeck, 2013].
Candidate wall materials are refractory metals, a class of metals that are very resistant to heat and wear. Tungsten is one of these refractory metals, it has the highest melting temperature of all metals, and a relatively high heat conductivity [Haynes, 2012]. In addition, it retains little fuel, and has a low erosion yield [García-Rosales et al., 1995; Haasz et al., 1998; Kirschner et al., 2000]. The actual tungsten erosion in a fusion reactor depends on the local plasma composition and temperature and therefore should be carefully monitored. Because of the high atomic number, tungsten impurities radiate away a substantial amount of power, deteriorating fusion performance when the core concentration of tungsten is above a few times $10^{-5}$ [Pütterich et al., 2010]. This low concentration requires on the one hand a minimization of the tungsten sources, e.g. by controlling divertor plasma parameters, and on the other hand the suppression of tungsten transport into the core plasma.

The next step in tokamak research, the International Thermonuclear Experimental Reactor, is currently being constructed in the south of France. The project aims to run at a $Q$ of 10, which means that the energy from fusion reactions will exceed the heating power by a factor of 10 [Ikeda, 2010]. ITER will feature a beryllium (Be) main wall and a full tungsten (W) divertor [Griffith, 2013; Pitts et al., 2009]. This combination of a low-Z material for the main wall and a refractory metal for the divertor is selected to give a large operational flexibility as well as
Figure 1.4: Two poloidal cross sections of the JET tokamak show the difference between the limiter configuration and the divertor configuration. The separatrix is the boundary between the core plasma and the Scrape-Off Layer. Figure Copyright ©EUROfusion 2014-2018.

the capability to handle large heat and particle fluxes to the divertor. In order to provide an integrated demonstration of the impact of this material combination, the JET tokamak is currently equipped with the ITER-Like Wall (ILW), which consists of solid beryllium limiters and a combination of bulk W and W-coated carbon fibre composite divertor tiles[Matthews et al., 2007, 2011]. Understanding divertor erosion in the JET ITER-Like Wall environment is an important step forward towards the successful exploitation of ITER. In this thesis, tungsten sputtering in JET was studied to obtain a consistent picture of tungsten erosion in terms of local plasma parameters, both during stationary and transiently increased plasma loads.

Plasma surface interaction in linear machines

Experiments in a tokamak provide an integrated test of the impact of wall materials on operational aspects, but a fusion reactor is a complex environment with limited diagnostic access. Linear plasma generators can help build a larger knowledge base because they offer a cost-effective, flexible way to investigate Plasma-Surface Interaction in reactor relevant conditions. In linear machines, candidate divertor materials can be tested in ITER-relevant plasma conditions, and studied with a wide array of plasma and surface diagnostics, both during and after plasma exposure. The ease of diagnostic access and control over the plasma parameters make linear plasma generators well-suited to develop and benchmark diagnostic techniques.
At DIFFER two linear plasma generators are operational, Pilot-PSI and Magnum-PSI, which create plasma conditions that mimic the projected conditions in the divertor of ITER\cite{van Eck et al., 2012; van Rooij et al., 2007}. The plasma parameters that are expected in the ITER divertor are high electron densities in the range $10^{20}$-$10^{21}$ m$^{-3}$ and low electron temperatures in the range 1-5 eV\cite{ITER, 1999}. To achieve these extreme conditions in a linear setup, both machines use a cascaded arc plasma source, and confine the plasma with a magnetic field. The electron temperature and density in Pilot-PSI and Magnum-PSI are measured with Thomson scattering. In the cascaded arc source, a feed gas such as hydrogen is ionized by an arc current. The source co-exhausts a large number of hydrogen molecules with the plasma due to the limited ionization efficiency. These molecules lead to plasma recombination reactions, and the importance of these processes is studied in the context of this thesis with emission spectroscopy.

In Pilot-PSI and Magnum-PSI the behaviour of materials under extreme heat and particle fluxes is investigated with a suite of surface and plasma diagnostics. Different damage mechanisms are studied in these controlled environments, such as e.g. physical sputtering and chemical erosion. Linear machines are also well equipped to study surface modifications that occur over longer timescales, such as retention of deuterium and tritium, because of the high fluences that can be reached. Linear machines provide an excellent opportunity to test new divertor concepts for future reactors such as liquid metal divertors by virtue of the ease of access and flexibility. In addition, diagnostic techniques can be tested in a controlled environment. In this thesis, tools to monitor tungsten erosion were benchmarked.

1.4 This thesis

In the previous sections, two extensive research fields were briefly introduced. On first glance, the two are very different, with the low temperature molecular plasmas used for the production of solar fuels at one and of the scale, and the atomic, fully ionized plasmas in a fusion reactor at the other end. However, on closer inspection, there are many similarities in both plasma physics and diagnostics in the topics studied in this thesis. All the plasmas under study have a low electron temperature in the range 1-5 eV, and a high electron density in the range $10^{18}$-$10^{21}$ m$^{-3}$. These plasmas are studied with optical techniques, passively with emission spectroscopy, and actively with laser-based spectroscopy.

A central theme in this thesis is the quantification of molecular processes (or chemical reactivity) in dense plasma environments on basis of insight in the thermal energy that is contained in the different degrees of freedom.
In all cases, optical methods are used to determine a characteristic temperature that governs the importance of various candidate reaction pathways. Particularly emphasized is the non-equilibrium character of the systems under study: a different temperature is assigned to the electrons, ions, neutral gas, and the vibrational and rotational degrees of freedom. In the following paragraphs I will briefly introduce the main research questions that are investigated for each of the subtopics.

Characterization of a solar fuels reactor

A microwave reactor is constructed to dissociate CO$_2$ into CO and O$_2$. This first step in the production of solar fuels can be performed efficiently in a plasma because of the non-equilibrium nature of the plasma. Plasma electrons excite vibrational degrees of freedom in the carbon dioxide molecule, while the gas temperature remains low. Our research question is: “How efficiently can we dissociate CO$_2$ using a plasma environment?” To answer this question, we investigate which processes are driving the chemistry in the plasma. Are dissociation reactions promoted by vibrational excitation, or do thermal processes play the dominant role? To this end a laser scattering diagnostic is built to measure gas densities in-situ to gain insight in the translational temperature in the plasma.

Residual gas entering high density hydrogen plasma

Linear plasma generators are an effective and flexible method to study Plasma Surface Interaction in divertor-grade conditions. Reactive molecules, a by-product of the plasma source, lead to unwanted plasma loss via Molecular Activated Recombination. The rates of these reactions depend strongly on the vibrational energy of the reacting molecules\cite{Janev2002}. Our research question is: “What is the importance of the several MAR mechanisms in the linear plasma generators Pilot-PSI and Magnum-PSI?” To determine the reaction rate coefficient, the vibrational temperature of the molecules is measured with spectroscopy on the Fulcher-α band. The molecular density in the center of the plasma column is estimated with an analytical model using the measured rotational and gas temperatures as input.

Spectroscopic study of tungsten erosion and migration

Quantification of particle fluxes from plasma facing components is generally done using the $\gamma_{XB}$ method, which links photon fluxes to particle fluxes by assuming a local balance between ionization and excitation, set by the electron temperature. For tungsten, this approach is extended to the low electron temperature range of 0.5-2 eV. To this end, a controlled amount of W is introduced into the high-density plasma of linear machine Pilot-PSI. Tungsten migration is studied with
spectroscopy on the WI 400.9 nm line, and the total photon fluxes are used to calculate inverse photon efficiencies. Although at the upper end of the studied temperature range the agreement is quantitative, at low temperature the measurements scale opposite to the ionization over the excitation rates. Based on numerical estimates of the ionization behaviour of the sputtered tungsten, we show that the measured scaling is caused by losses of neutral tungsten from the plasma.

**ELM-resolved divertor erosion in the JET ITER-Like Wall**

Divertor erosion is studied in JET in the ITER-Like Wall environment. The main research questions concern quantification of sputtering during ELMs and in-between ELMs, sputtering species identification, and the relation between the sputtered tungsten and the tungsten content of the plasma core. Particle fluxes to and from the outer divertor are quantified with emission spectroscopy using the $S_{XB}$ approach. A cross-calibration procedure is developed to obtain data with sufficient time resolution to resolve Edge-Localized Modes. During the ELMs, heat and particle fluxes are transiently increased, which both lead to enhanced erosion. The relative importance of erosion during ELMs and in-between ELMs is investigated. The sputtering species are different for inter- and intra-ELM sputtering, which indicates what fluxes to minimize to decrease tungsten sputtering. Transport of sputtered tungsten to the plasma core is investigated using Soft X-Ray emission to determine the core content.

### 1.5 Publications

This thesis is based on the following publications:

- **CO production in a MW plasma: A thermal equilibrium study**
  N. den Harder, D. C. M. van den Bekerom, M. F. Graswinckel, F. J. J. Peeters, J. M. Palomares, S. Ponduri, T. Minea, W. A. Bongers, M. C. M. van de Sanden, and G. J. van Rooij, To be submitted

- **Residual gas entering high density hydrogen plasma: rarefaction due to rapid heating**
  N. den Harder, D. C. Schram, W. J. Goedheer, H. J. de Blank, M. C. M. van de Sanden, and G. J. van Rooij, Plasma Sources Science and Technology, 24(2):025020 2015

- **Spectroscopic study of tungsten erosion and migration in high density low temperature plasmas**
  N. den Harder, M. F. Graswinckel, A. R. Lof, M. J. van de Pol, and G. J. van Rooij, To be submitted to the Journal of Nuclear Materials
• ELM-resolved divertor erosion in the JET ITER-Like Wall
  N. den Harder, S. Brezinsek, T. Pütterich, N. Fedorczak, G. F. Matthews, A.
  Meigs, M. F. Stamp, M. C. M. van de Sanden, G. J. van Rooij, and JET Contributors
  Nuclear Fusion, 56(2):026014 2016

The author of this thesis is co-author on the following publications:

• FDCDU15 - Carbon Dioxide Utilisation: Exploiting CO2 vibrational excitation
to achieve an energy efficient route for CO2 based artificial fuels
  G. J. van Rooij, D. C. M. van den Bekerom, N. den Harder, T. Minea, G. Berden,
  W. A. Bongers, R. A. H. Engeln, M. F. Graswinckel, E. Zoethout, and M. C. M.
  van de Sanden, Faraday Discussions 2015

• Migration of tungsten dust in tokamaks: role of dust–wall collisions
  S. Ratynskaia, L. Vignitchouk, P. Tolias, I. Bykov, H. Bergsåker, A. Litnovsky, N.
  den Harder, and E. Lazzaro, Nuclear Fusion 53(12):123002 2013

• Plastic adhesive impacts of tungsten dust with metal surfaces in plasma en-
nvironments
  S. Ratynskaia, P. Tolias, A. Shalpegin, L. Vignitchouk, M. De Angeli, I. Bykov,
  K. Bystrov, S. Bardin, F. Brochard, D. Ripamonti, N. den Harder, and G. De

• Fast camera observations of injected and intrinsic dust in TEXTOR
  A. Shalpegin, L. Vignitchouk, I. Erofeev, F. Brochard, A. Litnovsky, S. Bozhenkov,
  I. Bykov, N. den Harder, and G. Sergienko, Plasma Physics and Controlled
  Fusion 57(12):125017 2015

• ELM-induced W sputtering sources in JET
  S. Brezinsek, N. den Harder, and C. Guillemaut, Bulletin of the American Physical
  Society 2015

• Plasma operation with full W divertor - experiences from JET equipped with
  the ITER-Like Wall
  S. Brezinsek, M. Rubel, G.F. Matthews, R. Neu, A. Garcia-Carrasco, C. Giroud,
  C. Guillemaut, N. den Harder, A. Huber, S. Jachmich, J. Likonen, M. Mayer, I.
  Nunes, G. Sergienko, and JET contributors, 29th Symposium on Fusion Technology 2016
Chapter 2

CO production in a MW plasma: A thermal equilibrium study


Abstract

Plasma dissociation of CO\textsubscript{2} in a 2.45 GHz, 1 kW microwave reactor is studied with laser scattering, FTIR, and optical emission to quantify the contribution of non-thermal processes. Two operating regimes are identified as function of pressure: the diffuse and constricted plasma mode. Their occurrence is caused by microwave propagation behaviour, which changes with the electron-heavy particle collision frequency $\nu_{e-h}$.

In the diffuse mode, gas temperatures of 1500 - 3500 K are determined. The measured conversion degree, specific energy input, and temperature are used as input for a two-temperature thermal model, which is solved to obtain the gas temperature at the periphery of the reactor and the size of the hot zone. Solutions are found with edge temperatures of hundreds of K, and hot zone fractions which agree with the measured behaviour. The agreement shows that non-thermal processes are not needed to explain the reactor parameters in the diffuse discharge.

In the constricted mode, the radial plasma size is independent of power. A skin depth equal to the plasma size corresponds to electron densities of $10^{18}$ - $10^{19}$ m\textsuperscript{-3}. Temperatures in the central filament are in the range 3000 - 5000 K.

Both discharge modes are up to 50 % energy efficient in CO production. The Rayleigh signal in the afterglow increases, which could be interpreted as gas cooling, but the composition dependence of the Rayleigh scattering cross section makes this interpretation speculative.
2.1 Introduction

Anthropogenic emissions of greenhouse gases are at a historic high, and the associated changes in atmospheric composition have resulted in a global surface temperature increase\cite{IPCC2014c}. Concerns about human-induced climate change have led to an increased use of renewable sources for energy generation. Most of these sources are intermittent, and fluctuations lead to periods where the supply exceeds the demand, during which time energy storage is needed. In addition, most renewable sources produce electricity, while less than 20% of the total energy is consumed in that form\cite{IEA2012}. Converting electrical energy into chemical fuels would thus not only be useful for energy storage, but also for sector integration: deployment of sustainable energy in e.g. transportation. In addition, fuels are a long-term storage solution which is easily transportable over global distances.

A promising power to fuel approach is dissociating CO$_2$ in a microwave plasma. This approach has several advantages over traditional methods for chemical conversion, such as thermolysis and electrolysis\cite{Gomez2009, Huang2007}. Microwave reactors can be switched on subsecond timescales, which is ideal for grid balancing purposes. Since reactive species are generated in the plasma, no rare materials need to be used for catalysis. Power densities are high for microwave reactors, which enables compact plants. Microwave technology is relatively cheap, so that a significant amount of reactor downtime is not immediately prohibitive from a cost perspective.

Energy efficiencies of 80% have been demonstrated for CO$_2$ dissociation in microwave plasmas, albeit at low conversion degrees\cite{Rusanov1981}. Record efficiencies were reached in non-thermal plasmas, where different degrees of freedom have different temperatures. In these non-thermal plasmas, especially the vibrational modes are excited, which enhances rates for dissociation reactions. This enables high energy efficiencies since most of the energy invested in vibrational excitation contributes to dissociation, whereas thermal dissociation has an inherent energy efficiency limit of approximately 50 percent. To sustain the non-equilibrium between the gas temperature and the vibrational temperature, it is vital that a large fraction of the discharge energy is transferred from the plasma electrons to the vibrational modes. For CO$_2$ this is calculated to be the case for an electron temperature range of approximately 1-2 eV\cite{Rusanov1981}. A low gas temperature suppresses relaxation of the vibrational modes into translational excitation.

In this chapter, microwave propagation theory is outlined because the absorption behaviour dictates the plasma parameters, e.g. via the discharge size. The energy efficiency limits in case of thermal dissociation followed by quenching are studied computationally. A microwave reactor, designed for optimum diagnostic
access, is studied experimentally with laser scattering, FTIR and emission measurements. Optical emission is used to study the different modes of plasma operation at different pressures. With the laser diagnostic, neutral density profiles are determined via Rayleigh scattering. The local neutral density plays an important role in the microwave propagation via the electron-heavy particle collision frequency. The neutral density also gives insight in the temperature in the reactor, which provides a measure for the degree of non-equilibrium in the reactor. Neutral density profiles in the afterglow of the plasma give insight in the quenching behaviour. The composition of the effluent is measured with Fourier Transform InfraRed absorption spectroscopy. The measured conversion degree, specific energy input, and temperature are used as input for a two-temperature thermal model, which is solved to obtain the gas temperature at the periphery of the reactor and the size of the hot zone. The main aim of the current study is to quantify performance in a wide range of parameters and identify to what extent non-equilibrium processes are driving the CO₂ dissociation chemistry in the reactor.

2.2 Theory

2.2.1 Microwave propagation and absorption in plasmas

In the plasma reactor, a large range of pressures is accessible, and this leads to different microwave absorption behaviour via the associated change in electron-heavy particle collision frequency. Microwave absorption properties determine the plasma parameters, e.g. absorption over small length scales limits the plasma volume and results in a high power density. In this section, criteria are derived for wave propagation in plasmas with and without collisions. Analytic expressions are derived for the real and imaginary part of the refractive index, which are functions of the neutral density, and the electron temperature and density. With the refractive indices, reactor relevant parameters are calculated. Changes in absorption behaviour as function of the neutral density will be shown, and how plasma parameters such as the electron density can be estimated from bulk properties such as the plasma size.

The plasma frequency \( \omega_p \) expresses the electrostatic oscillation frequency in response to a small charge separation. The plasma frequency is given by:

\[
\omega_p = \sqrt{\frac{n_e e^2}{m_e \epsilon_0}}
\]  

(2.1)

and depends only on the electron density \( n_e \).
In the absence of collisions, the relative permittivity $\varepsilon_r$ depends on the plasma frequency as:

$$\varepsilon_r = 1 - \frac{\omega_p^2}{\omega^2} = 1 - \frac{n_e e^2}{m_e e_0 \omega^2}$$  \hspace{1cm} (2.2)

where $\omega$ is the angular frequency of the wave.

Since the index of refraction is given by $\sqrt{\varepsilon_r}$, and propagation of electromagnetic waves requires that the index of refraction is real, only waves that satisfy the condition $\omega > \omega_p$ can propagate in the plasma. For 2.45 GHz microwaves, this means that the critical electron density, at which $\omega$ is equal to the plasma frequency $\omega_p$, is $7.5 \times 10^{16}$ m$^{-3}$. As a consequence, microwave propagation is possible only at electron densities below this critical density. The expression for $\varepsilon_r$ given above is valid in the absence of collisions, penetration of microwaves below the plasma frequency may still be possible if collisions between electrons and heavy particles hinder the response of the electrons to the field and thus the shielding.

The effect of electron-heavy particle collisions is included in the following expression for the relative permittivity:

$$\varepsilon_r = 1 - i \frac{\sigma_\omega}{\varepsilon_0 \omega}$$  \hspace{1cm} (2.3)

with the conductivity $\sigma_\omega$, given by:

$$\sigma_\omega = n_e e^2 \frac{1}{m_e} \frac{\nu_{e-h} - i\omega}{\nu_{e-h} + i\omega} = \frac{n_e e^2}{m_e} \frac{\nu_{e-h} - i\omega}{\omega^2 + \nu_{e-h}^2}$$  \hspace{1cm} (2.4)

where $\nu_{e-h}$ is the collision frequency of the electrons with heavy particles. The real part of this equation expresses the Ohmic losses, the imaginary part describes inductive behaviour of the plasma. In collision dominated plasmas driven by 2.45 GHz microwaves, the real part is much larger than the imaginary part. Combining Equation 2.3 with Equation 2.4 yields an expression for $\varepsilon_r$ which, in contrast to Equation 2.2, includes electron-heavy particle collisions:

$$\varepsilon_r = 1 - \frac{\omega_p^2 (1 + i \nu_{e-h})}{\omega^2 + \nu_{e-h}^2}$$  \hspace{1cm} (2.5)

The collision frequency $\nu_{e-h}$ is calculated as the sum of two contributions:

$$\nu_{e-h} = \nu_{e-i} + \nu_{e-n} = n_i K_{e-i} + n_n K_{e-n}$$  \hspace{1cm} (2.6)

where $n_i$ and $n_n$ are the ion and neutral densities, and $K_{e-i}$ and $K_{e-n}$ are the rate coefficients for momentum transfer from electrons to ions and atoms.
The rate for electron-ion collisions is taken from Mitchner and Kruger [1973]:

\[ K_{e-i} = \frac{4 \sqrt{2\pi}}{3} \left( \frac{e^2}{4\pi\epsilon_0 m_e} \right)^2 \left( \frac{m_e}{k_B T_e} \right)^{3/2} \ln \sqrt{1 + \eta^2 \Lambda^2} \]  

(2.7)

The Coulomb logarithm \( \Lambda \) is given by \( \frac{3k_B T_e \epsilon_0}{e^2} \sqrt{\frac{r_k T_e}{e^2 \epsilon_0}} \). \( \eta \) is a factor close to one, \( \eta = 1 \) is used in all the calculations. \( T_e \) is the electron temperature. This formula is applicable for singly ionized plasmas and does not depend on the ion species.

\( K_{e-i} \) is calculated using the total electron scattering cross section taken from Itikawa [2002], which is shown in Figure 2.1. The cross section \( \sigma \) is converted to a rate using the following relation:

\[ K(T_e) = \int_{0}^{\infty} f(E, T_e) \sigma(E) \sqrt{\frac{2E}{m_e}} \, dE \]  

(2.8)

For the electron energy distribution function \( f(E, T_e) \) a Maxwell-Boltzmann distribution is used:

\[ f(E, T_e) = 2 \sqrt{\frac{E}{\pi}} \left( \frac{1}{k_B T_e} \right)^{3/2} \exp \left( -\frac{E}{k_B T_e} \right) \]  

(2.9)

Because the electron scattering cross section stays within the same order of magnitude in the energy range energy 1-100 eV, the rate calculation is not sensitive to the assumption of a Boltzmann distribution.
Rate coefficients for momentum transfer to the ions and neutrals are shown in Figure 2.2. At ionization degrees below $10^{-3}$ the $n_{\text{CO}_2} K_{e-\text{CO}_2}$ term is dominant in the collision frequency. Figure 2.3 shows $\nu_{e-n}$ as function of neutral density for various electron densities at an electron temperature of 1 eV to illustrate the contribution of both terms on the total collision frequency. At experimentally relevant neutral densities, the electron-ion term starts playing a role above electron densities of $10^{19}$ m$^{-3}$. Below this electron density the collision frequency is mainly determined by the electron-neutral term. Via the collision frequency, the neutral density determines the microwave propagation behaviour as will be shown by analysis of the refractive indices.

Figure 2.2: Rate coefficients for momentum transfer from electrons to ions and CO$_2$ atoms. $K_{e-i}$ is calculated using Equation 2.7, at an electron density of $10^{19}$ m$^{-3}$. $K_{e-n}$ is calculated from the Itikawa [2002] cross sections using Equation 2.8.

The refractive index consists of a real and imaginary part, and is (for nonmagnetic media) related to the relative permittivity as[Leins, 2010]:

$$n = n_{Re} + in_{Im} = \sqrt{\varepsilon_r}$$  \hspace{1cm} (2.10)

Taking the square of the refractive index leads to the following relation:

$$n^2 = n_{Re}^2 + 2n_{Re}n_{Im}i - n_{Im}^2 = \varepsilon_r = \varepsilon_{Re} + i\varepsilon_{Im}$$  \hspace{1cm} (2.11)

Separating the real and imaginary parts, this system of equations is solved to get
Figure 2.3: The collision frequency between the electrons and heavy particles as function of CO\textsubscript{2} density for various electron densities. At experimentally relevant neutral densities, electron-ion collisions only start playing a significant role above electron densities of 10\textsuperscript{19} m\textsuperscript{-3}.

an analytical solution for the refractive indices in terms of the relative permittivity:

\begin{align}
    n_{Re} &= \sqrt{\frac{1}{2} \left( \epsilon_{Re} + \sqrt{\epsilon_{Re}^2 - \epsilon_{Im}^2} \right)} \\
    n_{Im} &= \sqrt{\frac{1}{2} \left( -\epsilon_{Re} + \sqrt{\epsilon_{Re}^2 + \epsilon_{Im}^2} \right)}
\end{align}

Substituting the real and imaginary part of the relative permittivity described in Equation 2.5 results in:

\begin{align}
    n_{Re} &= \frac{1}{2} \left[ 1 - \frac{\omega_p^2}{\omega^2 + \nu_{c-h}^2} + \sqrt{1 - \frac{\omega_p^2(\nu_{c-h}^2 + \omega_p^2 - 2\omega^2)(\nu_{c-h}^2 + \frac{\omega_p^2}{\omega^2})}{(\omega^2 + \nu_{c-h}^2)^2}} \right] \\
    n_{Im} &= \frac{1}{2} \left[ \frac{\omega_p^2}{\omega^2 + \nu_{c-h}^2} - 1 + \sqrt{\nu_{c-h}^2\omega_p^2 + (\omega^2 - \omega_p^2)^2} \right] \left( \frac{\omega^2}{\omega_p^2 + \nu_{c-h}^2} \right)
\end{align}

The overall behaviour of the real and imaginary part of the refractive index as function of the electron and neutral density at a microwave frequency of 2.45 GHz is shown in Figure 2.4. These values are calculated for an electron temperature of 1 eV; results for an electron temperature of 0.5 and 2.0 eV are very similar.
It is seen that the real part of the refractive index shows different behaviour below and above a neutral density of $2.3 \times 10^{23}\text{ m}^{-3}$ for electron densities above the critical electron density.

Figure 2.4: The real and imaginary part of the refractive index as function of the CO$_2$ and electron density. The real part of the refractive index shows different behaviour below and above a neutral density of $2.3 \times 10^{23}\text{ m}^{-3}$ for electron densities below and above the critical electron density of $7.5 \times 10^{16}\text{ m}^{-3}$.

The real and imaginary part of the refractive index as function of the electron density are shown in Figure 2.5 by dashed and dotted lines. Solid lines indicate the reflectance. In this calculation, an electron temperature of 1 eV is used, and CO$_2$ as neutral species. When the neutral density is low, the electron-neutral collision frequency is low. In these conditions, the real part of the refractive index goes to zero while the imaginary part quickly grows as the electron density increases above the critical density. This abrupt change in refractive indices leads to a sudden increase in the reflection coefficient. Thus, at low neutral densities, microwave coupling is hindered above the critical electron density. This behaviour is described by Fridman [2008] as the diffuse regime. Because the electron density cannot exceed the critical density much at these low pressures, the plasma volume adjusts when the microwave power is increased.

Given that the neutral density is the dominant factor for the collision frequency, it is instructive to see how the refractive index changes as function of the neutral density. Figure 2.6 shows the real and imaginary part of the refractive index as function of the CO$_2$ density for various electron densities. When the electron density is below the critical electron density, the refractive index has a non-zero value over the complete range of neutral densities, i.e. microwave propagation is possible regardless of collision frequency. However, at higher electron densities, propagation is only possible above a certain neutral density. For a wide range of electron densities, the point where the refractive index becomes non-zero is situated around a neutral density of $2.3 \times 10^{23}\text{ m}^{-3}$.
Figure 2.5: The real (dashed lines) and imaginary (dotted lines) part of the refractive index as function of electron density at various neutral densities. The reflection coefficient is indicated with solid lines. At low neutral densities, the reflection jumps to 1 above the critical density. When the collision frequency $\nu_{e-h}$ increases, the criteria for propagation are relaxed.

Figure 2.6: The real (solid lines) and imaginary (dashed lines) part of the refractive index as function of the neutral density for various electron densities. The green line marks the neutral density at which the collision frequency $\nu_{e-h}$ equals the microwave frequency $\omega$ in the absence of e-i collisions.
2.3 \times 10^{23} \text{ m}^{-3} is approximately the neutral density at which the collision frequency $\nu_{e-h}$ equals the microwave frequency $\omega$. Above this neutral density, higher electron densities can be reached, but this will result in microwave absorption over a short length scale. Absorption length scales are characterized by the skin depth, which is defined as the distance over which the wave amplitude reduces by a factor $\frac{1}{e}$. Since the wave vector is given by $k = \frac{\omega}{c}n$, and only the imaginary part of the wave vector results in absorption, the skin depth is given by:

$$\delta_{\text{Skin}} = \frac{c}{\omega} \frac{1}{n_{im}} \quad (2.16)$$

The skin depth describes dissipative stopping, the incoming energy flux decays as given by the Beer-Lambert-Bouguer law:

$$S(x) = S_0 \exp \left( -\frac{2x}{\delta_{\text{Skin}}} \right) \quad (2.17)$$

The factor of two accounts for the fact that the energy flux is related to the square of the field, and the skin depth relates to the wave amplitude. As shown in Figure 2.7, the skin depth becomes on the order of millimeters as the electron density increases. This results in a plasma filament at higher electron densities, which is described by Fridman [2008] as the contracted regime.
When the relative permittivity becomes negative, the electromagnetic waves are unable to propagate. Under these conditions, the waves are reflected over a typical length scale:

\[ \delta_{\text{Reflection}} = \frac{c}{\omega \sqrt{|n_{\text{Re}}^2 - n_{\text{Im}}^2|}} \] (2.18)

This length scale is not related to energy dissipation, but corresponds to reflection. Parameter scans of the skin depth and the reflection length are shown in Figure 2.8. Note that the length scale for reflection only makes physical sense when the waves are reflected, which is roughly in the lower right quadrant of the figure.

![Figure 2.8: Length scales of absorption and reflection as function of the electron and neutral density.](image)

The refractive indices are also used to estimate microwave reflection, under the assumption that a plane wave is incident on a flat interface, where there is a sharp transition in refractive index. These assumptions are not satisfied in the reactor, but it is useful to have a rough estimate of the microwave reflection when scanning parameters over several orders of magnitude. The reflection coefficient is calculated with the Fresnel equation, given by:

\[ R = \frac{(n_{\text{Re}} - 1)^2 + n_{\text{Im}}^2}{(n_{\text{Re}} + 1)^2 + n_{\text{Im}}^2} \] (2.19)

A parameter scan of the reflection coefficient is shown in 2.9a. The length scale over which reflection takes place scales inversely to the reflection coefficient. Equation 2.19 and 2.17 can be combined to estimate the efficiency with which power is coupled into the plasma:

\[ \eta_{\text{MW}} = (1 - R) \exp \left( -\frac{2l}{\delta_{\text{Skin}}} \right) \] (2.20)

where \( l \) is the typical plasma size.
A scan of Equation 2.20 for a plasma size of 1 cm as function of the neutral and electron density is shown in 2.9b.

Figure 2.9: Reflection coefficient and absorption fraction as function of the electron and neutral density.

The analysis in this section is applied to plasmas driven by 2.45 GHz microwaves. At this microwave frequency, low power sources are inexpensive and readily available, and the size of magnetrons and waveguides is ideally suited for small-scale applications. However, 915 MHz microwaves have a higher electricity to microwave efficiency, and potentially provide more power per single magnetron. At microwave frequencies of 915 MHz the propagation behaviour is similar, but the numbers are different. The critical electron density is $1.0 \times 10^{16} \text{ m}^{-3}$, which might be too low to sustain plasma. At 1 eV, a neutral density of $8.5 \times 10^{22} \text{ m}^{-3}$ allows the formation of plasmas above the critical electron density.

On basis of these calculations, we make the following quantitative and qualitative observations for 2.45 GHz microwave propagation in CO$_2$ plasmas. In the absence of electron-neutral collisions, there is an upper limit on the electron density: $7.5 \times 10^{16} \text{ m}^{-3}$. Hence, electron densities in excess of this critical density can only be reached by virtue of the electron-neutral collisions. Sustaining plasmas with electron densities in excess of the critical density at low neutral density will be limited by reflection, even when electron-heavy particle collisions are taken into account. Calculating the electron-heavy particle collision frequency $\nu_{e-h}$ with the appropriate cross section for CO$_2$ shows that electron densities in excess of the critical density become accessible above neutral densities of $2.3 \times 10^{23} \text{ m}^{-3}$. This density is valid in a range around an electron temperature of 1 eV since the refractive indices are only weakly dependent on electron temperature. Below this neutral density, there will be a diffuse plasma with an electron density below the critical density. Above this neutral density, electron densities in excess of the critical density are not limited by reflection. However, as the electron density in-
creases, the skin depth, the length scale over which absorption takes place, decreases. Increasing neutral density softens this behaviour somewhat, but in general the plasma size will be limited as the electron density increases, resulting in a contracted plasma filament.

In conclusion, the neutral density, electron density, and the plasma size are linked as result of microwave propagation. The results outlined in this section can help exclude unphysical solutions of models which do not include these effects. It can also provide insights on limitations when scaling up the reactor. A reactor operating at 915 MHz will have a smaller operating window in terms of pressure in which the discharge is diffuse. In the contracted regime, increasing the microwave power will only lead to a marginally larger plasma volume because of skin effects. A larger reactor operating in this regime would thus need to increase the contact between gas and plasma, either by creating parallel reactors, or by influencing the gas flow in the reactor.

2.2.2 Gas flow dynamics

When the neutral density in the microwave reactor exceeds a threshold value, a plasma filament will form, which needs to be stabilized in the center of the reactor e.g. by a rotating flow pattern. Such a vortex flow can be realized in the experiment by tangential injection of the feed gas. However, the applied flow field will only be conserved if the flow is laminar i.e. smooth. In this section, the flow regime will be estimated, and the residence time of particles in the plasma will be calculated.

A characteristic number to classify the flow regime is the Reynolds number, a dimensionless quantity defined as the ratio of inertial to viscous forces. At Reynolds numbers lower than 1000, the viscous forces are dominant, and the flow will be laminar. At Reynolds numbers above 4000, inertial forces are dominant, which gives rise to turbulent flow. In the turbulent flow regime, there are chaotic eddies, vortices and other flow instabilities.

The mean velocity of gas in a tube is given by:

$$v_{\text{mean}} = \frac{\Phi}{\pi R_{\text{tube}}^2 n_0} \quad (2.21)$$

where $\Phi$ is the number of particles entering the tube per second, $R_{\text{tube}}$ is the radius of the flow tube, and $n_0$ is the neutral density. Inserting this relation in the expression for the Reynolds number yields:

$$Re = \frac{\rho_g v_2 R_{\text{tube}}}{\eta(p, T)} = \frac{2m_{\text{CO}_2} \Phi}{\pi R_{\text{tube}} \eta(p, T)} \quad (2.22)$$

Where $\rho_g$ is the gas density, $v$ is the gas velocity, $\eta$ is the dynamic viscosity of the
gas (Pa s), and $m_{\text{CO}_2}$ is the mass of a carbon dioxide molecule.

For a CO$_2$ flow of at most 10 slm which is above 300 K and flows with a uniform velocity in a tube with an inner diameter of 27 mm, the Reynolds number is always lower than 1000 [Fenghour et al., 1998]. This means that the flow is laminar in the complete parameter range studied in the reactor, and that an applied flow pattern will not be broken up by turbulence.

Given that the flow is laminar, there is Poiseuille flow, with the associated parabolic radial variation in the axial flow velocity for a tube with circular cross section as:

$$v(r) = \frac{2v_{\text{mean}}}{R_{\text{tube}}^2} (R_{\text{tube}}^2 - r^2)$$

(2.23)

It is assumed that in the experiment, the radial component of the velocity, i.e. the vortex flow, is superimposed on this parabolic axial velocity profile.

![Figure 2.10: Calculated residence times for a reactor with a 27 mm inner diameter quartz tube and an active volume of 43.2 mm length.](image)

When the mean velocity and the length of the plasma volume are known, the residence times are defined. Figure 2.10 shows calculated residence times when the length of the active volume is equal to the small dimension of the WR340 waveguides used in the experiment: 43.2 mm.

### 2.2.3 Thermolysis of CO$_2$ and quenching

One of the key performance indicators for processes that convert electricity to fuels is the energy efficiency. Plasma dissociation of carbon dioxide can potentially reach energy efficiencies of 80% as result of the non-equilibrium nature of the
plasma [Rusanov et al., 1981]. Thermal decomposition of \( \text{CO}_2 \) however has a lower, inherent, energy limit. In this section, equilibrium compositions will be calculated at different temperatures and pressures, and efficiency limits will be determined. A 0-D chemical kinetics model will be constructed. With this model, estimations will be made on timescales to reach equilibrium, and quenching rates needed to preserve the formed \( \text{CO} \). The main aim of this section is to calculate the exact energy efficiency limits in case of thermal dissociation with various quenching scenarios to quantify the importance of non-thermal processes.

Specialized computer programs are available to calculate the equilibrium composition of a given mixture as function of pressure and temperature. In this thesis, the NASA Computer program CEA is used, which is described in References Gordon and McBride [1994]; McBride and Gordon [1996]. The calculated equilibrium composition of a carbon dioxide mixture at 100 mbar is shown in Figure 2.11. The composition slightly shifts to \( \text{CO}_2 \) at increased pressures. The calculation includes the following species: \( \text{CO}_2, \text{CO}, \text{O}_2, \text{C}, \text{O}, \text{C}_2, \text{O}_3 \). Species for which the mole fraction is below \( 10^{-3} \), such as \( \text{C}, \text{C}_2, \text{and O}_3 \), are not shown in the graph.

![Figure 2.11: The equilibrium composition of a carbon dioxide mixture as function of temperature at a pressure of 100 mbar (Gordon and McBride, 1994; McBride and Gordon, 1996).](image)

The efficiency limit is calculated as the number of \( \text{CO} \) molecules \( n_{\text{mol,CO}} \), multiplied with the formation enthalpy per molecule \( \Delta H_{\text{CO}} \), divided by the total enthalpy change of the mixture \( \Delta H_{\text{mix}} \):

\[
\eta = \frac{n_{\text{mol,CO}} \Delta H_{\text{CO}}}{\Delta H_{\text{mix}}} \tag{2.24}
\]
A formation enthalpy $\Delta H_{\text{CO}}$ of 2.93 eV per molecule was used, which corresponds to the reaction $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$[Chase Jr., 1998]. This calculation assumes ideal quenching of the mixture, which means that the CO content is preserved. The role of oxygen radicals is not taken into account. If in a CO + O mixture all the O reacts with CO$_2$ to form extra CO and O$_2$, this increases the energy efficiency by 12%, thus at most 6 percentage point, since the $\Delta H$ of this reaction is only 0.35 eV per molecule[Chase Jr., 1998]. The ideal quenching efficiency is limited because only a fraction of the input energy is spent on the production of carbon monoxide. For example, as Figure 2.12 shows, when heating to 2000 K, less than 0.1 mole of CO is formed, while the total mixture is heated. As shown in Figure 2.13, the ideal quenching efficiency is not sensitive to the temperature and pressure, there is a large region in parameter space where efficiencies around 50% are attainable. This is a result of the weak pressure dependence of the equilibrium composition.

Since all the reactants and products are in the gas phase, and quenching is not instantaneous, chemical reactions continue during cooling. Some of these reactions consume carbon monoxide, reducing the energy efficiency. The temporal behaviour of the mixture during temperature ramps is studied computationally with a 0-D chemical kinetics model. Temperature-dependent rate coefficients of dominant reactions between the four included species CO$_2$, CO, O$_2$, and O are used as input. Table 2.1 shows constants to calculate rate coefficients as:

$$k(T) = k_0 \exp \left( -\frac{E_a}{k_B T} \right)$$

(2.25)
Reaction rates are calculated with the rate coefficients, e.g. the change in CO concentration resulting from reaction 1 is given by:

\[
\frac{dn_{\text{CO}1}}{dt} = k_1(T)n_{\text{CO}_2}n_{\text{CO}_2}
\] (2.26)

The total reaction rate for each reactant is the sum total of all the reactions. The temporal behaviour of an initial mixture is calculated by numerically integrating the differential equations over discrete time steps.

The outcome of the model depends critically on the input data, and the unknown uncertainties of the rate coefficients make an error estimate on the final answer difficult. As consistency check, the ratio between the forward and backward reaction rate coefficient are calculated using the principle of detailed balancing[Lieberman and Lichtenberg, 2005]. The equilibrium constant is related to the Gibbs free energy of a reaction as:

\[
K_{eq}(T) = \exp\left(-\frac{\Delta G(T)}{RT}\right)
\] (2.27)

The equilibrium constant only depends on thermodynamical data, which can be found in Chase Jr. [1998].
The equilibrium constant is also expressed in terms of a product of partial pressures of the reactants as:

$$K_{eq}(T) = \left(\frac{p}{p^*}\right)^{\alpha_g} \prod_j \left(\frac{p_j}{p}\right)^{\alpha_j}$$  \hspace{1cm} (2.28)

Where $p_j$ is the equilibrium pressure of component $j$, $\alpha_j$ is the stoichiometric coefficient of component $j$, which is negative for reactants and positive for products. $\alpha_g$ is the sum of the stoichiometric coefficients. The plimsoll symbol refers to standard conditions, which is at a pressure of 1000 mbar [Mcnaught and Wilkinson, 1997].

In equilibrium conditions, the forward and backward reaction rate will be the same, e.g. for reaction 1 and 9 in Table 2.1:

$$\hat{n}_{CO_2} \hat{n}_{CO_2} k_1(T) = \hat{n}_{CO} \hat{n}_{CO_2} k_9(T)$$

$$\left(\frac{\hat{n}_{CO_2}}{p}\right) \left(\frac{\hat{n}_{CO_2}}{p}\right) \left(\frac{p}{k_B T}\right)^2 k_1(T) = \left(\frac{\hat{n}_{CO}}{p}\right) \left(\frac{\hat{n}_{CO_2}}{p}\right) \left(\frac{p}{k_B T}\right)^3 k_9(T)$$  \hspace{1cm} (2.29)

This equation is rewritten, multiplying both sides with the ratio between pressures to read:

$$\left(\frac{\hat{n}_{CO}}{p}\right) \left(\frac{\hat{n}_{CO}}{p}\right) \left(\frac{\hat{n}_{CO_2}}{p}\right) \left(\frac{p}{p^*}\right) \left(\frac{p}{k_B T}\right)^2 k_1(T) \left(\frac{p}{p^*}\right)^3 k_9(T)$$  \hspace{1cm} (2.30)

Recognizing this as the expression for the equilibrium constant given in Equation 2.28, the relation between forward and backward reaction rates is written universally as:

$$K_{eq}(T) = \left(\frac{p}{k_B T}\right)^{-\alpha_g} \left(\frac{p}{p^*}\right)^{\alpha_g} \frac{k_1(T)}{k_9(T)}$$  \hspace{1cm} (2.31)

Although Equation 2.31 was derived on the assumption of thermal equilibrium between the components, the relation is also true for a system that is not in thermodynamic equilibrium. The only requirement is that the distribution of relative velocities of the colliding particles is Maxwellian at temperature $T$ [Lieberman and Lichtenberg, 2005].

The prefactors $k_0$ of the last eight reaction rate coefficients in Table 2.1 are corrected using detailed balancing. As an additional consistency check, Figure 2.14a shows the CEA thermal equilibrium composition together with the composition reached after numerically integrating the system of differential equations for 2.5 milliseconds. Time steps of a nanosecond and CO$_2$ as initial composition are used in the calculation. Although there are minor discrepancies, the overall behaviour is well reproduced, giving confidence that the set of rate coefficients adequately describes the behaviour of a thermal carbon dioxide mixture.
Table 2.1: Rate coefficients of reactions between CO$_2$, CO, O$_2$, and O. $k_0$ is given in m$^3$ s$^{-1}$ for bimolecular, and m$^6$ s$^{-1}$ for termolecular reactions. The first and last eight reactions are each others inverse[Butylkin et al., 1979].

<table>
<thead>
<tr>
<th>Index</th>
<th>Reaction</th>
<th>$k_0$</th>
<th>$E_i$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO$_2$ + CO$_2$ → CO + O + CO$_2$</td>
<td>$4.38 \times 10^{-10}$</td>
<td>5.58</td>
</tr>
<tr>
<td>2</td>
<td>CO$_2$ + CO → CO + O + CO</td>
<td>$4.38 \times 10^{-10}$</td>
<td>5.58</td>
</tr>
<tr>
<td>3</td>
<td>CO$_2$ + O$_2$ → CO + O + O$_2$</td>
<td>$3.72 \times 10^{-13}$</td>
<td>5.19</td>
</tr>
<tr>
<td>4</td>
<td>CO$_2$ + O → CO + O$_2$</td>
<td>$7.77 \times 10^{-15}$</td>
<td>1.57</td>
</tr>
<tr>
<td>5</td>
<td>O$_2$ + O$_2$ → O + O + O$_2$</td>
<td>$8.14 \times 10^{-12}$</td>
<td>5.14</td>
</tr>
<tr>
<td>6</td>
<td>O$_2$ + O → O + O + O</td>
<td>$1.99 \times 10^{-11}$</td>
<td>4.98</td>
</tr>
<tr>
<td>7</td>
<td>O$_2$ + CO → O + O + CO</td>
<td>$2.41 \times 10^{-12}$</td>
<td>5.12</td>
</tr>
<tr>
<td>8</td>
<td>O$_2$ + CO$_2$ → O + O + CO$_2$</td>
<td>$2.57 \times 10^{-12}$</td>
<td>5.14</td>
</tr>
<tr>
<td>9</td>
<td>CO + O + CO$_2$ → CO$_2$ + CO$_2$</td>
<td>$6.54 \times 10^{-42}$</td>
<td>0.13</td>
</tr>
<tr>
<td>10</td>
<td>CO + O + CO → CO$_2$ + CO</td>
<td>$6.54 \times 10^{-42}$</td>
<td>0.13</td>
</tr>
<tr>
<td>11</td>
<td>CO + O + O$_2$ → CO$_2$ + O$_2$</td>
<td>$6.51 \times 10^{-45}$</td>
<td>0.13</td>
</tr>
<tr>
<td>12</td>
<td>CO + O$_2$ → CO$_2$ + O</td>
<td>$1.23 \times 10^{-15}$</td>
<td>1.32</td>
</tr>
<tr>
<td>13</td>
<td>O + O + O$_2$ → O$_2$ + O$_2$</td>
<td>$6.81 \times 10^{-43}$</td>
<td>0.00</td>
</tr>
<tr>
<td>14</td>
<td>O + O + O → O$_2$ + O</td>
<td>$2.19 \times 10^{-42}$</td>
<td>-0.20</td>
</tr>
<tr>
<td>15</td>
<td>O + O + CO → O$_2$ + CO</td>
<td>$2.76 \times 10^{-43}$</td>
<td>0.00</td>
</tr>
<tr>
<td>16</td>
<td>O + O + CO$_2$ → O$_2$ + CO$_2$</td>
<td>$2.76 \times 10^{-43}$</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Figure 2.14: The overall behaviour of the system of equations matches the CEA equilibrium calculation. To illustrate the composition changes as the CO$_2$ mixture heats and cools, two different temperature evolutions are simulated.

With the system of differential equations, the effects of an arbitrary temperature evolution can be calculated. As an illustration, Figure 2.14b shows two identical temperature profiles with a different cooling rate. After an instantaneous temperature increase, concentrations reach steady with a characteristic equilibration time. When the mixture slowly cools, all the formed CO reacts back to CO$_2$. Faster quenching rates will preserve more of the formed CO. The equilibration times and the CO loss fraction will be quantified on basis of scans in equilibrium temperature and quenching rate.
The equilibrium composition is reached after a characteristic time. This time constant decreases with temperature, because the rate coefficients increase with temperature, as shown in Figure 2.15a. The equilibration time is calculated on basis of the CO concentration time derivative. Steady state is defined as a situation where the change in fractional pressure divided by the fractional pressure is less than $100 \text{ s}^{-1}$. The equilibration times are typically shorter than the residence times, which are on the order of hundreds of microseconds. This indicates that if the plasma is thermal, the composition will reach steady state.

Back-reactions during cooling lead to CO loss. Only at low temperatures, these reactions are suppressed, indicating the need for rapid quenching. Figure 2.15b shows the fractional loss of CO as function of linear cooling rate for three different initial temperatures. The fractional CO loss is sensitive to the initial temperature because it determines the composition of the cooling mixture. At higher temperatures, there are more oxygen radicals which react with CO to form carbon dioxide. Sufficiently high cooling rate can suppress most of the back reactions. Spatial effects are not included in these calculations. If the discharge would be inhomogeneous, where e.g. only a small fraction of the gas passes through the plasma, back reactions could be quenched by the abundance of carbon dioxide compared to the reaction products. 300 K is used as final temperature in the cooling ramp. The model is not detailed enough to determine the effect of different final temperatures since species which play a role in the chemistry at lower temperatures, such as ozone, are not included. Figure 2.16 shows the efficiency for thermal CO production as function of temperature and linear cooling rates, which includes the fractional CO loss.

![Equilibration times](image1)

![CO loss fractions](image2)

Figure 2.15: A CO$_2$ mixture reaches chemical equilibrium on a microseconds timescale, thus, high cooling rates are needed to suppress CO loss. The increasing O radical concentration with temperature leads to a larger fractional CO loss.
In summary, the thermal composition of a CO₂ mixture, and the energy efficiency of CO production is calculated with a model based on thermodynamic quantities. A 0-D chemical kinetics model is constructed on basis of 16 reactions between 4 species to investigate the dynamics of a thermal CO₂ mixture. Equilibrium compositions are reached on timescales below tens of microseconds if the mixture has a temperature in excess of 3000 K. Thermal CO production has an intrinsic energy efficiency limit of around 55 % because excess energy is spent in heating the reactants. In practice, the efficiency will be lower due to reactions of carbon monoxide and oxygen radicals to form carbon dioxide while the mixture cools down to room temperature. Linear cooling rates on the order of $10^9 \text{ K s}^{-1}$ inhibit back reactions, but the fractional CO loss depends critically on the initial composition of the cooling mixture. Still, when back reactions during cooling are taken into account, there are regions in parameters space where efficiencies in excess of 40 % are attainable.

2.2.4 Laser scattering and local plasma parameters

Scattering of light provides a non-intrusive way to study various plasma parameters in-situ. Lasers are an excellent light source to use in such a diagnostic setup since they provide spatially coherent, polarized light of high intensity. In this section, light scattering mechanisms of interest to this study will be introduced and explained in detail. This information will be combined to calculate spectra on basis
of estimated plasma parameters. The calculated spectra will be used to explain choices made in the construction of the laser scattering setup.

Generally in light scattering, the scattered power $P_{\text{scat}}$ is given by:

$$P_{\text{scat}} = P_i n_s \frac{d\sigma_s}{d\Omega} \Delta \Omega L_{\text{det}}$$  \hspace{1cm} (2.32)

where $P_i$ is the incident power, $n_s$ is the density of the scattering species, $\frac{d\sigma_s}{d\Omega}$ is the differential scattering cross section for scattering mechanism $s$, $\Delta \Omega$ is the solid angle of the collection optics, and $L_{\text{det}}$ is the length of the detection volume. In the context of this thesis, the three main scattering types are Rayleigh, Thomson, and Raman scattering.

Rayleigh scattering is light scattering by bound electrons in atoms, molecules, and particulates of small size compared to the wavelength of the light\cite{Rayleigh,1899}. It is generally used to diagnose atomic or molecular densities. In the solar fuels reactor it is used to measure gas densities, which are used to gain insight in microwave propagation and estimate temperatures.

Thomson scattering is light scattering by free electrons. Since the electrons are light, the Doppler broadening of the scattered light is detectable, so that the electron temperature as well as the electron density is measured. In the laser scattering setup constructed in this thesis the Thomson scattering contribution is not directly used. However the theory is outlined to estimate under what conditions the Thomson scattering contribution can be obtained from a laser scattering measurement.

Raman scattering is inelastic scattering of light on molecules, where rotational or vibrational transitions lead to a wavelength shift of the scattered light. This technique can be used to obtain molecular densities, and rotational or vibrational distributions. Experimentally the Raman scattering contribution was not used in this thesis, but Raman scattering is an important contribution to the calculated spectrum, and can obscure the Thomson scattering contribution depending on the plasma parameters.

Rayleigh Scattering

The total scattering cross section $\sigma_R$ for Rayleigh scattering on spherically symmetric particles is given, in units of m$^2$ per particle:

$$\sigma_R = \frac{8}{3\pi^3} \frac{\alpha_{SI}^2 \lambda_i^4}{\epsilon_0^2 \lambda_i^4}$$  \hspace{1cm} (2.33)

$\lambda_i$ is the wavelength of the incoming light. Note the strong wavelength dependence to the inverse fourth power. $\alpha_{SI}$ is the polarizability of the scattering species, which
has the SI units of F m². The polarizability is related to the refractive index \( n \) at heavy particle density \( n_h \), which is an experimentally accessible quantity:

\[
\alpha_{SI} = \frac{3\epsilon_0}{n_h} \left( \frac{n^2 - 1}{n^2 + 2} \right)
\]  

(2.34)

Figure 2.17: The electric field amplitude (gray wire mesh) and intensity (solid contour) of a dipole antenna oriented along the direction of the black arrow.

The total scattering cross section is not dependent on the scattering geometry. However, the incident light induces a dipole in the same direction as the incident field polarization, and this leads to the characteristic angular dependence of the intensity of the scattered field. A schematic of the dipole field distribution is shown in Figure 2.17. Geometry effects are captured in the differential scattering cross section, which reads:

\[
\frac{d\sigma}{d\Omega} = \frac{\pi^2 \alpha_{SI}^2}{\epsilon_0^2 \lambda^4} (1 - \sin^2 \theta \cos^2 \phi)
\]  

(2.35)

The angle \( \theta \) is the scattering angle, i.e. the angle between the incident light vector and the scattered light vector. The angle \( \phi \) is the angle between the polarization of the incoming light and the plane defined by the incoming light vector and the scattered light vector. In literature, the term cross section is often used as shorthand for either the total scattering cross section, the differential scattering cross section, or the differential scattering cross section at perpendicular angles. These distinct cross sections are related as:

\[
s_R = \oint_{4\pi} \frac{d\sigma_R}{d\Omega} d\Omega = \int_0^{2\pi} \int_0^\pi \frac{d\sigma_R}{d\Omega} \sin \theta d\theta d\phi = \frac{8\pi}{3} \frac{d\sigma_{R,\theta=\phi=90^\circ}}{d\Omega}
\]  

(2.36)

The previously described Rayleigh scattering theory only applies to spherically symmetric particles, and molecules are generally not spherical. Because of the spatial structure of molecules, the polarizability depends on the orientation with
respect to the applied electric field. As a result, the polarizability is no longer a single number, but a tensor which contains the polarizabilities for different orientations. However, since the molecules are randomly oriented, all orientations are averaged. The polarizability tensor then reduces to two parameters which are invariant with respect to rotation: the mean polarizability $\alpha$ and the anisotropy $\gamma$.

Literature values of these molecular properties are given for a selection of species in Table 2.4. The Rayleigh differential scattering cross section is expressed in terms of these two quantities as:

$$
\frac{d\sigma}{d\Omega} = \frac{\pi^2 a^2}{e_0^4 \lambda^4 \epsilon_0} \left( 1 + \frac{10 \gamma^2}{45 a^2} \right) \cdot (1 - \sin^2 \theta \cos^2 \phi)
$$

(2.37)

This expression is often rewritten in terms of $\rho_0$, which is defined as the ratio of horizontally-to-vertically polarized light scattered at 90° for unpolarized incident light. $\rho_0$ relates to $\alpha$ and $\gamma$ as:

$$
\rho_0 = \frac{6\gamma^2}{45a^2 + 7\gamma^2}
$$

(2.38)

The differential scattering cross section then reads in terms of $\rho_0$:

$$
\frac{d\sigma}{d\Omega} = \frac{\pi^2 a^2}{e_0^4 \lambda^4 \epsilon_0} \cdot (1 - \sin^2 \theta \cos^2 \phi)
$$

(2.39)

The ratio $\frac{6+3\rho_0}{6-7\rho_0}$ is generally called the King correction factor. When the incident light is linearly polarized at a 90° angle with respect to the observation direction, and the light is collected under a 90° angle with respect to the propagation direction, the vertically polarized, horizontally polarized, and sum of the two components is expressed in terms of an effective Rayleigh differential scattering cross section as:

$$
\frac{d\sigma_{R-V}}{d\Omega} = \frac{d\sigma_R}{d\Omega} \left( \frac{2 - \rho_0}{2 + \rho_0} \right)
$$

$$
\frac{d\sigma_{R-H}}{d\Omega} = \frac{d\sigma_R}{d\Omega} \left( \frac{\rho_0}{2 + \rho_0} \right)
$$

$$
\frac{d\sigma_{R-Tot}}{d\Omega} = \frac{d\sigma_R}{d\Omega} \left( \frac{2}{2 + \rho_0} \right)
$$

(2.40)

where the subscript $R - V$ indicates vertically polarized light and $R - H$ indicates horizontally polarized light arriving at the detection system. Literature Rayleigh scattering cross sections for various species of interest are given in Table 2.2. When Rayleigh scattering cross sections could not be found, they were calculated from the polarizabilities. Literature values for molecules include the King correction.
factor, and as such take into account depolarization effects. To apply these cross sections to the experimental geometry used in this thesis however, they still need to be multiplied by a factor \( \frac{2}{2 + \rho_0} \).

\[
\frac{\Delta}{\Delta^2} (10^{-32} \text{ m}^2) \quad \text{Reference}
\]

<table>
<thead>
<tr>
<th>Species</th>
<th>( \frac{d\sigma}{d\Omega} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.87</td>
<td>[Goldman, 1989]</td>
</tr>
<tr>
<td>H(_2)</td>
<td>1.35</td>
<td>[Sutton and Driscoll, 2004]</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>14.9</td>
<td>[Sneep and Ubachs, 2005]</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>4.43</td>
<td>[Sutton and Driscoll, 2004]</td>
</tr>
<tr>
<td>Li</td>
<td>1149</td>
<td>[Molof et al., 1974]</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>0.0017</td>
<td>[Cooke et al., 1977]</td>
</tr>
<tr>
<td>Na</td>
<td>1131</td>
<td>[Holmgren et al., 2010]</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>0.043</td>
<td>[Gray et al., 1988]</td>
</tr>
<tr>
<td>K</td>
<td>3608</td>
<td>[Holmgren et al., 2010]</td>
</tr>
<tr>
<td>K(^+)</td>
<td>1.28</td>
<td>[Opik, 1967]</td>
</tr>
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<td>Rb</td>
<td>4342</td>
<td>[Holmgren et al., 2010]</td>
</tr>
<tr>
<td>Rb(^+)</td>
<td>3.5</td>
<td>[Mitroy et al., 2010]</td>
</tr>
<tr>
<td>Cs</td>
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<td>[Amini and Gould, 2003]</td>
</tr>
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<td>Cs(^+)</td>
<td>10</td>
<td>[Safinya et al., 1980]</td>
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<td>C</td>
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<td>[Das and Thakkar, 1998]</td>
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<td>CO</td>
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<td>[Shardanand and Rao, 1977]</td>
</tr>
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<td>Ar</td>
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</tr>
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<td>[de Sande, 2002]</td>
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<tr>
<td>Kr</td>
<td>12.0</td>
<td>[Mitroy et al., 2010]</td>
</tr>
<tr>
<td>Xe</td>
<td>31.8</td>
<td>[Mitroy et al., 2010]</td>
</tr>
</tbody>
</table>

Table 2.2: Rayleigh scattering cross sections at 532 nm, 295 K, and \( \theta = \phi = 90^\circ \).

In some conditions, small particulates might be present in the reactor. When the size of the particulates is small, i.e. at least an order of magnitude smaller than the wavelength of the incident light, Rayleigh theory adequately describes the scattering behaviour. The polarizability for small spherical particulates is given by [Jones, 1979]:

\[
\alpha_{SI} = 3\varepsilon_0 V \left( \frac{n^2 - 1}{n^2 + 2} \right)
\]  

(2.41)

where \( V \) is the volume of the particulate, and \( n \) is the refractive index. The differential scattering cross section can thus be written:

\[
\frac{d\sigma_R}{d\Omega} = \frac{16\pi^4 \rho_0}{\lambda^4} \left( \frac{n^2 - 1}{n^2 + 2} \right)^2 \cdot (1 - \sin^2 \theta \cos^2 \phi)
\]  

(2.42)
where $r$ is the radius of the scattering particulate. Since the cross section depends on the sixth power of the particulates radius, the observed signal is heavily biased towards larger particulates. To put this into perspective, when in a CO$_2$ discharge 1 percent of the carbon atoms is part of graphite particulates, with bulk graphite properties [Stagg and Charalampopoulos, 1993], at a particle radius of 1 nm the Rayleigh scattering from the particulates is approximately equal to the Rayleigh scattering from the CO$_2$ molecules, and at a particulate radius of 10 nm the Rayleigh scattering from the particles is 3 orders of magnitude larger than the scattering from the molecules.

Thermal movement of the scattering species causes a Doppler broadening of the Rayleigh scattered light. The lineshape $f_R$ is given by:

$$f_R(\lambda) = \frac{1}{\lambda_i} \sqrt{\frac{m_i c^2}{4 \pi k_B T_B}} \exp\left(-\frac{m_i c^2}{4 k_B T_B \lambda_i} \left(\frac{\lambda - \lambda_i}{\lambda_i}\right)^2\right) \tag{2.43}$$

Note that the Doppler width for Rayleigh scattering is a factor of $\sqrt{2}$ larger than for spontaneous emission [Miles et al., 2001]. Since the Rayleigh scattering species typically have a low thermal speed on account of their large mass, this broadening is usually negligible compared to instrument broadening. For CO$_2$ the Doppler width at a temperature of 1 eV for incident light of 532 nm is only 0.009 nm, as is calculated with:

$$\Delta \lambda_{FWHM} = 4 \ln 2 \frac{k_B T_B}{m_i c^2 \lambda_i} \tag{2.44}$$

A gas composition needs to be assumed in the interpretation of Rayleigh scattering measurements, since a change in chemical composition cannot be deduced from the measurement directly. One option is to interpret measured data using the Rayleigh cross section of CO$_2$. Since the measurements are done in a reactive environment which produces a substantial amount of CO, this is not strictly correct. Because the Rayleigh scattering cross section for a stoichiometric mixture of carbon monoxide and oxygen is lower than for carbon dioxide, the density will be underestimated when assuming pure CO$_2$ as scattering species. At a specific energy input of 1 eV per molecule, when the reactor is 100 percent energy efficient in creating CO and O$_2$, the density will be underestimated by 10 percent when assuming pure CO$_2$ in the interpretation. However, this estimation is only valid when the microwave energy is distributed evenly over the CO$_2$ molecules in the reactor. When the power deposition profile is peaked, the assumption that there is mainly CO$_2$ in the detection volume breaks down.

If the effective Rayleigh scattering cross section of a mixture is known as function of temperature, the density can still be deduced in some cases. Recalling Equation 2.32, for a pure CO$_2$ mixture the CO$_2$ density $n_{CO_2}$ is directly obtained
from the Rayleigh scattering measurement. If instead there is a mixture with a different Rayleigh cross section present in the reactor, the density of the mixture $n_{\text{mix}}$ is related to the CO$_2$ density as:

$$n_{\text{CO}_2} = n_{\text{mix}} \left( \frac{d\sigma_{\text{mix}}}{d\Omega} \right) \left( \frac{d\sigma_{\text{CO}_2}}{d\Omega} \right)^{-1} = \frac{p}{k_B T_{\text{mix}}} \left( \frac{d\sigma_{\text{mix}}(T_{\text{mix}})}{d\Omega} \right) \left( \frac{d\sigma_{\text{CO}_2}}{d\Omega} \right)^{-1} \tag{2.45}$$

The temperature dependence is written explicitly in the last term. Note that the contribution of the electrons and ions to the pressure is negligible since their densities are orders of magnitude lower than the neutral density. With the measured pressure, the right hand side is only a function of temperature. The equilibrium composition is used to calculate the effective Rayleigh scattering cross section by summing the product of the cross sections and mole fractions, as shown Figure 2.18. Since the cross section decreases with temperature, there exists a unique solution to Equation 2.45. In the data analysis, the composition at 100 mbar is used, and depolarization properties of species other than CO$_2$ are not taken into account.

Figure 2.18: The equilibrium composition is used to calculated an effective cross section. The dashed lines indicate the cross sections for individual species.

The depolarization properties of the mixture change slightly with composition. When the differently polarized components of the scattered light are measured separately, it would provide a consistency check of the adaptive cross section procedure. Since the CO$_2$ depolarizes the scattered light more than CO or O$_2$, the ratio of the H and V polarized light changes when the the composition of the mixture changes. The cross section for the different polarizations, calculated with Equation 2.40 using information from Table 2.4, is shown in Figure 2.19.
Figure 2.19: The equilibrium composition is used to calculate an effective cross section for the different polarization components. The ratio of the two components changes with temperature because of the different depolarization properties of the scattering species.

Thomson Scattering

A full description of the Thomson scattering theory is available in literature such as Evans and Katzenstein [1969]. In this section a brief outline of Thomson scattering on low temperature plasmas is given. The differential scattering cross section for Thomson scattering is given by:

$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2}{4\pi \varepsilon_0 m e c^2}\right)^2 \cdot (1 - \sin^2 \theta \cos^2 \phi)$$

(2.46)

The cross section for Thomson scattering is large relative to Rayleigh scattering, the Thomson differential scattering cross section at perpendicular angles is $7.94 \times 10^{-30} \text{ m}^2$. Note that the total Thomson scattering cross section $\sigma_T$ can be calculated using Equation 2.36, which yields $6.65 \times 10^{-29} \text{ m}^2$.

Thomson scattering can be coherent or incoherent depending on the plasma conditions. The two cases result in different spectra, which contain different information about the plasma parameters. Thomson scattering is incoherent when the wavelength of the incident is much smaller than the Debye length, so that scattering happens over the length scale of random thermal electron density fluctuations. In the limit of incoherent scattering, the wavelength dependence of the Thomson scattered light is given by a Gaussian in case of a Maxwellian electron energy distribution. Coherent scattering occurs when the incident wavelength is much larger.
than the Debye length, and scattering takes place over length scales over which correlated fluctuations are possible. In this case, the scattering spectrum is no longer a Gaussian, but is described by a form factor which contains information about both the electron and ion energy distribution function. The importance of coherent effect is estimated with the scattering parameter $\alpha$ [Salpeter, 1960]:

$$\alpha = \frac{1}{|\vec{k}_s| \lambda_D}$$  \hspace{1cm} (2.47)

where $\lambda_D$ is the Debye length, given by:

$$\lambda_D = \sqrt{\frac{\varepsilon_0 k_B T_e}{e^2 n_e}}$$  \hspace{1cm} (2.48)

and $|\vec{k}_s|$ is the length of the differential scattering vector, which is given by:

$$|\vec{k}_s| = 2 \left(\frac{2\pi}{\lambda_i}\right) \sin\left(\frac{\theta}{2}\right)$$  \hspace{1cm} (2.49)

which simplifies to $\frac{4\pi}{\sqrt{2}\lambda_i}$ in the experimental scattering geometry where $\theta = 90^\circ$. Inserting these relations into the expression for the scattering parameter yields:

$$\alpha = \frac{\sqrt{2}}{4\pi} \frac{\lambda_i}{\lambda_D} = \frac{\sqrt{2}}{4\pi} \sqrt{\frac{e^2 n_e}{\varepsilon_0 k_B T_e}} \frac{\lambda_i}{\lambda_i}$$  \hspace{1cm} (2.50)

Even at low electron temperatures, coherent effects only start playing a role at significant electron densities. At an electron temperature of 1 eV for 532 nm incident light, $\alpha$ becomes 0.1 at an electron density of $1.5 \times 10^{20}$ m$^{-3}$. Since in the experimental setup used in this section the electron density is not expected to exceed $10^{20}$ m$^{-3}$ on basis of particle and power balance considerations, scattering will be incoherent. In the limit of incoherent Thomson scattering, Gaussian lineshape $f_\lambda$ of the scattered light is given by:

$$f_\lambda(\lambda) = \frac{1}{\lambda_i} \sqrt{\frac{m_e c^2}{4\pi k_B T_e}} \exp\left(-\frac{m_e c^2}{4k_B T_e} \frac{\lambda_i - \lambda}{\lambda_i}\right)$$  \hspace{1cm} (2.51)

The electron temperature can be extracted from the width of the scattered spectrum using the relation:

$$\Delta \lambda_{FWHM} = 4 \sqrt{\ln 2} \sqrt{\frac{k_B T_e}{m_e c^2}} \lambda_i$$  \hspace{1cm} (2.52)
Raman Scattering

In this section rotational Raman scattering will be briefly treated for simple linear molecules in the vibrational ground state. For CO\(_2\) and O\(_2\) this is an approximation, but the discrepancies introduced by this approximation are small [Penney et al., 1974]. Analogous to Equation 2.32, the amount of Raman scattered light for a single rotational transition is given by:

\[
P_{J \rightarrow J'} = P \rho_i \gamma_i \frac{d\sigma_{J \rightarrow J'}}{d\Omega} \Delta Q L_{det}
\]

(2.53)

where \(F(j)\) is the fraction of molecules in the initial state. For simple linear molecules, the only allowed rotational transitions are \(J \rightarrow J \pm 2\), where \(J\) is the initial rotational angular momentum quantum number. Neglecting higher order corrections, the energy of the individual rotational levels are given by:

\[
E_J = B \nu (J + 1)
\]

(2.54)

where \(B\) is the rotational constant for vibrational level \(\nu\). Values of \(B\) for molecules of interest are given in Table 2.3. For the allowed Raman transitions, the wavelengths are calculated from the energy levels as:

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

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

(2.55)

If the rotational levels are in thermal equilibrium at a given temperature \(T_{rot}\), the rotational population distribution is given by a Boltzmann distribution as:

\[
F(j) = \frac{g_J g_I (2J + 1)}{Q} \exp \left( - \frac{E_J}{k_B T_{rot}} \right)
\]

(2.56)

\(g_J\) and \(g_I\) are statistical factors, given in Table 2.3 for various molecules. \(Q\) is the rotational partition function, determined by the following sum over the rotational levels:

\[
Q = \sum_J g_J g_I (2J + 1) \exp \left( - \frac{E_J}{k_B T_{rot}} \right)
\]

(2.57)

In the case of perpendicular scattering (\(\theta = \phi = 90^\circ\)), the differential cross section for the Raman transition \(J \rightarrow J'\) is written as [Penney et al., 1974]:

\[
\frac{d\sigma_{J \rightarrow J', \perp}}{d\Omega} = \frac{4\pi^2 b_{J \rightarrow J'} \gamma^2}{45 e_0^2 \lambda_{J \rightarrow J'}^2}
\]

(2.58)
Table 2.3: Values of the statistical weight factor $g_J$ for even and odd rotational levels, the nuclear spin degeneracy $g_I$, and the rotational constant $B_0$ after Huber and Herzberg [1950]; Penney et al. [1974].

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$g_J$ even</th>
<th>$g_J$ odd</th>
<th>$g_I$</th>
<th>$B_0$ (10^-4 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2.38363</td>
</tr>
<tr>
<td>CO₂</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0.483786</td>
</tr>
<tr>
<td>N₂</td>
<td>6</td>
<td>3</td>
<td>1</td>
<td>2.46695</td>
</tr>
<tr>
<td>O₂</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1.78264</td>
</tr>
</tbody>
</table>

Values for $\gamma$, the anisotropy of the polarizability tensor, are given in Table 2.4. $b_{J \rightarrow J'}$ are the Placzek-Teller coefficients, which for simple linear molecules are calculated as:

\[
\begin{align*}
b_{J \rightarrow J+2} &= \frac{3(J+1)(J+2)}{2(2J+1)(2J+3)} \\
b_{J \rightarrow J-2} &= \frac{3(J-1)}{2(2J+1)(2J-1)} \\
b_{J \rightarrow J} &= \frac{J(J+1)}{(2J-1)(2J+3)}
\end{align*}
\]

(2.59)

As illustration the differential scattering cross sections are shown in 2.20a for Raman scattering on nitrogen with 532 nm incident light. Nitrogen is chosen as molecule since the rotational spacing is larger than for CO₂, resulting in a cleaner figure.

The intensities of the Raman transitions form a characteristic winged pattern around the central exciting line. The width of the pattern is mainly the result of a thermal population of rotational levels, higher levels being more populated at higher temperatures leading to a broader envelope. The product $F(J) \frac{d\sigma_{J \rightarrow J'}}{d\Omega}$ is shown as function of wavelength in 2.20b for perpendicular scattering of 532 nm light on nitrogen.

An exhaustive treatment of the geometry dependence of the Raman scattering differential cross section, or a full description of the influence of depolarization on the Raman signal is beyond the scope of this thesis. Vibrational Raman, a method which is able to measure parts of the vibrational distribution function, is also not treated. The Raman cross sections are used here to predict the amount of Raman signal in the total scattering spectra. When measuring Raman scattering in a plasma, the increased temperatures lead to population of higher vibrational states. Different selection rules for these states result in a more complex Raman spectrum [Barrett and Weber, 1970].
Figure 2.20: Perpendicular Raman cross sections for \( \text{N}_2 \) and the resulting spectrum at various rotational temperatures.

(a) \( \text{N}_2 \) differential cross sections for perpendicular Raman.

(b) Raman lines of \( \text{N}_2 \) molecules at various temperatures.

<table>
<thead>
<tr>
<th>Species</th>
<th>( \alpha , (10^{-40} \text{ Fm}^2) )</th>
<th>( \gamma , (10^{-40} \text{ Fm}^2) )</th>
<th>( \rho_0 ) (Percent)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>2.22</td>
<td>0.62</td>
<td>1.0</td>
<td>[Bogaard et al., 1978]</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>2.95</td>
<td>2.38</td>
<td>7.8</td>
<td>[Bogaard et al., 1978]</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>1.97</td>
<td>0.79</td>
<td>2.1</td>
<td>[Alms et al., 1975]</td>
</tr>
<tr>
<td>NO</td>
<td>3.35</td>
<td>3.33</td>
<td>11.4</td>
<td>[Bogaard et al., 1978]</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>1.74*</td>
<td>1.27</td>
<td>6.6</td>
<td>[Penney et al., 1974]</td>
</tr>
</tbody>
</table>

Table 2.4: Polarizabilities, polarizability anisotropies, and depolarization ratios for selected molecules at an incident wavelength of 532 nm. * For oxygen the static dipole polarizability is listed [Olney et al., 1997].

Calculated scattering spectra

The measured scattered spectrum are the sum of Rayleigh, Thomson, and Raman scattered light. To estimate which plasma parameters can be measured under what conditions, Figure 2.21 shows calculated spectra for four illustrative cases. The electron density is fixed at \( 10^{19} \text{ m}^{-3} \), and the electron temperature is kept constant at 1 eV. For the neutral density, two extreme cases are taken, a low neutral density of \( 10^{21} \text{ m}^{-3} \) and a high neutral density of \( 10^{24} \text{ m}^{-3} \). Spectra are calculated for two Gaussian instrument functions with a Full Width Half Maximum of 0.1 and 0.5 nm. For the Raman signal, a rotational temperature of 300 K is used.

In the calculated spectra, the Rayleigh scattered light dominates. By adjusting the instrument function, the ratio of the Rayleigh peak to the rest of the spectrum is varied, since if affects the width of the Rayleigh peak while the surface area stays constant. The Thomson signal could be measured under favourable conditions, i.e. a large instrument broadening and a neutral density that is at most 2 orders
of magnitude larger than the electron density. When the neutral density exceeds the electron density by more than 2 orders of magnitude, the Rayleigh peak will dominate the signal.

Different techniques are used to suppress the Rayleigh peak, such as a triple-grating spectrometer [de Sande, 2002] or a volume Bragg grating [Klarenaar et al., 2015] or with a mask inside a single-pass spectrometer [Brehmer et al., 2015]. If the ratio between the neutral and electron density becomes too large, the Thomson signal is be polluted by Raman signal, depending on the instrument function, electron temperature and gas temperature. The Thomson contribution can be increased by exploiting the inverse fourth power wavelength dependence of the Rayleigh and Raman scattering cross section. At longer wavelengths, the relative contribution of Thomson scattering increases, if e.g. a Ruby laser of 694.3 nm is used instead of a Nd:YAG laser at 532 nm, the Thomson contribution to the total spectrum is almost three times larger.
2.3 Experimental layout

2.3.1 Plasma reactor

In the plasma reactor, 2.45 GHz microwaves are generated by a 0.8 kW power supply. The microwaves are coupled to gas flowing in a 27 mm inner diameter quartz tube. The tube is inserted through the broad wall of a WR340 waveguide. A sliding short circuit is positioned at a quarter wavelength from the center of the quartz tube, so that the electric field at the plasma position is maximized. Note that the wavelength is the guide wavelength $\lambda_g$, which depends on the frequency and the mode of transmission. For the TE0 mode, the dominant mode in rectangular waveguides, the cutoff wavelength is twice the dimension of the broad wall of the waveguide. The guide wavelength is always longer than the wavelength in free space, and is calculated as:

$$\lambda_g = \frac{\lambda}{\sqrt{1 - \left(\frac{\lambda}{\lambda_{cut}}\right)^2}}$$

For 2.45 GHz waves in a WR340 waveguide, with dimensions 86.36 $\times$ 43.18 mm, the guide wavelength is 174 mm, so the sliding short is positioned at 44 mm from the center of the quartz tube. There is a 20 mm diameter hole in the sliding short, to perform optical measurements in the microwave cavity. The 14 mm thickness of the sliding short ensures a negligible microwave leakage, which was confirmed experimentally. The impedance of the plasma is matched with a three-stub tuner to establish efficient coupling of microwaves to the plasma. In the experiments, the reflected power never exceeded 1 percent of the input power.

![Diagram of microwave setup](image)

Figure 2.22: The microwave setup consists of a magnetron (1) and a three port circulator with a matched, actively cooled load (2) which serves to shield the source from reflected microwaves. A sliding short (5) and a three-stub tuner (3) maximize the electric field at the location of the plasma in the quartz tube (4).
Gas is injected tangentially into the quartz tube to create a rotating flow pattern, with gas flow rates between 0.1 and 10 standard liters per minute. The reactor is evacuated by a pump combination with adjustable speed, resulting in pressures between 1 and 1000 mbar.

The pressure is monitored with two different methods. For pressures up to 10 mbar, a PKR 260 Compact FullRange™ Gauge is used, above this range the measurement is not linear. At pressures above 10 mbar, an ASG2-1000 Active Strain Gauge is used. This pressure measurement relies on the deflection of a metal diaphragm, and is therefore independent of gas type. The accuracy of this gauge is ± 0.2 % full scale, which gives a measurement error of 2 mbar. The temperature coefficient is 0.03 % full scale per K, which gives a 30 mbar deviation when the gauge heats up 100 K.

2.3.2 Laser and focusing optics

A Continuum Powerlite™ DLS 8000 Nd:YAG laser is used as light source in the scattering setup. Frequency doubling yields 0.5 J per pulse at 532 nm. The 10 Hz laser has a shot-to-shot energy stability of 3.5 % (1.2 % RMS). The power drift is 5.0 %, which was measured during 8 hours with a ΔT of ± 3 °C. The timing jitter is 0.5 ns, which is small compared to the 5-7 ns pulse duration [Continuum, 2015].

An anti-reflection coated UV fused silica window is used to couple the laser into the reactor. Straylight from parasitic scattering of the laser is suppressed by placing the entrance window 2 meters away from the detection volume, and installing baffles in the vacuum. A critical aperture of 6 mm diameter is installed 505 mm in front of the detection volume, and a subcritical aperture of 12 mm diameter is placed 100 mm before the detection volume. The laser light is dumped approximately 2 meters after the detection volume in a beam trap installed in vacuum.

The laser beam is focused at the detection volume by a lens with a 2.4 m focal length. Since the beam divergence is 0.45 mrad, this results in a 1.08 mm diameter beam at the focus. The Rayleigh length, which expresses the distance along the propagation direction from the beam waist to the place where the area of the cross section is doubled, is 288 mm.

2.3.3 Importance of laser heating

In the experimental setup, 0.5 J pulses focused into a 1.1 mm diameter spot result in fluences of $5 \times 10^5$ J m$^{-2}$. In these conditions, the non-intrusiveness of the diagnostic needs to be verified. In this section, theoretical expressions for laser heating will be given, and experimental results will be discussed.
Analytical expressions for laser heating of an electron gas with electron-ion and electron-atom interactions were derived by Carbone et al. [2012, 2013]. The critical laser fluence $F_{\text{crit}}$ to achieve an electron heating of $\Delta T_e$ reads as follows:

$$F_{\text{crit}} = \frac{6\pi^2 m_e \epsilon c^3 k_B \Delta T_e}{e^2 \nu_{e-h} \lambda_i^2}$$

(2.61)

where $\nu_{e-h}$ is the collision frequency of the electrons with heavy particles, which is given above in Equation 2.6. The heated electrons will transfer the energy via collisions. At an electron temperature of 1 eV the electron-CO$_2$ collision rate is $6.8 \times 10^{-14}$ m$^3$ s$^{-1}$, which results in 68 collisions during the 10 nanosecond laser pulse at a neutral density of $10^{23}$ m$^{-3}$. This energy transfer is not taken into account in the derivation, so this expression provides the upper limit for laser heating of the electron gas. Since the neutral density is orders of magnitude larger than the electron density, it is assumed here that if the condition for electron heating is not exceeded, neutral heating by the laser is not of importance.

The critical laser fluence calculated for several experimental conditions is shown in Figure 2.23. A 10 % increase in electron temperature is taken as maximum allowed temperature variation. The electron density is fixed at $10^{19}$ m$^{-3}$ in all cases, but the results are not sensitive to this value since $\nu_{e-h}$ is dominated by electron-neutral collisions. The fluence reached when a 0.5 Joule pulse is focused to a spot with 1.08 mm diameter is shown in black. The experimental fluence exceeds the threshold for a $\Delta T_e$ of 10 % when the neutral density is sufficiently high. Since the neutral density at 300 K and 100 mbar is $2.4 \times 10^{24}$ m$^{-3}$, laser heating could play a role already at low pressures, provided that the neutral gas is room temperature.

Although the previous calculations illustrate that laser heating could play a role, experimentally the effects of laser heating were observed only at much higher fluences by Carbone et al. [2012]. To exclude perturbation of the gas or plasma by the laser in the current experiment, a scan was made in the laser power. Measured intensities are normalized by the pressure to account for scatter in the experimental conditions. For neutral gas, the Rayleigh scattered light shows a linear response as function of the laser power, indicating that processes which show a clear threshold, e.g. breakdown, do not occur. In a 3 slm CO$_2$ plasma created at 120 mbar and 830 Watt power input, the response is also linear, as shown in 2.24b. Although these measurements do not, a priori, exclude laser heating in the complete parameter range accessible, they do prove that laser heating is not important for pressures up to 120 mbar. As will be shown later, neutral densities measured in the plasma are lower than expected, in which case the critical fluence is much higher than the laser fluence.
Figure 2.23: Critical laser fluences for an electron heating of 10%. An electron density of $10^{19} \text{ m}^{-3}$ is used, but the results are not sensitive to this value since the $\nu_{e-h}$ is dominated by electron-neutral collisions. The fluence reached in the experiment is indicated in black.

![Graph showing laser fluence vs. neutral density for different electron temperatures.](image)

(a) Rayleigh scattering in CO$_2$.

(b) Rayleigh scattering in a CO$_2$ plasma.

Figure 2.24: Laser power scans in 120 mbar CO$_2$ and in a 3 slm CO$_2$ plasma at 120 mbar and 830 Watt power input. To eliminate scatter, the intensities are normalized to the pressure.

2.3.4 Data handling and calibration

Calibration and data analysis is straightforward for Rayleigh scattering, but for completeness the procedure is outlined in this section. Individual fibers are binned in the acquired spectra. Each bin is fitted with a Gaussian function to determine the amount of signal. The calibration of the detection branch sensitivity and straylight level is obtained from pressure scans.
Calibration spectra are acquired multiple times to measure statistical errors. Error propagation yields the error in the density determination. Variation in calibrations measured before and after experiments are an indication of the systematical error introduced by e.g. alignment changes over the course of the day. In most cases, both calibrations are within 10%. An example is shown in Figure 2.25. Note that the exposure time is varied, with single laser pulses being acquired at the upper end of the pressure range, so the statistical errors are different for the different points. The throughput always decreases towards the end of the day. Straylight levels are on the order of a few times $10^{21}$ m$^{-3}$ CO$_2$ density equivalent, i.e. a few times $10^{19}$ m$^{-3}$ electron density equivalent.

![Figure 2.25: Before and after experiments the signal intensity is measured as function of pressure to calibrate the sensitivity of the detection branch. Red points were measured during experiments. Similar throughputs over the course of the day indicate that the alignment of the optical system is stable. Intensity variations are used to calculate the statistical errors.](image)

2.3.5 Spectrometer and collection optics

Scattered light is collected at a 90° polarization and scattering angle by a 100 mm focal distance lens with a 51 mm diameter. The magnification of the collection optics results in an axial detection range of approximately 20 mm. The scattered light is transported with an array of 400 μm diameter fibers to a self-built, single-pass spectrometer in Littrow arrangement with a 0.3 m focal distance, 0.08 m diameter Littrow lens. A Jobin Ivon type 520-25-120 square grating is used which measures 11 x 11 cm$^2$, has a groove density of 1200 mm$^{-1}$ and is optimized for
first order diffraction. The grating efficiency is only about 20% as shown in Figure 2.28 [Horiba, 2015]. The grating angle of the spectrometer is calculated with Bragg’s law:

\[ 2 \sin \alpha = nk\lambda \]  

(2.62)

where \( n \) is the diffraction order, \( \alpha \) is the grating angle, \( k \) is the groove density and \( \lambda \) is the wavelength of the incident light. The grating angle \( \alpha \) is 0.325 radians, which is used to calculate the linear dispersion:

\[ \frac{d\lambda}{dx} = \frac{1}{knL \cos \alpha} \]  

(2.63)

where \( L \) is the focal length of the Littrow lens. The linear dispersion is 26 nm per cm at the surface of the image intensifier.

A third generation image intensifier of type EPM102G-04-22S made by KATOD is used to amplify the measured signal. The in-house constructed power supply for the image intensifier has a rise time of 9 ns at a load of 150 pF, when a 1000 V pulse is requested. In these conditions, the fall time is 8 ns. A Nikon 135mm f/2 DC and a Nikon AF-S 85mm f/1.8g lens are used to project the intensified spectrum with a magnification of 0.6 on the MANTA G-145B CCD camera. The pixel size of this camera is 6.45 \( \mu \)m, with a resolution of 1388 x 1038. The magnification of the lenses gives an effective pixel size of approximately 11 \( \mu \)m at the image intensifier. Combining this with the calculated linear dispersion of 26 nm per cm at the surface of the image intensifier results in a linear dispersion of 0.027 nm/pixel.

![Figure 2.26: A schematic of the spectrometer. Light enters via the slit (1), is reflected by a mirror (2) passes through the Littrow lens (3), refracts on the grating (4), passes the Littrow lens again, is amplified by the image intensifier (5), which is projected by lenses (6,7) onto the CCD (8).](image)

The linear dispersion of the spectrometer is measured using the spectral lines shown in Table 2.5. The literature wavelengths and the measured position on the CCD, together with a linear fit, are shown in Figure 2.27. The measured linear dispersion is 0.026 nm per pixel. The small discrepancy with respect to the calculated value is likely due to a slightly different magnification of the image intensifier screen projection onto the CCD.
Figure 2.27: The linear dispersion of the spectrometer was determined at 0.026 nm per pixel using spectral lamps.

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd:YAG</td>
<td>532</td>
</tr>
<tr>
<td>Ne I</td>
<td>533.08</td>
</tr>
<tr>
<td>Ne I</td>
<td>534.11</td>
</tr>
<tr>
<td>Ne I</td>
<td>540.06</td>
</tr>
<tr>
<td>Hg I</td>
<td>546.08</td>
</tr>
</tbody>
</table>

Table 2.5: Spectral lines used for the calibration of the spectrometer [NIST, 1976].

For an accurate characterization of the scattered light, the instrumental broadening should be known, since the measurement is a convolution of the spectrum with the instrument function. The instrument function is a convolution of all the different broadening mechanisms, e.g. the width of the entrance slit, the spatial resolution of the sensor, alignment imperfections, etcetera. Provided all broadening mechanisms are Gaussian, the total broadening is:

$$\Delta \lambda_{total} = \sqrt{\Delta \lambda_1^2 + \Delta \lambda_2^2 + \Delta \lambda_3^2 + \ldots}$$  (2.64)  

If the spectrometer is properly aligned, the instrumental FWHM is determined by the entrance slit, and is approximately the product of the entrance slit width and the linear dispersion:

$$\Delta \lambda_{instr} = \frac{w_{dia}}{knL} \cos \alpha$$  (2.65)
where \(w_{\text{slit}}\) is the width of the entrance slit [Palmer and Loewen, 2005]. A slit width of 10 \(\mu m\) results in an instrument FWHM of 0.03 nm. The measured spectral resolution depends on the sampling at the exit slit, i.e. the spatial resolution of the detector. Detector limited sampling occurs when the instrument FWHM is narrower than the spectral width of the detector channels. When the instrument FWHM is equal to the sampling interval, there is critical sampling. Oversampling occurs when the instrument FWHM is larger than twice the sampling interval. Since the linear dispersion is measured at 0.026 nm/pixel, a slit width of 10 \(\mu m\) will result in about 1 pixel per instrument FWHM, close to critical sampling.

The etendue characterizes the ability of an optical system to accept light. It is a function of the area of the emitting source and the solid angle that the systems entrance pupil subtends from the source. The throughput of an optical system is determined by the element with the smallest etendue. In the experimental setup, the etendue of the spectrometer is limiting, which means that increasing e.g. the etendue of the collection optics, will not lead to an increased signal. The etendue for a spectrometer is calculated as:

\[
G = \frac{h_{\text{slit}} k n A_{\text{grating}} \Delta \lambda_{\text{instr}}}{L} = \frac{A_{\text{slit}} A_{\text{grating}}}{L^2} \cos \alpha
\]  

(2.66)

where \(h_{\text{slit}}\) is the slit heigth, \(A_{\text{slit}}\) is the area of the entrance slit, and \(A_{\text{grating}}\) is the grating area [Lerner and Thevenon, 2015]. Because the etendue is inversely proportional to the local length of the Littrow lens squared, a short spectrometer will have a much better throughput. The spectrometer used in the laser scattering setup has an etendue of 0.64 \(\times \) 10\(^{-8}\).

The quantum efficiency of the Manta G-145B camera is shown in Figure 2.28. The quantum efficiency is measured by the manufacturer, without protection glass or filters, and the actual value is approximately 10 percent lower. Although Sony does not publish full well capacities, the CCD in the Manta G-145B camera, the Sony ICX285 (type 2/3), is reported to have a full well capacity of 18000 photoelectrons based on dynamic range and signal to noise calculations [Hornberg, 2006].

Low signal-to-noise ratios in the case of weak signals require long integration times. However, since the intensifier-CCD combination is uncooled, dark current and its associated noise levels will also increase at long acquisition times.

Gaussian noise, which has a probability density function according to a normal distribution, can arise in the CCD sensor e.g. due to poor illumination or high temperature, and in the electronic circuit of the camera, e.g. due to transmission. In the case of the Manta G-145 camera, the Gaussian noise shows no clear dependence on the exposure time below 1 second. This indicates that at these time scales, noise sources in the readout and transmission dominate. At timescales exceeding 1 second, a small time-dependent contribution is seen.
Salt-and-pepper noise consists of highly intense pixels in dark areas, and low intensity pixels in illuminated areas. This type of noise can be caused by malfunctioning of the camera, e.g. memory cell failure or errors in the image digitizing or transmission. Photodiode leakage currents can also give rise to salt-and-pepper noise at long exposure time. Salt-and-pepper noise can be mostly eliminated by dark frame subtraction. The noise behaviour of the Manta G-145B camera is studied by measuring spectra in the absence of light with varying exposure times. The amount of saturated pixels shows a power law behaviour, with a prefactor of about 10 and an exponent of around 1.7 when the exposure time is given in seconds, as shown in Figure 2.29.

2.3.6 Optical emission imaging

Optical emission of the plasma in the reactor is studied using a Manta G-146B camera. The quantum efficiency is shown in Figure 2.28. The emission is focused with a 1 inch diameter 75 mm focal distance lens at a distance of 284 mm which subtends a solid angle of $6.3 \times 10^{-3}$ steradian. The magnification results in a field of view of approximately 20 by 20 mm. A vignetting correction is applied using a homogeneous discharge.
Figure 2.29: The saturated pixel fraction of the Manta G-145B camera shows a power law dependence on the exposure time. Extrapolating, the sensor completely saturates at an exposure time of 20 minutes.

2.3.7 FTIR

The effluent is led through a gas cell inside a Varian 670 FTIR spectrometer. Spectra are taken at a resolution of 0.09 cm\(^{-1}\) so that the individual rovibrational peaks are resolved. CO densities are deduced from a fit of the spectrum. In the fit procedure, a spectrum is calculated using molecular data from the HITEMP database, taking into account pressure broadening, Doppler broadening, and instrument broadening\[\text{Rothman et al., 2010}\]. Room temperature is assumed since the FTIR measurement cell is located a few meters away from the discharge.

\[
\text{CO}_2 \rightarrow (1 - \alpha)\text{CO}_2 + \alpha\text{CO} + \frac{\alpha}{2}\text{O}_2 \tag{2.67}
\]

The energy efficiency is calculated using the enthalpy \(\Delta H\) of 2.93 eV per molecule, and the measured conversion degree \(\alpha\) [Chase Jr., 1998].

\[
\eta = \frac{\alpha \Delta H \Phi \epsilon}{P_{in}} \tag{2.68}
\]

\(\Phi\) is the flow rate in molecules per second, and \(P_{in}\) is the input power in Watt.
2.4 Results

2.4.1 Operating regimes in microwave discharges

In the microwave reactor, different modes of plasma operation are observed as function of pressure. At low pressures the plasma is diffuse, the plasma emission is relatively homogeneous over the radius of the quartz tube. At higher pressures, the plasma constricts, and forms a filament in the middle of the reactor. The difference between the diffuse and constricted regime is illustrated by two optical emission measurements shown in Figure 2.30. An emission image obtained at a pressure of 42 mbar and a power input of 221 Watt, corresponding to the diffuse regime, is shown in 2.30a. An image obtained at 170 mbar and 420 Watts, corresponding to the constricted regime, is shown in 2.30b.

![Image](a) Optical emission at a pressure of 42 mbar and 221 Watt input power.  
![Image](b) Optical emission at a pressure of 170 mbar and 420 Watt input power.

Figure 2.30: Two illustrative cases to show the difference between the diffuse and contracted operating regime.

To illustrate that the two operating regimes are not gradually different, but separated by a sharp transition, the emission FWHM as function of input power is shown in 2.31a for a fixed flow rate of 13 slm. Note that the emission FWHM, although line-integrated, is representative of the plasma size, since the width of a Gaussian function is invariant under an Abel transformation [Abel, 1826]. In the constricted regime the radial extent of the plasma is independent of input power, while in the diffuse regime the plasma radius increases when the input power is increased. In addition to the pressure dependence, these measurements suggest there is also a minimum input power for the plasma to fully constrict. For both regimes the total emission intensity increases with power input as shown in 2.31b. Deviations from this trend are attributed to emission outside of the observation volume.
The FHWM of the radial emission profile increases with power below approximately 130 mbar. Above this pressure the plasma width constricts to a few mm, and becomes independent of the microwave power.

The emission intensity increases with power. At higher pressures, the emission is more intense. Deviations from the trend at higher power input is due to emission outside of the detection volume.

Figure 2.31: The FHWM and total intensity of the optical emission of the plasma.

The existence of the two regimes is caused by the differences in microwave propagation at different electron-heavy particle collision frequency [Fridman, 2008]. At low pressures, the collision frequency \( \nu_{e-h} \) is not sufficiently high to enable electron densities above the critical electron density of \( 7.5 \times 10^{16} \text{ m}^{-3} \). This results in a diffuse plasma, where the plasma volume adjusts to satisfy the power balance. At increased pressures, above \( \text{CO}_2 \) densities of approximately \( 2.3 \times 10^{23} \text{ m}^{-3} \), the collision frequency is high enough to enable the formation of plasma with electron densities in excess of the critical electron density. As the electron density increases the skin depth becomes smaller, limiting the plasma size. The filament is stabilized in the middle of the reactor by a rotating flow pattern which is realized by tangential injection of the feed gas.

The results section is divided into separate parts which describe the measurements in the diffuse and the constricted regime. This choice is made because the diffuse and contracted regime behave differently in terms of plasma parameters such as the electron density. The homogeneity of the diffuse regime allows the estimation of bulk properties with a two-temperature model. In the constricted regime, the plasma sizes obtained from optical emission measurements are used to estimate electron densities via the skin depth.

### 2.4.2 Low pressure operation: diffuse regime

Rayleigh scattering measurements in the center of the microwave plasma interpreted on basis of the \( \text{CO}_2 \) Rayleigh cross section yield a neutral density of \( 7 \times 10^{22} \text{ m}^{-3} \) at 100 mbar and a specific energy input of 1 eV per molecule. This neutral
density corresponds to temperatures on the order of 1 eV. In this temperature regime, the CO$_2$ is fully dissociated into C and O, and this dissociation degree is reached on timescales that are well below the residence time. In these conditions, interpreting the Rayleigh signal assuming pure carbon dioxide as scattering species is unrealistic.

It is possible to interpret the Rayleigh scattering measurements in a way that takes into account the local dissociation degree, as outlined in the theory section in Equation 2.45. This method requires knowledge of the composition as function of temperature. As first approximation, a thermal CO$_2$ mixture is assumed, for which the effective cross section is shown in Figure 2.18. Since the effective cross section decreases by a factor of 3.5 going from room temperature to 5000 K, the measured signal will decrease by the same factor at a constant density. Interpreting the measurements on basis of the effective cross section will thus yield higher densities. All density and temperature values presented in this section are interpreted on basis of the effective cross section of a thermal mixture unless explicitly stated otherwise.

Axial profiles of the neutral density are measured with laser scattering for different radial locations. There are only minor axial variations in the neutral density for all the measurements in the microwave cavity. As the power increases, the neutral density becomes radially homogeneous, as shown in 2.32b. The ratio of the on-axis and 5 mm off-axis density approaches 1 as the power increases. This is verification that the discharge is homogeneous over a large fraction of the reactor radius in the diffuse regime.

Figure 2.32: Axial profiles of the neutral density measured at different radii show minor variations. In the diffuse regime, the plasma becomes radially homogeneous as the input power increases.

An overview of all the on-axis laser scattering measurements in the diffuse plasma is shown in Figure 2.33. Although different flow settings are used in the experiment, the measured densities are not dependent on the flow, and overlap
when plotted as function of pressure and input power. Most neutral densities measured in the center of the diffuse plasma are below a neutral density of $2.3 \times 10^{22} \text{ m}^{-3}$. As established in Section 2.2.1, below this neutral density the formation of high electron density plasmas is hindered by reflection, and the plasma volume will adjust while the electron density in the plasma stays around a critical electron density of $7.5 \times 10^{16} \text{ m}^{-3}$. The calculated neutral density was based on CO$_2$ in the electron-heavy particle collision frequency, if the plasma composition is properly accounted for in the calculation, the neutral density needed to sustain higher electron density plasmas might be slightly different.

Figure 2.33: The neutral density in the center of the discharge for various pressures.

Since the neutral density varies between $5 \times 10^{22}$ and $25 \times 10^{22} \text{ m}^{-3}$, and mostly flows of 13 slm are used, the mean flow speed varies between 40 and 200 m/s. When the width of the waveguide, 43.2 mm, is used as plasma length, the residence time varies from 0.2 to 1 ms. As shown in 2.15a, thermal compositions are reached on a shorter microseconds timescale, depending on the gas temperature.

Although the neutral densities are only a function of input power at fixed pressure, the energy efficiencies are also dependent on the flow rate. As Figure 2.34 shows, this results in different energy efficiencies for the same specific energy input. Since the plasma parameters are similar, we attribute the different energy efficiencies to a residence time effect. Thermal compositions are reached at short timescales, more plasma time only increases losses.

Energy efficiencies close to 50 percent are reached at 103 mbar and 1 eV specific energy input. At a flow of 13 slm, this corresponds to a conversion degree
of almost 15 percent. Conversion degrees as function of microwave power are shown in Figure 2.35 for various pressures. The conversion scales linearly with the power, with a different slope at different pressures. The offset results in a hyperbolic behaviour of the energy efficiency as function of input power.

The measured energy efficiency is below the limit of 52 percent that is calculated in the theory section for a thermal mixture which is instantaneously quenched. The composition and temperature for a thermal mixture at 100 mbar is shown as function of energy input in Figure 2.12. At a specific energy input of 1 eV per molecule, the temperature is below 2000 K, the conversion degree is only 2 percent, and the efficiency in those conditions is 6 percent. This does not correspond with the measured values, which is an indication that a one-temperature calculation is an oversimplification.

To estimate if the measured conversion degree and specific energy input can be reproduced by a model which assumes a thermal composition, a two-temperature model is introduced. In this model, the conversion degree $\alpha$ and the specific energy input $E_{in}$ are parametrized by three variables: the fraction of particles in the hot zone $\beta$, and two temperatures:

\begin{align*}
\alpha &= (1 - \beta)\alpha(T_{\text{low}}) + \beta\alpha(T_{\text{high}}) \\
E_{in} &= (1 - \beta)E_{in}(T_{\text{low}}) + \beta E_{in}(T_{\text{high}})
\end{align*}

Back reactions during quenching of the mixture are not considered. The record energy efficiency measurements with a conversion degree of 15 % at 1 eV specific
energy input are reproduced with this model if 17 % of the gas is 3250 K and 83 % of the gas is 720 K. Since radially outwards the surface area per annulus is larger, and the cold gas is denser, this results in a hot zone diameter of 19 mm if the density increase due to dissociation is neglected. This shows that CO production in optimum conditions is reproduced on basis of a thermal two-temperature model. The hot zone diameter is compatible with experimental observations, and the temperature of the cold zone allows for some gas heating next to the plasma.

With the measured conversion degree $\alpha$, the specific energy input $E_{in}$, and the on-axis temperature $T_{high}$ deduced from Rayleigh scattering measurements as input, the two-temperature model was solved for the hot zone fraction $\beta$ and the temperature of the low temperature reservoir $T_{low}$. Figure 2.36 shows the hot zone fraction for a variety of measurements done at CO$_2$ flow rates ranging from 3 to 13 slm. Although the efficiency (i.e. CO production) depends on flow and pressure, the hot zone fraction scales well with the specific energy input. This is consistent with the emission measurements of the plasma size, which were found to increase with input power. The 100 mbar power scans where the efficiency is optimal still have an appreciable cold zone temperature of 470 K and above. In some cases, unphysical solutions were found. This was the case for some of the 3 slm data, which has a high specific energy input, a $T_{high}$ between 2300 and 2900 K, but a low conversion. We attribute this to CO losses via back reactions, so that the conversion degree which is measured downstream is not representative for the CO production.
It could be argued that a stepped temperature profile is unrealistic, since in the reactor the temperature profile will be smooth, due to heat convection and conduction from the hot to the cold zone. To assess what influence this has on the conversion degree and the specific energy required, a Boltzmann-step function is introduced for the temperature profile:

$$T(r) = (T_{\text{max}} - T_{\text{min}}) \left( 1 - \frac{1}{1 + \exp \left( \frac{r - R_{\text{edge}}}{R_{\text{width}}} \right)} \right) - \frac{1}{1 + \exp \left( \frac{r - R_{\text{edge}}}{R_{\text{width}}} \right)} + T_{\text{min}}$$  \hspace{1cm} (2.70)

$T_{\text{max}}$ and $T_{\text{min}}$ are the temperatures in the center and at the edge, $R_{\text{edge}}$ is the location of the boundary between the two zones, and $R_{\text{width}}$ is an adjusting parameter for the width of the transition between edge and center region. The average of e.g. the temperature is then calculated by the following integral over the reactor radius:

$$T_{\text{avg}} = \frac{\int_{0}^{R_{\text{max}}} T(r)n(r)2\pi r dr}{\int_{0}^{R_{\text{max}}} n(r)2\pi r dr}$$  \hspace{1cm} (2.71)

Figure 2.37 shows three profiles with a central temperature of 3250 K, an edge temperature of 300 K, an edge location of 10 mm for a reactor diameter of 27 mm at 100 mbar. The edge width is varied to investigate the effects on the average temperature, conversion, and specific energy input. Table 2.6 shows the radially averaged quantities of the profiles. Variations at the edge of the reactor have a
large effect on the average because the surface area is large, and the colder gas is denser. This analysis shows that also relatively smooth profiles can still produce significant quantities of CO without wasting large amounts of energy in heating gas to temperatures which do not contribute to CO production. As an example, a profile with a central temperature of 3250 K, an edge temperature of 300 K, an edge location of 10.3 mm and an edge width of 1 mm has a conversion degree of 0.15 at a specific energy input of 1.1 eV per molecule.

![Figure 2.37: Several hypothetical temperature (solid) and density (dashed) profiles calculated with the Boltzmann step function at a pressure of 100 mbar.]

<table>
<thead>
<tr>
<th>$R_{\text{edge}}$ (mm)</th>
<th>$T_{\text{avg}}$ (K)</th>
<th>$\alpha$</th>
<th>$E_{\text{in}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1149</td>
<td>0.127</td>
<td>0.927</td>
</tr>
<tr>
<td>2</td>
<td>1595</td>
<td>0.129</td>
<td>1.19</td>
</tr>
<tr>
<td>3</td>
<td>1733</td>
<td>0.010</td>
<td>1.17</td>
</tr>
</tbody>
</table>

Table 2.6: Average temperature, conversion, and specific energy input for the three temperature profiles shown in Figure 2.37. Since colder gas is more dense, variations at the edge of the reactor have a large effect on the average.

Figure 2.38 shows the gas temperatures in the reactor for various operating conditions. The power scan at 101 mbar falls in the temperature range where the CO production is maximum, i.e. where the highest efficiencies are attainable. At the lower end of the measured temperature range, the residence time exceeds the chemical equilibration time. At 2500 K, the equilibration time is 0.4 ms, but this rapidly increases to 1.6 ms at 2250 K, 7 ms at 2000 K, and 9.8 ms at 1750 K. Although this is not compatible with the assumption made in the Rayleigh data
analysis that the composition is in thermal equilibrium, the effect is small since at low temperatures the effective cross section is close to the CO₂ cross section.

Figure 2.38: The gas temperature in the center of the discharge.

The measured gas temperatures and CO production rates are consistent with a thermal composition and a sufficiently peaked temperature profile. In order to reach high energy efficiencies, it is vital that produced CO does not react back to CO₂. Back reactions are suppressed by quick cooling. Mixing with colder CO₂ from the edge of the reactor is beneficial in this respect for two reasons, firstly it is a cooling mechanism, and secondly the CO is diluted so that oxygen radicals are less likely to react with the carbon monoxide. The first aspect, the influence of cooling rates on CO loss, is investigated in the theory section with a 0-D model. Cooling rates of at least a few times 10⁸ K/s are needed to keep the fractional CO loss below 20%. The cooling rate of the gas is estimated from downstream Rayleigh scattering measurements, in the afterglow of the plasma. The measured cooling rates are on the order of 10⁶ K/s, which is insufficient to prevent back reactions. Although the cooling rates are modest, the intensity of the Rayleigh scattering does increase in the afterglow, as shown in 2.39b for a constricted discharge. Due to the variation of the effective cross section in this temperature range, the signal variation only translates to a minor temperature variation. Further interpretation of these measurements is speculative without knowing the exact composition. Maybe the composition does not change and the signal increases because of cooling. Maybe the signal increases due to inward diffusion of CO₂, which has a higher Rayleigh scattering cross section. In any case, the temperatures measured in the afterglow are still around 3000 K, so the quenching might take place farther downstream.
2.4.3 High pressure operation: contracted regime

As the pressure increases, there is a transition in plasma shape: the plasma contracts to a filament in the middle of the reactor. This is a result of the increased collision frequency $v_{e-h}$, which enables microwave propagation at electron densities above the critical density. Because of the high power density in the small volume of the filament, the electron densities are estimated to be on the order of $10^{18} - 10^{19} \text{ m}^{-3}$ with a simple power balance [van Rooij et al., 2015]. Indirect support for this electron density estimation is deduced from the plasma size. Since microwave propagation is limited by the skin effect, which changes with the electron density, the electron density is related to the plasma size. The radial extent of the plasma is on the order of millimeters, which corresponds to an electron density in the range $10^{18} - 10^{19} \text{ m}^{-3}$ as shown in Figure 2.7. The filament is stabilized in the center of the reactor by the rotating flow pattern realized by axial injection of the carbon dioxide.

Axial profiles of the neutral density are measured with laser scattering for different radial locations. 2.39a shows profiles measured in similar discharges. As in the diffuse discharge, there are only minor variations in the axial direction. In the radial direction, there are large differences between the low neutral density in the plasma filament and the larger densities in the periphery.

![Graphs showing axial profiles of the neutral density and CO$_2$ equivalent density](image)

(a) In the contracted regime, there are pronounced radial gradients in the neutral density profiles, a consequence of the peaked power deposition profile.

(b) The CO$_2$ equivalent density increases in the afterglow, but the temperature decrease is modest as result of the temperature dependent cross section used in the analysis.

Figure 2.39: Axial profiles of the neutral density in the microwave cavity and afterglow of the plasma for contracted discharges.

A summary of the on-axis neutral density measurements is shown in Figure 2.40. The measured densities and temperatures are shown as function of specific energy input since the measured values do not seem to overlap when plot as function of input power, but the paucity of measurements does not allow further conclusions.
The neutral temperatures in the filament are somewhat higher than measured in the diffuse discharge, but not by a large margin. The measured on-axis neutral densities all exceed the calculated $n_0$ of $2.3 \times 10^{23}$ m$^{-3}$ needed to sustain the constricted discharge mode.

The energy efficiencies for the constricted regime are shown in 2.41a. The maximum energy efficiency in the constricted regime is close to 50 percent, similar to values obtained in the diffuse regime. In contrast to operation at lower pressures, the energy efficiency scales with the specific energy input.

In the contracted plasma regime, the optical emission is peaked in the center of the reactor. This is a consequence of the peaked power deposition profile. The deposited power is transferred to the periphery by conduction. This situation is similar to electric arc discharges, although arcs generally operate at higher heavy
particle temperatures. The behaviour of electrical arc discharges is described by the Elenbaas-Heller equation, which has analytical solutions as derived by Shaw [2006]. The gas temperature profiles that result from the Elenbaas-Heller equation are not as peaked as the optical measurements suggest, these gradual profiles are not a good starting point for a two temperature approximation. Since the measured efficiencies in the contracted regime most likely result from a complex interplay of plasma-chemical processes, more measurements of the plasma parameters are needed for a factual discussion on the importance of non-equilibrium, vibrationally excited processes, in the contracted discharge.

2.5 Conclusions

A microwave plasma reactor for the dissociation of carbon dioxide is studied with laser scattering, FTIR, and optical emission measurements. Two regimes of operation are identified, a diffuse mode of operation at low pressures, and a constricted discharge at increased pressures, which is caused by differences in microwave propagation. At low pressures, the collision frequency $\nu_{e-h}$ is not sufficiently high to enable electron densities above a critical electron density of $7.5 \times 10^{16} \text{ m}^{-3}$. In this regime the plasma volume adjusts to satisfy the power balance. At increased pressures, above CO$_2$ densities of approximately $2.3 \times 10^{23} \text{ m}^{-3}$, the collision frequency is high enough to enable the formation of plasma with electron densities in excess of the critical electron density. As the electron density increases the skin depth becomes smaller, limiting the plasma size.

In the diffuse regime, the neutral density is constant along the axial direction. In the central 10 mm of the reactor, the density profile becomes homogeneous at increasing input power. The radial plasma size, estimated from optical emission measurements, increases with the input power, a feature that sets the diffuse regime apart from the contracted regime. Central gas temperatures in the range 1500 - 3500 K are inferred from Rayleigh scattering measurements. A two-temperature thermal model is constructed to relate the conversion degree $\alpha$, the specific energy input $E_{in}$, a hot zone fraction $\beta$, and a $T_{low}$ and $T_{high}$. Measured conversion degrees and specific energy inputs are combined with temperatures inferred from Rayleigh scattering measurements to obtain solutions for $T_{low}$ and $\beta$. The hot zone fractions $\beta$ are found to scale with the specific energy input. Record efficiencies approaching 50 % are measured, in which case a $T_{low}$ of 470 K is needed to satisfy the specific energy input. Afterglow measurements are used to estimate cooling rates.

In the constricted regime, a small plasma filament forms in the middle of the reactor. The radial size of the filament does not increase with increasing input
power. The electron density is estimated to be in the range $10^{18} - 10^{19}$ m$^{-3}$ based on the size of the plasma in combination with the calculated skin depth. Also in this regime, energy efficiencies approach 50%.

Contributorship statement

N. den Harder is the main author of the chapter. He constructed the experiment and laser scattering diagnostic, conducted the experiments and data analysis, investigated microwave-plasma coupling and (thermal) reaction kinetics: he is guarantor. D. C. M. van den Bekerom conducted FTIR measurements and data analysis. M. F. Graswinckel provided assistance in the construction of the experiment. F. J. J. Peeters, J. M. Palomares, S. Ponduri, W. A. Bongers, and M. C. M. van de Sanden provided input in interpretation. T. Minea assisted during experiments. G. J. van Rooij directed the conception and design of the experiment, gave input on the acquisition, analysis, and interpretation of the data, and assisted in drafting and revising the chapter.
Chapter 3

Residual gas entering high density hydrogen plasma: rarefaction due to rapid heating

Based on: Plasma Sources Science and Technology 24, 025020, (2015)

Abstract

The interaction of background molecular hydrogen with magnetized (0.4 T) high density (1-5 \times 10^{20} \text{ m}^{-3}) low temperature (\sim 3 \text{ eV}) hydrogen plasma was inferred from the Fulcher band emission in the linear plasma generator Pilot-PSI. In the plasma centre, vibrational temperatures reached 1 eV. Rotational temperatures obtained from the Q(\nu = 1)-branch were systematically \sim 0.1 \text{ eV} lower than the Q(\nu = 0)-branch temperatures, which were in the range of 0.4-0.8 eV, typically 60% of the translational temperature (determined from the width of the same spectral lines). The latter is attributed to preferential excitation of translational degrees of freedom in collisions with ions on the timescale of their in-plasma residence time. Doppler shifts revealed co-rotation of the molecules with the plasma at an order of magnitude lower angular velocity, confirming that the Fulcher emission connects to background molecules. A simple model estimated a factor of 90 rarefaction of the molecular density at the centre of the plasma column compared to the residual gas density. Temperature and density information was combined to conclude that ion-conversion molecular assisted recombination dominates plasma recombination at a rate of 1 \times 10^{-15} \text{ m}^3 \text{ s}^{-1}. The observations illustrate the general significance of rapid molecule heating in high density hydrogen plasma for estimating molecular processes and how this affects Fulcher spectroscopy.
3.1 Introduction

Low temperature hydrogen plasma is, amongst others, characterized by the significant presence of \( \text{H}_2 \) molecules. The significance lies not so much in their relative abundance, but merely in their importance for opening up reaction pathways for the plasma ions. As a consequence, the properties of these molecules often determine main system properties such as plasma recombination (of interest for e.g. in the exhaust of fusion devices, see Krasheninnikov et al. [1997]; Reiter et al. [1997]), ionization and dissociation rates, and negative ion formation efficacy (both of interest for reactive species generation for materials processing in semiconductor industry [Bacal et al., 1981; Gorse et al., 1992; Sawada and Fujimoto, 1995]).

The present research in the linear plasma generator Pilot-PSI [van Rooij et al., 2007] was conducted to reveal exactly one of such a system property, namely the plasma recombination rate, and in addition, to identify the exact molecular process responsible for plasma recombination. The various molecular plasma loss mechanisms, termed “Molecular Activated Recombination” (MAR) were suspected to be relevant on basis of previous work: de Graaf et al. [1993]; Shumack et al. [2008]. Out of the different MAR mechanisms, negative-ion-mediated MAR

\[
e + \text{H}_2 \rightarrow (\text{H}_2^-)^* \rightarrow \text{H} + \text{H}^- \quad (3.1)
\]

\[
\text{H}^+ + \text{H}^- \rightarrow \text{H} + \text{H}(n = 3) \quad (3.2)
\]

and ion-conversion MAR

\[
\text{H}^+ + \text{H}_2 \rightarrow \text{H} + \text{H}_2^+ \quad (3.3)
\]

\[
e + \text{H}_2^+(v') \rightarrow \text{H}(1s) + \text{H}(n \geq 2) \quad (3.4)
\]

are the most important [Janev, 2002]. The rate of both recombination reactions is not only determined by the molecular density, but also strongly dependent on the rovibrational excitation of the reactants. An increase in the rovibrational energy of the molecules speeds up the reaction, whilst the reaction rate is enhanced by many orders of magnitude for the higher lying vibrational levels.

A wide range of active laser spectroscopic techniques is capable of measuring (vibrationally excited) hydrogen molecules, such as the LIF (Laser Induced Fluorescence) [Vankan et al., 2004], CARS (Coherent Anti-Stokes Raman Spectroscopy) [Meulenbroeks et al., 1996], REMPI (Resonance-Enhanced MultiPhoton Ionization) [Bonnie et al., 1988] and FWFM (Four-Wave Frequency Mixing) [Stutzin et al., 1989]. We chose for a passive spectroscopy approach that gives immediate overview over (parts of) the relative distribution over vibrational levels and that is commonly
used in laboratory as well as fusion experiments [Fantz, 2002; Gritsinin et al., 1998; Heger et al., 2001; Shikama et al., 2007; Tomasini et al., 1996]. In particular, we studied the molecular emission of the diagonal Fulcher-\(\alpha\) band [Fulcher, 1913] \((d^3\Pi_u \rightarrow a^3\Sigma^+_g)\) to determine vibrational temperatures [Fantz and Heger, 1998]. The vibrational temperature was subsequently used to calculate the effective rate for both recombinative reactions invoking available vibrationally resolved rate constants, which are taken from Reiter [2005]. Similarly, the rotational temperature of the excited state was determined and, with assumptions about the excitation mechanism, projected to the ground state rotational temperature Herzberg [1989]. The latter is often interpreted as the gas temperature. We determined the gas temperature independently from the Doppler broadening of the spectral lines and compared the two results. Doppler shifts were used to quantify the rotational motion and to assess the coupling between molecules and plasma ions. Finally, the molecular density in the plasma centre was inferred from these temperature measurements, enabling estimation of the absolute importance of the main MAR mechanisms.

The experimental observations reported here represent a general example of how fast molecule heating in high density hydrogen plasma affects the reaction rates of molecular processes and their overall importance. Furthermore, it illustrates how it affects the interpretation of Fulcher spectroscopy. These findings are not only of relevance for laboratory experiments, but also for future fusion devices such as ITER, in which the plasma conditions in the regions of the strike points at the divertor target are close to those in the present study [ITER, 1999; Pitts et al., 2009].

### 3.2 Method

#### 3.2.1 Instrumentation

The linear plasma generator Pilot-PSI is used to generate hydrogen plasma beams of typically 12 mm wide (density FWHM), with a peak density and temperature of \(1.5 \times 10^{20} \text{ m}^{-3}\) and 1-3 eV, in a magnetic field of 0.4 T. At these densities and temperatures, the collisionality is high, so that the electron and ion energy distributions are close to Maxwellian. Lifetimes of \(\text{H}_2^+\) and \(\text{H}_3^+\) ions are short, and protons are the majority ions. The ionization degree inside the plasma beam is high, more than 80% in the conditions used in this paper [Shumack et al., 2011].

A schematic of the device is shown in Figure 3.1. The plasma source is a cascaded arc [Kroesen et al., 1990], in which discharge currents ranging from 80 to 250 A were drawn between three tungsten cathodes and a copper-tungsten nozzle. Hydrogen gas flows are varied between 1 and 4 standard liters per minute.
Figure 3.1: Schematic of the Pilot-PSI experiment. Optical Emission Spectroscopy and Thomson Scattering were performed at an axial distance of 5 cm from the cascaded arc source.

The plasma expands from a high pressure ($\sim 10^4$ Pa) in the cathode chamber to a low pressure ($\sim 2$ Pa) in the 1 m long, 0.4 m diameter vacuum vessel. The vessel pressure, monitored by a membrane gauge at the plasma source side of the vessel, is adjustable by adjusting the rotation speed of the booster pump. A set of five field coils surrounding the vacuum vessel is used to generate the 0.4 T magnetic fields used in present experiments. Magnetic fields of up to 1.6 T can be generated. More details of the experiment can be found in van Rooij et al. [2007].

Profiles of electron density and temperature are measured 5 cm downstream of the cascaded arc source anode by means of Thomson Scattering [van der Meiden et al., 2008]. Optical Emission Spectroscopy is performed using the High RESolution spectrometer (HiRES), a single-pass spectrometer in Littrow configuration [Shumack et al., 2008]. Light is collected at an axial distance of 5 cm from the plasma source, perpendicular to the magnetic field axis, at the same position as where Thomson Scattering is performed. An array of 40 individual 0.4 mm diameter quartz fibers is used to relay the light to the HiRES spectrometer. In this way, a spectral range of approximately 4 nm can be investigated over the whole radius of the plasma jet for each discharge. The spatial resolution is 0.7 mm. The measurements are line-of-sight integrated.

A relative intensity calibration is carried out using a USS-1200C integrating sphere. The instrument function is measured using an argon lamp. The instrument function is Gaussian shaped and has a 17 pm FWHM. Since the emission lines studied are also Gaussian shaped, the measured width is corrected for instrumen-
tal broadening using the relation:

\[
\Delta \lambda_{\text{Doppler}}^2 = \Delta \lambda_{\text{Measured}}^2 - \Delta \lambda_{\text{Instrument}}^2
\]  

(3.5)

3.2.2 Vibrational temperatures from the Fulcher band

The Fulcher-\(\alpha\) band consists of the radiative transitions between the various vibrational and rotational levels of the upper \(d^3\Pi_u\) and lower \(a^3\Sigma_g^+\) electronic levels of the hydrogen molecule. Here, it is summarized how the vibrational and rotational temperature of the \(X^1\Sigma_g^+\) electronic ground state are determined from the relative line intensities in the Fulcher \(\alpha\) band.

Evaluation of the ground state vibrational temperature starts with calculation of the energy levels of the hydrogen molecule according to Herzberg [1989]:

\[
E(\nu, J) = T_e + \omega_e (\nu + \frac{1}{2}) - \omega_x (\nu + \frac{1}{2})^2 + B_v (J + 1)
\]

(3.6)

with

\[
B_v = B_e - \alpha_e (\nu + \frac{1}{2})
\]

(3.7)

\(\nu\) and \(J\) are the rotational and vibrational quantum numbers, and the other symbols represent constants listed in Table 3.1. It is assumed that the vibrational energy levels of the electronic ground state are populated according to a Boltzmann distribution, so that the distribution over the energy levels is known as function of \(T_{\text{vib}}\).

The upper Fulcher state population is then calculated using the transition probabilities, which can be found in Fantz and Wunderlich [2006], or Franck-Condon factors as listed in Fantz and Heger [1998].

<table>
<thead>
<tr>
<th>State</th>
<th>(T_e)</th>
<th>(\omega_e)</th>
<th>(\omega_x)</th>
<th>(B_e)</th>
<th>(\alpha_e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X^1\Sigma_g^+)</td>
<td>0</td>
<td>0.546</td>
<td>0.01504</td>
<td>0.00754</td>
<td>0.000380</td>
</tr>
<tr>
<td>(a^3\Sigma_g^+)</td>
<td>11.89</td>
<td>0.330</td>
<td>0.00888</td>
<td>0.00424</td>
<td>0.000207</td>
</tr>
<tr>
<td>(d^3\Pi_u)</td>
<td>13.97</td>
<td>0.294</td>
<td>0.00822</td>
<td>0.00376</td>
<td>0.000192</td>
</tr>
</tbody>
</table>

Table 3.1: Molecular constants of hydrogen for electronic states of interest in eV after the NIST [1976], database of Diatomic Molecules.

Electron impact excitation is assumed as the dominant population mechanism of the upper Fulcher state. Because the excitation energy of approximately 14 eV is large compared to the electron temperature, an additional factor is needed that accounts for the fraction of electrons with sufficient energy for excitation. Combining all these factors leads to the following expression for the upper Fulcher state population.
The state population as function of $T_{\text{vib}}$ and $T_e$:

$$f(\nu') \propto \sum_{\nu_0} q_{\nu'\nu_0} e^{\frac{E(\nu_0)}{k_B T_{\text{vib}}}} e^{-\frac{\Delta E_{\text{vib}}}{k_B T_e}}$$

(3.8)

<table>
<thead>
<tr>
<th>Branching ratio</th>
<th>$H_2$</th>
<th>$D_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu' = 0 \rightarrow \nu'' = 0$</td>
<td>0.8887</td>
<td>0.8708</td>
</tr>
<tr>
<td>$\nu' = 1 \rightarrow \nu'' = 1$</td>
<td>0.7459</td>
<td>0.6953</td>
</tr>
<tr>
<td>$\nu' = 2 \rightarrow \nu'' = 2$</td>
<td>0.6134</td>
<td>0.5429</td>
</tr>
<tr>
<td>$\nu' = 3 \rightarrow \nu'' = 3$</td>
<td>0.4917</td>
<td>0.4122</td>
</tr>
<tr>
<td>$\nu' = 4 \rightarrow \nu'' = 4$</td>
<td>0.3817</td>
<td>0.3019</td>
</tr>
</tbody>
</table>

Table 3.2: Branching ratios for the $d^3\Pi_u \rightarrow a^3\Sigma^+_g$ transition of $H_2$ and $D_2$ after Fantz and Heger [1998].

The measured intensities divided by the branching ratios, which are listed in Table 3.2, are compared directly with the calculated population distributions [Fantz and Heger, 1998]. Varying $T_{\text{vib}}$ in the calculation the sum of squares is minimized, which yields the vibrational temperature.

| $\nu'' = 0$ | 0.0980 | 0.2958 | 0.3387 | 0.1975 | 0.0601 | 0.0092 | 0.0006 | 0.0001 | 0.0000 |
| 1 | 0.1641 | 0.1676 | 0.0000 | 0.1648 | 0.3001 | 0.1645 | 0.0357 | 0.0029 | 0.0004 |
| 2 | 0.1685 | 0.0338 | 0.0854 | 0.1060 | 0.0104 | 0.2447 | 0.2631 | 0.0802 | 0.0077 |
| 3 | 0.1400 | 0.0000 | 0.1157 | 0.0006 | 0.1230 | 0.0247 | 0.1238 | 0.3200 | 0.1377 |
| 4 | 0.1039 | 0.0125 | 0.0709 | 0.0336 | 0.0600 | 0.0420 | 0.0944 | 0.0312 | 0.3278 |
| 5 | 0.0735 | 0.0289 | 0.0269 | 0.0686 | 0.0300 | 0.0865 | 0.0001 | 0.1193 | 0.0001 |
| 6 | 0.0511 | 0.0369 | 0.0056 | 0.0669 | 0.0840 | 0.0475 | 0.0431 | 0.0238 | 0.0894 |
| 7 | 0.0357 | 0.0375 | 0.0001 | 0.0477 | 0.0299 | 0.0950 | 0.0636 | 0.0037 | 0.0598 |
| 8 | 0.0253 | 0.0343 | 0.0012 | 0.0284 | 0.0414 | 0.0001 | 0.0436 | 0.0332 | 0.0061 |

Table 3.3: Franck-Condon factors for the $d^3\Pi_u \leftarrow X^1\Sigma^+_g$ transition in $H_2$ as calculated in Fantz and Heger [1998].

### 3.2.3 Rotational temperatures from the Fulcher band

The relative spectral line intensities within the Q-branch ($\Delta \ell = 0$) are used to determine the rotational temperature [Herzberg, 1989]. Some lines are disturbed by nearby lying lines, these lines cannot be used in the analysis, see Table 3.5. The line intensity is converted to a relative population of the upper Fulcher state by taking into account the degeneracy of the upper state, and the transition strength. The relative population is then plotted on a logarithmic axis versus the energy of the
ground state, given by Equation 3.6. If the upper level is populated according to a Boltzmann distribution, the points show a linear dependence with slope $-E_i/k_B T_{rot}$.

This approach is only valid when the rotational distribution in the ground state follows a Boltzmann distribution. Energy exchange between the rotational and translational degrees of freedom takes place via inelastic molecule-molecule collisions, if these collisions dominate the rotational temperature will be equal to the gas temperature [Astashkevich et al., 1996]. Surface association of hydrogen molecules could lead to an overpopulation of higher rotational levels, but we assume that these processes are of minor influence, and that the lower levels are quickly thermalized. Absorption studies on similar plasmas confirm that the ground state lower rotational levels are Boltzmann populated with a temperature equal to ambient temperature [Vankan et al., 2004].

The ground state rotational distribution is assumed to be exactly imaged onto the excited state. No angular momentum is transferred during the electron impact excitation, and the excitation rate coefficients are independent of the rotational quantum number [de Graaf, 1994; Lavrov et al., 1981].

Since the lifetime of the upper Fulcher state is about 31 ns, and $\nu_{coll}/p \approx 6 \times 10^4$ s$^{-1}$Pa$^{-1}$, only at pressures above 500 Pa collisional redistribution of the upper state population becomes important [Astashkevich and Lavrov, 2002; Phelps, 1990]. At 500 Pa, the time between collisions is equal to the radiative lifetime of the upper Fulcher state. Because the pressures during the experiments are well below this value, redistribution can be neglected, i.e. the measured distribution reflects the ground state distribution [Garg et al., 2008; Gritsinin et al., 1998; Tomasini et al., 1996].

<table>
<thead>
<tr>
<th>branch</th>
<th>(0-0)</th>
<th>(1-1)</th>
<th>(2-2)</th>
<th>(3-3)</th>
<th>(4-4)</th>
<th>(5-5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>601.8299</td>
<td>612.1787</td>
<td>622.4815</td>
<td>632.706</td>
<td>642.8119</td>
<td>652.7355</td>
</tr>
<tr>
<td>Q2</td>
<td>602.3757</td>
<td>612.7246</td>
<td>623.0258</td>
<td>633.2482</td>
<td>643.3510</td>
<td>653.2644</td>
</tr>
<tr>
<td>Q3</td>
<td>603.1909</td>
<td>613.5395</td>
<td>623.8391</td>
<td>634.0575</td>
<td>644.1498</td>
<td>654.0525</td>
</tr>
<tr>
<td>Q4</td>
<td>604.2716</td>
<td>614.6186</td>
<td>624.9150</td>
<td>635.1282</td>
<td>645.2107</td>
<td>655.0880</td>
</tr>
<tr>
<td>Q5</td>
<td>605.6091</td>
<td>615.9565</td>
<td>626.2495</td>
<td>636.4618</td>
<td>646.5251</td>
<td>656.2796</td>
</tr>
<tr>
<td>Q6</td>
<td>607.1996</td>
<td>617.5462</td>
<td>627.8369</td>
<td>638.0317</td>
<td>648.0868</td>
<td>657.9321</td>
</tr>
<tr>
<td>Q7</td>
<td>609.0374</td>
<td>619.3812</td>
<td>629.6622</td>
<td>639.8452</td>
<td>649.8794</td>
<td>659.6834</td>
</tr>
<tr>
<td>Q8</td>
<td>611.1088</td>
<td>621.4507</td>
<td>631.7233</td>
<td>641.8908</td>
<td>651.9008</td>
<td>661.6679</td>
</tr>
<tr>
<td>Q9</td>
<td>613.4077</td>
<td>623.7457</td>
<td>634.0085</td>
<td>644.1498</td>
<td>654.1394</td>
<td>663.8577</td>
</tr>
</tbody>
</table>

Table 3.4: Wavelengths in nm of the first nine lines of the Q-branch with $\Delta \nu = 0$ of the hydrogen Fulcher-$\alpha$ band after Crosswhite [1972].
3.2.4 Translational temperature determination

The translational or gas temperature of the molecular hydrogen is determined from Doppler broadening of the emission line using the following relation:

$$T_{\text{gas}} = \frac{mc^2}{8k\ln 2} \left( \frac{\Delta \lambda_{\text{FWHM}}}{\lambda} \right)^2$$

(3.9)

Since we operate at a comparatively low magnetic field of 0.4 T, Zeeman splitting is small compared to the instrument function and can thus be neglected in the lineshape analysis, as shown in Shikama et al. [2007].

### Studied lines Coinciding lines

<table>
<thead>
<tr>
<th>Upper level</th>
<th>Lower level</th>
<th>λ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{1}\Sigma_{u}^{+}$</td>
<td>$c^{3}\Pi_{u}$</td>
<td>603.1465</td>
</tr>
<tr>
<td>$H^{1}\Sigma_{g}^{+}$</td>
<td>$B^{3}\Sigma_{u}^{+}$</td>
<td>603.1909</td>
</tr>
<tr>
<td>$h^{3}\Sigma_{g}^{+}$</td>
<td>$c^{3}\Pi_{u}$</td>
<td>603.1909</td>
</tr>
<tr>
<td>$g^{3}\Sigma_{g}^{+}$</td>
<td>$c^{3}\Pi_{u}$</td>
<td>603.2171</td>
</tr>
<tr>
<td>$^Q(0-0)(3)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^Q(1-1)(2)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^Q(1-1)(3)$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.5: Lines overlapping studied transitions after Crosswhite [1972].

3.3 Results

3.3.1 Vibrational temperature and reaction rates

The vibrational excitation of the Pilot-PSI plasma beam was evaluated under representative operational conditions: $3 \times 10^{20} \text{ m}^{-3}$ and 3 eV (radial profiles of density and temperature are plotted in Figure 3.2). The spectral regions containing the Q-branch of the first three vibrational transitions used for the analysis are plotted in Figure 3.3. The width of the four separate spectral regions is determined by the spectral coverage of the spectrometer. The spectra were recorded in consecutive discharges. The rotational lines, which are annotated in the spectrum, show the 3:1 alternating intensity pattern caused by the hydrogen spin isomers. The combination of the Boltzmann distribution over the different states and the increasing degeneracy of higher lying states leads to the fact that e.g. the $Q(0-0)5$ peak is more intense than the $Q(0-0)1$ peak. There are some peaks which show an anomalous intensity, Crosswhite [1972] learns that these peaks are blended with other lines. Disturbed lines which are excluded in the data analysis are listed in Table 3.5.
Figure 3.2: Radial profiles of the electron temperature and density are measured by Thomson Scattering. Molecules diffusing into the plasma beam are heated to a vibrational temperature of 1 eV over a path length of less than 1 cm.

Figure 3.3: Fulcher emission measured in the centre of the profiles shown in Figure 3.2. The vibrational temperature determined at this radial position is approximately 1 eV.

The Q1 line intensities were determined by fitting the line profiles with the Gauss function. An offset was allowed to account for continuum emission, which is significant at the high electron densities studied here [Meulenbroeks et al., 1994]. The first rotational peak in each vibrational branch was thus used to represent the
population distribution in the upper Fulcher state. Vibrational temperatures in the
ground state were obtained with the sum of squares minimization outlined in the
previous section. This was repeated for each point along the vertical viewing cord
covering the entire plasma beam diameter, yielding the vibrational temperature
profile shown in Figure 3.2. The peak vibrational temperature of 1 eV demon-
strates that the molecules are significantly heated by the plasma over a path length
on the order of the plasma radius. At room temperature, hydrogen molecules
travel this distance in microseconds, indicating that the heating takes place on this
short timescale. Comparable vibrational temperatures of around 1 eV have been
observed earlier in tokamaks by Fantz et al. [1999] under comparable electron
densities and temperatures using the same procedure.

The 1 eV vibrational temperature is used as input to calculate the reaction rates
for negative-ion mediated MAR and ion-conversion MAR with the vibrationally
resolved rates from Reiter [2005]. A Boltzmann distribution is assumed also for
the higher vibrational levels, although these were not directly probed [Capitelli et al., 2010]. At an electron temperature of 3 eV and a vibrational temperature
of 1 eV, the rate for negative-ion-mediated MAR is $2 \times 10^{-16}$ m$^3$s$^{-1}$ and the rate
for ion-conversion MAR is $1 \times 10^{-15}$ m$^3$s$^{-1}$. Reaction rates for the two different
MAR mechanisms fall within one order of magnitude thus both processes are of
significance for plasma recombination under these conditions. Although these
rates are greatly enhanced (an order of magnitude for the ion-conversion chan-
nel) compared to rates calculated without vibrational excitation, these are still
not as high as assumed in previous experiments to explain the observed molecule
depletion in the plasma column of Pilot-PSI [Shumack et al., 2008]. This hints at
the importance of other mechanisms which also cause a hollow molecule density
profile.

3.3.2 Rotational and gas temperature determination

Rotational temperatures were measured close to the plasma source exit when the
plasma was freely expanding (i.e. zero magnetic field, all other results in this work
were obtained in a magnetic field of 0.4 T). These measurements are useful for
connecting the present experiments with existing literature, and serve as a bench-
mark for the experiments under magnetized conditions. The results of an axial
scan at two different source input power levels are shown in Figure 3.4. Rotational
temperatures of up to 0.25 eV were found, which are significantly higher than ro-
tational temperatures reported before in literature using a similar plasma source
[de Graaf, 1994]. The measured rotational temperatures are close to the electron
temperature measured by probes in expanding hydrogen plasmas [Veremiyenko,
2006]. The higher rotational temperatures are a consequence of operating at higher
power: an energy input of around 2 eV per molecule for the discharge with the highest rotational temperature was used. The rotational temperature cools in the expansion, as shown in Figure 3.4. The measurements in the free expansion are already an indication that we perform Fulcher spectroscopy under extreme conditions not previously explored.

![Figure 3.4: The rotational temperature in a freely expanding plasma is close to the electron temperature [Veremiyenko, 2006] and cools in the expansion. The source was operating at 3 slm hydrogen with two different power inputs.](image)

The magnetic field confines the plasma into a narrow beam, which increases the electron density by orders of magnitude. The radial H₂ emission profile also changes significantly when the magnetic field is switched on. The broad emission profile contracts to a more narrow, flat top profile. The measured emission is line integrated and hence a flat top profile corresponds to a hollow emission profile. As an illustration, Figure 3.5 shows a measured profile and the Abel-inverted profile. The inversion is performed by fitting Gaussians and using their invariance under Abel-inversion. The emission profile exhibits undoubtedly a minimum in the center. The exact value in the center, or the hollowness, is too sensitive to details in the inversion process to be quantified. A hollow emission profile means that the molecule density profile is even more hollow because the plasma density and temperature profiles are peaked. However, since the emission intensity depends non-linearly on the electron temperature and density, a quantitative statement on molecule depletion in the centre of the plasma beam is not possible to make on basis of this data.
Figure 3.5: The radial profile of the Q(0-0)1 intensity shown in Figure 3.6 for the magnetized plasma. Since the line-integrated measurement has a flat top profile, the Abel-inverted profile is hollow. This is a strong indication that the concentration of molecules is depleted towards the center of the plasma beam.

Figure 3.6: Two spectra measured at a source current of 250 A and a hydrogen flow rate of 3 slm. In the magnetized plasma the hydrogen molecular spectrum changes: different H2 electronic states give rise to transitions overlapping with Fulcher peaks, and the relative line intensities within the Q-branch change. The Q(0-0)3 peak is comparatively intense because of overlap with other H2 emission lines, see Table 3.5.
The rotational line intensity distributions in the Fulcher emission change drastically when the magnetic field is switched on, as is seen in Figure 3.6: rotational excitation is strongly increased in the magnetized plasma compared to the freely expanding plasma, most likely due to shorter mean free paths at the increased plasma densities. For example, the $Q_{(0-0)}^{(4)}$ peak more than doubles in intensity while the height of the $Q_{(0-0)}^{(1)}$ peak stays approximately constant. This behavior is reflected in the Boltzmann plots shown in Figure 3.7. Indeed, rotational temperatures of up to 0.85 eV are found.

![Figure 3.7: Boltzmann plots for various plasma conditions, both freely expanding and magnetized. Note the absence of the Q(0-0)3 peak for the magnetized cases because of coinciding lines.](image)

In order to compare these high rotational temperatures with the actual gas temperature, we have evaluated the Doppler broadening of the rotational lines. The first line of the Q(0-0) and Q(1-1) branch was used to determine the translational (i.e. gas) temperature. Figure 3.8 shows the spectra of Figure 3.6 in more detail together with Gaussian fits to illustrate the broadening of the emission lines. Details of the line profile also confirm that the lines listed in Table 3.5 are a superposition of multiple lines. Within present work, these lines are simply disregarded, since the determination of the intensity of the overlapped lines was found to lead to ambiguous results.

Zeeman splitting as main cause of the line broadening was excluded by measuring a spectrum at 1.6 T and verifying that the line shape is still Gaussian, as shown in Figure 3.9. Since the Zeeman splitting scales with the field and with the inverse of the squared quantum number, and we see a negligible contribution at
1.6 T for the lowest rotational lines, we estimate that the Zeeman contribution at lower fields is less than ten percent [Shikama et al., 2007]. It has therefore been neglected in the line shape analysis for the gas temperature determination.

Figure 3.8: This detail of Figure 3.6 shows the first four Q(0-0) peaks with Gaussian fits. The Q(0-0)3 peak is disturbed by nearby lying peaks and is not used in the rotational temperature determination. The broadening of the peaks for the magnetized case indicates a higher gas temperature.

Figure 3.10 shows a radial profile of the gas temperature and the rotational temperature. The rotational temperature is consistently lower than the translational temperature around the plasma center. We note that the rotational temperature data is only available near the plasma center as signal intensities become too low at the plasma edge for a stable Boltzmann fit.

Figure 3.11 shows the rotational temperature in the middle of the beam as function of the gas temperature for a variety of discharges in order to get insight into the correspondence of the gas temperature and the rotational temperature. It demonstrates that the mismatch between the translational temperature and rotational temperature is a systematic effect. It is also clear that the Q(0-0) branch yields a higher rotational temperature than the Q(1-1) branch. In literature a higher rotational temperature is usually obtained from the lower vibrational branches, e.g., in Fantz [2002]; Heger et al. [2001].

A possible explanation for the imbalance between the rotational and gas temperature is that there is not sufficient time for molecule-molecule collisions to equilibrate these different degrees of freedom at the time scale of heating [Astashkevich et al., 1996]. This heating takes evidently place in the plasma by collisions with the hot plasma ions. Inspection of energy transfer cross sections for
Figure 3.9: The first Q(0-0) peak with Gaussian fit at a field strength of 1.6 T. At 1.6 T the line shape stays Gaussian, this indicates that Zeeman splitting is not the main broadening mechanism. Comparing Q(0-0) lines with higher quantum numbers gives an upper bound to the amount of broadening expected at lower fields.

Figure 3.10: A gas and rotational temperature profile in the magnetized plasma beam. Central temperatures are extracted from the spectrum shown in Figure 3.6.

collisions between hot hydrogen ions and cooler molecules learns that the energy of the ions is preferentially transferred into the translational degrees of the hydrogen molecules [Phelps, 1990]. As molecule densities are much lower than ion densities, the subsequent equilibration cannot take place during the time that the
molecules reside in the plasma column. The consequence of this explanation is that the measured gas and rotational temperatures do not represent the residual gas properties throughout the vessel but only within the plasma column.

Additional support for this transient molecule heating by the plasma beam is the average rotation speed of the molecules. In Pilot-PSI, the ions rotate around the beam with velocities of a few km s\(^{-1}\) because of \(E\times B\) drift [Veremiyenko, 2006]. This shows in spectra by the Doppler shift of the emission lines, which results from the velocity component of the emitter parallel to the spectroscopy observation chord. The molecules pick up some of this rotation, which is calculated from the Doppler shift of the molecular emission lines with the relation \(v = \frac{\Delta \lambda}{\lambda_0} c\). Analysis of these Doppler shifts yields the velocity profiles shown in Figure 3.12. Note that the measured Doppler shifts are a few picometers, which is on the order of the linear dispersion of the spectrometer. The observed rotation speeds range from 500 to 1500 m s\(^{-1}\), about an order of magnitude lower than the ion rotation velocity. This is yet another indication that the present molecular spectroscopy experiments probe the molecules at the same time scale as these are heated.

The consequence of the molecule heating inside the plasma column is rarefaction of the molecule density. According to the momentum balance, \(nkT = \text{constant}\), so the density of the molecules should decrease proportionally with the gas temperature increase. To estimate the importance of this effect, we constructed a model in which heating of the molecular influx by a stationary plasma column

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Figure 3.11: Measured rotational temperatures as function of gas temperature for two vibrational branches. Each point represents one discharge. Lines are shown to guide the eye. Shots without magnetic field are denoted by a triangle.
is evaluated. This simple model includes the following three terms in the power balance: the Maxwellian influx of cold molecules, the Maxwellian outflux of heated molecules and a term which describes the heating by the plasma. Dissociation of the molecules in the plasma is neglected for simplicity. The Maxwellian power flux is given by the area of the boundary region multiplied by the particle flux and the energy per particle. The heating term is given by the interaction volume multiplied with the amount of collisions per volume unit and the energy transfer per collision. The cross sections were taken from the work by Phelps [1990]. The expressions for the terms in the power balance are thus:

\[
P_{\text{in}} = 2\pi RL \, \frac{1}{4} n_0 v_0^2 k_B T_0
\]
\[
P_{\text{out}} = 2\pi RL \, \frac{1}{4} n_b v_b^2 k_B T_b
\]
\[
P_{\text{heating}} = \pi R^2 L \, n_b n_e v_i^2 k_B T_i m_i / m_e
\]  

(3.10)

where subscript 0 denotes the background gas properties, and \( b \) are the plasma heated molecules. In order to estimate the rarefaction, the power balance \( P_{\text{out}} = P_{\text{in}} + P_{\text{heating}} \) is solved for the density ratio between the cold gas outside the beam and the heated molecules inside the plasma:

\[
\frac{n_0}{n_b} = \frac{R n_e v_i^2 3 T_i m_i}{m_0 v_0^2 T_0 \left( \sqrt{n/T_0} - 1 \right)}
\]

(3.11)
Taking a radius $R$ of 5 mm, an electron density $n_e$ of $3 \times 10^{20}$ m$^{-3}$, and assuming heating of the molecules to a temperature of 1 eV by ions of 3 eV, the density ratio equals approximately 90. Although the model is very simple, it illustrates that heating alone can lead to a significant dilution of the molecules when comparing the centre of the plasma beam to the colder periphery.

A hollow H$_2$ density profile under similar conditions was indirectly observed before with spectroscopy on atomic hydrogen [Shumack et al., 2008]. Strongly enhanced rates for ion-conversion MAR were needed to explain the observed profiles. With this contribution we show that although the rates are significantly enhanced with respect to the lowest level, rarefaction because of heating is the dominant mechanism behind the observed hollow H$_2$ density profiles.

### 3.4 Conclusions

H$_2$ vibrational temperatures were determined from the Q-branch spectrum of the Fulcher-$\alpha$ band. The vibrational population was used to compute effective reaction rates for negative-ion-mediated MAR and ion-conversion MAR, which are strongly enhanced with respect to the rates for the lowest vibrational level.

H$_2$ rotational temperatures were determined from the Q-branch spectrum of the Fulcher-$\alpha$ band. In addition, translational temperatures were measured using line shape analysis. The translational temperature measured was systematically higher than the rotational temperature. This was explained by collisions with ions, since the cross section for momentum exchange is larger than for rotational excitation. The velocity profiles of the molecules were found to follow the ion velocity profile, giving a strong indication of coupling between molecules and plasma species. The main implication of the efficient heating of the molecules is rarefaction. Since from the momentum balance, $n_kT$ is constant, the density of the molecules goes down proportionally with the temperature increase. This leads to a dilution of the molecules when comparing the centre of the plasma beam to the colder periphery. This effect, combined with the dissociation of the molecular influx, leads to a hollow density profile for the hydrogen molecules and thus causes a decreased effectiveness of molecular assisted processes.

These observations illustrate the general significance of rapid molecule heating in high density hydrogen plasma, e.g. in tokamak exhausts, for estimating molecular processes. Just taking residual gas properties on basis of e.g. wall temperatures and background pressure information is no longer justified. Furthermore, estimating gas temperatures on basis of rotational temperatures from Fulcher spectroscopy is compromised as both degrees of freedom may well be out of equilibrium.
Contributorship statement

N. den Harder performed and analyzed the experiments, drafted and revised the chapter, he is guarantor. D. C. Schram assisted with the data interpretation, and contributed the Doppler shift interpretation. W. J. Goedheer and M. C. M. van de Sanden provided input in interpretation. H. J. de Blank helped with the construction of the two temperature model. G. J. van Rooij directed the conception and design of the experiment, contributed to the acquisition, analysis, and interpretation of the data, and assisted in drafting and revising the chapter.
Chapter 4

Spectroscopic study of tungsten erosion and migration in high density low temperature plasmas

Based on: forthcoming publication in the Journal of Nuclear Materials

Abstract

Tungsten erosion and migration is studied on basis of WI 400.9 nm emission in the low temperature (0.5-2 eV), high density (1-6 × 10^{20} m^{-3}) plasma parameter regime that is relevant for ITER strike point areas. Inverse photon efficiencies are determined in various plasma conditions from absolute line emission using a controlled tungsten source. The results demonstrate that the inverse photon efficiency is close to literature values around 2 eV, but increases strongly as temperature decreases. This increase is attributed to escape of neutral tungsten from the plasma, an effect that is qualitatively reproduced in modeling of the tungsten migration pattern.
4.1 Introduction

Tungsten has a combination of material properties that make it suited as plasma facing material in a fusion reactor. Tungsten has the highest melting temperature of all metals, in addition to a high heat conductivity, which makes it durable under high heat flux conditions\cite{Haynes2012}. In addition, it retains little fuel, and has a low erosion yield by virtue of its large atomic weight\cite{Garcia-Rosales1995, Haasz1998, Kirschner2000}. The high atomic number of tungsten however also brings a disadvantage, since a high-Z impurity is an efficient radiator at high plasma temperatures. In view of radiative losses it is important to understand W as an impurity source and have the tools to monitor the W erosion and migration in situ.

Tungsten erosion is commonly quantified with the $S/\Sigma_B$ method. This method relates line-of-sight integrated photon fluxes to particle fluxes\cite{Behringer1989, Behringer1987}. It is assumed that all particles are lost via ionization. The relation between photon and particle fluxes then condenses into one number, the $S/\Sigma_B$ value, which captures the ionization/excitation balance and as such is strongly dependent on the electron temperature. At low electron temperatures, the ionization rate decreases drastically, which results in long ionization mean free paths. When the ionization mean free paths become on the order of the system size, loss processes other than ionization, such as particle escape, become significant, and the the main assumption behind the $S/\Sigma_B$ approach is no longer satisfied.

Knowing the limits of the $S/\Sigma_B$ method in low temperature plasmas is of interest, since in ITER the heat flux power deposition width will be on the order of centimeters\cite{ITER1999}. The reference separatrix electron density will be around $3 \times 10^{19} \text{ m}^{-3}$. Near the strikepoints, the electron temperature will be low, especially during fully detached operation. This can lead to ionization mean free paths for tungsten which are larger than the system size, invalidating spectroscopic particle flux determination with the $S/\Sigma_B$ approach. In this chapter we calculate and experimentally determine for tungsten below what electron temperature particle escape becomes significant for a given system size.

Tungsten erosion and migration is spectroscopically monitored in the low temperature ($0.5$-$2$ eV), high density ($1$-$6 \times 10^{20} \text{ m}^{-3}$) plasma of the linear machine Pilot-PSI. A probe is used to introduce a controlled quantity of tungsten into the plasma. This is realized by exposing the probe to a high flux of argon ions which are accelerated by a negative bias to sputter the tungsten. Sputter yields are computed by relating the mass loss to the ion fluence, which are compared with literature values to verify the probe behaviour. Using the mass loss measurements at 100 eV impact energy as calibration, the sputter yields are then measured in the energy range of 40-200 eV by spectroscopic techniques as an additional consistency
check. Both results confirm that the probe behaves as expected, and that it is suitable to introduce a predictable amount of tungsten into the plasma.

With the probe as a controlled tungsten source, we measure spatially resolved absolute photon fluxes for the tungsten 400.9 nm emission line for various plasma conditions in the electron temperature range of 0.5-2 eV. From these measurements, the $\frac{S}{X_B}$ value is determined as function of electron temperature. Loss fractions of neutral tungsten are calculated for the cylindrical geometry in the experiment as function of the electron temperature, which are compared with the loss fractions estimated from the $\frac{S}{X_B}$ values. Measured spatial emission profiles and ionization mean free paths are compared with modeled profiles and calculated mean free paths.

4.2 Method

4.2.1 Experimental layout

![Figure 4.1: Schematic of the Pilot-PSI setup. Plasma conditions were measured 2 cm in front of the target with a Thomson scattering setup. Optical emission spectroscopy was scanned axially to map out the complete emission plume.](image)

Experiments are performed in the linear plasma generator Pilot-PSI[van Rooij et al., 2007]. Plasmas are generated using a cascaded arc discharge[Kroesen et al., 1990]. In the cascaded arc source, discharge currents between 50 and 200 A are drawn at voltages around 100 V leading to input powers in the range 5-25 kW. Argon gas flows in the source vary between 0.8 and 2.5 standard liters per minute. The plasma expands from a high pressure (~10⁴ Pa) in the cathode chamber to
a low pressure (∼2 Pa) in the a 1 m long, 0.4 m diameter vacuum vessel. The expanding plasma, with flow velocities on the order of 1 km s\(^{-1}\), is confined using a magnetic field of 0.4 T. A schematic of the setup is shown in Figure 4.1.

The electron density and temperature 2 cm in front of the probe are monitored using a Thomson Scattering setup [van der Meiden et al., 2008]. A radial electron temperature and density profile is shown in Figure 4.2. Electron densities and temperatures are in the range that is relevant to the projected conditions in the ITER divertor [ITER, 1999].

Optical Emission Spectroscopy is performed using the High RESolution spectrometer, a single-pass spectrometer in Littrow configuration [Shumack et al., 2008]. An array of 40 individual 0.4 mm diameter quartz fibers relays the light to the HiRES spectrometer. In this way, a spectral range of approximately 4 nm is investigated over the whole diameter of the plasma column. The spectrometer is absolutely calibrated using an USS-1200C integrating sphere.

![Figure 4.2](image)

Figure 4.2: Radial electron temperature and density profiles measured by Thomson Scattering at 2 cm distance from the target. Over the inner 80% of the plasma, the temperature only drops by 10%.

The probe geometry is shown in Figure 4.3. The tungsten probe is clamped into a copper heat sink. The copper heat sink is shielded from the plasma by a boron nitride plate. The heat sink and BN-plate are clamped to a target holder with a molybdenum clamping ring. The back of the heat sink is electrically insulated from the target holder with an aluminium oxide plate (not shown). As a result, the probe is electrically insulated from the molybdenum clamping ring.
The incident particle flux is determined from the ion saturation current collected by the probe. The 100 Volt negative potential of the probe ensures that all electrons are repelled, this is verified by recording the I-V characteristic in a separate experiment. Because of the magnetic field geometry, the effective surface of the probe is the same as the plasma facing surface leading to a negligible influence of collection effects[Veremiyenko, 2006]. Secondary electron emission by ion impact is negligible under the conditions used in the experiment, since the secondary electron emission coefficient for tungsten is smaller than 0.1 for argon ion impact energies of up to 1 keV[Hagstrum, 1956]. The floating potential is approximately zero, so the potential of the probe is equal to the energy of the incoming particles.

Because it is expected that the ionization mean free paths will be large in the studied electron temperature range, redeposition of sputtered material will be low even for large probes. Thus the probe size is chosen as a trade-off between plasma uniformity over the probe surface and the dynamic range of the mass loss and spectroscopic measurement. A probe diameter of 1.6 mm is used.
4.2.2 $S/\chi_B$ method

Optical emission spectroscopy is used to quantify particle fluxes with the $S/\chi_B$ method. In this technique, the line integrated photon flux is related to a particle flux via the inverse photon efficiency. Assumed is that ionization is the only loss process for the particles. Balancing electron impact ionization and radiative decay then leads to an expression that relates the line of sight integrated emission to the influx of particles. This inverse photon efficiency is sometimes referred to as the $S/\chi_B$ value because it has the form of an (ionization rate)/(branching ratio x excitation rate) [Behringer et al., 1989; Behringer, 1987]. The $S/\chi_B$ value connects the incoming particle flux, $\Gamma_w$, to the line integrated emission of a spectral line, $I_W$ (photons sr$^{-1}$ m$^{-2}$ s$^{-1}$), as follows:

$$\Gamma_w = 4\pi S/\chi_B I_W$$

(4.1)

Experimentally the $S/\chi_B$ value can thus be obtained as [Nishijima et al., 2009, 2011]:

$$S/\chi_B = \frac{\Gamma^{Spt}_w}{4\pi I_W} = \frac{Y_W \Gamma_i}{4\pi I_W}$$

(4.2)

Where $\Gamma^{Spt}_w$ is the flux of sputtered particles, $Y_w$ is the sputter yield of the relevant projectile-target combination, and $\Gamma_i$ is the incident ion flux.

Calculating the WI 400.9 nm $S/\chi_B$ value from first-principles is not trivial. In high density plasmas, the coronal approximation, which assumes that excitation is collisional and decay radiative, breaks down, because other processes such as collisional redistribution and cascade contributions play a more significant role. In these cases a collisional-radiative model is needed to obtain the $S/\chi_B$ value. The case of tungsten is especially cumbersome because of the closely lying ground states. Although there is theoretical data on the inverse photon efficiencies for tungsten [Beigman et al., 2007], experimentally verified $S/\chi_B$ values are sometimes preferred. In this case, a fit is used that combines measurement data from several tokamaks [Laengner et al., 2013]:

$$\frac{S}{\chi_B}(T_e) = 53.7 \left(1 - 1.04 \exp \left(-\frac{T_e}{22.1}\right)\right)$$

(4.3)

However, the underlying results are scarce in the low temperature range, as illustrated by the unphysical negative values of the formula below 0.9 eV. Since all the quantities in Equation 4.2 are experimentally accessible in Pilot-PSI, the literature values of inverse photon efficiency can be extended towards lower electron temperatures in the current experiment. However, these measurements need to be supported by calculations to validate that the conditions to apply the $S/\chi_B$ approach are met.
4.2.3 W migration and particle escape

The $\mathcal{S}/XB$ approach assumes that ionization is the only loss process the sputtered neutrals. A crude way to check this assumption is to compare the ionization mean free path of the sputtered tungsten to the system size. The ionization mean free path is defined as:

$$\lambda_{\text{mfp}} = \frac{v_W}{n_e < v_{iz}>} \tag{4.4}$$

where $v_W$ is the speed of the sputtered W atoms, $n_e$ is the electron density, and $< v_{iz}>$ is the ionization rate of W neutrals at the relevant electron temperature.

In order to estimate the speed of the sputtered W particles, it is necessary to know the energy of the sputtered particles. The energy spectrum of the sputtered particles is well described by a Thompson distribution [Stangeby, 2000; Thompson, 1968]:

$$\frac{dY}{dE} = \frac{2E_{\text{bind}}(E_{\text{bind}} + E_{\text{max}})^2}{E_{\text{max}}^2 (E + E_{\text{bind}})^3} \tag{4.5}$$

The maximum energy $E_{\text{max}}$ which the sputtered particle can have is given by:

$$E_{\text{max}} = E_0\gamma(1 - \gamma) - E_{\text{bind}} \tag{4.6}$$

where $E_0$ is the energy of the incoming projectile, and $\gamma$ is $\frac{4m_1m_2}{(m_1 + m_2)^2}$, the maximum energy fraction that can be transferred [Stangeby, 2000]. $E_{\text{bind}}$ is the surface binding energy. The most probable energy for the Thompson distribution, which does not depend on the energy and mass of the incoming ions, is half of the surface binding energy. For $E_{\text{bind}}$ the enthalpy of vaporization of 8.36 eV per atom is used, which leads to a most probable thermal ejection speed of 1.5 km s$^{-1}$ [Haynes, 2012].

The W ionization rate as function of electron temperature was taken from the ATOM code [Vainshtein et al., 2011]. In this rate, stepwise ionization is not taken into account. Since this effect may be significant at densities of the order of $10^{20}$ m$^{-3}$ used in these experiments, ionization rates are likely underestimated. The ATOM ionization rate is expressed by the following formula:

$$< v_{iz} > = 10^{-8}A \frac{\sqrt{\beta(\beta + 1 + D)}}{(\beta + \gamma)(\beta + 1)}e^{-\beta_{iz}} \tag{4.7}$$

where $\beta = Ry/T_e$ and $\beta_{iz} = E_{iz}/T_e$. Ry is the Rydberg energy. An ionization energy $E_{iz}$ of 7.86 eV is used. $T_e$ is the electron temperature. The used adjusting parameters are: $A = 60.4$ m$^3$ s$^{-1}$, $\gamma = 0.048$ and $D = -0.3$ [Vainshtein et al., 2011].
### Table 4.4: Calculated ionization mean free paths at an electron density of $10^{20}$ m$^{-3}$

<table>
<thead>
<tr>
<th>Electron temperature (eV)</th>
<th>Ionization rate (m$^3$ s$^{-1}$)</th>
<th>Ionization mean free path (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-21}$</td>
<td>$10^{-6}$</td>
<td>$10^3$</td>
</tr>
<tr>
<td>$10^{-18}$</td>
<td>$10^{-3}$</td>
<td>$10^0$</td>
</tr>
<tr>
<td>$10^{-15}$</td>
<td>$10^0$</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>$10^{-12}$</td>
<td>$10^3$</td>
<td>$10^{-6}$</td>
</tr>
</tbody>
</table>

Figure 4.4: Calculated ionization mean free paths at an electron density of $10^{20}$ m$^{-3}$. Large mean free paths indicate that in low temperature conditions, the particles may escape the 1 cm radius plasma beam without ionizing, violating the assumptions underlying the $S/\Sigma_B$ approach.

With the described values, the mean free path varies over 6 orders of magnitude in the regime of plasma parameters studied. The critical parameter is the electron temperature, as shown in Figure 4.4. At a density of $10^{20}$ m$^{-3}$ and a temperature of 2 eV, the mean free path is 6 mm, which is smaller than the width of the density profile. At plasma temperatures below 2 eV the ionization mean free path is higher, indicating that particle loss will start playing a role in the experiment, provided that the rates are accurate in the high density conditions.

The fraction of the sputtered neutrals which leaves the system without being ionized is estimated using the system size $L$, $n_e$, and $T_e$ as input. We first define that particles can escape the system when the ionization mean free path is larger than the system size. Equation 4.4 is then be solved for $v$ at $\lambda_{nfpL}$ to yield an escape velocity, which is be converted into an escape energy $E_{esc}^W$.

$$E_{esc}^W = \frac{1}{2}m_Wv^2 < v \sigma_{iz}^2 >^2 L^2 \quad (4.8)$$

Since particles below this energy stay in the system, and the energy distribution of the sputtered particles is given by Equation 4.5, the escape fraction is calculated as:

$$f_{esc}^W = 1.0 - \int_{0}^{E_{esc}^W} \frac{2E_{\text{bind}}(E_{\text{bind}} + E_{\text{max}})^2}{E_{\text{max}}^2} \frac{E}{(E + E_{\text{bind}})^3} dE \quad (4.9)$$
When the angular distribution of the sputtered species is known, this approach is suitable to calculate the expected pattern of W migration into the plasma for a point source. When the energy of the impacting argon ions is high, the sputtered species angular distribution is well described by a $\cos(\alpha)$ distribution [Emmoth, 1981]. This leads to the following distribution of the sputtered species in the plasma:

$$n(r, \alpha) = \left(1 - f_{\text{esc}}^{\text{er}}(n_e, T_e, L_{\text{tr}}/\sin(\alpha))\right) \cos(\alpha) \exp(-l/\lambda_{\text{mfp}})$$

(4.10)

The first term describes the escape of particles from the plasma column. The effective path length is smaller for particles sputtered at a larger angle to the surface normal. The second term describes the angular distribution of the source. Artificially, a cutoff term is introduced to ensure that the concentration at outside of the plasma column is zero. The last term describes the exponential decay due to ionization of the sputtered neutrals that stay in the plasma. The $\lambda_{\text{mfp}}$ is calculated using Equation 4.4, with as $\bar{v}_W$ the average velocity of the particles that remain in the plasma. Escape fractions for various plasma radii at an electron density of $10^{20}$ m$^{-3}$ are shown in Figure 4.5 as function of electron temperature. A calculated migration pattern is shown in Figure 4.6 for a plasma radius of 10 mm, an electron density of $10^{20}$ m$^{-3}$ and an electron temperature of 2.0 eV. Although the calculated plume is much smaller than the plasma column, already 12 percent of the sputtered particles escape without being ionized in the plasma. This is an important result because it shows that already at the upper end of the temperature range that is studied in the experiment, particle losses play a significant role.
4.3 Results

4.3.1 W source characterization and sputter yield

To confirm that the probe is usable as a controlled W source, the sputter yield is measured by relating the mass loss to the ion fluence. The W rod is weighed using a precision microbalance. The probe is then exposed to plasma and biased to obtain the desired impacting ion energy. The current is monitored to obtain the particle flux. After plasma exposure the W rod is weighed again. The sputter yield is then calculated from the total ion fluence and the mass loss.

The total ion fluence per experiment is determined by integrating the current traces for the collective exposures. In some shots arcing occurs, but the current spikes are filtered out. The arcing does not influence the mass loss measurement since arcing occurs between the back of the heat sink and the target holder. The current limit of the power supply results in a temporary drop in the voltage of the probe. Although as a consequence of the voltage drop there is no sputtering during arcs, the short time duration limits the impact on the measurement. A current trace of a discharge in which there is considerable arcing is shown in Figure 4.7.

The energy of the incoming ions is adjusted via the biasing voltage of the probe. Since the plasma potential is approximately zero, the incoming particle energy can be directly related to the potential. Analysis of the I-V characteristics confirm at a probe voltage of -40 V and below there is ion saturation.
In the determination of the sputter yield by a mass loss measurement it is crucial that redeposition is low. Redeposition of tungsten on the probe would lead to an underestimation of the sputter yield in the mass loss measurement. After the experiment the redeposition pattern is studied. The sputtered tungsten redeposits over a large area, even the inner part of the molybdenum clamping ring is covered with a layer of tungsten. Since the tungsten redeposits over an area that is more than two orders of magnitude larger than the surface of the probe, we conclude that redeposition has a negligible influence on the mass loss measurement.

If the probe behaves as expected, the sputter yields determined by mass loss should agree with literature values. Although there is some scatter in the sputter yields because of experimental uncertainties, the mass loss measurements agree well with conclusions from the TRIM.SP code [Eckstein, 2007]. This is an experimental validation that the probe is suitable to introduce a controlled amount of tungsten in the plasma.

In addition to the weight loss measurements, the sputter yield is also determined spectroscopically. In these cases the intensity of the neutral tungsten emission line at 400.9 nm is monitored with the HiRES spectrometer. In the individual spectra, the W emission line is fit with a Gaussian function. The width of the Gaussian is determined by instrument broadening. Argon emission lines in the spectral region near the tungsten 400.9 nm line necessitate the use of a high-resolution spectrometer. The intensity of the spectral line 3.5 mm in front of the probe is related to the tungsten influx using the mass loss measurement at -100 V bias as
Figure 4.8: Measured sputtering yields for low energy argon ions on a tungsten surface. The dotted line is the literature value obtained with TRIM.SP simulations [Eckstein, 2007].

calibration point. Spectroscopic sputter yield measurements agree well with the predictions of the TRIM.SP code, although there is some discrepancy at low ion energies as shown in Figure 4.8. This could be a result of a changed W migration pattern at lower sputtering energies. Lower sputtering energies lead to a lower maximum energy of the sputtered particles which could give a more localized emission pattern. This more compact emission pattern could lead to an underestimation of the amount of tungsten emission, because the assumption that the local emission intensity at 40 eV is the same fraction of the total emission intensity as at 100 eV breaks down. The sputter yield deviations at lower temperature could also be the result of a small negative plasma potential, which results in a slightly lower impact energy than would be expected on basis of the probe potential.

The overall agreement between the observed sputter yield and the probe potential is a good indication that the probe behaves as expected, and that it can be used to generate a controlled tungsten influx.

4.3.2 W migration and $S/\chi_B$ values

$S/\chi_B$ values are experimentally determined using Equation 4.2. The spatial intensity distribution of the tungsten 400.9 nm line is measured to determine the local photon flux. Since the emission plume is larger than the observation volume of the spectrometer, several spectra are taken at various axial positions in the plasma. The emission plume is then integrated to obtain the total photon flux.
During the experiments, the electron density and temperature profiles directly in front of the probe are measured with Thomson scattering. Electron densities used during the experiments are in the range $1-6 \times 10^{20} \text{ m}^{-3}$. Electron temperatures vary between 0.5 and 2 eV. The FWHM of the electron density profiles is typically 12 mm.

The radial profile of the tungsten emission is approximately Gaussian as shown in Figure 4.9. The axial profiles of the tungsten emission are adequately described by exponential decay, as shown in Figure 4.10. A full profile is shown in Figure 4.11. When the electron temperature is lower than 1 eV however, the decay is not mono-exponential anymore, as illustrated in Figure 4.12. This is an indication that ionization is not the only loss process but other processes play a role as well. As seen in the calculation, sputtered atoms exit the plasma column without ionizing, leading to dilution of the plume of sputtered particles. Deposition of the sputtered tungsten over a large area is further confirmation that not all the tungsten is ionized in the plasma beam.

![Figure 4.9](image)

**Figure 4.9:** A radial profile of the WI 400.9 nm emission intensity at an axial distance of approximately 4 mm from the surface of the probe. The profile has a Gaussian-like shape, as indicated by the blue line.

Calculated ionization mean free paths are higher than measured values. This can be caused by the used ionization rate, or the effective speed of tungsten neutrals in the plasma. Firstly, at the electron densities in Pilot-PSI, stepwise ionization can play an important role. Since these effects are not included in the rate, the ionization rate will be underestimated, leading to an overestimation in the calculated mean free path. Secondly, the plasma flow towards the tungsten
probe drags along tungsten neutrals leading to a shorter mean free path in the experiment. Balancing the Bohm flux with the collected flux leads to a plasma flow velocity of approximately 0.5 km s\(^{-1}\) in the studied discharges. Since the velocity of the sputtered tungsten atoms is approximately 1.5 km s\(^{-1}\), this could lead to a considerable modification of the emission profile.

![Graph showing exponential decay](image)

Figure 4.10: An axial profile of the WI 400.9 nm emission intensity. The intensity decay shows exponential behaviour, with a decay length of 1.6 mm. The electron temperature was 1.5 eV at an electron density of \(6 \times 10^{20}\) m\(^{-3}\).

Because the \(S/\lambda_B\) value depends on the total number of photons, modification of the plume shape by plasma drag does not change the numerical value. The influence of different processes on the ionization rate is something that should be captured in the \(S/\lambda_B\) value. However, the decay profiles at low temperature show multi-exponential behaviour. This is an indication that multiple loss processes play a role, while the \(S/\lambda_B\) assumes ionization as only loss process.

When additional loss channels are present, a straightforward interpretation of the measurement data in terms of an \(S/\lambda_B\) value is no longer valid. The additional loss process adds an extra term to the \(S/\lambda_B\) value that depends on the experimental geometry, resulting in an \(S+L/\lambda_B\) value, where \(L\) indicates particle loss. Since \(L\) will be a positive number, the inverse photon efficiency will thus be overestimated. At a measured \(S+L/\lambda_B\) of 100, if the true \(S/\lambda_B\) is 20, the loss fraction is four times as large as the ionization, and eighty times as large as the excitation. With the calculated loss fractions shown in Figure 4.5 in combination with the multimachine fit for the \(S/\lambda_B\) values, \(S+L/\lambda_B\) values can be calculated. Note that there are some assumptions in this approach, such as the cosine distribution of the sputtered material, which
Figure 4.11: A full spatial profile of the WI 400.9 nm emission intensity. The intensity decay shows exponential behaviour, with a decay length of 1.6 mm. The electron temperature was 1.5 eV at an electron density of $6 \times 10^{20} \text{ m}^{-3}$.

Figure 4.12: An axial profile of the WI 400.9 nm emission line at low electron temperature where the intensity decay is not purely exponential anymore. The electron temperature was 0.7 eV at an electron density of $1.6 \times 10^{20} \text{ m}^{-3}$.

...can instead be butterfly-shaped at low sputtering energies. Also the ionization rate may not be completely accurate in the high density, low temperature conditions. However, the calculated and measured $S + L / X_B$ values qualitatively agree, as shown in Figure 4.13. Since the multimachine fit given by Equation 4.3 becomes negative...
below 0.9 eV, a fit was made to the $S_{XB}$ value in the range 0 to 2.5 eV, where the fit function was forced to go through the origin. When the particle losses become very close to 1, the correction becomes unreliable, which occurs at an electron temperature of approximately 1 eV. The onset of particle losses at around 2 eV however is well predicted by the model. As shown both in experiment and calculation, particle losses start playing a major role at electron temperatures below approximately 2 eV for system sizes on the order of 1 cm.

Figure 4.13: Measured $S_{XB}$ values of the 400.9 nm WI line for various plasma parameters. A multimachine fit of high-$T_e$ data points is shown in blue. On basis of the calculated escape fraction at an electron density of $1 \times 10^{20}$ m$^{-3}$ and system size of 5 mm, a correction factor is shown in red. At electron temperatures below 1 eV, the escape fraction is very close to one, which leads to erroneous results for the calculated correction factor.

<table>
<thead>
<tr>
<th>$T_e$ (eV)</th>
<th>$n_e$ ($10^{20}$ m$^{-3}$)</th>
<th>$\lambda_{mfp}$ (mm)</th>
<th>$\lambda_{em}$ (mm)</th>
<th>$S_{XB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>1.6</td>
<td>18560</td>
<td>4.5</td>
<td>1120</td>
</tr>
<tr>
<td>0.8</td>
<td>2</td>
<td>3219</td>
<td>11</td>
<td>183</td>
</tr>
<tr>
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</tr>
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<td>2.5</td>
<td>15</td>
<td>1.3</td>
<td>95</td>
</tr>
<tr>
<td>1.5</td>
<td>6.0</td>
<td>6.2</td>
<td>1.6</td>
<td>85</td>
</tr>
<tr>
<td>1.7</td>
<td>5.0</td>
<td>5.0</td>
<td>2.2</td>
<td>14</td>
</tr>
</tbody>
</table>

Table 4.1: Experimental plasma conditions, calculated ionization mean free paths $\lambda_{mfp}$, and measured mean free paths $\lambda_{em}$ and $S_{XB}$ values of the 400.9 nm WI line.
4.4 Conclusions

A probe mount was constructed to introduce a controlled amount of tungsten into the low temperature high density plasma of the linear machine Pilot-PSI. The 1.6 mm diameter tungsten probe was exposed to an argon plasma and negatively biased to obtain different impact energies. The sputter yield of argon on tungsten at 80 and 100 eV was determined by mass loss measurements in combination with the ion fluence as measured by the I-V characteristics. Sputter yields in the 40-200 eV range were determined with spectroscopy on the W 400.9 nm emission line. Both methods compare well with literature sputter yields. This consistency check shows that the probe can be used to introduce a controlled amount of tungsten into the plasma.

Spatial profiles of the 400.9 nm neutral tungsten emission line were studied in various plasma conditions. The measured ionization mean free paths were shorter than the calculated values, this was attributed to the underestimation of the tungsten ionization rate in high density plasmas, and to ion drag on the sputtered neutrals. At low electron temperatures the ionization mean free paths were on the order of the plasma size, which resulted in additional loss processes that are not captured in the $\gamma_{XB}$ value. At the upper end of the electron temperature range which was studied, measured $\gamma_{XB}$ values were close to literature values. As shown both in experiment and calculation, particle losses start playing a major role at electron temperatures below approximately 2 eV for system sizes on the order of 1 cm.

Contributorship statement

N. den Harder is main author, performed the experiments and data analysis, he is guarantor. M. F. Graswinckel, A. R. Lof, and M. J. van de Pol contributed to the experimental design, and measurements. G. J. Van Rooij directed the conception and design of the experiment, data acquisition, analysis, and interpretation, and assisted in drafting and revising the chapter.
Chapter 5

ELM-resolved divertor erosion in the JET ITER-Like Wall

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Abstract

Tungsten gross erosion in H-mode plasmas is quantified in the outer divertor of the JET ITER-Like Wall environment with optical emission spectroscopy on the 400.9 nm atomic neutral tungsten line. A novel cross-calibration procedure is developed to link slow, high spectral resolution spectroscopy and fast photomultiplier tube measurements in order to obtain ELM-resolved photon fluxes. In the inter-ELM phase, W erosion is mainly due to impurity sputtering by beryllium, with sputter yields of approximately $10^{-4}$ with respect to the total flux. Sputtering during ELMs, which accounts for more than 50% of the total gross erosion, varies independently from the inter-ELM erosion. The amount of W erosion during ELMs is only partly explained by beryllium sputtering, indicating that during ELMs sputtering by deuterons plays a role. The total W outer divertor source is found to linearly increase with the power crossing the separatrix, whilst divertor fueling in excess of $10^{22}$ D$_2$ s$^{-1}$ can break this trend.

The influence of the W source rate on the tungsten content of the core plasma is investigated using Soft X-Ray emission to determine the tungsten content. At low source rates the content is determined by the source, but at higher source rates, other mechanisms determine the total tungsten content. Indications of impurity flushing by ELMs is seen at ELM frequencies above approximately 40 Hz. The inner/outer divertor asymmetry of the W source during ELMs is investigated, and the outer divertor W source is larger by a factor of $1.8 \pm 0.7$. 

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5.1 Introduction

ITER will feature a full tungsten (W) divertor and a beryllium wall cladding [Griffith, 2013; Pitts et al., 2009]. Beryllium is used because it is a low-Z oxygen getter. Tungsten is selected since it has a high melting temperature, a relatively high heat conductivity, and a low erosion yield [García-Rosales et al., 1995; Haasz et al., 1998; Haynes, 2012; Kirschner et al., 2000]. The combination of a low-Z material for the main wall, and a refractory metal for the divertor, is selected to give a large operational flexibility as well as the capability to handle the large heat and particle fluxes to the divertor. In order to provide an integrated demonstration of the impact of this material combination, the JET tokamak is currently equipped with the ITER-Like Wall (ILW), which consists of solid beryllium limiters and cladding, as well as a combination of bulk W and W-coated carbon fiber composite divertor components [Matthews et al., 2007, 2011; Neu et al., 2013].

Although material properties of W make it an ideal candidate for use in fusion reactors, there is a strict limit on the tolerable amount of W in the plasma core. This is because tungsten can radiate until deep in the plasma core, which is a power loss mechanism. An acceptable fusion performance is only attainable when the W core concentration is a few times $10^{-5}$ at most [Pütterich et al., 2010]. This low concentration requires on the one hand a minimization of the net tungsten sources via detached divertor operation, and on the other hand the suppression of tungsten transport to the plasma core.

Given the requirement on the tungsten core concentration, it is important to get an overview of the critical parameters for the erosion of tungsten components, notably the divertor, both during steady state and transient events such as Edge Localized Modes. Sputtering during ELMs might show a different dependence on the plasma parameters, since the intra-ELM source may be linked to pedestal parameters rather than edge conditions. Also simulations indicate that a large fraction of the intra-ELM W-source might promptly redeposit, compared to the inter-ELM contribution [Tskhakaya and Groth, 2015]. In addition, intra-ELM sources might be different in the efficiency with which the sputtered particles reach the core plasma, i.e. have a different divertor screening.

In this paper tungsten gross erosion in the outer divertor of the JET ITER-Like Wall environment is quantified by optical emission spectroscopy under a wide range of H-mode plasmas. The emphasis is on the time dependence of the W source, so that the transient Edge Localized Modes are resolved, and the inter- and intra-ELM contributions can be distinguished. ELM-resolved W source information is obtained via a novel cross-calibration procedure between the 40 ms time resolution divertor spectroscopy and the 0.1 ms time resolution Photo Multiplier Tube (PMT) measurements through optical filters [Meigs et al., 2010; Morgan et al.,
Both spectroscopic methods look at neutral tungsten emission at 400.9 nm. Although the PMT measurements provide a high time-resolution absolute photon flux, the signal is polluted by non-W contributions passing through the narrowband filter. The degree of overestimation depends on the divertor conditions. With this calibration, these contributions are accounted for, and the W-source can be quantified with 0.1 ms time resolution, which is approximately 20 data points per ELM. The inter-ELM W-source is examined in terms of local plasma parameters. Impurities such as Be, C, and O which can cause W sputtering are identified, and the measured sputter yield is compared with literature values as an additional consistency check. Sputtering species during ELMs are considered. The tungsten source per ELM is linked to pedestal parameters. The total intra-ELM source is discussed in relation to global physics parameters. The tungsten core content is related to the tungsten source. Core contents and sources are used to calculate tungsten confinement times and study flushing of impurities by ELMs.

5.2 Method

Particle fluxes are derived from line-of-sight integrated absolute photon fluxes using the number of ionizations per emitted photon. This inverse photon efficiency is sometimes written as $\frac{S}{X_B}$ because it has the form of an (ionization rate)/(branching ratio $\times$ excitation rate) [Behringer et al., 1989; Behringer, 1987]. Although high-Z elements are cumbersome to model, theoretical $\frac{S}{X_B}$ data is available for W [Beigman et al., 2007]. In this paper, experimentally derived $\frac{S}{X_B}$ values for the WI transition at 400.9 nm were applied, which are widely used and agree well with theoretical data [Laengner et al., 2013]. The numerical value is based on results from several tokamaks:

$$\frac{S}{X_B}(T_e) = 53.7 \{1 - 1.04 \exp\left(\frac{-T_e}{22.1}\right)\}$$  (5.1)

$\frac{S}{X_B}$ values for the beryllium emission lines, which are only weakly dependent on the electron density, were obtained from ADAS for the experimental electron density range of of $10^{18}$ to $10^{19}$ m$^{-3}$ [Summers, 2004; Summers et al., 2006]. All inverse photon efficiencies used in this contribution are shown in Figure 5.1 for an electron density of $10^{19}$ m$^{-3}$.

The $T_e$ dependence of the $\frac{S}{X_B}$ values necessitates the incorporation of an electron temperature measurement in the impurity flux determination. The divertor electron temperature in JET is measured by an array of Langmuir probes. The current-voltage characteristics of these flush mounted probes are fitted with a four parameter model, which gives an electron temperature as well as a total particle flux [Gunn et al., 1995]. In the determination of the inter-ELM $\frac{S}{X_B}$ values, the electron temperatures as measured by the probe system were used. During the
Inverse photon efficiency

WI 401nm
BeII 436nm
BeII 527nm

Electron temperature (eV)

Figure 5.1: The inverse photon efficiencies for the relevant spectral lines. The BeII $\gamma_{XB}$ values were taken from Summers [2004], and the WI value was taken from Laengner et al. [2013].

ELMs, a fixed temperature of 100 eV was assumed, giving $\gamma_{XB}$ values of 53 and 58 for the WI 401 nm and the BeII 527 nm emission lines. At temperatures above a few times ten electronvolts, the $\gamma_{XB}$ values are only weakly dependent on the electron temperature, so the particle flux determination is not very sensitive to this assumption. If the electron temperature during ELMs would be 50 eV instead of the assumed 100 eV, the tungsten flux would be a 10 percent overestimation, and the beryllium flux would be overestimated by 15 percent.

Different systems are available to quantify divertor photon fluxes at JET. The KT3 system images optical emission from the divertor region via an optical mirror link system. The rectangular lines-of-sight have a toroidal extent of 2 mm and a poloidal size of 25 mm. Several spectrometers make up the KT3 system. The spectrometer equipped to study the WI emission is designated KT3B [Meigs et al., 2010], a 0.75 meter Czerny-Turner spectrometer, which uses a 1200 lines/mm grating for the 400 nm wavelength range. Exposure times of 40 ms are used.

The KS3 system uses fibre-optics to image the divertor [Morgan et al., 1985]. The KS3 lines of sight are circular with a diameter of 33 mm, and cover the complete inner and outer divertor. Plasma emission is observed by Photo Multiplier Tubes through a filterscope to isolate the relevant spectral line. The KS3 system simultaneously monitors BeII emission at 436.1 nm, DI emission at 656.3 nm, and WI emission at 400.9 nm with 0.1 ms time resolution. The average FWHM of the filters used to observe the WI 400.9 nm line is 0.89 ± 0.03 nm.
The tungsten content of the plasma was calculated from the Soft X-Ray emission. The SXR emission is deconvolved, and the tungsten content is then calculated using electron temperature and density profiles in combination with the tungsten cooling factor known from literature [Pütterich et al., 2010].

![Figure 5.2: A Cross section of JET in which the lines of sight monitored by the various spectroscopy systems are indicated][van Rooij et al., 2013].

5.3 Results

5.3.1 Cross-calibration and ELM-resolved photon fluxes

In order to study W erosion ELM-resolved, fast WI photon fluxes needed, such as provided by the PMT system. However, the spectral resolution is poor since the FWHM of the used filters are on the order of 1 nm. This leads to an overestimation of the tungsten signal due to contribution from the continuum background, as illustrated by Figure 5.3 in which a KT3B spectrum is overlaid with the KS3 filter shape.

To estimate the influence of background on the signal, the WI line intensity determined with the KT3B spectrometer is compared to the PMT signal over the flat top of several JET discharges. In this comparison the PMT data is time-integrated over the exposure windows of the spectrometer. A weighted sum of different KT3B
poloidal channels is calculated to match the PMT spatial resolution. Figure 5.4 shows the result of such comparison for the strikepoint location. In all the considered discharges, regardless of ELM frequency, there is a linear scaling between the WI line intensity and the PMT signal, but the PMT signal is consistently higher due to the background contribution. The majority of the offset observed in the PMTs is due to Bremsstrahlung. There is also additional background, possibly plasma light that is not completely attenuated by the filter. Notwithstanding the physics behind the fit parameters, a fit with a good coefficient of determination is a reliable way of reconstructing the WI line intensity from the PMT signal in combination with KT3B data. This cross-calibration yields the WI line intensity with a time resolution of 0.1 ms, sufficient to resolve individual ELMs with approximately 20 data points for each ELM.

Several discharges were investigated with the cross-calibration procedure. Only discharges with the strikepoint on the semi-horizontal outer divertor target plate were studied. Discharges for which the \( r^2 \) of the fit was below 0.6 were excluded from further analysis. Since for a good fit quality a sufficiently large \( W \) photon flux was needed, these criteria resulted in a set of H-mode discharges with a significant amount of tungsten erosion. The set of discharges shows widely varying operating parameters, with the toroidal field strength ranging from 1.5 to 2.7 T, plasma currents from 1.5 to 2.5 MA, and heating powers between 5 and 23 MW.
To distinguish between the inter- and intra-ELM contribution, the ELMs need to be assigned. This was done based on the amplitude and derivative of the PMT signal. The sum of the inter- and intra-ELM contribution was compared with the integral of the PMT signal as additional check for the ELM assignment.

![Graph](image)

Figure 5.4: Comparison between the WI line intensity and the observed PMT signal. A linear relation is found, although an appreciable part of the PMT signal is offset from background emission.

Emission of beryllium in the outer divertor is measured using a different PMT array with filters centered on the 527 nm emission line of singly ionized beryllium. A cross-calibration is not done for these signals, mainly since the beryllium emission is less localized, which makes it less straightforward to compare the PMT signals with spectroscopy data. If the background behaviour in the beryllium emission is similar to the tungsten background behaviour, the intra-ELM flux is accurate, while the inter-ELM flux will be an overestimation.

Since this procedure is only applicable on the outer divertor, where there is overlap between the spectrometer and filtered PMT observation chords, all sources given in this contribution are outer divertor sources, unless explicitly mentioned otherwise. Outer divertor particle fluxes are spatially integrated over the strike-point and in the toroidal direction without taking into account shadowing effects or other toroidal asymmetries. In effect this assumes a global plasma-wetted fraction of 1.0. If there is shadowing, the plasma exposed part of the surface will catch a higher flux so that to first order the average surface flux is similar to the perfectly symmetric case.
### 5.3.2 Inter-ELM W erosion and local plasma parameters

The main erosion mechanism for W in tokamaks is physical sputtering. Figure 5.5 shows the sputter yield for various elements, calculated with the revised Bohdansky formula using ERO-TEXTOR data [García-Rosales et al., 1995; Kirschner et al., 2000]. In JET a typical inter-ELM electron temperature is around 25 eV, and a typical particle flux is $10^{23} \text{ m}^{-2} \text{s}^{-1}$. Since the threshold energy for tungsten sputtering by deuterium is above 200 eV, only heavy impurities can sputter during the inter-ELM phase. In practice however, the incoming ions are not monoenergetic, and will carry $2kT_i$ to the wall, in addition to the $3Z_i kT_e$ due to acceleration through the Debye sheath [Stangeby, 2000]. In addition, not all particles will arrive at normal incidence. Averaging over the angular and energy distribution was performed as in Abramov et al. [1989]; Kirschner et al. [2000], which yields the sputter yield as function of electron temperature. The sputter yield for e.g. beryllium ions on tungsten then no longer shows clear threshold behaviour, although the threshold impact energy is 51 eV. Note that the angular distribution could be different than assumed, and this will have a significant effect on the sputter yield, as found by experiment and modeling [Borodin et al., 2014; Schmid et al., 2010].

![Figure 5.5: Various sputter yields at normal incidence as function of the impact energy](image)

Figure 5.5: Various sputter yields at normal incidence as function of the impact energy [García-Rosales et al., 1995; Kirschner et al., 2000]. Because of the threshold behaviour, inter-ELM sputtering by fuel species will be negligible.

The sputter yield also changes when there is surface modification or when surface layers are present [Bizyukov and Krieger, 2007]. Simulations of impurity migration show that layers of material are present at several locations in the JET divertor [Schmid et al., 2015]. These effects however are neglected in this paper.
because the surface is most likely pristine tungsten, since the outer divertor is a net erosion zone [Brezinsek and contributors, 2015]. This is a consequence of the flux balance of impinging beryllium ions and re-eroded beryllium. A large fraction of the impinging beryllium ions reflect as neutral species, the rest is locally deposited [SDTrimSP, 2015]. The deposited beryllium is immediately re-eroded by deuterons from the plasma. Due to the low impurity concentration in the plasma, the balance between deposition and re-erosion is shifted towards re-erosion of beryllium from the surface. With the $\gamma_{XB}$ technique, the incoming and re-eroded flux cannot be distinguished.

Previously, in the JET ILW environment, in L-mode discharges beryllium was found as the dominant sputtering impurity [van Rooij et al., 2013]. Since there are no Be components in the divertor in the JET-ILW, all beryllium ions flowing into the divertor are from the main chamber [Brezinsek and contributors, 2015]. Figure 5.6 shows the inter-ELM sputter yield in terms of the beryllium influx as function of electron temperature. Drawn in the Figure are the sputter yields for various charge states of beryllium. There is reasonable agreement between measured and literature sputter yields, which is an indication that in the inter-ELM phase, beryllium is the main sputtering species. The largest uncertainty in this measurement is the beryllium photon flux, which could be overestimated due to background emission. Correcting for this spurious signal would lower the beryllium flux, resulting in an increased sputter yield.

![Figure 5.6: Inter-ELM tungsten sputter yield by beryllium as function of the divertor electron temperature. Although there is some scatter in the measured sputter yields, the overall behaviour is indicative of W physical sputtering by beryllium.](image)
Relating the inter-ELM W sources to the total particle flux, i.e. including species which do not sputter, is commonly done to estimate the performance of operating scenarios in terms of wall erosion. For the studied discharges, effective sputter yields on the order of $10^{-4}$ are found. This is a result of the low impurity concentration, the beryllium fraction in the incoming particle flux is on the order of $10^{-3}$. Figure 5.7 shows the effective sputter yield as function of divertor electron temperature. Clearly seen is that the sputter yield is lower at lower electron temperatures. This is mainly a result of the lower beryllium fraction in the total flux at these low electron temperatures. The reason behind the lower beryllium fraction at decreasing electron temperatures could not be identified because of the varying conditions in which the data were taken. It maybe a combined effect of a smaller main chamber Be source and suppressed migration.

![Figure 5.7: Inter-ELM tungsten effective sputter yield as function of the divertor electron temperature as measured by probes. Because of the low beryllium concentration, the sputter yield in terms of total flux is low.](image)

5.3.3 Inter- and intra-ELM contributions

With the ELM-resolved signal it is possible to disentangle the inter- and intra-ELM contribution to the total W erosion, as shown in Figure 5.8. Since the studied discharges were not detached, and all have an electron temperature above 10 eV, the inter-ELM sources are relatively constant. The intra-ELM sources however vary over roughly one order of magnitude. For the H-mode discharges considered, the intra-ELM W source accounts for a large fraction of the total W source [Giroud et al., 2013]. The intra-ELM source seems independent from the inter-ELM source.
Note that the use of a constant $S/X_B$ value could lead to an underestimation of the W-source, when the electron temperature excursion during an ELM is sufficient to lead to a higher $S/X_B$ value for the intra-ELM photon flux. The ELM-resolved beryllium influxes show different behaviour, the inter-ELM flux dominates by approximately a factor of two, and the intra-ELM flux varies over about a factor of two.

![Figure 5.8](image)

Figure 5.8: Inter- and intra-ELM W outer divertor sources shown as function of the total W source. The inter-ELM sources are relatively constant, while the intra-ELM sources show a large variation. Already at a modest total source, the intra-ELM fraction is dominant.

The increase in WI emission during ELMs, a direct measure for the increase in erosion, had a time duration of $0.8 \pm 0.1$ ms, estimated from the temporal FWHM. Since this small time duration accounts for at least half of the tungsten source, the source strength during an ELM is strongly enhanced. While the inter-ELM tungsten influx is $9 \times 10^{18}$ s$^{-1}$, during an ELM the W source is $5 \times 10^{20}$ s$^{-1}$ on average, a 60 fold increase. Metastable long-lived electronically excited states of tungsten can affect fast emission measurements. Since the time scale of emission dynamics during an ELM agrees with ELM durations measured with IR cameras, these effects are not important for the present analysis [Sieglin et al. 2013].

The high source strength during ELMs is mainly caused by the increased temperature of the particles arriving at the divertor plates, which increases the sputter yield. The beryllium flux also increases during ELMs, but only a factor of 2, although this could be slightly higher because of the overestimated inter-ELM flux. Since the Be on W sputter yield is known from literature as function of temperature, in principle an effective ELM ion temperature could be deduced from the
observed sputter yield, assuming that beryllium is the only sputterer. However, because the sputter yield is almost constant at temperatures above a few hundred electronvolts, in practice this procedure is not feasible. Although the literature sputter yield is only weakly temperature dependent at ELM-relevant ion temperatures, the observed sputter yield shows variations, and at higher pedestal electron temperatures increases above the maximum sputter yield for beryllium on tungsten. The observed flux ratio between beryllium and tungsten is shown in Figure 5.9 together with the literature sputter yield for fully ionized beryllium ions on tungsten. Since at higher pedestal electron temperatures the observed sputter yields exceeds the literature yield, sputtering by beryllium alone cannot explain the observed tungsten source. This indicates that at increased pedestal temperatures, sputtering by fuel species becomes important. This behaviour is already expected from literature sputter yields shown in Figure 5.5, combined with an educated guess on the divertor plasma parameters during an ELM. A detailed analysis on sputtering during Type I ELMs can be found in Guillemaut et al. [2015].

![Figure 5.9: The intra-ELM sputter yield of Be on W as function of the pedestal electron temperature. The red line indicates the literature sputter yield of fully ionized beryllium. Sputter yields above the red line indicate a contribution of fuel species to the sputtering.](image)

5.3.4 Intra-ELM W erosion and pedestal parameters

Since during ELMs particles are transported from the hot pedestal region to the target plates, it is instructive to analyze the intra-ELM W source as function of pedestal parameters. Figure 5.10 shows the average tungsten source for individual
ELMs as function of the confined energy loss for various fueling rates. Different majority gas fueling rates in units of electrons per second are indicated with different colours. Pulses with at least half a MW of ICRH during the flat top phase are indicated with a star. This figure shows that low fueling rates lead to larger ELMs, which gives a high W source per ELM [Guillemaut et al., 2015]. However, this is offset by the low ELM frequency, so that the total W influx can still be low. High fueling rates lead to a lower W influx per ELM, although the energy loss per ELM is not necessarily smaller.

![Figure 5.10: The average W outer divertor source per ELM shown as function of the drop of diamagnetic energy during an ELM for several fueling rates. RF-heated shots are indicated with a star. In pulses with a similar fueling, the W ELM source shows a linear dependence on the energy loss.](image)

5.3.5 Total W sources and global physics parameters

Although the limited number of studied pulses prohibits a rigorous scaling analysis, some global physics parameters clearly correlate with the observed W-source. Note that although these global quantities can obscure the underlying physics, these correlations are still useful from an operational point of view. Of the studied parameters, the power crossing the separatrix shows the most convincing correlation. Figure 5.11 shows, for several JET pulses, the total W-source as function of the power crossing the separatrix which is calculated as: \( P_{\text{SEP}} = P_{\text{NBI}} + P_{\text{ICRH}} + P_{\text{Ohmic}} + \frac{dW_{\text{DIA}}}{dt} - P_{\text{Rad,bulk}} \). For a given fueling rate, the W source linearly increases with power crossing the separatrix. Fueling above \( 10^{22} \text{ s}^{-1} \) does decrease the W source, but low fueling does not lead to a highly increased W source. Pulses with ICRH
show in general a higher W outer divertor source, but the overall effect is small. ICRH is expected to increase the W influx because of RF induced sheath effects [Lerche et al., 2015; Perkins, 1989]. The correlation between the W sources and $P_{\text{SEP}}$ is mainly the result of the increased ELM frequency at higher $P_{\text{SEP}}$. For type I ELMs, the energy loss per ELM does not vary significantly with heating power, but the ELM frequency increases as $P_{\text{SEP}}$ increases, due to a faster build up of the edge pressure gradient [Zohm, 1996].

![Figure 5.11: Total W outer divertor sources shown as function of the power crossing the separatrix for several fueling rates. RF-heated shots are indicated with a star. In pulses with a similar fueling, W sources shows a linear dependence on $P_{\text{SEP}}$, through the increased ELM frequency at higher $P_{\text{SEP}}$.](image)

5.3.6 Gross W erosion and plasma W content

Relating the ELM-resolved tungsten sources with the tungsten content of the plasma could give insight in the combined effects of divertor screening and pedestal transport. Divertor screening is expected to be high, PIC calculations indicate that the promptly redeposited fraction of the eroded tungsten will exceed 97 percent even in the most favourable conditions, and during ELMs the redeposited fraction will be higher still [Tskhakaya and Groth, 2015]. Although it will be difficult to single out the effect of redeposition on the global tungsten content of the plasma, it is instructive to evaluate the tungsten content in terms of the tungsten source.

As shown in Figure 5.12, the total W content shows a weak dependence on the source below source rates of $0.4 \times 10^{20} \text{ s}^{-1}$. The large spread in the data is an indication that although the source rate plays a role, transport mechanisms are
more important for the tungsten content of the main plasma, which is consistent with earlier observations [Casson et al., 2015]. The ratio between the total W content and the total source can be used to estimate an effective confinement time or penetration factor of the tungsten ions [Dux et al., 2011; Lipschultz et al., 2001]. Since here this factor is calculated in terms of only the outer divertor source, the tungsten confinement time will be lower in practice. Tungsten confinement times in the range from 1 to 10 ms were found, which is comparable to results obtained in JET by Fedorczak et al. [2015].

The measured tungsten confinement times show a dependence on the ELM frequency, decreasing when the ELM frequency is higher. However, since the source increases with the ELM frequency, and the total tungsten content does not show large variations, numerically, the observed variation in confinement time is mostly caused by variations in the W source. Both quantities are plotted as function of the ELM frequency in Figure 5.13. An increased ELM frequency leads to an increased source, except at the highest ELM frequency where the ELM signature is fuzzy. The tungsten content of the plasma increases with the source at low ELM frequencies, but around 40 Hz this trend reverses and the content decreases, in contrast with the source which still increases. This is a sign of flushing of W out of the main plasma by ELMs [Fedorczak et al., 2015; Pütterich et al., 2012]. This is in line with observations that low ELM frequencies often leads to a high core radiation levels [Matthews et al., 2013].

Figure 5.12: The total W content of the plasma as function of the total W outer divertor source. RF-heated shots are indicated with a star. There is some correspondence between the tungsten source rate and the core concentration, but the large scatter indicates that other processes are at play as well.
5.3.7 Inner and outer divertor contributions

The inner and outer divertor PMT signals were compared in order to estimate the relative contribution of the inner and outer divertor W source. To compare the signals on an equal footing, no cross-calibration was performed, hence the inter-ELM sources could not be studied. The outer divertor W source is larger during ELMs by a factor of $1.8 \pm 0.7$. Given the scatter in the data, no systematic dependencies could be found. An asymmetry in ELM energy loads by a factor of about 2 was found previously in JET. Whether the inner or outer divertor is favoured is dependent on the direction of the ion $\mathbf{B} \times \nabla \mathbf{B}$ drift [Eich et al., 2007].

5.4 Conclusions

W sources are studied in the JET ITER-Like Wall environment with optical emission spectroscopy for the C33 campaign. A cross-calibration method is developed to link fast PMT measurements with 40 ms time resolution spectra to obtain 0.1 ms resolution WI photon fluxes. Inter-ELM W erosion is dominated by the impurity beryllium. Of the total flux, the beryllium fraction is on the order of $10^{-3}$, which results in effective sputter yields on the order of $10^{-4}$. These observations are similar to earlier findings in L-mode discharges [van Rooij et al., 2013].
Intra-ELM erosion dominates the total W source. The intra-ELM source varies over one order of magnitude while the inter-ELM source remains approximately the same, making ELM control an important priority when considering the total W source. Sputtering during ELMs is largely explained by beryllium sputtering, although at higher pedestal electron temperatures sputtering by deuterium becomes significant.

Larger ELMs in terms of pedestal energy loss are found to give a larger tungsten source per ELM. The total tungsten source correlates well with $P_{\text{SEP}}$, mainly due to the increased ELM frequency at higher $P_{\text{SEP}}$.

Although some correspondence is seen between the tungsten source and the total tungsten content of the plasma, the large spread in the data is an indication that although the source rate plays a small role, transport mechanisms are more important for the core content. Tungsten confinement times calculated on basis of the total tungsten content and the outer divertor source vary between 1 and 10 ms. In discharges with type I ELMs, the source increases with increasing ELM frequency. This contrasts with the plasma tungsten content, which increases with the source until at an ELM frequency of approximately 40 Hz the trend reverses and the content decreases while the source is still increasing. This is interpreted as a sign of ELM flushing.

Inner and outer divertor sources are compared on the basis of the total photon flux. Intra-ELM W fluxes are asymmetric, where the outer divertor flux is larger by a factor of $1.8 \pm 0.7$.

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Contributorship statement

N. den Harder analysed and interpreted the data, and drafted and revised the chapter, he is guarantor. S. Brezinsek provided essential input in the interpretation. T. Püttterich analyzed the SXR measurements. N. Fedorczak, G. F. Matthews, and M. C. M. van de Sanden provided input in the interpretation. A. Meigs and M. F. Stamp operated the KT3 and PMT spectroscopy diagnostics and associated software. G. J. van Rooij directed the analysis and interpretation of the data, and assisted in drafting and revising the chapter. The JET Contributors provided the experiment.
Chapter 6

Summary and conclusions

In the context of this thesis, high density low temperature plasmas were studied for a wide variety of applications. In all cases, spectroscopic methods were employed, and interpretation of experimental data was supported by modeling. The common theme was the determination of a characteristic temperature, by spectroscopic means, to assess the importance of various plasma-physical or plasma-chemical processes. Particularly emphasized was the non-thermal character of the systems under study: a different temperature was assigned to the electrons, ions, neutral gas, and the vibrational and rotational degrees of freedom.

Applications of the studied plasmas relate to the research theme “energy”. As outlined in the introduction, drastic changes in the energy supply chain are needed in the 21st century to ameliorate the greenhouse effect. The plasmas in this thesis are studied in view of CO₂ free energy production. In Chapter 2, an energy storage method was researched, more specifically, the reduction of CO₂ into CO in a microwave plasma reactor. This is a first step in the production of fuels using renewable energy and carbon dioxide, and thus a way to store electrical energy in chemical bonds. Energy efficiency is crucial for the viability of this technique, therefore special attention was paid to the contribution of non-thermal processes. Fully non-thermal CO₂ dissociation can be performed with energy efficiencies of 80 % by avoiding loss processes such as gas heating. Chapters 3 through 5 dealt with the behaviour of tungsten under the extreme power and particle loads encountered in a fusion reactor. This topic was studied in linear machines as well as a tokamak environment. In Chapter 3, the role of molecules in a linear plasma generator was investigated. Molecules lead to plasma loss via Molecular Assisted Recombination, and quantification of these processes is the first step towards optimization of the linear device. Chapter 4 dealt with a spectroscopic study of tungsten erosion and migration in a linear machine. In this chapter the \( \gamma_{_{XB}} \) approach, which is commonly used to relate photon fluxes to particle fluxes, was benchmarked at low electron temperature conditions. In this case, in spite of the high electron
density, the ionization mean free path exceeds the system size below an electron temperature of 2 eV, and the standard $S/X_B$ approach breaks down. Loss fractions were calculated which can be used to analyze the gross erosion of W in these conditions. In Chapter 5, tungsten erosion in the JET ITER-Like Wall environment was researched, with focus on the importance of ELMs. Since each individual chapter is relatively self-contained, the results are summarized in separate subsections.

CO production in a MW plasma: A thermal equilibrium study

CO$_2$ dissociation, a first step in the production of solar fuels, is potentially energy efficient when performed in a microwave plasma because of the non-equilibrium nature of the plasma. This reaction was studied computationally and experimentally. The main aim was to develop a good understanding of CO$_2$ dissociation in thermal conditions by modeling, and then apply this knowledge to determine the importance of non-equilibrium processes in the experiment.

An equilibrium model was used to determine inherent energy efficiency limits of thermal dissociation. A maximum efficiency of approximately 50 percent is attainable in the case of thermal dissociation in the temperature range 3000 - 4000 K, if the quenching is ideal, i.e. the produced CO does not react back. A 0-D chemical kinetics model was constructed to investigate the influence of different quenching scenarios on the energy efficiency. Fast quenching rates on the order of 10$^9$ Kelvins per second are needed to preserve the formed CO.

A 2.45 GHz, 0.8 kW, microwave reactor was characterized with laser scattering, FTIR, and optical emission. Two regimes of operation were identified, a diffuse plasma at low pressures, and a constricted discharge at increased pressure. Their occurrence was attributed to microwave propagation behaviour, which changes with the electron-heavy particle collision frequency $v_{e-h}$. At low pressures, the collision frequency $v_{e-h}$ is not sufficient to enable electron densities above a critical electron density of $7.5 \times 10^{16}$ m$^{-3}$. In this regime the plasma volume adjusts to satisfy the power balance. At increased pressures, above CO$_2$ densities of approximately $2.3 \times 10^{23}$ m$^{-3}$, the collision frequency is sufficiently high to enable the formation of plasma with electron densities in excess of the critical electron density. As the electron density increases the skin depth becomes smaller, limiting the radial plasma size.

In the diffuse regime, the neutral density profile is radially homogeneous in the central 10 mm of the reactor at 800 W power input. The radial plasma size, estimated from optical emission measurements, increased with input power, a feature that sets the diffuse regime apart from the contracted regime. Central gas temperatures in the range 1500 - 3500 K were inferred from Rayleigh scattering measurements. A two-temperature thermal model was constructed to relate
the conversion degree $\alpha$, the specific energy input $E_{in}$, a hot zone fraction $\beta$, and a $T_{low}$ and $T_{high}$. Measured conversion degrees and specific energy inputs were combined with temperatures inferred from Rayleigh scattering measurements to obtain solutions for $T_{low}$ and $\beta$. The hot zone fractions $\beta$ were found to scale with the specific energy input. Record efficiencies approaching 50% were measured, in which case a $T_{low}$ of 470 K is needed to satisfy the specific energy input. The agreement between model and measurement shows that non-thermal processes are not needed to explain the reactor parameters in the diffuse discharge. However, the two-temperature model does assume ideal quenching, which is unrealistic given the cooling rates which are estimated from afterglow measurements. This might be an indication that the cold gas at the periphery plays a role in the quenching of the mixture, or that non-equilibrium processes are at play.

In the constricted regime, a small plasma filament formed in the middle of the reactor. The radial size of the filament did not increase with increasing input power. The electron density was estimated in the range $10^{18} - 10^{19}$ m$^{-3}$ based on the size of the plasma in combination with the calculated skin depth. Temperatures in the central filament were in the range 3000 - 5000 K. Also in this regime, energy efficiencies approach 50%.

These results show that CO$_2$ reduction can be performed in a microwave reactor with high energy efficiencies. However, the observed efficiencies do not exceed thermal efficiencies, given that the produced CO does not react back, through a combination of fast cooling and mixing with carbon dioxide from the periphery. If the plasma is completely thermal, there is little room from improving the energy efficiency. As literature indicates, energy efficiencies that clearly exceed the thermal limit are attainable, so reactor modifications should be made to reach a non-equilibrium plasma. Promising improvements are: pulsing the plasma to decrease the overall gas temperature which influences vibrational-translational quenching rates, using a supersonic expansion to decrease the amount of back-reactions in the afterglow, or seeding a low ionization potential impurity to influence the electron energy distribution function.

**Residual gas entering high density hydrogen plasma**

Linear plasma generators are an effective and versatile method to study Plasma Surface Interaction. However, creating divertor-grade conditions in a linear machine is challenging. Pilot-PSI and Magnum-PSI use cascaded arc sources, which have a limited ionization efficiency and thus co-exhaust reactive molecules, which lead to plasma loss via Molecular Assisted Recombination reactions. The rate of these reactions depends strongly on the vibrational temperature of the reacting molecules. The interaction of background molecular hydrogen with magnetized
(0.4 T) high density (1-5 × 10²⁰ m⁻³) low temperature (~ 3 eV) hydrogen plasma was investigated via Fulcher band emission in the linear plasma generator Pilot-PSI.

H₂ vibrational temperatures were determined from the Q-branch spectrum of the Fulcher-α band. In the plasma centre, H₂ vibrational temperatures reached 1 eV. At this temperature, ion-conversion MAR dominates plasma recombination at a rate of 1 × 10⁻¹⁵ m³ s⁻¹.

H₂ rotational temperatures were determined from the Q(0-0) and Q(1-1) spectrum. In addition, translational temperatures were obtained from line shape analysis. Q(ν = 1)-branch rotational temperatures were systematically ~ 0.1 eV lower than the Q(ν = 0)-branch temperatures, which were in the range of 0.4-0.8 eV. The Q(ν = 0)-branch temperature was typically 60 % of the translational temperature. This is an indication that the molecules are heated by the ions on the plasma residence timescale, since ion-molecule collisions preferentially excite the translational degrees of freedom in the molecule. Additional confirmation of the coupling between background molecules and the ions came from Doppler-shift analysis, which revealed co-rotation of the molecules with the plasma at an order of magnitude lower angular velocity. A model was constructed on basis of the power balance to estimate the molecular density in the beam compared to the periphery. Using the translational temperature measurements as input, a factor of 90 rarefaction is reached due to the heating.

These observations show that the temperatures of background H₂ molecules diffusing into a high density hydrogen plasma are mainly determined by molecular properties such as cross sections for momentum transfer, rotational excitation, and vibrational excitation. Since this situation is qualitatively similar to background molecules diffusing into the central plasma filament of the solar fuels reactor, calculating the energy loss functions for this system could give insight in the expected degree of non-equilibrium between the different degrees of freedom of the background molecules.

Spectroscopic study of tungsten erosion and migration

Quantification of particle fluxes from plasma facing components is generally done using the $\tilde{\gamma}_{XB}$ approach, which relates photon fluxes to particle fluxes. This method assumes a local balance between ionization and excitation, set by the electron temperature. The validity of this approach for tungsten in the ITER-relevant plasma parameter regime, i.e. low temperature (0.5-2 eV) and high density (1-6 × 10²⁰ m⁻³), was studied in a linear plasma generator. To this end, a controlled amount of W is introduced into the plasma by sputtering a probe with argon ions, and the erosion and migration behaviour is studied on basis of WI 400.9 nm emission.
As a consistency check, the sputter yield of argon on tungsten at 80 and 100 eV was determined by mass loss measurements in combination with the ion fluence as measured by the probe I-V characteristics. Sputter yields in the 40-200 eV range were determined with spectroscopy. Both methods compared well with literature sputter yields. This shows that the probe is a suitable method to introduce a controlled amount of tungsten into the plasma.

Spatial profiles of the 400.9 nm neutral tungsten emission line were measured in various plasma conditions. At the lower end of the electron temperature range, the ionization mean free paths were on the order of the plasma size, which results in additional loss processes. As a consequence, the observed photon fluxes were too low, leading to artificially high $\tilde{\gamma}_{XB}$ values since these additional losses are not consistent with the assumption that ionization is the only loss process of the charge state under observation. With the literature ionization rate, and assumptions on the angular and energy distribution of the sputtered species, the loss fraction was estimated. At an electron density of $10^{20}$ m$^{-3}$, the calculated loss fraction is above 10 percent when the electron temperature is below 2 eV in the experimental geometry. This indicates that only at the upper end of the electron temperature range, particle escape becomes less important. This was reflected in the measured $\tilde{\gamma}_{XB}$ values, which were close to literature values only at the upper end of the studied electron temperature range. These experiments show that below an electron temperature of 2 eV a cautious interpretation of tungsten emission is warranted if one of the system dimensions is below 1 cm, even at high densities.

ELM-resolved divertor erosion in the JET ITER-Like Wall

Divertor erosion in the JET ITER-Like Wall environment was studied with the goal of getting a consistent picture of inter-ELM and intra-ELM erosion in terms of edge plasma parameters, and to assess the influence of gross erosion on the tungsten content of the plasma. Particle fluxes to and from the outer divertor were quantified with emission spectroscopy using the $\tilde{\gamma}_{XB}$ approach. A cross-calibration method was developed to link fast PMT measurements with 40 ms time resolution spectra to obtain 0.1 ms resolution WI photon fluxes. This method was applied to H-mode discharges with a wide range of operating parameters, the toroidal field strength ranging from 1.5 to 2.7 T, plasma currents from 1.5 to 2.5 MA, heating powers between 5 and 23 MW, and different gas puffing scenarios.

Inter-ELM W erosion was dominated by the impurity beryllium. Of the total flux, the beryllium fraction was on the order of $10^{-3}$, which resulted in effective sputter yields on the order of $10^{-4}$. These observations are similar to earlier findings in L-mode discharges [van Rooij et al., 2013].
Intra-ELM erosion accounted for the majority of the W source. Intra-ELM erosion varied over one order of magnitude while the inter-ELM source remained approximately the same, making ELM control an important priority when aiming to minimize the total W source. Sputtering during ELMs was largely explained by beryllium sputtering, although at higher pedestal electron temperatures sputtering by fuel species becomes significant. Larger ELMs in terms of pedestal energy loss were found to give a larger tungsten source per ELM. The total tungsten source correlated well with the power crossing the separatrix $P_{\text{SEP}}$, mainly due to the increased ELM frequency at higher $P_{\text{SEP}}$.

Erosion measurements obtained from photon fluxes only give information on gross erosion. Since a large part of the eroded W will promptly redeposit, and W transport to the core is determined by the plasma parameters, it is not a priori clear that a higher gross erosion will result in a larger core tungsten content. To investigate the correspondence between the tungsten source and the total tungsten content of the plasma, the measured W sources were compared with core contents determined via Soft X-Ray emission. Although some correspondence was seen between the tungsten source and the total tungsten content of the plasma, the large spread in the data is an indication that although the source rate plays a small role, transport mechanisms are more important for the core content, which is consistent with earlier observations. Tungsten confinement times calculated on basis of the total tungsten content and the outer divertor source varied between 1 and 10 ms. In discharges with type I ELMs, the source increased with increasing ELM frequency. This contrasted with the plasma tungsten content, which increased with the source until at an ELM frequency of approximately 40 Hz the trend reverses and the content decreases while the source is still increasing. This was interpreted as a sign of increased outward transport of tungsten impurities at increased ELM frequency.

These results show that inter-ELM sputtering can be minimized by reducing the beryllium flux to the divertor or, more generally, the impurity content. Minimizing the intra-ELM sputtering, the largest part of the source, is more difficult, which is illustrated by the correlation between power crossing the separatrix and the total W source observed in JET. However, if the ELM frequency is above approximately 40 Hz, the core tungsten content stays relatively constant while the source still increases. This shows that transport mechanisms play an important role in determining the tungsten content of the plasma, and that tungsten screening can be maximized by increasing the ELM frequency.
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About the author

I, Niek den Harder, was born on the third of April 1989 in Ouderkerk aan de Amstel, Nederland. I attended elementary school at “De Akker” in Amstelveen, and high school at the “Van Lodenstein College” in Amersfoort, which I finished in 2006 at the gymnasium level. I studied Chemistry at the University of Utrecht, and obtained my bachelors degree cum laude in 2009 with a project titled “Analytical gradients with ZORA Spin-Orbit in GAMESS-UK” in the Theoretical Chemistry group of Joop van Lenthe.

Afterwards, I enrolled for the “Nanomaterials: chemistry and physics” master. The plasma physics course inspired me to do my masters internship in the FOM institute for plasma physics Rijnhuizen in Nieuwegein. I obtained my degree cum laude in 2011 on the topic “Optical Emission Spectroscopy on the linear plasma generator Pilot-PSI” under the supervision of Gerard van Rooij in the Low Temperature Plasma Physics and Heating group LTPP-H.

Subsequently, I started my PhD under the supervision of Gerard van Rooij. In the context of the original research plan, centred around the transport of tungsten particulates in fusion plasmas, I performed dust injection experiments on the linear machine Pilot-PSI and provided assistance with dust dropping during several campaigns on the TEXTOR tokamak at the Forschungszentrum Jülich in Germany. The scope of the project broadened to spectroscopy of tungsten in low temperature plasmas, which was studied in linear machines, i.e. Pilot-PSI and Magnum-PSI, and in the JET tokamak at the Culham Centre for Fusion Energy in the UK where I was seconded for three months. During the transition to the FOM institute DIFFER, i.e the Dutch Institute For Fundamental Energy Research, the solar fuels research department was founded, where I was involved from the start. In this department, I applied diagnostics to low temperature microwave plasmas.

After my PhD, I will perform computational work on neutral beam injection systems in the ITER Technology and Diagnostics group of the Max-Planck-Institut für Plasmaphysik in Garching, Germany.