Plasma chemistry and kinetics in a magnetized hydrogen plasma expansion: a study of negative ions

Citation for published version (APA):

DOI:
10.6100/IR735309

Document status and date:
Published: 01/01/2012

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Plasma chemistry and kinetics in a magnetized hydrogen plasma expansion

A study of negative ions

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op dinsdag 28 augustus 2012 om 16.00 uur

door

Willem-Jan Egbert Nicolaas van Harskamp

geboren te Oss
This work is supported by the European Communities under the contract of Association between EURATOM and FOM and carried out within the framework of the European Fusion Programme.

Printed and bound by: Printservice Technische Universiteit Eindhoven.
Cover design: Paul Verspaget, Verspaget & Bruinink, Nuenen.

A catalogue record is available from the Eindhoven University of Technology Library

ISBN: 978-90-386-3201-8, NUR 926

Trefwoorden: plasmadiagnostiek / laserspectroscopie / moleculaire rotatie - vibratie / waterstof kinetiek / negatieve waterstof ionen / plasma expansie / modelling / wederzijdse neutralisatie proces
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Abstract    You are about to start reading my PhD thesis entitled *Plasma chemistry and kinetics in a magnetized hydrogen plasma expansion*. It deals with a fundamental study into the important reaction processes in a hydrogen plasma expansion that is weakly magnetized. In this chapter I will give a historical background and a status overview of hydrogen plasma expansions.

*Willem-Jan van Harskamp*
1.1 Energy demand

One of the greatest challenges in realizing a sustainable future is sustainable energy generation since it is ultimately the basis of the global economy. Today, we are mostly dependent on nonrenewable fossil fuels [1] that have been and will continue to be a major cause of pollution and climate change. Because of these problems, and the problems associated with the decline of harvesting cheap oil and gas all around the world, finding sustainable alternatives is becoming increasingly urgent. Therefore, it is important to innovate and invest in new energy sources like solar, water and wind power to create a diverse energy mix.

Another promising energy source that can be added to the energy mix is nuclear fusion, which is based on a nuclear reaction in which light nuclei are fused under release of vast amounts of energy. The fusion fuel (primarily deuterium and lithium) exists abundantly in the Earth’s ocean to supply the world’s energy needs for millions of years and is therefore an infinitely renewable energy resource. Furthermore, no greenhouse gases are emitted in the fusion process and it does not depend on the weather conditions. However, one of the main problems with fusion is that the primary plasma fuel, a mixture of the hydrogen isotopes deuterium and tritium, must be burned at a temperature of 150 million degrees. This temperature can be sustained in Tokamak devices, by confining a hot plasma in an external magnetic field.

In 2005 an agreement was reached on the construction of the next generation Tokamak device, called ITER (International Thermonuclear Experimental Reactor) [2]. This nuclear fusion device is being built in Cadarache, France where 33 nations are collaborating to realize the first plasma in 2020. Its target is to achieve a power multiplication factor of 10 (i.e. the power generated from the fusion reactions exceeds the power needed to sustain the high plasma temperature by a factor of ten) during pulses of 500 seconds or longer [3]. The maximum plasma temperature attainable by ohmic heating in a tokamak is insufficient to start the fusion reactions and therefore additional heating tools, e.g. high-frequency electromagnetic waves and Neutral Beam Injection (NBI), are needed [4]. After the ignition conditions are reached in the fusion plasma the
alpha particles have sufficient energy to keep the plasma hot but the additional heating tools are required for controlling the plasma.

Figure 1.1: Scheme of the neutral beam injection principle: ions are denoted in red and neutral atoms in green. [5]

1.2 Neutral beam injection

Generating energetic neutral beam atoms by means of NBI is not at all straightforward. The only way to form the high energetic neutral beam atoms is to produce large amounts of ions first, then to accelerate the ions in a strong high-voltage electric field and finally neutralize the accelerated beam, see figure 1.1. The accelerated ions get neutralized by charge-exchange interactions with a gas cloud, but some leave the cloud in a charged state. These residual ions must be deflected by a dedicated electromagnet to a cooled ion dump. Finally, a powerful vacuum pumping is used to remove the slow atoms from the neutralizing gas cloud. The fast neutral atoms that are created by the neutral beam system are injected into the fusion plasma and penetrate deep before they deposit their energy.

In the Joint European Torus (JET) positive ions are created and subsequently accelerated and neutralized to get 80 keV neutral deuterium atoms, but in ITER energies up to 1 MeV/nucleon are mandatory to penetrate the center of the fusion plasma. At these high energies it is not possible to use positive ions since
the neutralization cross-section at impact velocities higher than 100 keV is small. Fortunately, negative ions (either $\text{H}^-$ or $\text{D}^-$) have a neutralization efficiency of 60\% at 1 MeV/nucleon [6, 7], but they have additional problems compared to positive ions because they suffer from co-extracted electrons that have to be removed from the beam. The co-extracted electrons result in the stripping of negative ions by collisions. Furthermore, negative ions are destroyed by fast mutual neutralization processes with positive ions [8–10]. Nevertheless, much progress has been achieved the last couple of years as demonstrated by two pioneering NBI systems at LHD (180 keV of $\text{H}^0$ and 360 keV of $\text{D}^0$) [11] and JT-60SA (500 keV of $\text{D}^0$) [12].

1.3 Production of negative hydrogen ions

The fundamental processes leading to negative ion production are Volume Production by dissociative attachment and Surface Production by surface electron attachment. The latter process is being used in all present negative ion based NBI systems because of its much better performance, especially at lower pressures since the stripping losses due to collisions with the background gas are minimized. The main disadvantage using volume production of $\text{H}^-$ is that a high background gas pressure is required which leads to early dissociation of the negative ions and a high stray electron current (10 to 100 times the negative ion current) is produced.

The most efficient negative hydrogen ion sources use cesium (Cs) deposited surfaces at a pressure of 0.3 Pa [13–16]. With a cesium coating the surface production of negative ions is drastically increased due to the reduction of the material work function. The surface effect, i.e. the conversion of neutral or positive hydrogen ions to negative ions is given by

$$H, H_p^+ + \text{wall} \rightarrow \text{H}^-, \quad p = 1, 2, 3. \quad (1.1)$$

For neutral beam injection in ITER a Radio Frequency (RF) source will be used for the creation of a plasma in which among other species hydrogen atoms are created to form negative ions at cesium covered surfaces. Recent developments at the
IPP (Max-Planck-Institut für Plasmaphysik) in Garching show that RF sources can match the ITER conditions. Eventually, cesium-free negative ion sources are demanded for the next generation fusion reactors due to its toxicity and long term operation stability. To this end alternative methods to create negative ions are explored. One possible route is via nonmetallic surfaces, including polycrystalline graphite and highly-oriented pyrolytic graphite (HOPG) which give so far the best surface production of negative ions at carbon surfaces [17, 18]. The negative ion yield obtained on a polycrystalline graphite surface is comparable to that found on Cs or Ba-covered surfaces [19].

Another route producing negative ions is by volume processes, where the precursor is a ro-vibrationally excited hydrogen molecule (denoted by H$_{rv}$). These ro-vibrationally excited molecules inherit an internal energy up to 4.5 eV. Moreover, the ro-vibrational excitation of hydrogen molecules is of a metastable character, because radiative transitions within the electronic ground state $X^1 \Sigma^+_g$ are dipole forbidden and transitions occur only via collisions with other molecules, atoms or surfaces. Among others, these reactions are dissociation, ionization, charge exchange or Dissociative Attachment (DA). However, this method producing negative hydrogen ions is a no go for the NBI in ITER due to the fact that each electron

![Figure 1.2: Two-step volume production of negative ions in a tandem source.](image-url)
1. GENERAL INTRODUCTION

1.3. PRODUCTION OF NEGATIVE HYDROGEN IONS

has to produce more than 40 negative ions since the extracted electron/ion ratio has to be kept below 1. In addition, the source has to operate at very low pressure.

Volume sources are developed in order to maximize the production of negative ions by the DA process. The search for high intense H\(^-\) sources by volume production was initiated in 1977 by the observation at the Ecole Polytechnique in Palaiseau, France. For this they used a tandem source which consists of two regions separated by a magnetic filter, the driver and the extraction chamber, see figure 1.2 [20]. The driver contains a RF or filament heating region. In the driver the hydrogen molecules are excited by fast electrons (5-10 eV) to high internal energy. Then a magnetic filter is used to reduce both the electron density and electron temperature. In the expansion chamber the electron temperature is lowered to 1-2 eV so that the DA reaction rates are maximized while minimizing the destruction of negative ions by electron and ion interactions. The DA process for producing negative ions is given by

\[
\text{H}_2^\text{rv} + e^- \rightarrow \text{H}_2^- \rightarrow \text{H} + \text{H}^-.
\]

The potential curve of the metastable H\(_2^-\) ion is shown in figure 1.3. The metastable H\(_2^-\) ion fragments into a H atom and a H\(^-\) ion [21].

High ro-vibrationally excited hydrogen molecules can also be produced by surface association\(^*\) processes on low-temperature surfaces. Atomic hydrogen is effectively absorbed on metals. When in this situation a new hydrogen atom comes to the wall a hydrogen molecule can be formed by wall association in a so called Eley-Rideal type process [23, 24]:

\[
\text{H} + \text{H}_{\text{wall}} \rightarrow \text{H}_2^\text{rv}.
\]

With wall association an important part of the dissociation energy (4.5 eV) becomes available for ro-vibrational excitation of a hydrogen molecule.

Ro-vibrational hydrogen molecules are for example formed at the wall of a fusion reactor [25–28], at the surface of interstellar dust grains [29, 30] and at copper surfaces [31].

\(^*\)The term wall recombination is commonly used in literature but not used in this thesis to avoid confusion with "real" recombination e.g., dissociative recombination.
1.3. PRODUCTION OF NEGATIVE HYDROGEN IONS

1. General Introduction

An example distribution of ro-vibrationally excited H₂ densities, measured with Vacuum-Ultra Violet Laser Induced Fluorescence (VUV-LIF) [32, 33], in a hydrogen plasma expansion is shown in figure 1.4. The H₂ density distribution is a superposition of two different Boltzmann distributions for the ro-vibrational states. Lower rotational states (J<7) of each vibrational state follow a Boltzmann distribution described by a lower temperature which is close to the temperature of the background gas. However, higher rotational states follow a Boltzmann-like distribution with a much higher temperature similar to the vibrational temperature. These non-equilibrium ro-vibrational H₂ populations are not unique but measured in several different plasmas [34–37].

The DA process can be enhanced by several orders of magnitude if the precursor of H⁻, the ro-vibrationally excited molecule, has a high internal energy. The rate of H⁻ production can change eight orders of magnitude when the vibrational state changes from \( v=0 \) to \( v=9 \) [38], see figure 1.5. The DA process increases even more when the rotational states \( J \) are taken into account.

In figure 1.5 the dissociative attachment cross-section as function of the electron energy for different rotational \( J \) and vibrational \( v \) states are given [38]. From

Figure 1.3: Simplified potential energy diagram of hydrogen. [22]
1.4. Expanding hydrogen plasmas

The presence of negative hydrogen ions ($H^-$) and their effect on the excited state densities of atomic hydrogen is investigated in a linear plasma generator called PLEXIS, which is an acronym for PLasma EXpansion in Interaction with Surfaces. The PLEXIS setup is mainly designed for diagnostic studies and has many resemblances with other linear plasma generators like the Pilot-PSI and Magnum PSI setups from FOM institute DIFFER where conditions close to the diverter plates of ITER are simulated. The plasma source is mounted on a moveable arm inside the expansion vessel (of PLEXIS) so that spatial and radial measurements can be performed along the full plasma expansion while keeping the diagnostics...
1.4. Expanding Hydrogen Plasmas

General Introduction

Figure 1.5: The production of negative hydrogen ions by dissociative attachment as function of the electron energy for the rotational state \( J=0 \) in the vibrational states \( v=0, 2, 4, 6 \) and \( 8 \).

fixed. For the creation of the plasma a cascaded arc is used. This plasma source was first introduced by Maecker in 1956 [39] for spectroscopic studies in near equilibrium plasmas, see figure 2.2 in Chapter 2. At the university of Kiel, detailed studies were made on hydrogen line broadening by Wiese et al [40]. The cascaded arc plasma was also used to study deviations from thermal equilibrium [41] in Eindhoven. Since the fundamental study of hydrogen kinetics in plasmas is important for the realization of hydrogen negative ion (H\(^-\)) or hydrogen neutral (H) sources much effort was done to understand the expansion in a low pressure vessel.

The plasma expansion in a low pressure vessel was extensively studied by Van de Sanden [42–44], De Graaf [45, 46], Meulenbroeks [47–49] and Mazouf-fre [50–52] in which they established that noble gas plasmas and ground-state
H₂ molecules behave in first order identical to a hot gas expansion. The behavior of the reactive species is different since ions recombine anomalously fast (at 100 Pa) [45, 47]. The mechanism responsible for the fast recombination of ions is Molecular Activated Recombination (MAR). In the first few centimeters of the plasma expansion charge exchange between atomic ions (H⁺) and ro-vibrationally excited molecules (H₂rv) occur, followed by dissociative recombination of the formed molecular ion (H₂⁺). The ro-vibrationally excited molecules necessary for the charge exchange process are not produced in significant amounts by the arc since the kinetic energies (in the order of 1 eV) are not high enough for direct excitation but they are formed at the nozzle surface. Vankan et al showed that an increasing nozzle size increases the amount of H₂rv and reduces the amount of atomic hydrogen due to surface association processes [53]. The important processes that are present in expanding hydrogen plasmas are shown in figure 1.6.

![Figure 1.6: Schematic representation on the important processes taking place in the magnetized H₂ plasma expansion.](image)

To avoid the fast MAR processes that are present in the non-magnetized hy-
1.4. Expanding Hydrogen Plasmas

Expanding hydrogen plasma at moderate pressures (∼100 Pa) and exploiting a high density of charged particles, the background pressure is lowered and an external magnetic field is applied. The result is a bright light emitting plasma column with two distinct regions. At a specific distance from the source of the expansion a sharp transition from a red light emitting plasma (dominated by Hα emission) to a blue light emitting plasma (dominated by Hβ and Hγ emission) occurs [54–56], see figure 1.7. The transition from red to blue light emission depends on the plasma settings, e.g. background pressure, input power, magnetic field strength, hydrogen flow and nozzle length.

![Figure 1.7](image)

**Figure 1.7:** A typical magnetized hydrogen plasma expansion created by a cascaded arc in which two distinct regions are observed, namely an ionizing red light emitting plasma and a recombining blue light emitting plasma.

In the blue light emitting plasma population inversion of the excited states \( n=4, 5 \) and \( 6 \) with respect to \( n=3 \) is observed. In literature, the population inversion of \( n=4, 5 \) and \( 6 \) with respect to \( n=3 \) is mostly attributed to three-body recombination as recently reported in ref.[57] using a radio frequency source. However, Qing et al concluded that three-body recombination cannot be responsible for the observed population inversion in the magnetized hydrogen expansion because a too low electron density and a too high electron temperature is measured [58]. Qing showed with a collisional radiative model that molecular processes must be important in the population of the excited states and proposed the molecular mutual neutralization of \( \text{H}_2^+ \) and \( \text{H}^- \) as a mechanism to produce excited atoms of
1. General introduction

1.5 This thesis

The levels $n=2-9$:

$$H^+_2 + H^- \rightarrow H(n) + H_2, \quad \text{with } n = 2 - 9. \quad (1.4)$$

Eerden et al applied a multi-crossing Landau-Zener model to calculate the molecular mutual neutralization cross-section as a function of the quantum states $n$ [10]. The calculated cross-section is rather large and has a maximum efficiency of excitation in the outgoing channels for the states $n=4, 5$ and 6. The importance of this reaction was further explored by van den Dungen [56] where the production rate of each excited state in the blue light emitting plasma correlates very well with the shape of the cross-section of the molecular mutual neutralization process.

1.5 This thesis

In this work further evidence is provided that atomic processes alone cannot explain the distinct emissions observed in the two different color regions. Therefore, molecular processes such as dissociative recombination [59] and processes involving negative ions\footnote{With processes involving negative ions we mean all the mutual neutralization processes that lead/not lead to excited hydrogen atoms: The atomic mutual neutralization process of $H^+ + H^-$, the molecular mutual neutralization process of $H_2^+ + H^-$ and the molecular mutual neutralization process of $H_3^+ + H^-$.} are suspected to be key in the understanding of the underlying mechanisms. The relevance of this work is to underpin the importance of these molecular processes in atomic regimes of hydrogen containing plasmas.

To understand the plasma chemistry and kinetics in the magnetized hydrogen plasma expansion in more detail several research questions need to be answered:

1. Can we explain the two distinct color regions in the plasma?

2. Why do we observe such a sharp transition from red to blue light emission?

3. How important are the molecular processes in the population of excited states of atomic hydrogen?
4. Is the molecular mutual neutralization process of $\text{H}_2^+ + \text{H}^-$ present in the plasma and does it lead to excited hydrogen atoms?

5. Can we understand the observed population inversion of $n=4-7$ with respect to $n=3$ in the blue light emitting plasma?

To answer several of these research questions a Collisional Radiative model (CR-model), developed at the Max-Planck-Institut für Plasmaphysik [60], is used to prove that molecular processes are present in the plasma (Chapter 5). The CR-model calculates the spatially resolved excited state densities of atomic hydrogen ($n=2$ up to $n=9$) which are compared with the measured excited state densities as determined using two diagnostics: tunable diode laser absorption spectroscopy for the first excited state $n=2$ (Chapter 4) and absolute optical emission spectroscopy for $n=3-9$ (Chapter 3). By comparing experiment with simulation the important population process to the excited states of atomic hydrogen can be investigated.

A novel time dependent photo-detachment technique is introduced and used to prove (and to corroborate the CR-model results) that processes involving negative ions are present in the plasma (Chapter 6). The photo-detachment technique is based on the detachment of $\text{H}^-$ coupled with optical detection of the disappearing Balmer emission light resulting from the mutual neutralization processes. This technique therefore provides a direct measurement of the processes involving negative ions and under certain conditions the negative ion density can be determined.

To answer the research questions about the chemistry and kinetics in the magnetized hydrogen plasma expansion, this thesis work is divided into the following chapters:

- In chapter 2, the experimental setup and the used diagnostics are explained. Furthermore, a study of different system settings is given.

- In chapter 3, the magnetized hydrogen plasma expansion is investigated by determining the excited state densities $n=3$ and higher of atomic hydrogen with absolute optical emission spectroscopy.
In chapter 4, the first excited state density of atomic hydrogen $n=2$ is determined by means of tunable diode laser absorption spectroscopy.

In chapter 5, the population processes in the plasma are investigated with a collisional radiative model.

In chapter 6, a novel photo-detachment technique is implemented in which the negative ions are probed with a laser in combination with an optical detection system to detect the change of the Balmer line emission.
Bibliography


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Experimental arrangement

2.1 The experimental setup

The experimental setup on which all experiments described in this thesis are conducted is called PLEXIS, which is an acronym for PLasma EXpansion in Interaction with Surfaces. In the chapters 3 to 6 the setup is only shortly explained. In this chapter I will give a more detailed overview of the setup and all the used diagnostics.

2.1.1 The PLEXIS setup

A schematic of the linear plasma generator PLEXIS is shown in figure 2.1. The 

Figure 2.1: A schematic overview of PLEXIS from the side. The cascaded arc is mounted on a movable arm. The vacuum pumps keep the background pressure around 9 Pa inside the vessel. Four Helmholtz coils (MC) can apply a varying axial magnetic field strength up to 180 mT.
2. EXPERIMENTAL ARRANGEMENT

2.1. THE EXPERIMENTAL SETUP

setup consists of a cascaded arc plasma source placed inside a 3 m long cylindrical low pressure vessel, with a diameter of 30 cm and multiple windows for diagnostic measurements.

During experiments the background pressure in the vessel is kept constant at about 9 Pa by a three stage pumping system, subsequently a single stage rotary pump, a booster pump and a roots pump. The cascaded arc is mounted on a movable arm inside the low pressure vessel which allows for spatial and axial measurements throughout the plasma expansion while keeping the diagnostics fixed at the window ports.

2.1.2 The plasma source

The cascaded arc which serves as the plasma source for the experiments, consists of three tungsten-lanthanum cathodes, four water-cooled copper plates that are separately insulated by PVC spacers and vacuum sealed by rubber O-rings, and a copper anode end plate, see figure 2.2. The hydrogen gas flows with 3000 sccm (1.25 \cdot 10^{21} \text{ H}_2 \text{ particles/s}) at a pressure of 10^4 \text{ Pa} through a channel of 4 mm diameter. With an input power of 6.8 kW a partially ionized and nearly fully dissociated hydrogen plasma is produced. Due to the large pressure difference between plasma source and vacuum vessel a supersonic expansion is formed. This introduces a shock when the pressure of the jet approaches the background.
2.1. THE EXPERIMENTAL SETUP

pressure, after which the plasma expands sub-sonically [1]. Outside the expanding jet recirculation cells are present [2].

The amount of charged particles that expand in the low pressure vessel depend strongly on the size of the nozzle that is mounted at the end of the anode end plate, see figure 2.3. Vankan and Gabriel have shown with experiments that in the anode nozzle significant losses of electrons, H\(^+\) and H atoms occur due to recombination and H\(_2\)\(^+\) formation at the surface [3, 4]. To achieve the smallest loss of ions, electrons and atoms an open nozzle is mounted at the anode end plate of the cascaded arc to reduce the interaction of plasma with surface. The different nozzles sizes that are investigated in this thesis work are shown in table 2.1.

![Figure 2.3: Three different nozzle sizes that investigated by mounting it at the end of the anode end plate.](image)

**Table 2.1:** The different nozzles, used in this work, are listed below.

<table>
<thead>
<tr>
<th>Name</th>
<th>Inner diameter [mm]</th>
<th>Length [mm]</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open nozzle</td>
<td>9.6</td>
<td>7.4</td>
<td>Copper</td>
</tr>
<tr>
<td>Short nozzle</td>
<td>4</td>
<td>7.4</td>
<td>Copper</td>
</tr>
<tr>
<td>Long nozzle</td>
<td>4</td>
<td>14</td>
<td>Copper</td>
</tr>
<tr>
<td>Very long nozzle</td>
<td>4</td>
<td>30</td>
<td>Copper</td>
</tr>
</tbody>
</table>
Charged particles

An external parallel magnetic field is applied to the plasma expansion to reduce the outward diffusion and thus increasing the plasma density. For this four Helmholtz coils mounted around the vessel are used to produce an uniform parallel magnetic field over a length of approximately 1.4 meter. The current in the coils can be increased up to 400 A to create a maximum magnetic field strength of about 180 mT, see figure 2.4. The magnetic field strength is measured to be constant in the expansion vessel and the measured absolute value changes less than 10% spatially.

The magnetized hydrogen plasma expansion obtained with an open nozzle differs in several ways from the one obtained with a short nozzle, as shown in figure 2.5. When an open nozzle is mounted on the anode end plate the generated plasma expansion is longer then when a short or long nozzle is mounted. In the presented thesis work it will be shown that the length of the magnetized hydrogen
2.1. The Experimental Setup

The experimental setup is greatly influenced by the used nozzle surface area and the applied external magnetic field strength.

![Image of plasma expansion comparison](image_url)

**Figure 2.5**: Comparison of the magnetized hydrogen plasma generated with (a) an open nozzle and (b) a short nozzle.

Figure 2.5 shows an open nozzle plasma expansion and short nozzle plasma expansion with the same experimental settings except a different external magnetic field strength. A larger magnetic field strength is needed for obtaining sufficient plasma density in the expansion when a short nozzle instead of an open nozzle is used. For the experiments with the open nozzle, having an inner diameter of 9.6 mm, a magnetic field of 14 mT is applied and for the short nozzle, having an inner diameter of 4.0 mm, a magnetic field of 42 mT is applied. In chapter 3, the two different plasma expansions are investigated in detail. When a long nozzle is mounted at the anode end plate, the amount of ions in the plasma expansion due to surface association processes is much less than with an open and short nozzle. Therefore, a magnetic field strength of 100 mT is necessary to get sufficient plasma density. The result is a completely blue plasma expansion of about 12 cm long.

The applied external magnetic field has a large influence on the motion of the charged particles in the plasma, unlike the neutrals which are less affected. The charged particles that move towards the walls (perpendicular to the magnetic
field lines) feel a Lorentz force and are deflected into a circular cyclotron motion around the magnetic field lines. The strength of the magnetic confinement is given by the Hall parameters:

\[ H_{ei} = \Omega_{ei} \tau_{ei} = \frac{6.3 \cdot 10^{22} T_{e}^{3/2} B_{ext}}{n_{e} \ln \Lambda} \]  

(2.1)

and

\[ H_{ii} = \Omega_{ii} \tau_{ii} = \frac{2.0 \cdot 10^{21} T_{i}^{3/2} B_{ext}}{A_i^{1/2} n_{e} \ln \Lambda} \]  

(2.2)

These parameters describe the electron, \( H_{ei} \), and ion confinement, \( H_{ii} \). The Hall parameter consists of the time between collisions \( \tau \) with the cyclotron frequency \( \Omega \). The temperatures of the electrons and ions are given by \( T_e \) and \( T_i \) respectively [in eV]. The applied external magnetic field is \( B_{ext} \) [in T] and \( n_e \) is the electron density [in m\(^{-3}\)]. The atomic mass number of the ions is given by \( A_i \) and \( \ln \Lambda \) is the Coulomb logarithm which is typically between the values 6-9 in this work.

When the Hall parameter is above 1 the species are considered to be confined by the magnetic field lines. For typical experimental conditions the electron Hall parameter varies from 4 to 13 in the red light emitting plasma and 5 in the blue light emitting plasma. The ion Hall parameter remains below 1, so strictly speaking they are not confined by the external magnetic field. The ions are however indirectly confined by the negative electron charge so that the outward diffusion of the charged particles is limited by electron diffusion.

### 2.2 Diagnostics

The diagnostics that are used on the hydrogen plasma expansion are explained below. With the help of Optical Emission Spectroscopy (OES), Tunable Diode Laser Absorption Spectroscopy (TDLAS) and Two-photon Absorption Laser Induced Fluorescence (TALIF), all the relevant densities of atomic hydrogen can be determined, i.e. the ground state density and the excited state densities of \( n=2 \) up to \( n=15 \). With a novel photo-detachment technique the importance of the mutual neutralization process is tested by detaching the extra electron of the negative ion.
by a laser. A double Langmuir probe setup is used for determining the electron parameters $T_e$ and $n_e$.

### 2.2.1 Optical emission spectroscopy for H($n=3$-$15$)

Optical Emission Spectroscopy (OES) is used to detect the visible part of the emission spectrum originating from the hydrogen plasma. Densities of excited H atoms are measured by means of OES on the Balmer line series. The emitted light from the plasma expansion is collected by a lens system and transported with an optical fiber to a Czerny-Turner spectrometer in which the dispersed light from the grating is detected by a CCD camera. To obtain absolute population densities of the excited states $n=3$ up to 15 a calibration of the optical system is carried out by comparison measurements using a tungsten ribbon lamp.

### 2.2.2 Tunable diode laser absorption spectroscopy for H($n=2$)

The first excited state, $n=2$, can not be determined with OES since it emits to the ground state in Vacuum Ultra Violet (VUV). Therefore, the first excited state is determined with Tunable Diode Laser Absorption Spectroscopy (TDLAS) by measuring the absorption on the $H_\alpha$ line from $n=2$ to $n=3$. The absorption spectrum of the plasma is measured as the tunable diode laser scans its wavelength range around the $H_\alpha$ line. For the TDLAS set-up a continuous wave TLB-7005 external-cavity diode laser with a power of 4 mW, operating according to the Littman-Metcalf principle, is used [5].

### 2.2.3 Two-photon LIF for H($n=1$)

The reason for using the non-linear TALIF technique, to measure the ground-state atomic hydrogen density, is that the transition between ground-state hydrogen $H(n=1)$ to the excited state $H(n=3)$ needs single photons in the VUV-range of the spectrum around 102.6 nm. This would make the setup for absorption spectroscopy and ordinary LIF very complicated because photons in the VUV and UV-range are absorbed in open air and a complete vacuum pathway of the laser light should be necessary. With TALIF, two photons with only a wavelength of 205 nm
are necessary to excite the ground-state atomic hydrogen. This wavelength is not absorbed in open air which makes it a useful technique.

A Nd:YAG laser pumped dye laser operates at a wavelength of around 615 nm. The laser beam is frequency tripled using two crystals, resulting in a tunable wavelength around 205 nm with a 8 ns pulse length. The fluorescence signal in this LIF process is detected at 656 nm (H$_\alpha$ emission) with a photo multiplier tube, giving information on density and temperature of the ground state density of atomic hydrogen. The densities are calibrated using a two photon transition in a known amount of krypton [6].

![Figure 2.6](image_url)

**Figure 2.6:** Example of a measured spectral profile of the two photon transition in atomic hydrogen (solid square) and Gaussian fit (red line). The relative change in laser power at different wavelengths are indicated by grey solid circles (see the right axis). The fluorescence is detected at the H$_\alpha$ line. The area of the peak is a direct measure of the H density after calibration with krypton. The local temperature is deduced from the Doppler broadening of the line after deconvolution with the laser spectral profile.
2.2.4 Photo-detachment

In chapter 6 we will prove by experiment that both the atomic and molecular mutual neutralization process are present in the plasma:

\[ \text{H}^+ + \text{H}^- \rightarrow \text{H}(n) + \text{H}, \quad \text{with } n = 2 \text{ and } 3 \]  

(2.3)

and

\[ \text{H}_2^+ + \text{H}^- \rightarrow \text{H}(n) + \text{H}_2, \quad \text{with } n = 2 - 9. \]  

(2.4)

To prove the presence of these two population processes experimentally, a novel time dependent \( \text{H}^- \) detection technique is demonstrated. Since the electron affinity of a negative hydrogen ion is 0.75 eV a Q-switched Nd:YAG laser is used with photon energies of 1.15 eV and 2.3 eV. The different photon energies are used to distinguish photo-ionization from photo-detachment, as discussed in Chapter 6. The laser pulses are introduced to the plasma to destroy the negative hydrogen ions that are present. Consequently, the Balmer emission is temporally lowered assuming that the mutual neutralization processes are important in the plasma. The re-population of typical Balmer levels herein is monitored by looking at the time constant of the repopulation process and the maximal amount of the excited state that is destroyed. This detection technique therefore provides an indirect measurement of \( \text{H}^- \) and a direct evidence of the presence of mutual neutralization processes.

2.2.5 Double Langmuir probe

A double Langmuir probe is used to determine the electron temperature \( T_e \) and electron density \( n_e \) in the magnetized expanding hydrogen plasma. The measurement is performed by applying a potential difference between two floating probes and measuring the current passing through the probes to get a symmetrical current-voltage plot [7], see figure 2.7. The situation is more complicated when a sufficiently strong magnetic field is applied to the plasma. In chapter 3, it will be shown that the double Langmuir probe setup can be used to determine the electron temperature and electron density when a weak external magnetic field of \( B < 50 \text{ mT} \) is applied to the plasma.
Figure 2.7: I-V characteristic of a double Langmuir probe. The electron temperature can be obtained from the slope of the double probe characteristic and the electron density from the ion saturation currents.

2.3 Collisional radiative model

In Chapter 5 a Collisional Radiative model (CR-model) is used to show that both the atomic and molecular mutual neutralization process are present in the plasma. The CR-model calculate the densities of excited states as functions of electron temperature, electron density and other present species by using balance equations:

\[
\frac{dn_n}{dt} + \vec{\nabla} \cdot n_n \vec{w}_n = \left( \frac{dn_n}{dt} \right)_{CR},
\]

where \( C \) stands for collision and \( R \) for radiation. The left side of this equation describes the increase in density \( n_n \) of an excited state \( n \) over time and must be related to an increase of flow due to divergence (\( \vec{w}_n \) is the velocity) and to the net result of population and depopulation processes. The right hand side describes the change in density of state \( n \) due to elementary processes like inelastic collisions and radiation. To ease the calculations done with the CR-model, often the
fact is utilized that the different processes which are dominant for reaching the equilibrium population of the species or states have different time scales. The ground state densities of atoms, molecules and ions depends on transport processes, typically $10^{-4}$ s, while the excited state densities are established on a time scale of $10^{-7}$ s and faster. Therefore, the ground state densities can be considered as quasi-constant input values for the CR-model. This information makes it possible to assume a Quasi Steady State Solution (QSSS) in many situations:

$$0 = \left( \frac{dn_n}{dt} \right)_{CR} = P_n - n_nD_n. \quad (2.6)$$

The processes are now grouped in production terms $P_n$ and destruction terms $D_n$. When assuming QSSS, the atomic state density can be determined by the ratio of production and destruction $n_n = P_n / D_n$. The output from the CR-model can be used to construct an Atomic State Distribution Function (ASDF) which relates the excited state densities per statistical weight of atomic hydrogen as function of the quantum states $n$.

In Chapter 3, a standard CR-model from the Eindhoven University of Technology is applied in which only atomic processes are included. In Chapter 4, 5 and 6, an extended CR-model from the IPP (Max-Planck-Institut für Plasmaphysik) in Garching, Germany, is applied which includes molecular processes. This extended CR-model is developed for low pressure and low temperature plasmas in which the newest available data from literature is used [8].
Bibliography


Population inversion in a magnetized hydrogen plasma expansion as a consequence of the mutual neutralization process *

Abstract  A weakly magnetized expanding hydrogen plasma is dominated by red light emission (dominated by H$_{\alpha}$ emission) in the first part and after a specific distance a sharp transition to a blue light emitting plasma (dominated by H$_{\beta}$ and H$_{\gamma}$ emission) is observed. The blue light emission is associated with population inversion of the electronically excited atomic hydrogen states $n=4$-6 with respect to $n=3$. By comparing the measured densities with the densities using an atomic collisional radiative model, we conclude that atomic recombination processes cannot account for the large population densities observed. Therefore, molecular processes must be important for the formation of excited states. This is further corroborated at the transition from the red light emission to the blue light emission where a hollow profile of the excited states $n=4$-6 in the radial direction is observed. This hollow profile is explained by the molecular mutual neutralization process of H$_3^+$ and H$^-$, which has a maximum production for excited atomic hydrogen 1-2 cm outside the plasma center.

3.1 Introduction

The development of efficient sources of reactive hydrogen radicals is important in many research fields and applications. For instance, atomic hydrogen radicals serve as primary reactive particles for surface modification or thin film deposition [1, 2]. For fusion plasma heating, one of the main research challenges is to develop efficient negative ion sources. A promising route is via dissociative attachment of ro-vibrationally excited hydrogen molecules $\text{H}_2^{\text{rv}}$ [3]. Studying the kinetics of $\text{H}_2^{\text{rv}}$ is of key importance in understanding negative ion formation processes in both volume and surface reactions [4]. The ro-vibrationally excited molecules are an important precursor in volume reaction produced Molecular Activated Recombination (MAR) processes [5–7]. In this paper the importance of several MAR processes will be examined. Especially, the formation of excited atom production via the mutual neutralization process of $\text{H}^-$ and $\text{H}_2^+$ will be discussed in detail [8–11].

A wall stabilized cascaded arc attached to a low pressure vessel has been shown to be a reliable source for the production of well-defined fluxes of atomic and molecular radicals, see figure 2.2 of Chapter 2. This kind of plasma source was first introduced by Maecker as a light source using argon as the carrier gas [12]. The study of expanding argon plasmas was continued by Kroesen et al as a particle source in a deposition chamber [13]. This method of deposition showed to be efficient and fast to grow hydrogenated amorphous carbon films (a-C:H). The fundamental aspects of argon plasmas expanding from a cascaded arc was studied extensively by van de Sanden et al [14, 15].

Work on hydrogen as a carrier gas was first done by de Graaf et al [5] and Meulenbroeks et al [16] by looking at the dynamics and kinetics of a non-magnetized expanding hydrogen plasmas at a pressure of 100 Pa. It was demonstrated that in the hydrogen expansion an anomalously high recombination occurs, which leads to a very effective destruction of ions and electrons. To avoid this fast recombination an external magnetic field and a low background pressure were used to produce a hydrogen plasma expansion with two distinct regions. This separation is observed as a sharp transition from a red light emitting plasma
3.1. INTRODUCTION

3. POPULATION INVERSION

to a blue light emitting plasma as reported in [17–19], see figure 3.1. Akatsuka et al [20] measured, with Optical Emission Spectroscopy (OES), the occurrence of population inversion in the downstream plasma. The population mechanism in the blue light emitting plasma is generally believed to be three-body recombination as recently reported in ref.[21] using a Radio Frequency (RF) plasma. However, Qing et al [22] concluded that three-body recombination cannot be responsible for the observed population inversion in the magnetized hydrogen expansion because of the too low electron density and too high electron temperature [23]. Both parameters were obtained with a Langmuir double probe. They showed the importance of molecular processes and proposed molecular mutual neutralization of $\text{H}_2^+$ and $\text{H}^-$ as a mechanism to produce highly excited atomic hydrogen. A multi-crossing Landau-Zener model was applied to calculate the molecular mutual neutralization cross-section as a function of the quantum states $n$ [24]. The calculated cross-section is rather large and has a maximum efficiency of excitation in the outgoing channels for the states $n=4$, 5 and 6. The importance of this reaction was further explored in ref.[19] where the production rate of each excited state in the blue light emitting plasma correlates very well with the shape of the cross-section of the molecular mutual neutralization process. In this paper we report on the production of excited H atoms in a magnetically confined hydrogen expansion. An important precursor for the formation of excited H atoms is $\text{H}_2^{\text{rv}}$ which is produced via wall association process at the anode nozzle of the arc and the reactor vessel [7]. These $\text{H}_2^{\text{rv}}$ molecules flow into the plasma locally producing $\text{H}^-$ ions via the dissociative attachment process [25]. The $\text{H}^-$ ions recombine with $\text{H}_2^+$ to form hydrogen atoms in highly excited states, causing population inversion. This work continuous the discussion of MAR processes in a cascaded arc [19, 22]. New evidence for the existence of MAR processes is given by examining atomic state distributions and using a collisional radiative model. These results show the promising possibility of using a wall stabilized cascaded arc as a $\text{H}^-$ ion source.
3. POPULATION INVERSION

3.2 EXPERIMENTAL SETUP AND DIAGNOSTICS

Figure 3.1: The low pressure vessel is surrounded by four Helmholtz coils to provide an axially magnetic field that can be changed in strength. The cascaded arc is mounted on a movable arm that allows 3D displacement in the reactor vessel. In this way spatially resolved measurements can be performed while the diagnostic tools remain fixed. The emission of the expanding plasma is dominated by red $H_\alpha$ emission in the first part of the plasma expansion after which a sharp transition to a blue light emitting plasma is observed. This sharp transition from red to blue depends on many settings like e.g. the background pressure, arc current and magnetic field strength.

3.2 Experimental setup and diagnostics

3.2.1 Plasma source and expansion

The cascaded arc that serves as the plasma source for the experiments, consists of three tungsten-lanthanum cathodes, four water-cooled copper plates that are separately insulated by PVC spacers and vacuum sealed by rubber O-rings, and a copper anode end-plate.

The hydrogen gas flows with 3000 sccm ($1.25 \cdot 10^{21}$ $H_2$ particles/s) and at a pressure of $10^4$ Pa through a channel of 4 mm diameter. With an input power of
6.8 kW a partially ionized and nearly fully dissociated hydrogen plasma is produced. It has been shown that in the anode nozzle significant losses of electrons, \( \text{H}^+ \) and \( \text{H} \) atoms can occur because of recombination and \( \text{H}_2^+ \) formation at the surface. Therefore, an open and a short nozzle (see Chapter 2) are used since they give the smallest loss of ions, electrons and atoms [25]. The plasma expands

![Emission spectrum](image)

**Figure 3.2:** An emission spectrum obtained with OES in the blue part of the hydrogen plasma expansion at \( z=25 \) cm. The radiation from the lower excited states \( n<6 \) are not shown here. The experimental conditions are as follows: open nozzle, \( I_{\text{arc}}=45 \) A, \( V_{\text{arc}}=150 \) V, \( \phi_{\text{H}_2}=3000 \) sccm, \( p_{BG}=9.3 \) Pa, and \( B_z=14 \) mT.

in a 3 meter long and 30 cm diameter stainless steel cylindrical vessel at a background pressure of 9 Pa. The pressure gradient between the cascaded arc and the expansion vessel forces the plasma to expand, first supersonically and then, after the formation of a shock, subsonically into the background [26]. Four Helmholtz coils mounted around the vessel are used to produce an uniform magnetic field of 14 mT over a length of approximately 1.4 meter when the open nozzle is used at the end of the plasma source and a magnetic field of 42 mT is applied when the short nozzle is used. A higher magnetic field strength is necessary to confine suf-
efficient charged particles when a short nozzle is used (instead of an open nozzle) due to more wall association processes. In figure 3.2, an emission spectrum obtained with OES in the blue emitting part of the plasma expansion is shown using an open nozzle configuration. The plasma expansion that is created in this work is known to be far from thermal equilibrium [27].

3.2.2 Optical emission spectroscopy

Optical Emission Spectroscopy (OES) is used to detect the visible part of the emission spectra originating from the plasma, see figure 3.1. An optical system consisting of 2 lenses creates an 1:7 image of the plasma expansion on an optical fibre which guides the collected light to a spectrometer with a spatial resolution of 70 µm. The latter is based on wavelength dispersion by a Czerny-Turner monochromator and the detection is performed by a light sensitive CCD detector. A typical spectrum in the blue light emitting plasma is shown in figure 3.2. In the red light emitting part of the plasma expansion intensive Fulcher-α band emission from the hydrogen molecule \((a^3\Pi_u - a^3\Sigma^+_d)\) is observed (with an open nozzle configuration) around 600 nm indicating high electron temperatures \((T_e > 1 \text{ eV})\), see figure 3.3. The excited state population is determined by electron (de)excitation processes, which depend exponentially on the electron temperature. The total Fulcher-α band emission therefore increases exponentially with the electron temperature. Experiments with the short nozzle configuration showed no Fulcher-α band emission in the plasma expansion indicating that the electron temperature is not so high \((T_e < 1 \text{ eV})\).

Absolute calibration of the measured line intensities is achieved with a tungsten ribbon lamp. The intensity of the emission is proportional to the density of the upper level \(u\). For an optically-thin plasma [22], the spectral emission coefficient \(j_\lambda(\lambda)\) (in W m\(^{-4}\) sr\(^{-1}\)) is given by

\[
j_\lambda(\lambda) = \frac{1}{4\pi} n_u A_{ul} E_{ul} \varphi(\lambda), \tag{3.1}
\]

where label \(u\) and \(l\) stands for the upper and lower level respectively. \(n_u\) is the density of the upper level \(u\), \(A_{ul}\) (in s\(^{-1}\)) the Einstein coefficient for spontaneous
3.2. EXPERIMENTAL SETUP AND DIAGNOSTICS

3. POPULATION INVERSION

**Figure 3.3:** An emission spectrum obtained with OES in the red emitting part of the hydrogen plasma expansion at $z = 4$ cm with an open nozzle configuration. The emission of the Fulcher band is between 570 to 640 nm and at 656 nm Hα emission is observed.

The energy of the photon that is emitted and the line shape function of the transition, which is normalized, i.e. $\int \varphi_{\lambda}(\lambda) d\lambda = 1$. The spectral radiance $L_{ul}$ along the Line-Of-Sight (LOS) is given as (in W m$^{-3}$ sr$^{-1}$)

$$L_{ul}(\lambda) = \int_{LOS} j_{\lambda}(\lambda) dy = \frac{1}{4\pi} A_{ul} E_{ul} \varphi_{\lambda}(\lambda) \int_{LOS} n_{ul} dy. \quad (3.2)$$

The integration of the spectral radiance over the wavelength gives the radiance, $\Lambda_{ul}$ of the line (in W m$^{-2}$ sr$^{-1}$):

$$\Lambda_{ul} = \int L_{ul}(\lambda) d\lambda \equiv \hat{L}_{ul} \Delta \lambda. \quad (3.3)$$

The $\hat{L}_{ul}$ value can be obtained from an emission measurement and calibrated absolutely with the known spectral density of the tungsten ribbon lamp. The uncertainty of the absolute density calibration with the tungsten ribbon lamp is 10%. The line width is $\Delta \lambda$ at Full Width Half Maximum (FWHM) of the Balmer transition. Equation (3.3) shows that the population density $n_{ul}$ of level $u$ depends
linearly on $\Lambda_{ul}$,

$$\hat{n}_u = \int_{\text{LOS}} n_u dy = \frac{4\pi\Lambda_{ul}}{A_{ul}E_{ul}} = \hat{L}_{ul}\Delta\lambda\frac{4\pi}{A_{ul}E_{ul}}. \quad (3.4)$$

With the optical setup a lateral profile is measured, i.e. the integrated LOS density. Abel inversion is used to determine the radially resolved densities. The spatial resolution of the optical setup is 3 mm, which is much smaller than the plasma radius. The magnetized plasma expansion has cylindrical symmetry so that Abel inversion of the measured line of sight profile can be applied [28]:

$$n(r) = \frac{-1}{\pi} \int_r^\infty \frac{\partial\hat{n}(\Delta r_{\text{LOS}}(y), y)}{\partial y} \frac{1}{\sqrt{y^2 - r^2}} dy. \quad (3.5)$$

Here, $\hat{n}(\Delta r_{\text{LOS}}(y), y)$ is the density along the LOS and $n(r)$ is the spatially resolved density (in m$^{-3}$). The LOS data is analyzed with a purely centralized Gaussian line profile [29]. The observed line profile is a combination of two radial Gaussian profiles, a narrow profile for the plasma core and a broad profile for the background. At the transition from a red to blue light emitting plasma a lateral dip at the center axis is observed. The dip in the center of the density profiles can be simulated by adding a third Gaussian with a negative area to the total density profile.

### 3.2.3 Langmuir double probe

A Langmuir double probe is used to determine the electron temperature $T_e$ and electron density $n_e$ in the magnetized expanding hydrogen plasma. The measurement is performed by applying a potential difference between two floating probes and measuring the current passing through the probes to get a symmetrical current-voltage plot [30]. The situation is more complicated when a sufficiently strong magnetic field is applied to the plasma. This will then reduce the electron current collected by the probe. However, the double probe theory is still valid in a magnetized plasma if the Larmor radii for ions and electrons are much larger than the Debye length. Assuming that $n_e=10^{18}$ m$^{-3}$, $B_0=14 \cdot 10^{-3}$ T and $T_e=0.3$ eV the Larmor radii are $\rho_i = 3.2 \cdot 10^{-3}$ m and $\rho_e = 7.0 \cdot 10^{-5}$ m for ions and electrons respectively. These two are larger than the Debye length $\lambda_D = 4 \cdot 10^{-6}$
m. The influence of the negative ions on the probe theory is small if the density is much lower than the positive ion density [21]. Furthermore, it is assumed that \( \text{H}_2^+ \) is dominant over \( \text{H}^+ \) in the blue light emitting plasma. The two probes are both 3.7 mm long and 0.8 mm in diameter. The diameter was chosen in such a way that it is much smaller than all relevant mean free path lengths and larger than the Debye length.

It is important to know whether the charged particles in the plasma expansion are magnetized or not. For this the electron cyclotron radius must be smaller than their mean free path in the plasma. The electrons are magnetized once the electron Hall parameter \( H_{ei} \) is higher than unity. The electron Hall parameter for the conditions assumed above can be calculated with

\[
H_{ei} = \frac{e}{\rho_e} = \frac{6.3 \cdot 10^{22} \cdot T_e^{3/2} B_0}{n_e \ln \Lambda} \approx 25.
\] (3.6)

This is higher than unity, and therefore the electrons are following the magnetic field lines. The ion Hall parameter can be calculated with

\[
H_{ii} = \frac{\lambda_{ii}}{\rho_i} = \frac{2 \cdot 10^{21} \cdot T_i^{3/2} B_0}{A_i^{1/2} n_e \ln \Lambda} \approx 0.9.
\] (3.7)

This shows that the ions are only marginally magnetized. The main conclusion is that for both the open nozzle and short nozzle configuration the electrons are magnetized while this is not true for the ions.

### 3.3 Atomic collisional radiative model

A Collisional Radiative Model (CR-model) can be used to determine which processes are responsible for the observed population inversion in the blue light emitting plasma. A CR-model relates the densities of excited states to those of atomic- and ionic ground states. The atomic CR-model requires four input parameters to calculate the mass balance for all excited states [31] namely \( T_e, n_e \), the gas temperature \( T_{\text{gas}} \) and the ground state density of atomic hydrogen \( \text{H}(n=1) \). These parameters are derived from experiments conducted on the magnetized hydrogen.
plasma. The population processes that are included in the used CR-model are listed in table 3.1. In table 3.1 the numerical values of the four input parameters of the CR-model are shown. Both the electron density and temperature are derived from the Langmuir double probe measurements. Probe measurements have only been performed for $z > 16 \text{ cm}$ when an open nozzle is used since the probe is glowing close to the arc. The gas temperature is determined with the open nozzle configuration from Tunable Diode Laser Absorption Spectroscopy (TDLAS) by investigating the Doppler broadening of the H$_\alpha$ absorption signal, see Chapter 4. The ground state density $H(n=1)$ is obtained with Two-Photon Laser Induced Fluorescence (TALIF). From the densities of the CR-model an Atomic State Distribution Function (ASDF) can be constructed [35]. Knowledge of the ASDF is of fundamental importance since it describes how excited states in atoms and ions are populated at a given electron temperature $T_e$, electron density $n_e$ and neutral ground-state density $H(n=1)$.

From the ASDF the coefficients of total recombination and ionization can be calculated which are required for the particle- and energy source terms in plasma-transport equations.
### 3.4 Experimental results

The spatially resolved densities of $n=3$ up to $n=15$, obtained from the Abel inverted OES measurements, are presented. In order to understand the important reaction mechanisms in the magnetized hydrogen plasma expansion, the obtained excited state density results of the open nozzle configuration will be compared with that of the short nozzle configuration. The results from both studies are obtained with the same experimental settings except for the strength of the applied magnetic field and of course, the diameter of the nozzle. From these data atomic state distribution functions are constructed. Subsequently, the excited state densities are compared with the simulated densities from the standard CR-model.

#### 3.4.1 Spatially resolved densities

**Open nozzle configuration**

The Abel inverted contour plots of $n=3$ up to $n=6$ for the plasma expansion in which an open nozzle is used is shown in figure 3.4.

In figure 3.4(a), the density per statistical weight of $n=3$ is shown (in m$^{-3}$). The background emission at the edges is fitted with a broad Gaussian profile and the center core is fitted with a narrow Gaussian profile. The background emission at the edges are due to metastable species in the recirculating background gas. The local excited state density profiles show that the expansion starts out with a very narrow lateral profile. After the transition, which occurs at $z=18-20$ cm, the

---

**Table 3.2:** The four input parameters that are obtained in the blue light emitting plasma and used as input in the standard CR-model.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Obtained via</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_e$</td>
<td>double probe</td>
<td>[0.9-0.1 eV]</td>
</tr>
<tr>
<td>$n_e$</td>
<td>double probe</td>
<td>$[3 \times 10^{18} - 2 \times 10^{17} \text{ m}^{-3}]$</td>
</tr>
<tr>
<td>$T_{gas}$</td>
<td>TDLAS</td>
<td>700 K</td>
</tr>
<tr>
<td>$H(n=1)$</td>
<td>TALIF</td>
<td>$10^{20}$ m$^{-3}$</td>
</tr>
</tbody>
</table>
3. Population inversion

3.4. Experimental results

Figure 3.4: The contour plot of Abel inverted H-atom density profiles $n=3, 4, 5$ and $6$ (in m$^{-3}$) divided by the statistical weight $g_n$. The excited state densities are obtained with an open nozzle mounted at the end of the cascaded arc.
Figure 3.5: The contour plot of Abel inverted H-atom density profiles \( n=3, 4, 5 \) and 6 (in \( \text{m}^{-3} \)) divided by the statistical weight \( g_n \). The excited state densities are obtained with a short nozzle mounted at the end of the cascaded arc.

profile broadens in the blue light emitting plasma.

In figure 3.4(b), the density per statistical weight of \( n=4 \) is shown. The dens-
ity of \( n=4 \) is low in the red part of the plasma expansion where \( \text{H}_\alpha \) emission is dominant and it increases rapidly after the red-blue transition. An interesting feature is an observed hollow profile in the red-blue transition at \( z=18-20 \) cm.

In figure 3.4(c) and 3.4(d) we see the density per statistical weight of \( n=5 \) and 6 respectively. The densities are low in the red light emitting plasma region and after the red-blue transition we observe that the densities of both \( n=5 \) and 6 reach a maximum. Note that in the red light emitting plasma region for \( n=6 \) no lateral OES scans are obtained due to the low signal to noise ratio.

**Short nozzle configuration**

The Abel inverted contour plots of \( n=3 \) up to \( n=6 \) for the plasma expansion in which an short nozzle is used is shown in figure 3.5. A hollow profile is observed in the contour plots of the open nozzle case and absent in the short nozzle results. In both cases the excited state density profiles appear to be very narrow in the red part of the plasma, in contrast to the profiles in the blue light emitting plasma.

In case of the short nozzle all excited state densities first experience a rapid decrease which declines after 1 cm from the exit of the arc. Then the excited state densities are about 1 order smaller for the short nozzle compared with the open nozzle. After a minimum, which is not nearly as steep as for the open nozzle, the densities of \( n=4-6 \) start increasing. In the blue afterglow the higher excited state densities exceed the density of \( n=3 \), which is decreasing slowly. Note that in the red light emitting plasma region for \( n=6 \) no lateral OES scans are obtained due to the low signal to noise ratio.

**Radial profiles**

The hollow profile for the excited states \( n=4, 5 \) and 6 is obtained in the red-blue transition when an open nozzle is mounted at the anode endplate, see figure 3.6. From this we conclude that the maximum population inversion is observed towards the edge of the plasma, at \( r=1.2 \) cm, while in the center, at \( r=0 \) cm, no population inversion is observed.
3.4. EXPERIMENTAL RESULTS

3.4.2 Atomic state distribution function

From the excited state densities we can construct an ASDF. In the left part of figure 3.7 two ASDF’s are shown for the open nozzle configuration and on the right side two ASDF’s are shown with a short nozzle configuration. In the graphs...
$I_n$ is defined as $E_+ - E_n$, with $E_+$ the ionization energy of the hydrogen atom and $E_n$ the energy of excited state $n$. On the top left of figure 3.7 an ASDF in the center of the plasma expansion at $z=7$ cm is shown, which resembles the typical ASDF of an ionizing plasma of medium electron density [35]. In bottom left of figure 3.7 an ASDF in the blue light emitting plasma, i.e. at $z=33$ cm from the arc exit, is shown. In the blue light emitting plasma we clearly observe that population inversion of $n=4-6$ with respect to $n=3$ is detected. This shows that there is an input source to the excited states $n=4, 5$ and 6. In the top right of figure 3.7 and ASDF in the red emitting plasma is shown when a short nozzle is mounted at the anode endplate. In the bottom right of figure 3.7, an ASDF at $z=18$ cm is shown. Here we also observe population inversion of $n=4, 5$ and 6 with respect to $n=3$.

3.4.3 The electron temperature and electron density in the plasma

Open nozzle configuration

The electron temperature of the plasma inside the cascaded arc was determined to be around 1.5 eV and the electron density $10^{21-22}$ m$^{-3}$ [36]. From the Hall parameter it follows that the plasma charged particles are not magnetized inside the cascaded arc because of the high electron densities.

Since the Langmuir double probe cannot measure close to the arc exit when an open nozzle is mounted at the anode endplate due to thermoemission of the probe, the electron temperature and electron density cannot be measured in the first 16 cm of the plasma expansion with the mentioned diagnostic. Fortunately, the values of $n_e$ and $T_e$ in the red first part of the expanding plasma column can be determined by the observation of the Fulcher system of H$_2^*$ and the asymptotic behavior of highly excited states of atomic hydrogen. The highly excited states of atomic hydrogen are shown in figure 3.8.

The presence of significant Fulcher radiation shows that the electron temperature is relatively high in the first part of the expansion (open nozzle configuration). The electron temperature can be determined from the absolute density of
3.4. EXPERIMENTAL RESULTS

Open nozzle

Figure 3.7: The atomic hydrogen population density per statistical weight is shown at an axial distance of 7 and 33 cm from the exit of the arc. Both are measured on-axis at \( r=0 \) mm. In the red region a typical ASDF of an ionizing plasma is observed and in the blue light emitting plasma population inversion of \( n=4, 5, 6 \) and 7 with respect to \( n=3 \) is observed.

the Fulcher band via the following balance:

\[
n_e n_{H_2} k^{\text{exc}} = n_{H_2}^* (A_F + n_e k^{\text{de-exc}}).
\] (3.8)

Here \( k^{\text{exc}} = k_0^{\text{exc}} \exp (-E_F/k_B T_e) \) (in \( \text{m}^3\text{s}^{-1} \)) is the electron excitation rate from the ground state \( n_{H_2}(X^1\Sigma_g^+) \) with \( k_0^{\text{exc}} \approx 10^{-15} \text{ m}^3\text{s}^{-1} \) [37], \( A_F=2.5 \cdot 10^7 \text{ s}^{-1} \) the transition probability of the Fulcher transition [38] and \( k^{\text{de-exc}} \approx 1 \cdot 10^{-12} \text{ m}^3\text{s}^{-1} \) the electron de-excitation rate [39]. Furthermore, \( n_{H_2}^* (d^3\Pi_u) \) is the upper state density of the Fulcher band emission and \( n_{H_2} \) is the density of molecular
3. POPULATION INVERSION

3.4. EXPERIMENTAL RESULTS

Figure 3.8: The excited state density as function of the axial position for $n=3$ up to $n=9$ measured on-axis.

hydrogen determined from the ideal gas law. The density of $n_{H_2}$ depends on the gas temperature that is 3500 K close to the arc and drops to 1000 K close to the red-blue transition. The electron temperature can be determined from equation (3.8) with

$$kT_e = \frac{E_F}{\ln\left(\frac{n_{H_2} n_e k_{exc}^e}{n_{H_2}^2 (A_F + n_e k_{de-exc}^e)}\right)}.$$ (3.9)

The electron temperatures obtained with equation (3.9) are shown in figure 3.9a. Since $n_e k_{de-exc}^e > A_F$ in the first 16 cm of the plasma expansion, the electron density drops out.

The electron density in the red part of the plasma expansion can be evaluated by analyzing the excited state distribution, see figure 3.8. The excited states close to the ionization threshold $I_n=E_i-E_n\approx 0$ are represented by the Saha distribution:

$$\frac{n_e^S}{g_n} = \frac{n_e n_i}{g_e g_i} \left(\frac{h^2}{2\pi m_e k_B T_e}\right)^{3/2} \exp\left(\frac{I_n}{k_B T_e}\right),$$ (3.10)

where $g_n$ is the statistical weight of level $n$, $m_e$ the electron mass, $h$ the constant of Planck and $k_B$ the Boltzmann constant. From the overpopulation factor $b_n = n_n/n_n^S$ [35], which relates the excited states densities with the Saha dens-
3.4. EXPERIMENTAL RESULTS

3. POPULATION INVERSION

Figure 3.9: The on-axis electron temperature and electron density with a) the open nozzle configuration and b) the short nozzle configuration.

ity, we calculate that $b_{6-9}$ $\approx$ 1 are close to Saha while the lower excited states are overpopulated with respect to Saha $b_{3-5}$ $>$ 1. The electron density can be determined from equation 3.10, assuming that $n_e = n_i$, $g_e$ = 2 and that the higher excited states are in Saha. The value of $T_e$ obtained from the Fulcher band emission is used in these data since at higher electron densities the overpopulation factor should vary as $b_n = 1 + C T_e ^{-5.5}$, where $C$ is a constant [35].

Note that the overpopulation factor of the lower Balmer levels is due to MAR processes and only for a smaller amount to direct excitation of H atoms by electrons. Dissociative excitation of H$_2$ leading to excited H atom states is here improbable as this excitation is via a repulsive state and thus requires substantial energy.

In figure 3.9(a), we observe that the electron density decreases only slightly from $z$=17 cm to $z$=24 cm, but decreases significantly for larger $z$ values. It should be noted that the decrease in density starts just in front of the maximum population inversion. With an increasing magnetic field the current out of the cascaded arc extends further into the vessel and thereby increases the electron density. The magnetic field is therefore responsible for shifting the red-to-blue transition and also confining the plasma better.

The electron temperature, measured with the Langmuir double probe, is 0.9 eV
at $z=17$ cm and decreases to 0.1 eV at $z=24$ cm from the exit of the arc. After $z=24$ cm the electron temperature remains more or less constant between 0.1-0.15 eV. Increasing the magnetic field strength does not increase the electron temperature.

The electron temperature determined with the absolute Fulcher band emission and the Langmuir double probe clearly shows a nice overlap between $z=17$-19 cm. The comparison of the electron density with the Saha method and the Langmuir double probe shows us that there is overlap as well.

The uncertainty in the observation of the Fulcher system of $H_2^*$ and the asymptotic behavior of highly excited states of atomic hydrogen are approximate and is estimated to be 30%.

Short nozzle configuration

The double Langmuir probe is also used to determine $T_e$ and $n_e$ in plasma expansion when a short nozzle is mounted at the anode endplate, see figure 3.9(b). When comparing $T_e$ and $n_e$ for an open nozzle and a short nozzle, the most obvious difference is the size of the properties in the first part of the plasma, see figure 3.9(a) and (b). Both the electron temperature and electron density start out higher in the plasma expansion generated with an open nozzle. Comparing the open nozzle and short nozzle configuration for $n_e$ and $T_e$ in both shape and value in the blue light emitting plasma we observe the same parallelogram structure.

3.5 Discussion

First, the main population processes in the red emitting part of the plasma will be outlined. Secondly, the hollow profile in the red-blue transition (open nozzle configuration) will be discussed followed by the main processes in the blue light emitting plasma.
3.5. DISCUSSION

3.5.1 The red light light emitting plasma region

As shown in figure 3.4 the densities of excited states is highest measured for \( n=3 \) in the red light emitting part of the plasma expansion. A dominant process in the red light emitting plasma expansion to produce excited atoms is Molecular Activated Recombination (MAR). The creation of this reaction is done in two steps. First, a molecular ion is produced by charge exchange with a proton [40]:

\[
\text{H}_2^{rv} + \text{H}^+ \rightarrow \text{H}_2^{+;rv} + \text{H}(n = 1). \quad (3.11)
\]

In this step, the hydrogen molecule needs to be ro-vibrationally excited since this reaction is otherwise endothermic with an energy deficit of 2.1 eV. The second step is dissociative recombination of \( \text{H}_2^{+;rv} \) in which two hydrogen atoms are produced, i.e. one in the ground state and another in an excited state:

\[
\text{H}_2^{+;rv} + e^- \rightarrow \text{H}(n = 1) + \text{H}(n = 2, 3). \quad (3.12)
\]

Notably, to produce an excited hydrogen atom in a state with \( n \geq 4 \), the ro-vibrationally excited hydrogen molecule should have an internal energy of at least 3.7 eV. Vankan et al showed with VUV-LIF experiments that the internal energy of \( \text{H}_2^{rv} \) close to the arc is not much higher than 2.5 eV [7]. This shows that dissociative recombination is only important in the red part of the plasma expansion populating \( n=2 \) and \( n=3 \). The population of the higher excited states \( n=4 \) and \( n=5 \) can be formed by collisional excitation from \( n=3 \) due to the high electron temperature \( (T_e > 1 \text{ eV}) \).

3.5.2 The red-blue transition

The hollow profile obtained in the red-blue light emitting transition, at \( z=18-22 \) cm, suggests that there is an inward flow of \( \text{H}_2^{rv} \) from the vessel wall producing \( \text{H}^- \) ions [41]. Since the positive ions and electrons are mostly confined in the center of the plasma and the ro-vibrationally excited molecules are more dense away from the center axis of the plasma an optimum of the dissociative attachment process occurs. Hence, the negative ions form a hollow profile and react with the positive molecular ions via the molecular mutual neutralization process to form...
the highly excited states that are observed. The importance of charged particles at the red to blue transition is shown by the influence of the magnetic field on the transition. With an increasing magnetic field the current out of the cascaded arc extends further into the vessel and thereby increases the electron density. The magnetic field is therefore responsible for shifting the red-to-blue transition and also confining the plasma better. Increasing the magnetic field strength does not increase the electron temperature significantly. These results are also confirmed with Thomson scattering by Shumack *et al* [42]. The magnetic field dependence shows that the transition can not be explained by flow patterns, e.g. recirculation cells, because the ionization degree of the plasma is too low to alter the flow because of the presence of charged particles.

In the plasma expansion with a short nozzle configuration a large amount of $H_x^+$ is produced at the nozzle. The reason for the complete absence of a hollow profile at the red-to-blue transition might be that the amount of $H_x^+$ produced via wall association processes at the vessel wall is insignificant compared to the amount of $H_x^+$ produced at the nozzle surface.

### 3.5.3 The blue light emitting plasma

Because of the low electron temperature and relatively high electron density in the blue region, three particle recombination, i.e. $H^+ + e^- + e^- \rightarrow H(n) + e^-$, can become significant on the center axis, i.e. $r$=0 mm. To investigate the importance of three particle recombination on the density of the excited states, an ASDF is constructed from the simulation results of the standard CR-model, see figure 3.10.

The ASDF at $z$=33 cm shows that the CR-model predicts the densities to be more than two orders of magnitude lower than measured. The reason that three-body recombination cannot explain the high densities of the excited states is because the electron densities in the plasma are too low. To discuss the importance of three-body recombination in the blue light emitting plasma the mass balance is used:

$$n_e^3 \cdot k^{3b, \text{rec}} = \frac{n_4}{c_4}. \quad (3.13)$$
3.5. Discussion 3. Population inversion

Figure 3.10: The simulation results that are obtained with an atomic CR-model are compared with the data retrieved from OES at $z=33$ cm. The excited state densities that are obtained with the CR-model are more than two orders of magnitude lower than the OES measurements and the maximum population input is at $n=8$ instead of $n=5$. Note that the measurement is done on-axis ($r=0$ mm) at $z=33$ cm with an open nozzle configuration.

Here, $k^{3b,rec}$ is the three-body recombination coefficient given by $k^{3b,rec}=1.7 \cdot 10^{-39} \cdot T_e^{-9/2}$ $m^6$s$^{-1}$ with $T_e$ in eV and $\tau_4$ the lifetime of state $n=4$. Since $\tau_4^{-1}=A_4=3 \cdot 10^{-7}$ s$^{-1}$, $n_e=3.4 \cdot 10^{17}$ m$^{-3}$ and $T_e=0.16$ eV, the maximum value at $z=33$ cm of $n_4$ is $2 \cdot 10^9$ m$^{-3}$. The value measured with OES is two orders of magnitude higher than obtained with the atomic CR-model. This makes it very improbable that only atomic processes are responsible for the measured high densities in the magnetized hydrogen plasma. Similar results are obtained using a short nozzle configuration.

Therefore, molecular processes such as dissociative recombination and processes with negative ions must populate the excited states of atomic hydrogen. Furthermore, the production rate of each excited state [19] correlates very well with the shape of the cross-section of the molecular mutual neutralization of H$_2^+$ and H$^-$ [24]. To study the importance of these molecular processes an extended
3. Population inversion

3.6 Conclusion

The magnetized hydrogen plasma expansion shows a typical red light emitting region in the first part of the expansion after which a sharp transition to a blue light emitting plasma is observed. The Balmer emission lines of the plasma are investigated with optical emission spectroscopy to determine the absolute densities of electronically excited hydrogen states of \( n=3 \) up to \( n=15 \). From these measurements we observed population inversion of \( n=4-6 \) with respect to \( n=3 \) in the blue light emitting plasma. The electron temperature in the red light emitting part of the plasma is determined from the absolute Fulcher band emission and the electron density from the Saha method by looking at the excited state densities that are close to Saha when an open nozzle configuration is used. In conjunction with the Langmuir double probe measurements a complete picture of \( n_e \) and \( T_e \) is given in the plasma on-axis.

An important part of this paper is devoted to the discussion which population mechanisms are responsible for the population inversion in the blue light emitting plasma. The two most likely population mechanisms proposed for the population inversion in the blue light emitting plasma are three-body recombination of \( \text{H}^+ \) with two electrons and molecular mutual neutralization of \( \text{H}_2^+ \) with \( \text{H}^- \). The importance of the latter process is shown at the red-blue light emitting transition where a hollow profile of the excited states \( n=4-6 \) is observed when an open nozzle is mounted at the anode endplate. The hollow profile could indicate a lateral inflow of \( \text{H}_2^+ \), produced at the reactor walls. This can lead to an increase in asymmetric charge exchange and therefore tip the balance between molecular and atomic recombination. The position of the red to blue light emitting transition is however strongly influenced by the magnetic field strength. This excludes the possibility that the transition is purely caused by flow patterns like recirculation cells. The magnetic field dependence means that the electron density and temperature play an important role in the transition.

Comparing the measured densities with the densities calculated on the basis
of the measured $T_e$ and $n_e$, using an atomic collisional radiative model, leads to the conclusion that atomic recombination processes can not account for the large population densities observed. Therefore, molecular processes such as dissociative recombination and processes with negative ions are suspected to be key in the understanding the mechanisms in the blue light emitting plasma.
Bibliography


Chapter 4

Detailed H($n = 2$) density measurements in a magnetized hydrogen plasma jet

Abstract The first excited state density, $n=2$, is determined with tunable diode laser absorption spectroscopy (TDLAS) on the Balmer-alpha transition to investigate how important molecular processes such as dissociative recombination are in the plasma. The relevance of the presented work is to underline these molecular processes in atomic regimes of hydrogen containing plasmas. The density of $n=2$ is $1 \cdot 10^{17}$ m$^{-3}$ close to the plasma source and decreases gradually along the plasma column to $10^{14}$ m$^{-3}$ at 20 cm from the plasma source exit. The presented results show that creating a stable hydrogen laser in the visible light, i.e. population inversion of $n=3$ with respect to $n=2$, is not possible due to the population of $n=2$ by dissociative recombination of H$_3^+$ ions. A collisional radiative model is used to substantiate the presence of molecular processes in the plasma.

4.1 Introduction

Negative ion sources for neutral beam injection (NBI) in fusion devices are used in a low pressure surrounding and rely mainly on hydrogen particles picking up an electron from a cesium surface [1–4]. For the next generation fusion devices cesium-free negative ion sources need to be developed. To this end alternative methods to create negative ions are explored. One possible route is via non-metallic surfaces, including polycrystalline graphite and highly-oriented pyrolytic graphite (HOPG) which give so far the best surface production of negative ions at carbon surfaces [5, 6]. The negative ion yield obtained on a polycrystalline graphite surface is comparable to that found on Cs or Ba-covered surfaces [7].

Another viable route is through volume processes, where the precursor of \( \text{H}^- \) is a ro-vibrationally excited hydrogen molecule (denoted by \( \text{H}_2^v \)). These molecules are formed by association processes at surfaces [8–13]. The rate coefficient for the dissociative attachment process in which negative atomic hydrogen atoms are formed, depends very strongly on the ro-vibrational excitation of the hydrogen molecule; the rate changes eight orders of magnitude when going from \( v = 0 \) to \( v = 9 \) [14]. The dissociative attachment process for producing negative ions by volume processes is given by

\[
\text{H}_2^v + e^- \rightarrow \text{H}_2^- \rightarrow \text{H} + \text{H}^-.
\]  

(4.1)

The metastable \( \text{H}_2^- \) ion fragments fast into a H atom and a \( \text{H}^- \) ion [15].

For the creation of the plasma expansion a cascaded arc is used as a plasma source [16]. The cascaded arc has been studied extensively in Eindhoven by Kroesen [17] and van de Sanden [18, 19]. From earlier work, it is known that the cascaded arc provides high fluxes of excited and reactive species such as ions, radicals and ro-vibrationally excited molecules albeit at relatively low electron temperatures of 0.2-0.3 eV [20–23]. To exploit a high plasma density and reduce the fast molecular activated recombination (MAR) processes a low background pressure of 7-10 Pa in combination with an external parallel magnetic field is used. By applying the magnetic field a 40 cm long confined plasma column
with a width of 2-4 cm is created. At about 20 cm from the arc exit a sharp transition from an ionizing red light emitting plasma to a recombining blue light emitting plasma occurs [24, 25], see figure 4.1. The exact shape and position of the red to blue transition depends on the system settings, e.g. background pressure, magnetic field, hydrogen flow, and both nozzle length and geometry.

Figure 4.1: The magnetized hydrogen plasma jet created by a cascaded arc. The visible part of the plasma jet, i.e. the red and blue emitting region, is roughly 40 cm long in total and the red-to-blue transition occurs at approximately 20 cm from the arc exit. The four Helmholtz coils (indicated as "Coils") apply an external magnetic field to the plasma.

To investigate the population processes in the plasma the excited state densities of atomic hydrogen have to be determined. In our previous paper we reported on the measurement of excited state densities of $n=3$ up to $n=15$ by optical emission spectroscopy (OES) and a discussion on the important population processes in the plasma was started [25]. To determine the spatially resolved first excited state density of $n=2$, tunable diode laser absorption spectroscopy (TDLAS) and Abel inversion [26] are used. Shumack et al showed how the first excited state density can be determined with TDLAS [27]. They measured close to the exit of the arc where the electron density and temperature are high so that fine structure is small compared to Doppler and Stark broadening. The first excited state density ($n=2$) is important to determine since it gives us valuable information about the dissociative recombination processes of $\text{H}_2^+$ and $\text{H}_3^+$ in the plasma.
4. ABSORPTION SPECTROSCOPY

4.1. INTRODUCTION

In the previous paper it was also shown that atomic processes alone cannot explain the two distinct plasma regions (the red and blue light emitting plasma) and therefore we concluded that molecular processes such as dissociative recombination and processes with negative ions are suspected to be key in the understanding of the underlying mechanisms. A summary of the important population processes to the excited states of atomic hydrogen, as discussed in ref.[25], is shown in table 4.1.

Table 4.1: The dominant reaction mechanisms for the production of the excited hydrogen atoms in the magnetized hydrogen plasma [25, 28].

<table>
<thead>
<tr>
<th>Reaction process</th>
<th>Production of H((nl))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2^+ + e^- \rightarrow H((nl)) + H)</td>
<td>dissociative recombination</td>
</tr>
<tr>
<td>(\text{H}^+ + \text{H}^- \rightarrow H((nl)) + H)</td>
<td>atomic mutual neutralization</td>
</tr>
<tr>
<td>(\text{H}_2^+ + \text{H}^- \rightarrow H((nl)) + \text{H}_2)</td>
<td>molecular mutual neutralization</td>
</tr>
<tr>
<td>(\text{H}^+ + e^- + e^- \rightarrow H((nl)) + e^-)</td>
<td>three-body recombination</td>
</tr>
<tr>
<td>(\text{H}_3^+ + e^- \rightarrow H((nl)) + \text{H}_2)</td>
<td>dissociative recombination</td>
</tr>
</tbody>
</table>

To give additional prove that molecular processes are present in the plasma an extended collisional radiative model (CR-model) is used [29]. To investigate the population processes with the CR-model the electron density and electron temperature needs to be determined. These plasma parameters were obtained with a double Langmuir probe, in ref.[25], but close to the arc probe glowing occurs due to the high electron temperature. Therefore, Stark broadening is included in the fitting of the Balmer-alpha absorption lineshape (obtained from the TDLAS measurements) to determine the electron density in the first 9 cm of the expansion.

In the blue light emitting plasma, population inversion is observed between the level pairs \(n=3-4, n=3-5, n=4-5\) and \(n=3-6\) with optical emission spectroscopy. The molecular mutual neutralization process of \(\text{H}_2^+\) and \(\text{H}^-\) was introduced to be an important population process to explain the highly excited state densities that were obtained with the experiments. The presence of this population process could explain the two differently observed plasma regions [25]. The cross-sectional data of the molecular mutual neutralization process was calcu-
lated by Eerden et al. The calculations by Eerden showed that the excited state densities of \( n=2-9 \) are mainly populated and that it has a maximum for \( n=4-7 \) [30]. The observed population inversion has already been observed by several other groups in hydrogen-like plasmas by for example Bohn [31]. Very closely related is the work presented by Akatsuka et al [32] and Shibagaki et al [33]. However, it was never experimentally verified if population inversion with respect to \( n=2 \) occurs. This may give more information about the potential creation of a continuous wave laser in the visible region. Theoretically, population inversion of \( n=3 \) with respect to \( n=2 \) has been shown by Ali et al [34]. Since the main input in the blue emitting plasma is to the excited states \( n=4-7 \) population inversion of \( n=3-7 \) with respect to \( n=2 \) could occur.

In the presented work, the first excited state density of atomic hydrogen along the full plasma length is determined and more data points on the wings of the plasma are measured to get a more accurate fitting procedure. In the blue light emitting plasma fine structure has to be included in the fitting procedure since the gas temperature is lower than in the red light emitting plasma. The molecular activated recombination processes along the full plasma length will be investigated by looking at the first excited state density. A collisional radiative model will be used to substantiate the conclusions from the experiments.

### 4.2 Experimental setup and diagnostics

#### 4.2.1 Plasma source

The linear plasma generator called PLEXIS (PLasma EXpansion in Interaction with Surfaces), consists of a cascaded arc plasma source [16] placed inside a stainless steel expansion chamber. The cascaded arc is mounted on a movable arm, which allows for spatial measurements while keeping the diagnostics fixed at the window ports. The plasma is ignited by three cathodes and it is sustained inside by four insulated stabilizing plates with a bore diameter of 4 mm. The hydrogen flow is 3000 sccm in the cascaded arc at a pressure of approximately \( 10^4 \) Pa. The current through each of the cathodes is 15 A and the discharge
4. Absorption spectroscopy

4.2. Experimental setup and diagnostics

The voltage is around 150 V, giving a total input power to the plasma of 6.8 kW. A short open nozzle is mounted at the end of the plasma source as it provides optimal conditions for studying population inversion [35]. The open nozzle has an inner diameter of 9.6 mm and is 7 mm long. Subsequently, the plasma can freely expand into a low pressure surrounding of 8 Pa. Due to the large pressure difference between plasma source and vacuum vessel a supersonic expansion is formed. This introduces a shock when the pressure of the jet approaches the background pressure, after which the plasma expands sub-sonically [36]. Four Helmholtz coils are mounted around the vessel, as shown in figure 4.1, to produce an axial uniform magnetic field of 14 mT over a length of approximately 1.4 m to confine the charged particles in the plasma.

4.2.2 Absorption spectroscopy

The TDLAS set-up is based on a continuous wave TLB-7005 external-cavity diode laser with a power of 4 mW, operating according to the Littman-Metcalf principle [37, 38]. The diode laser has a tunable range from 656.33 to 656.60 nm around the H$_\alpha$ line. The absorption spectrum of the plasma is measured as the tunable diode laser scans its wavelength range. The change in the laser frequency is monitored with an etalon, that has a free spectral range of $9.95 \pm 0.07$ pm (approximately 6.9 GHz). The short term line width of the laser is $<500$ kHz for a period of 50 ms. The measurement time of one spectrum is approximately 1 minute. For this period the line width is estimated to be 10 MHz, using the Root Allen theorem [39]. This shows that in analyzing the line profiles of the absorption spectrum, the laser line width does not have to be taken into account. The polarization of the laser is chosen horizontally, parallel to the magnetic field so the Zeeman splitting of the H$_\alpha$ line can be neglected. The laser intensity is measured before it enters the vessel, behind the etalon and 2.5 m after the laser bundle passes the plasma reducing the amount of direct plasma light on the detector, see figure 4.2. The first photo-diode is used for the wavelength calibration, the second for the background signal and the last photo-diode is used to measure the absorption signal. Brewster windows are mounted on the diagnostic ports of the
plasma vessel to minimize interference effects from the laser beam. The spatial resolution is 3 mm and determined by the laser diameter inside the plasma.

The absorption of the laser light along its optical path is determined by the Lambert-Beer law, given by

$$I(\nu) = I_0(\nu) \exp \left( - \int_0^L \sigma_{23}(\nu) n_2 dl \right),$$  \hspace{1cm} (4.2)

where $I_0(\nu)$ and $I(\nu)$ are the intensities of the laser [in W] respectively before and after absorption, at the laser frequency $\nu$ [in s$^{-1}$]. The frequency dependent absorption cross-section of the He transition is indicated by $\sigma_{23}$ [in m$^2$], and $n_2$ is the local $H(n=2)$ density [in m$^{-3}$], which is integrated over the absorption path length $L$ [in m]. The absorption cross-section of the He line $\sigma_{23}$ is given by

$$\sigma_{23}(\nu) = \frac{c^2}{64 \pi \nu_3^2} \sum_{k=1}^{7} A_{32k} \nu_k G(\nu - \nu_{32}^k),$$  \hspace{1cm} (4.3)
which is a summation over the individual sub-transitions that make up the H\textsubscript{\alpha} line, as given in table 4.2. The 7 sub-transitions are indicated by $k$, with $A_k^{nm}$ the Einstein coefficients [in s$^{-1}$], $g_k^U$ the degeneracy of the upper state, $\nu_k^{nm}$ the transition frequency, and $G$ the lineshape of each transition. The central frequency of the H\textsubscript{\alpha} line, averaged over the sub transitions, is given by $\nu_{\alpha \Omega}$ and $c$ indicates the speed of light.

**Table 4.2:** The wavelength, energy and transition probabilities of the optically allowed transitions between the excited states $n = 2$ and $n = 3$ [42].

<table>
<thead>
<tr>
<th>k</th>
<th>Frequency [cm$^{-1}$] (vacuum)</th>
<th>Transition $m-n$</th>
<th>$g_k^U$</th>
<th>$g_k^S$</th>
<th>$A_{nm}$ [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15233.4006</td>
<td>2$p-3d$</td>
<td>2</td>
<td>4</td>
<td>$5.388 \times 10^7$</td>
</tr>
<tr>
<td>2</td>
<td>15233.3655</td>
<td>2$s-3p$</td>
<td>2</td>
<td>4</td>
<td>$2.245 \times 10^7$</td>
</tr>
<tr>
<td>3</td>
<td>15233.3029</td>
<td>2$p-3s$</td>
<td>2</td>
<td>2</td>
<td>$2.104 \times 10^6$</td>
</tr>
<tr>
<td>4</td>
<td>15233.2571</td>
<td>2$s-3p$</td>
<td>2</td>
<td>2</td>
<td>$2.245 \times 10^7$</td>
</tr>
<tr>
<td>5</td>
<td>15233.0709</td>
<td>2$p-3d$</td>
<td>4</td>
<td>6</td>
<td>$6.465 \times 10^7$</td>
</tr>
<tr>
<td>6</td>
<td>15233.0347</td>
<td>2$p-3d$</td>
<td>4</td>
<td>4</td>
<td>$1.078 \times 10^7$</td>
</tr>
<tr>
<td>7</td>
<td>15232.9370</td>
<td>2$p-3s$</td>
<td>4</td>
<td>2</td>
<td>$4.209 \times 10^6$</td>
</tr>
</tbody>
</table>

The lineshape function $G$ is based on both Doppler and Stark broadening. Any other broadening effects are negligible under the experimental conditions of the investigated plasma. The Stark broadening, caused by collisions of the charged particles, only becomes significant at electron densities above $10^{19}$ m$^{-3}$ [43, 44]. Below this density the lineshape function can be described purely by a Gaussian, since at those conditions the thermal motion of the particles is the main broadening mechanism, i.e. Doppler broadening. In thermal equilibrium this results in a single Gaussian profile with a full width half maximum (FWHM) $\Delta\nu_D$ described by

$$\Delta\nu_D = 2\nu_{\alpha \Omega}\sqrt{\frac{2k_B T_{\text{gas}} \ln 2}{mc^2}}.$$  \hspace{1cm} (4.4)

Here $k_B$ is the Boltzmann constant, $T_{\text{gas}}$ the gas temperature and $m$ the mass of
4.2. EXPERIMENTAL SETUP AND DIAGNOSTICS

4.3. ABSORPTION SPECTROSCOPY

The Stark broadening of the $H_\alpha$ absorption line results in a Lorentzian lineshape. For low electron densities, around $10^{19}$ m$^{-3}$ and lower, the Stark broadening is best described with the impact approximation [45, 46], see figure 4.3. The impact approximation includes a contribution for the motion of the ions. The quasi-static approximation, by Kepple and Griem [47, 48], neglects the motion of the ions which gives a serious underestimation of the Stark broadening at electron densities below $10^{22}$ m$^{-3}$ [43, 44]. The FWHM of the Stark broadening $\Delta \nu_S$, determined by Stehlé and Feautrier [45, 50] using the impact approximation, is given by

$$\Delta \nu_S = \frac{1.55 \cdot 10^{-10} n_e}{\pi} \sqrt{\frac{m}{T_i M_e}} \left[ 27.54 + \ln \left( 10^6 \frac{T_D T_i m_e}{n_e m'} \right) \right]. \quad (4.5)$$

**Figure 4.3:** Comparison of different calculations for the Stark broadening FWHM. For $n_e < 10^{19}$ m$^{-3}$ the impact approximation [45] shows good agreement with Full Computer Simulation Methods (FCSM)$^A$ simulations by Olchawa et al [43]. At higher densities the FCSM$^A$ by Gigosos et al [49] and the FCSM$^B$ overlap. The quasi-static approximation [47] shows a serious underestimation of the broadening at $n_e < 10^{22}$ m$^{-3}$. 
Here the reduced mass \( m' \) is \( m_i \frac{m_x}{m_i + m_x} \) with \( m_i \) and \( m_x \) respectively the ion perturber and emitter mass. The reduced temperature \( T_D \) is \( T_i T_e/(T_i + T_e) \) with \( T_i \) and \( T_e \) the ion and electron temperature respectively [in K]. The electron mass is given by \( m_e \) [in kg]. The derivation of eq.(4.5) uses a cut-off procedure to avoid problems with low impact parameters (strong collisions), which only makes it valid for \( T_i > 2000 \) K [46]. The Stark broadening is assumed to be the same for all sub-transitions.

The convolution of a Doppler and Stark broadened lineshape gives a Voigt profile for the lineshape function \( G \). The total combined lineshape of the H\( \alpha \) line is a summation over the 7 shifted lineshapes, as described in eq.(4.3). The actual absorption spectrum, described by the absorption \( X_{abs} \), is given by

\[
X_{abs}(\nu) = 1 - \frac{I(\nu)}{I_0(\nu)} \approx \sigma_{23}(\nu) N_{2\ LOS}.
\] (4.6)

The approximation on the right hand side follows from eq.(4.2) for an optically thin plasma [51]. Note that in the above approximation a constant cross-section is assumed along the laser’s line of sight (LOS). The integral over the local density along the laser’s LOS is replaced by the integrated LOS density \( N_{2\ LOS} \) [in m\(^{-2}\)], which is defined as

\[
N_{2\ LOS} = \int_0^L n_2 dl.
\] (4.7)

Each measurement has to be calibrated with a reference measurement to compensate for loss of laser power elsewhere in the system, e.g. by interference in the optics. The actual measured absorption \( X_{abs, \ meas} \), is therefore described by

\[
X_{abs, \ meas}(\nu) = 1 - \frac{I_{abs}(\nu)/I_{abs, \ D}(\nu)}{I_{ref}(\nu)/I_{ref, \ D}(\nu)} \cdot C_{norm}.
\] (4.8)

Here the intensities, \( I(\nu) \) and \( I_0(\nu) \), from the absorption measurement are divided by the intensities from a reference measurement. During a reference measurement the magnetic field is turned off and the plasma source is moved away so that during the reference measurement no laser absorption is measured. The absorption and reference measurements are indicated with respectively the subscripts \( abs \) and \( ref \). Also included in eq.(4.8) is a normalization factor, \( C_{norm} \), which sets the absorption baseline to zero. The normalization factor compensates
for small system fluctuations between absorption and reference measurements, e.g. the photo diode sensitivity, and is typically between 0.996 - 1.004. To avoid measuring spectra in the saturation regime, the absorption has been recorded as function of the laser power. All data have been obtained with laser powers below the saturation regime.

The local excited state densities are obtained with Abel inversion by fitting lateral LOS density profiles with a series of Gaussians [25, 26].

### 4.3 Results

#### 4.3.1 Absorption spectra

The absorption spectra measured with the TDLAS set-up at $z=0.5$ cm from the nozzle exit is shown in figure 4.4. The spectrum is averaged over 4000 scans at a frequency of 81 Hz resulting in a measurement time of about 1 minute. The residue in figure 4.4 shows that close to the arc Stark broadening significantly improves the fit values on the wings of the absorption profile. The absorption measurement is combined with a reference measurement as described in eq.(4.8), since the system changes gradually over the course of several minutes due to temperature changes of the vessel wall. In figure 4.5, the absorption spectra at two other positions are shown namely $z=5$ cm and $z=19$ cm. All obtained spectra in the first 9 cm of the plasma expansion are fitted with Stark broadening included. Further downstream Doppler broadening is sufficient for the fitting of the line profile due to an electron density that is lower than the electron density in the first part of the expansion. An asymmetric line profile in the frequency spectrum is visible after $z=9$ cm which indicates the presence of fine structure. In figure 4.5, the fine structure at $z=19$ cm is visible due a low gas temperature of 1000 K and a low electron density of $3 \times 10^{18}$ m$^{-3}$.

The presence of Stark broadening in the absorption spectra for $z<9$ cm also enables the estimation of the LOS averaged electron densities. The Stark broadening is used to estimate the electron density at $z=0.5$ cm at around $10^{20}$ m$^{-3}$, as shown in figure 4.6. The electron densities determined from Stark broadening
4.3.2 The local excited state densities of H($n = 2$)

The local excited state densities of H($n=2$) [in m$^{-3}$] are obtained with Abel inversion performed on the determined LOS densities. In figure 4.7, the measured LOS density profiles are fitted with a series of Gaussians. The minimum detectable absorption is 10$^{-4}$ and the maximum measured absorption is 0.1. The LOS density decreases from $1.55 \times 10^{15}$ m$^{-2}$ at $z=0.5$ cm down to the detection limit of $10^{12}$ m$^{-2}$ at $z=33$ cm. This gives TDLAS a dynamic range of three orders of magnitude in detecting the first excited state density of atomic hydrogen. The uncertainties of the first excited state density obtained

\textbf{Figure 4.4:} Absorption spectrum at $z=0.5$ cm in the plasma expansion. The experimental data is fitted with two different strategies. The red line includes Doppler and fine structure in the fitting procedure and the blue line includes Doppler, fine structure and Stark broadening. The residue of both fitting procedures are shown at the bottom.

overlap well with previous measured electron densities using the Saha equation [25].
4.3. RESULTS

4. ABSORPTION SPECTROSCOPY

Figure 4.5: Absorption spectra at $z=5$ cm and $z=19$ cm in the plasma expansion. The experimental data at $z=5$ cm is fitted with two different strategies. The red line includes Doppler and fine structure in the fitting procedure and the blue line includes Doppler, fine structure and Stark broadening. The experimental data at $z=19$ cm is not fitted with Stark broadening due to the low electron density.

with TDLAS are expected to be around 6% in the red emitting plasma and the uncertainties increase to 10-20% in the blue emitting plasma due to the lower absorption signal.

In figure 4.8, the local H($n=2$) density measurements per statistical weight in the plasma vessel are shown. The contour plot is constructed by using a standard interpolation technique between the data points. The plasma expansion starts at $z=0$ cm and $r=0$ cm. The local excited state density profiles show that the expansion starts out with a very narrow lateral profile. After the transition to the blue light emitting plasma the profile broadens and a small increase of density is observed. The increase of the first excited state ($n=2$) in the blue light emitting plasma is believed to be caused by dissociative recombination of $H_3^+$ ions. The $H_3^+$ ions are created by $H_2^+$ collisions with the background gas of $H_2$ as demonstrated by de Graaf in a non-magnetized hydrogen plasma expansion [23]:

$$H_2^+ + H_2 \rightarrow H_3^+ + H.$$  \hspace{1cm} (4.9)
Figure 4.6: The on-axis electron densities are determined from the Stark broadening in the absorption spectra and these results are compared with earlier work [25].

The presence of H$_3^+$ ions in the plasma can be shown by increasing the pressure: the increase of H$_3^+$ with increasing background pressure has been observed by looking at the intensity of the blue emitting plasma. The increased collisions of H$_2^+$ ions with the background gas diminishes the excitation in H($n$=4-7) through the molecular mutual neutralization process of H$_2^+$ and H$^-$. Dissociative recombination of H$_3^+$ can occur via two different reaction channels [52]. The products are either three hydrogen atoms in their ground state or a molecule and an excited atom. The latter reaction is given by:

$$H_3^+ + e^- \rightarrow H_2 + H(n).$$  \hspace{1cm} (4.10)

Since the distribution of the excited states in this process is not exactly known, the cross-sectional data and branching ratios are used from experiments performed by Datz et al in a storage ring [53]. Datz showed that dissociative recombination of H$_3^+$ ions mainly populate the first excited state of n = 2.

In the first part of the expansion direct excitation from the ground state is important for the population of $n=2$ due to the high electron temperature of 2 eV. Further downstream the electron temperature drops gradually until $z=18$ cm.
After that distance from the arc, the electron temperature drops fast and direct excitation plays no role in the formation of \( n=2 \) due to the too low electron temperature of \( \sim 0.2 \) eV. Therefore, another reaction should be responsible for the increase of \( n=2 \) in that region. As already mentioned the \( \text{H}_2^+ \) ion is formed along the plasma column due to MAR-processes and it is key in explaining the high density of the first excited state in the blue emitting plasma. Janev et al have shown that the dissociative recombination rate of \( \text{H}_2^+ \) ions producing \( n=2 \) is \( k=2 \cdot 10^{-15} \, \text{m}^3/\text{s} \) at an electron temperature of 0.2 eV [28].

The on-axis local densities of the excited states obtained with both TDLAS
and OES are shown in figure 4.9. For \( z > 20 \text{ cm} \) the excited state densities show population inversion for the higher excited states \( n=4 \) and 5 with respect to \( n=3 \). However, the high density of \( n=2 \) along the full plasma length makes population inversion of the higher excited states with respect to \( n=2 \) not possible.
4.3. RESULTS 4.3.3 Temperature profiles

The temperature of the \( n=2 \) atoms is obtained from the fitted full width half maximum (FWHM) of the Balmer-alpha absorption transition spectra. In figure 4.10, the temperature profiles determined from the fits are shown. In figure 4.10a we see the on-axis temperature while in figure 4.10b and 4.10c the lateral profiles at respectively \( z = 11 \) cm and \( z = 17 \) cm are shown. From the on-axis temperature profile we observe that the plasma expansion cools from 2100 K at \( z = 0.5 \) cm to 1100K for \( z = 7 \) cm. A faint indication of a shock at \( z = 9 \) cm is observed but the uncertainties in the temperature prevent a clear determination of the temperature rise. The shock at \( z = 9 \) cm is confirmed with Two-Photon Absorption Laser Induced Fluorescence (TALIF) measurements on the ground state density of atomic hydrogen and the gas-expansion theory, \( z_m = 1.8 \times 10^{-2} (\dot{\Phi}/p_b)^{1/2} (AT_s)^{1/4} \approx 9 \) cm. Here \( z_m \) is the position at which the shock occurs [in cm], \( \dot{\Phi} \) the flow [in scc/s], \( p_b \) the background pressure [in Pa], \( A \) the mass number and \( T_s \) the tem-

Figure 4.9: On-axis local densities of the excited states, the lines are a guide to the eye. For \( z > 20 \) cm the excited state densities show population inversion for the higher excited states \( n=4,5 \) and 6 with respect to \( n=3 \) but not with respect to \( n=2 \).
perature of the plasma in the source which is 1.5 eV [54]. Further downstream in the plasma, at an on-axis position of \( z=20 \) cm, clear local heating in the gas temperature is observed. This rise in temperature is preceded at \( r=2 \) cm for \( z=17 \) cm, which is exactly at the transition where the plasma changes from the red to the blue light emitting plasma. Here, we will argue that this local heating may be caused by a double layer. The strength of the magnetic field, which mainly affect the charged particles, changes the shape and position of the red to blue transition. Measurements of the electron density and temperature have shown that the plasma is divided into two different regions. The red emitting plasma is characterized by a high electron temperature with \( T_e > 1 \) eV, while the blue afterglow is relatively cold with an electron temperature \( T_e \) around 0.2 eV. The resulting temperature gradient could sustain the double layer.

The first excited state density is mainly populated by dissociative recombination of both \( \text{H}_2^+ \) and \( \text{H}_3^+ \) and direct excitation of atomic hydrogen. Charge exchange of an ion with an excited state of atomic hydrogen is a very efficient process which can couple the excited states to the ions [55]. This introduces a coupling between the neutral excited states and the ions in the plasma. The temperature of the H atoms in the \( n=2 \) excited state can thus also contain a component from the ion temperature and therefore give an overestimation of the neutral gas temperature.

The uncertainties in the gas temperature are mainly caused by Stark broadening in the absorption spectra for \( z<9 \) cm. The Stark parameter that is required to analyze these spectra gives some degree of freedom in the analysis. By looking at the chi-square value and the residue we observe a clear improvement of the fit by including Stark broadening. For \( z>9 \) cm a small Stark component could still be present but it does not improve the residue much. Neglecting Stark effect for \( z>9 \) cm could lead to an overestimation of the temperature of about 100 K. Since this contribution is small, the trends in the temperature profile will remain the same.

A second contribution to the uncertainty of the gas temperature for \( z<9 \) cm is the initial supersonic expansion of the plasma. The expansion causes a net outflow of the neutral particles with velocities around 7000 m s\(^{-1}\) [56].
4.3. RESULTS

4. ABSORPTION SPECTROSCOPY

Figure 4.10: The gas temperature profiles as determined from the Doppler broadening of the absorption spectra. The lines between the data points are a guide to the eye. a) Shows the on-axis gas temperature as function of $z$ and in b) and c) lateral gas temperature profiles at $z=11$ cm and $z=17$ cm are given respectively.

Doppler broadening measured with TDLAS is averaged along the LOS of the measurement. Any outflow of particles to the sides will therefore be averaged out in all directions, resulting into an additional Doppler broadening of the spectra. The Doppler broadening caused by the expansion can be significant compared to the measured Doppler broadening. The initial expansion of the plasma can thus lead to an overestimation of the gas temperature as determined from the Doppler broadening. Lateral temperature profiles indicate that this effect could be important up to $z=5$ cm.
4.3.4 A collisional radiative model

In the previous paper we have shown, with an atomic CR-model, that atomic processes cannot account for the large population densities observed in the plasma. Therefore, it was concluded that molecular processes must play a dominant role in the formation of excited state densities of atomic hydrogen in the plasma. The molecular mutual neutralization process of $\text{H}_2^+$ with $\text{H}^-$ was proposed to be very important for the population of $n=4$-7 in the blue emitting plasma [25]. In this work an extended CR-model is used in which channels of molecular species and negative ions are added [29]. In figure 4.11, an atomic state distribution function (ASDF) is constructed in the blue light emitting plasma at $z=25$ cm. The spatially

![Figure 4.11](image_url)
resolved excited state densities per statistical weight of $n=2$ up to $n=9$ are plotted versus the quantum state $n$.

In figure 4.11, the importance of the dissociative recombination process of $\text{H}_3^+$ in the blue emitting plasma is simulated with the $\text{C}_\text{H}_3^+$ channel. The simulation result shows that the dissociative recombination process of $\text{H}_3^+$ is mainly responsible for the population of $n=2$. The density of $n_{\text{H}_3^+}=3 \cdot 10^{18}$ m$^{-3}$ is simulated with an uncertainty of 50%. The second excited state $n=3$ mainly by dissociative recombination of $\text{H}_2^+$ (denoted by $\text{C}_\text{H}_2^+$) and atomic mutual neutralization (denoted by $\text{C}_{\text{H}^-}$). Note that excitation and de-excitation processes are not important in the blue emitting plasma due to the low electron temperature of 0.2 eV. From figure 4.11 we observe that the $\text{C}_{\text{H}^-}$ channel is very important for populating $n=3-8$. The $\text{C}_{\text{H}^-}$ channel is a superposition of the molecular mutual neutralization process of $\text{H}_2^+$ with $\text{H}^-$ and the atomic mutual neutralization of $\text{H}^+$ with $\text{H}^-$. The atomic mutual neutralization process mainly populates the $n=3$ state and the molecular mutual neutralization process mainly $n=4-7$ [30]. The simulation results of the excited states $n=4-7$ only show a good resemblance with the experimental results when the molecular mutual neutralization is included. In an upcoming paper the simulation results on the magnetized hydrogen plasma expansion will be thoroughly explained and discussed [57].
4.4 Conclusion

Spatially resolved measurements on the first excited state density have been performed to show that molecular activated recombination processes are dominantly present in the hydrogen plasma expansion that is weakly magnetized. Previous studies have shown that ro-vibrationally excited hydrogen molecules are created at the nozzle surface [13]. These molecules penetrate into the low pressure surrounding creating negative ions via the dissociative attachment process. Since the ro-vibrationally excited hydrogen molecules inherit internal energy, charge exchange with H\(^+\) is possible to create H\(_2\)\(^+\) ions. The created H\(_2\)\(^+\) ions interact with the background gas to form H\(_3\)\(^+\) ions or populate the excited states \(n=4-7\) via the molecular mutual neutralization process. The presence of H\(_3\)\(^+\) ions in the blue light emitting plasma has been simulated with the extended CR-model and is \(n_{H_3^+}=3 \cdot 10^{18} \text{ m}^{-3}\) with an uncertainty of 50\%. The production of H\(_3\)\(^+\) ions is strongly influenced by the background pressure. Maintaining a low background pressure reduces the conversion of H\(_2\)\(^+\) ions into H\(_3\)\(^+\) ions, and thereby minimizes the destruction of the blue light emission. The dissociative recombination process of H\(_3\)\(^+\) producing \(n=2\) is believed to be the main reason why population inversion of the excited states \(n=3-7\) with respect to \(n=2\) is not observed in the blue light emitting plasma.
Bibliography


Chapter 5

Application of a collisional radiative model in a magnetized hydrogen plasma expansion

Abstract  In this chapter a collisional radiative model is described that simulates the processes that determine the (de-)population of excited states of atomic hydrogen in a magnetized hydrogen plasma expansion. The high excited state densities of atomic hydrogen, present in the blue light emitting plasma region, is attributed to the molecular mutual neutralization process of H₂⁺ and H⁻ forming a hydrogen molecule and an excited atom. The low electron temperature and high negative ion density in the blue light emitting plasma region gives optimal conditions for populating \( n=4-7 \) by the molecular mutual neutralization process as will be demonstrated by simulation. The simulation results demonstrate that the negative hydrogen ion density is \( 10^{16} \) m\(^{-3} \) in the red light emitting plasma region and increases in the blue light emitting plasma region to \( 10^{17} \) m\(^{-3} \).
5.1 Introduction

Studying hydrogen plasmas is of great importance from a fundamental point of interest since hydrogen is the most abundant molecule in the known universe and also the simplest to work on, from a theoretical point of view. From an application point of interest, hydrogen containing plasmas are studied because of their potential in surface modification, thin film deposition [1, 2] and for the creation of negative ions in particle accelerators [3] and in neutral beam injectors for fusion devices [4]. In the work presented here the hydrogen plasma under investigation is expanding in a low pressure surrounding and is created by a cascaded arc plasma source. When an external magnetic field is applied in the parallel direction of the expansion a confined plasma column is created with two distinct regions [5–8]. At a specific position from the source of the expansion a sharp transition from an "ionizing" red light emitting plasma (dominated by H\(_\alpha\) emission) to a "recombining" blue light emitting plasma (dominated by H\(_\beta\) and H\(_\gamma\) emission) occurs, see figure 5.1. The transition of red to blue light emission is not well understood but it is known that the exact shape and position of the transition depends on the system settings, e.g. background pressure, input power, magnetic field strength, hydrogen flow, and nozzle length. A Collisional Radiative model (CR-model) is applied in this work to identify the relevant processes in the plasma. Previous studies on the same kind of plasma expansion have shown that atomic processes alone cannot explain the two different regions in the magnetically confined expanding plasma due to the too low electron temperature and too low electron density [8, 9]. Therefore, molecular processes are suspected to be key in the understanding of the underlying mechanisms.

To identify the relevant processes in the magnetized hydrogen plasma expansion the local excited state densities of atomic hydrogen need to be measured by several diagnostics. The first excited state density of hydrogen (\(n=2\)) is determined with Tunable Diode Laser Absorption Spectroscopy (TDLAS) by looking at the H\(_\alpha\) absorption line and the higher excited state densities of \(n=3\) up to \(n=15\) are determined from the Balmer line emission with absolute Optical Emission Spectroscopy (OES). Since both diagnostics measure line of sight profiles, Abel
5.1. INTRODUCTION

Collisional radiative model inversion is applied to get the local excited state densities [10]. The results of

\[
\begin{align*}
\text{n}=2 & \quad \text{n}=3 & \quad \text{n}=4 & \quad \text{n}=5 & \quad \text{n}=6 & \quad \text{n}=7 & \quad \text{n}=8 & \quad \text{n}=9 \\
\text{z (cm)} & \quad 0 & \quad 10 & \quad 20 & \quad 30 & \quad 40 \\
\end{align*}
\]

Figure 5.1: The on-axis local excited state densities of atomic hydrogen, known from Abel inversion, are determined for \( n=2 \) up to 9 as function of \( z \). By applying an external magnetic field to the plasma of 14 mT a 40 cm long plasma column is created with two distinct plasma regions. The used system settings: a hydrogen flow of \( \phi_{H_2} = 3000 \) sccm, a background pressure of 9 Pa and an input power of 6.8 kW.

From figure 5.1 it is observed that population inversion of the excited states \( n=4, 5 \) and 6 with respect to \( n=3 \) is present in the blue emitting plasma region.

The excited state densities are discussed in detail in [8, 11] and are shown in figure 5.1. For the interpretation of these spectroscopically measured densities population models are needed. Such models calculate the population densities of excited atoms depending on the plasma parameters.
This population inversion has also been observed by Akatsuka et al albeit with a different plasma source [12]. In literature, the population process to the excited states in the blue emitting plasma region has been ascribed to be three-body recombination, i.e. the recombination of a proton (H\(^{+}\)) with two electrons, as recently reported by Shibagaki [13] for observations in a RF-plasma. When discussing three-body recombination in this work we implicitly also include radiative recombination to the discussion. In the thesis work of Qing, three-body recombination was excluded as being an important population process for \(n=4, 5\) and 6 in the blue light emitting plasma region because to account for the high densities the required electron density must be one order of magnitude higher and the electron temperature lower that measured with the diagnostics [9]. The simulation results from a Collisional Radiative model (CR-model) showed that atomic processes have a minor contribution to the population of the excited states in the blue light emitting plasma region [8]. Therefore, additional prove was given that molecular processes play a key role in the formation of the highly excited states. The importance of molecular processes in non-magnetized hydrogen plasma expansions were discussed extensively by both de Graaf [14] and Meulenbroeks [15] at intermediate pressure (100 Pa) and by Eerden et al [16] in magnetized hydrogen plasma expansions at low pressure (10 Pa). In the latter case the molecular mutual neutralization process

\[
\text{H}_2^+ + \text{H}^- \rightarrow \text{H}(n) + \text{H}_2, \quad \text{with } n = 2 - 9 \quad (\text{A}^* - \text{process}) (5.1)
\]

for populating the excited states of atomic hydrogen was proposed to be important (abbreviated by A\(^*\)-process, where A\(^*\) stands for atomically excited). The cross sections for populating \(n=2-9\) were calculated with a multi-crossing Laundau-Zener approximation valid at collision energies below 10 eV, see figure 5.2. There is a non monotonic behavior of partial cross sections observed as function of \(n\), with a maximum of efficiency of excitation for the quantum states \(n=4, 5\) and 6. This suggests that if the molecular mutual neutralization process is present in the plasma it populates the excited states \(n=4, 5\) and 6 dominantly. The negative ions that are necessary for equation (5.1) are created in the plasma by dissociative attachment of \(\text{H}_2^{+} + e^- \rightarrow \text{H} + \text{H}^- [17–20]\). The plasma expansion that is under
investigation has optimal conditions for creating these negative ions, i.e. low pressure (2-10 Pa), high ro-vibrational energy of the hydrogen molecule $H_2^{\nu}$ [21] and low electron temperatures (0.15-2 eV) [8].

![Figure 5.2: Partial cross-sections for the mutual neutralization processes of $H_2^+ + H^- \rightarrow H(n) + H_2$ and $H^+ + H^- \rightarrow H(n) + H$ as function of the quantum state $n$ and the center of mass energy $E_{CM}$ as calculated by Eerden et al [16]. When the cross-sectional data of Janev is used for the molecular mutual neutralization processes no excited $H$ states are populated [22]. The cross-sections for dissociative recombination of $H_2^+ + e^- \rightarrow H(n) + H$ as function of the quantum state $n$ and an electron temperature of $T_e=2$ eV are given by Janev [22].](image)

The performed calculations on the cross-sectional data of the molecular mutual neutralization process by Eerden et al assumes that all the released energy of the neutralization process is transferred to the hydrogen atom (A*-process) while it could also be transferred to the internal energy of the molecules (M*-process, where M* stands for molecularly excited). Moreover, Janev [22] suggest that all the released energy by the process is transferred to the ro-vibrational states of $H_2^{\nu}$.
and not to the excited states of atomic hydrogen at all:

$$H_2^+ + H^- \rightarrow H(n) + H_2^{rv}, \quad \text{with } n = 1 \quad (M^* - \text{process}). \quad (5.2)$$

Note that the available energy of the given process can electronically excite the molecule as stated by Janev. An important aim of this chapter is the determination of the branching ratio of the A*-process and M*-process.

In this work a CR-model for hydrogen, based on the flexible solver Yacora, is used which includes channels based on molecular species and negative ions [23]. The CR-model uses the most recent data available in literature and was tested successfully in predicting the absolute electron density in an ECR plasma with high dissociation degree and low ionization degree [23]. Furthermore, the model was successfully applied in RF ion sources for determining the negative hydrogen ion densities by looking at the H$_\alpha$/H$_\beta$ line ratios [24]. We will show with simulations that the molecular mutual neutralization process is active in the blue emitting plasma region and that a mixture of two different cross-sectional data is necessary to bring the simulations in agreement with the experimentally determined excited state densities of $n=2$ up to 9. The two different cross-sectional data that are used for molecular mutual neutralization process is the A*-process where the excited atom states are populated and the M*-process where the released energy is transferred solely to the ro-vibrational levels of the molecules and keeping the H atom in the ground state, see table 5.1.

<table>
<thead>
<tr>
<th>Population process</th>
<th>H($n$)</th>
<th>input energy to $H_2^{rv}$</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2^+ + H^- \rightarrow H(n) + H_2^{rv}$</td>
<td>$n=2$-$9$</td>
<td>Only the excess energy</td>
<td>A*-process [16]</td>
</tr>
<tr>
<td></td>
<td>$n=1$</td>
<td>All the available energy</td>
<td>M*-process [22]</td>
</tr>
</tbody>
</table>

It is checked if the mixture of the A*- and the M*-process can be brought into agreement with the observed population inversion of the higher excited states with respect to $n=3$ satisfactory in the blue light emitting plasma region. The relevance of the two population channels in the blue light emitting plasma region,
namely the A*-process and the M*-process is estimated along the on-axis plasma column to determine the branching ratio.

5.2 Experimental setup

For the creation of the hydrogen plasma a cascaded arc is used. The cascaded arc is a wall stabilized thermal plasma source and was first introduced by Maecker in 1956 [25]. The plasma source consists of three tungsten-lanthanum cathodes, four water-cooled copper plates that are separately insulated by PVC spacers and vacuum sealed by rubber O-rings, and a copper anode end-plate, see figure 5.3.

Figure 5.3: The plasma under investigation is generated from flowing hydrogen using a wall-stabilized cascaded arc. Inside the channel the pressure is $10^4$ Pa and the temperature 1-1.5 eV [26]. The zero position ($z=0$ cm) starts at the end of the nozzle and is indicated by an asterisks (*).

The hydrogen gas flows with 3000 sccm ($1.25 \cdot 10^{21}$ H$_2$ particles/s) at a pressure of $10^4$ Pa inside the plasma source through a channel of 4 mm diameter. With an input power of 6.8 kW a partially ionized and nearly fully dissociated hydrogen plasma is produced that is known to be far from thermal equilibrium [27]. A short open nozzle is mounted at the end of the plasma source as it provides optimal conditions for studying population inversion [8]. The open nozzle reduces the contact area with the hot plasma compared with a small diameter nozzle and thereby
minimizes the production of $\text{H}_2^+$ molecules by H atom recombination. Via charge
exchange these $\text{H}_2^+$ molecules induce the conversion of $\text{H}^+$ into molecular ions
($\text{H}_2^+$) which are subsequently quickly lost via recombination processes. It tran-
spires that an open nozzle increases the total ionization and dissociation degree in
the plasma expansion [21, 28]. The pressure gradient between the high pressure
cascaded arc and the low pressure expansion vessel forces the plasma to expand,
first supersonically and then, after the formation of a shock, subsonically into the
background [29]. The background pressure in the expansion vessel is typically
9 Pa in this work. Four Helmholtz coils mounted around the vessel produce an
uniform magnetic field of 14 mT over a length of approximately 1.4 meter to
confine the plasma expansion.

5.3 The CR-model

Collisional radiative models (CR-models) describe the population of excited states
as function of the plasma parameters such as electron density, temperature and
neutral density [30]. CR-models are used for the calculation of source terms in
modeling and for plasma diagnostics. Several plasma diagnostics are based on
the determination of the absolute densities of excited state densities with emission
and absorption spectroscopy. The densities that are obtained from the diagnostics
must then be related to the densities of atoms in the ground state and to the ions.
The CR-models are formed by using mass balances of all excited states:

$$ \frac{dn_n}{dt} + \nabla \cdot n_n \vec{w}_n = \left( \frac{dn_n}{dt} \right)_{CR}, $$

(5.3)

where $C$ stands for collision and $R$ for radiation. The left side of this equation
describes the increase in density $n_n$ of an excited state $n$ over time and must be
related to an increase of flow due to divergence ($\vec{w}_n$ is the velocity) and to the net
result of population and depopulation processes. The right hand side describes
the change in density of state $n$ due to elementary processes like inelastic colli-
sions and radiation. To ease the calculations done with the CR-model, often the
fact is utilized that the different processes which are dominant for reaching the
equilibrium population of the species or states have different time scales. The
ground state densities of atoms, molecules and ions depends on transport processes, typically $10^{-4}$ s, while the excited state densities are established on a time scale of $10^{-7}$ s and faster. Therefore, the ground state densities can be considered as quasi-constant input values for the CR-model. This information makes it possible to assume a Quasi Steady State Solution (QSSS) in many situations:

$$0 = \left( \frac{dn_n}{dt} \right)_{CR} = P_n - n_n D_n. \quad (5.4)$$

The processes are now grouped in production terms $P_n$ and destruction terms $D_n$. When assuming QSSS, the atomic state density can be determined by the ratio of production and destruction:

$$n_n = \frac{P_n}{D_n}. \quad (5.5)$$

The time dependence of the population density $n_n$ in the investigated plasma can be described by the following rate equation:

$$\frac{dn_n}{dt} = \sum_{m>n} A_{mn} n_m - \sum_{n>m} A_{nm} n_n + n_e \left( \sum_{m>n} k_{mn} n_m - \sum_{n>m} k_{nm} n_n \right) + n_e \left( (k_{n_{\text{rec}}} + k_{n_{\text{3b,rec}}} n_e) n_{H^+} - k_{n_{\text{ion}}} n_n \right) + X_n, \quad (5.5)$$

where $A_{mn}$ and $A_{nm}$ are the transition probabilities for spontaneous emission. The rate coefficients for excitation and de-excitation by electron collisions are given by respectively $k_{mn}$ and $k_{nm}$. The rate coefficients for three-body recombination and radiative recombination of H$^+$ with density $n(H^+)$ is given by $k_{3b,\text{rec}}$ and $k_{\text{rec}}$ respectively and the rate coefficient for ionization of state $n$ is given by $k_{\text{ion}}$. The contribution to the excited states by molecular induced processes is presented by $X_n$ which consists of:

$$X_n = n_{H^-} n_{H_2^+} k_{mn} + n_{H^-} n_{H+} k_{amr} + n_e n_{H_2^+} k_{dr} + n_e \left( k_{H_2^+,n} n_{H_3^+} + k_{H_3^+,n} n_{H_2^+} + k_{de} n_{H_2} n_{H_2} \right). \quad (5.6)$$

These equations can be constructed for all excited states, resulting in a system of coupled ordinary differential equations.
The solution of equation (5.5) can be expressed in terms of population coefficients [31]:

\[ R_{on} = \frac{n_n}{n_e \cdot n_0}, \]  

(5.7)

where \( n_0 \) denotes the density of the ground state or another species with quasi-constant density. If the population density \( n_n \) depends on more than one species \( S \) with quasi-constant density, additional coupling processes have to be considered by calculating population coefficients for each of these species. Then \( n_n \) is the result of a summation:

\[ n_n = n_e \cdot \sum_S R_{Sn} n_S. \]

(5.8)

where \( R_{Sn} \) are the population coefficients for coupling of the different species \( S \) to the excited states and \( n_S \) the ground state densities of these species.

**Figure 5.4:** The population density of an excited state in the hydrogen atom can be coupled to six species with quasi-constant density. The electron density, electron temperature and gas temperature is also used as input to the model.

The CR-model is executed with the flexible package called Yacora which requires as input the heavy particle temperature \( T_{gas} \), the electron temperature \( T_e \), the electron density \( n_e \) and six hydrogen species with quasi-constant densities. The densities of the six species that are used as input to the model are...
the atomic hydrogen density $H$, the molecular hydrogen density $H_2$ determined with the ideal gas law, the molecular ion densities $H_2^+$ and $H_3^+$, the negative ion density $H^-$ and the proton density $H^+$, see figure 5.4. The Yacora package has many advantages compared to other solvers since it includes non-linear processes like heavy particle collisions and self absorption due to optical thickness of the emission lines.

In this work only the excited states of $n=2$ up to 9 are compared to the experimental results on the excited states since they are the most relevant for determining the important population processes in the plasma. The atomic population processes are grouped into two different channels: $C_H$ is the group of atomic processes that populate the excited states via excitation, de-excitation, spontaneous emission and ionization, and $C_{H^+}$ consists of three-body recombination and radiative recombination, see table 5.2.

<table>
<thead>
<tr>
<th>Channel</th>
<th>Population process to $H(n)$</th>
<th>Rate coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_H$</td>
<td>$H(m) + e^- \rightarrow H(n &gt; m) + e^-$</td>
<td>$k^{mn}$ [22]</td>
</tr>
<tr>
<td></td>
<td>$H(m) + e^- \rightarrow H(n &lt; m) + e^-$</td>
<td>$k^{nm}$ [22]</td>
</tr>
<tr>
<td></td>
<td>$H(m) \rightarrow H(n &lt; m) + h\nu$</td>
<td>$k^{em}$ [32]</td>
</tr>
<tr>
<td></td>
<td>$H(m) + e^- \rightarrow H^+ + e^- + e^-$</td>
<td>$k^{ion}$ [22]</td>
</tr>
<tr>
<td>$C_{H^+}$</td>
<td>$H^+ + e^- + e^- \rightarrow H(n) + e^-$</td>
<td>Three-body recombination $k^{3b,rec}$ [31]</td>
</tr>
<tr>
<td></td>
<td>$H^+ + e^- \rightarrow H(n) + h\nu$</td>
<td>Radiative recombination of $H^+$ $k^{rec}$ [31]</td>
</tr>
</tbody>
</table>

Molecular induced reaction processes in the hydrogen plasma are considered since atomic population processes were not sufficient to explain the high density of the excited states. These reactions automatically cause the introduction of hydrogen molecules and molecular ions, as listed in table 5.3. The first molecular channel in table 5.3 is $C_{H_2}$ which includes dissociative excitation of $H_2$ as a population process to the excited states. Due to a low electron temperature ($T_e < 6$ eV) throughout the plasma it is not expected to be an important population process. The second channel is $C_{H_2^+}$ which consists of dissociative recombination of $H_2^+$ and dissociation of $H_2^+$ into a proton, an electron and an excited hydrogen
atom. The vibrational temperature of the H$_2^+$ molecule is assumed to be 2000 K in this work. The third molecular channel is C$_{\text{H}}^-$ and includes atomic mutual neutralization and molecular mutual neutralization. The two mutual neutralization processes are expected to be very important in the plasma since the population rates are very high [16]. The atomic mutual neutralization process is strictly speaking an atomic population process, but it is coupled to the H$^-$ species and therefore incorporated in this channel. Important to note, as discussed in the introduction, is that the molecular mutual neutralization process includes a mixture of the cross-sectional data of Janev et al [22] (the M*-process) and Eerden et al [16] (the A*-process). Finally, the C$_{\text{H}}^+$ channel is implemented in the CR-model which includes dissociative recombination of H$_3^+$.

The contribution of all six channels to the excited states will be shown separately in the same ASDF. In this way the dominant population processes can be highlighted and by adding the six channels a comparison with the experimental data can be made.

For constructing the CR-model for atoms, several thousand reactions have to be known. The cross sections, rate coefficients and transition probabilities which have been used in our model are taken from articles from various authors [16, 22, 31, 33]. The accuracy of the CR-model results depend strongly on the accuracy of the used input data.

The CR-model includes the 40 energetically lowest lying excited states of atomic hydrogen to obtain an equilibrium with the Saha ion states. The main reactions are radiation and electron collision processes with atoms, molecules and ions. The only two heavy particle collision processes in the CR-model are atomic and molecular mutual neutralization. The ground state density of atomic hydrogen is used as a fixed parameter for the solution of the process due to its quasi-constant character. Therefore, important processes like the stripping of negative ions by electrons need not to be included in the model since it only populates the ground state density of atomic hydrogen.

In this work all the input rate coefficients of the CR-model are calculated based on a Maxwellian energy distribution of the electrons. This is justified in our plasma expansion since the ionization degree is sufficiently high in the red
5.4. Results

The input densities and temperatures for the various species in the CR-model are discussed first. Secondly, a benchmark study on the most likely cross-sectional data for the molecular mutual neutralization process of $\text{H}_2^+$ and $\text{H}^-$ in the plasma is given. Thirdly, the important population processes at one position in the red light emitting plasma are discussed and also at one position in the blue light emitting plasma. Finally, a sensitivity study is presented to determine the uncertainty and correctness of the obtained densities.

The electron temperature and density

It is very important to measure the electron temperature and electron density in the plasma accurately since otherwise wrong conclusions about the important
The electron temperature and density measurements in the plasma are extensively discussed in [8] and the results are shown in figure 5.5. The electron temperature is determined from the intensive Fulcher-\( \alpha \) band emission from the hydrogen molecule \((\sigma^3 \Pi_u - \sigma^3 \Sigma_u^+ )\) in the red light emitting plasma region and by a double Langmuir probe in the blue light emitting plasma region. The electron density in the red light emitting plasma region can be evaluated by analyzing the higher excited state densities assuming Saha and by a double Langmuir probe in the blue light emitting plasma region.

**Figure 5.5:** The on-axis electron temperature and electron density at different axial positions from the plasma source [8]. This data is used as input for the CR-model.

The electron density is \(10^{20} \text{ m}^{-3}\) close to the arc exit and is decreasing one order of magnitude over a length of 20 cm. This decay is much slower than in a non-magnetized hydrogen plasma expansion since the magnetic confinement decreases the radial expansion of the plasma. After \(z=20\) cm of expansion, a transition from the red light emitting plasma region to the blue light emitting plasma region occurs. The electron density just after this transition remains constant until \(z=25\) cm, after which the density drops fast to \(10^{17} \text{ m}^{-3}\) at \(z=35\) cm.
The electron temperature is about 2 eV close to the arc exit and drops gradually along the red emitting plasma column. At \( z = 17 \) cm, which is just before the red to blue transition, the electron temperature drops fast from 0.9 eV to 0.2 eV in 6-7 cm after which the electron temperature remains constant along the plasma column.

The applied magnetic field reduces the mobility of the charged particles across the magnetic field. This has as consequence that the source current spreads out in the expansion vessel. This spreading out in the expansion vessel happens until the resistance of the axial and radial current path are equal and the current from the source returns to the anode to close the circuit, see figure 5.6. The influence of the magnetic field on the plasma current is large. A larger magnetic field strength increases the penetration length of the current in the expansion, resulting in a longer red light emitting plasma region. The central heat input of the current by ohmic heating can be calculated if the axial electric field and conductivity are known:

\[
Q_{\text{ohmic}} = \sigma_\parallel |E_z|^2
\]  

(5.9)

where \( \sigma_\parallel \) is the conductivity parallel to the magnetic field and \( E_z \) is the axial electric field. The current density close to the arc exit is \( j(z) = \frac{I_{\text{arc}}}{\pi r_{\text{channel}}^2} = 9.0 \times 10^5 \) A m\(^{-2}\), with a current from the arc of \( I_{\text{arc}} = 45 \) A and a radius of
the current channel of $r_{\text{channel}}=4$ mm. The conductivity from Spitzer [35] is $\sigma_{||} \approx 2 \times 10^4 \frac{\rho^{3/2}}{\ln \chi} \Omega^{-1} m^{-1}$ resulting in an axial electric field of $E_z = j(z)/\sigma_{||}=90$ V m$^{-1}$. With equation (5.9) we find that the central heat input by ohmic heating close to the arc exit is approximately $10^3$ W m$^{-3}$.

The current originating from the source decreases along the plasma column and closes the circuit at $z=17-18$ cm, i.e. ohmic heating is not present in the plasma expansion after 17 cm. After 17 cm a fast decreasing electron temperature is observed while the electron density is conserved. The distance over which the electron temperature drops from 0.9 eV to 0.2 eV is 7 cm which agrees well with calculations from the energy conservation equation, see appendix B. The fast decrease in electron temperature and slow decrease in electron density can be explained by elastic collisions of electrons with both ions and neutrals.

**The heavy particle temperature**

The temperature of the first excited state is determined from the width of the Balmer-alpha absorption lineshape, obtained from Tunable Diode Laser Absorption Spectroscopy (TDLAS). The temperature of the first excited state of atomic hydrogen is assumed to be representative for the gas temperature. The gas temperature drops from 2000 K close to the arc exit to 700 K in the blue light emitting plasma region where it remains constant [11]. The temperature on the ground state density of atomic hydrogen are performed with TALIF and show similar results with the TDLAS temperature measurements, as shown in figure 5.7. The density of $H_2$ ($n_{H_2}$) in the plasma is determined from the obtained gas temperature in combination with the ideal gas law ($p = n_{H_2} k_B T_{\text{gas}}$).

**The atomic ground state density**

Vankan *et al* showed that when an open nozzle (as used in this work) is attached to the anode end plate of the source, the H atom flux weakly depends on the flow. This suggests that the dissociation degree inside the arc is almost 100% [28]. Vankan also showed that the hydrogen atom flux density, determined with Two-Photon LIF (TALIF), is $\Phi(H)=9.8 \times 10^{30}$ s$^{-1}$ at $z=0.2$ cm indicating that the
dissociation degree is 40% just after the anode nozzle exit [28]. The dissociation degree characterizes the source strength, i.e. the capability of producing H radicals, and it is expressed as follows:

$$
\beta = \frac{\Phi_H}{2\Phi_{H_2}} = \frac{n(H)}{n(H) + 2n(H_2)}.
$$

Here $\Phi_H$ is the ground-state atomic hydrogen flux and $\Phi_{H_2}$ the gas flow of molecular hydrogen at the gas inlet. Under our experimental conditions the molecular gas flow is $\Phi_{H_2} = 1.25 \times 10^{21}$ s$^{-1}$. The dissociation degree is determined (using TALIF measurements) to be 10% at $z=1$ cm and it increases to 14% at $z=4$ cm after which the dissociation decreases again. After the red to blue transition a fast decreasing dissociation degree is observed as measured before by Mazouf-fre [36]. An explanation for the increase in dissociation degree after 4 cm of expansion is not known yet. The fast decreasing dissociation degree in the first 10 mm of the expansion (100% in the arc, 40% at $z=0.2$ cm and 10% at $z=1$ cm) is explained by diffusion of H atoms in the radial direction [36, 37]. Note that at $z=0$ cm, the expansion already started for 7 mm and that association processes on the wall already occurred.

The plasma becomes optically thick for Lyman-α if the ground state density

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{figure5.7.png}
\caption{The heavy particle temperature is measured with both TALIF and TDLAS [11].}
\end{figure}
of atomic hydrogen, $n_H$, is sufficiently high. The ground state densities can maintain inside the plasma expansion for several cm before escaping in radial direction. It is expected that only in the first 3-4 cm of the plasma expansion self absorption due to opacity is present. This results in a higher $n=2$ density than observed with TDLAS. Further downstream in the plasma expansion ($z > 3-4$ cm) self absorption is not expected to be present. The influence of self absorption due to opacity is discussed extensively by Behringer et al [38] and it would be interesting to investigate the importance it in the first several cm of the plasma expansion.

**The positive hydrogen ions**

Many plasma diagnostics have been applied to the plasma for determining the temperature and density of several species like, the electron density $n_e$, the electron temperature $T_e$, the atomic ground state density $n_H$, the molecular density of $n_{H_2}$ and the gas temperature $T_{gas}$. However, not all the required species for the CR-model are measured like e.g. $H^+$, $H_2^+$, $H^-$ and $H_3^+$. To estimate the densities of these species a one dimensional flow model in which charge neutrality is satisfied has been included. The absolute density of $H^+$ is known to be close to the electron density and the amount of $H_2^+$ is approximately in the order of $10^{16}$ m$^{-3}$. Detailed analysis show that the amount of $H_2^+$ cannot be an order of magnitude higher since then the input to $n=3$ would become one order of magnitude too high (for more information see the sensitivity study). The $H_2^+$ ions are created by charge exchange of $H^+$ ions with ro-vibrationally excited molecules $H_2^{v}$ via:

$$H_2^{v} + H^+ \rightarrow H_2^+ + H.$$  \hspace{1cm} (5.11)

This charge exchange reaction is endothermic with an energy deficit of 2.1 eV and is about resonant when the molecule has a vibration excitation of $v = 4$ [14].

Simulations with the CR-model showed that the $H_3^+$ ion was important to include to balance quasi-neutrality in the plasma. Otherwise, too much $H_2^+$ is created which overestimates the population to the excited state $n=3$ by the mutual neutralization and dissociative recombination. $H_3^+$ ions are created by $H_2^+$
5.4. Results

Collisions with the background gas of H\textsubscript{2} [14]:

\[ \text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}. \quad (5.12) \]

Dissociative recombination of H\textsubscript{3}\textsuperscript{+} can occur via two different reaction channels [39]. The products are either three hydrogen atoms in their ground state or a molecule and an excited atom. The latter reaction is given by

\[ \text{H}_3^+ + e^- \rightarrow \text{H}_2 + \text{H}(n). \quad (5.13) \]

The cross sectional data and branching ratios are determined from experiments in a storage ring [33]. These experiments show that dissociative recombination of H\textsubscript{3}\textsuperscript{+} mainly populates the first excited state of the H atom (H\textsubscript{2}(n=2)). When the H\textsubscript{3}\textsuperscript{+} channel (C\textsubscript{H\textsubscript{3}+}) was not added in the CR-model, more H\textsubscript{2}\textsuperscript{+} was available, due to charge-neutrality, for populating \(n=3\). This resulted in an order of magnitude too high density of \(n=3\) when compared to the experimental data. Furthermore, the simulated density of \(n=2\) was underestimated with respect to the experimental data in the blue light emitting plasma region. Therefore, one of the key challenges in this work was obtaining a good agreement of the modeling results for the excited states \(n=2\) and \(n=3\) with experimental data. Including dissociative recombination of H\textsubscript{3}\textsuperscript{+} in the CR-model provided a solution to this problem: more population to the first excited state via the dissociative recombination process of H\textsubscript{3}\textsuperscript{+}. More H\textsubscript{3}\textsuperscript{+} also implies less H\textsubscript{2}\textsuperscript{+} presence due to quasi-neutrality resulting in a lower production through this process of the \(n=3\) state.

The negative hydrogen ions

In the plasma negative hydrogen ions are created by the dissociative attachment process of ro-vibrationally excited hydrogen molecules H\textsubscript{2}\textsuperscript{rov} with electrons \(e^-\) [22]:

\[ \text{H}_2^{\text{rov}} + e^- \rightarrow \text{H}_2^- \rightarrow \text{H}^- + \text{H}. \quad (5.14) \]

The dissociative attachment process can be enhanced by several orders of magnitude if ro-vibrationally excited molecules (H\textsubscript{2}\textsuperscript{rov}) are present. The rate of dissociative attachment increases by eight orders of magnitude when the vibrational excitation is changed from \(v = 0\) to \(v = 9\) [40].
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5.4. RESULTS

There are several processes that involve negative ions which can populate the atomic excited state densities. One population process is the atomic mutual neutralization process given by:

\[ H^+ + H^- \rightarrow H(n) + H, \quad \text{with } n = 2 \text{ and } 3. \]  \hfill (5.15)

This reaction has been calculated with a single-crossing Laundau-Zener approximation by Bates et al [41] and Olsen et al [42] and shows a good agreement with experimental data. The excited state densities of \( n=1 \) and \( n=4 \) in equation (5.15) are not populated, since the corresponding non-adiabatic couplings are both too weak. The population to the excited states of \( n \geq 5 \) do not exist at all due to the weak coupling. The ratio of the cross sections in equation (5.15) for \( n=2 \) and \( 3 \) strongly depends on the electron energy. The population to \( n=2 \) can therefore be neglected in the considered energy range relevant for this work.

The other population process to the excited states is the molecular mutual neutralization process as described by Eerden et al [16]:

\[ H^+ + H_2^- \rightarrow H(n) + H_2, \quad \text{with } n = 2 - 9. \]  \hfill (5.16)

The ionization energy of \( H_2 \) is 15.42 eV and the binding energy of \( H^- \) is 0.75 eV. This leaves 14.67 eV to excite the hydrogen atom. As the ionization energy of atomic hydrogen is only 13.6 eV, all states can be populated in this reaction leaving some energy for the ro-vibrational excitation of the resulting \( H_2 \) molecule.

To calculate the rate of the molecular mutual neutralization process to the excited states a detailed analysis is needed on the ratio of the \( A^* \)-process and \( M^* \)-process, as discussed in the next section. The destruction of \( H_2^+ \) ions and \( H^- \) ions in the plasma can be demonstrated by increasing the pressure since the increased collisions with the background gas diminishes the excitation in \( H(n=4-7) \) through the \( A^* \)-process.

Since there are both \( H_3^+ \) ions and \( H^- \) ions present in the plasma [11], the reaction of

\[ H_3^+ + H^- \rightarrow H_2 + H + H(n) \]  \hfill (5.17)

could also produce atomic hydrogen in excited states. For this to happen the energy available to excite an excited atom is 10.15 eV, close to the energy of the
first electronically excited state of the H atom. This process could excite \( n = 2 \) when the \( \text{H}_3^+ \) molecule has internal energy. Especially, since the \( \text{H}_3^+ \) and \( \text{H}^- \) ions are dominantly present in the blue light emitting plasma region as shown by the simulation results (see upcoming sections). This population process is not included in the extended CR-model since it has not been studied so far either experimentally or theoretically.

### 5.4.1 The input densities of the species that are used in the CR-model

The importance of the species \( n_{\text{H}_2}, n_{\text{H}}, n_{e}, n_{\text{H}^+}, n_{\text{H}_3^+}, n_{\text{H}^-} \) and \( n_{\text{H}_3^+} \) have been discussed extensively in the previous sections and the absolute densities that are used for the modeling in CR-model are shown in figure 5.8. In the left graph of figure 5.8 the densities of \( n_{\text{H}_2}, n_{\text{H}} \) and \( n_{e} \) are shown and in the right graph that of \( n_{\text{H}^+}, n_{\text{H}_3^+}, n_{\text{H}^-} \) and \( n_{\text{H}_3^+} \).

![Figure 5.8](image-url)

**Figure 5.8:** The density of the various species that are used as input for the CR-model as function of \( z \) (on-axis). The lines between the data points are a guide to the eye.
5. COLLISIONAL RADIATIVE MODEL

5.4. RESULTS

5.4.2 Using the different cross sectional data of the molecular mutual neutralization process

We know that negative ions are created in the plasma by dissociative attachment and that they play a role in the population of the excited states. Therefore, it is important to deduce the correct cross-sectional data of the molecular mutual neutralization process which involve negative ions. This is done by using different cross-sectional data as input to the model and making a comparison with the experimental results for all excited states of $n=2$ up to $n=9$. In the $A^*$-process most energy is transferred to the excited atom states ($n=2-9$) and only the excess energy is transferred to the ro-vibrational states of $H_{2}^{+}$. In the $M^*$-process all the released energy is transferred solely to the excited molecules while keeping the hydrogen atom in the ground state. The cross-sectional data of both channels is investigated in the blue light emitting plasma region where the molecular mutual neutralization processes is dominantly present, see the ASDF in figure 5.9.

![Graph](attachment:image.png)

**Figure 5.9:** Overview of the cross-sectional data that is used for $H_{2}^{+} + H^{-} \rightarrow H(n) + H_{2}$ in the CR-model.

To obtain the best overlap of simulations with experiments a mixture of $A^*$ and $M^*$-process is necessary. The simulation results show that about 84% of the
molecular mutual neutralization process is populating the excited states as described by the A*-process and 16% to the ro-vibrational states of the molecules as described by the M*-process. Note that other population process, like dissociative recombination and atomic mutual neutralization, are also included in the ASDF. Simulation results show that the ratio of the A*-process and the M*-process in the remains constant along the z-axis in the blue light emitting plasma region (within the uncertainty of the modeling). The obtained ratio could also be an indication that the cross-sectional data as calculated by Eerden et al for the A*-process is too high.

In the appendix the results of the simulated excited state densities of \( n = 2 \) up to \( n = 9 \) are shown as function of \( z \) and compared with the experimentally determined densities. In figure 5.14 of the appendix, a good agreement of the simulations with the experiments is obtained along the whole relevant plasma expansion of 30 cm. Furthermore, population inversion of \( n = 4-5 \) with respect to \( n = 3 \) is well simulated at different positions in the blue light emitting plasma region.

5.4.3 The relevant reaction processes in the plasma

The contributions of the various population processes to the excited states of atomic hydrogen, as calculated with the CR-model, can be shown schematically by the so called Atomic State Distribution Function (ASDF). The summation of all the contributing reaction processes to the excited state densities per statistical weight are compared with the experimentally determined excited state densities.

The important reaction processes in the red light emitting region

A constructed ASDF in the red light emitting plasma at \( z = 13 \) cm is shown in figure 5.10. The contribution of the six excitation channels for the population of the excited states are all separately included by an ASDF with open data points. The summation of the six excitation channels is given as the red solid triangle (red ▲). This figure shows that the \( \text{C}_\text{H}^- \) channel has a main input to the \( n = 3 \) state. The input to \( n = 3 \) is expected since the atomic mutual neutralization of
5. COLLISIONAL RADIATIVE MODEL

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Figure 5.10: The on-axis excited state densities per statistical weight as function of the quantum states at \( z = 13 \) cm. The following plasma parameters are used as input to the model: \( n_{H^+} = 2.5 \times 10^{20} \text{ m}^{-3} \), \( n_{H^-} = 2 \times 10^{21} \text{ m}^{-3} \), \( n_{H_2^+} = 1.0 \times 10^{16} \text{ m}^{-3} \), \( n_{H^{-}_3} = 1 \times 10^{17} \text{ m}^{-3} \), \( n_{H^{-}_4} = 1 \times 10^{16} \text{ m}^{-3} \) and \( n_{H^+} \approx n_e = 2.4 \times 10^{19} \text{ m}^{-3} \). The experimental data is given by the solid black square (black ■). The lines in between the data points are a guide to the eye.

\( H^+ \) and \( H^- \) is important in the red light emitting plasma region as discussed in [8]. Furthermore, the molecular mutual neutralization is also present in the red light emitting plasma region, but to a much lesser extent than in the blue light emitting plasma region. The different population processes that are included in the channels are listed in table 5.2 for the atomic processes and in table 5.3 for the molecular processes. The \( C_{H^+} \) channel consists of three-body recombination and radiative recombination which are mainly populating \( n \geq 7 \) in the red light emitting plasma region. This result shows us that the assumption used in [8] to determine the electron density is correct by assuming Saha equilibrium for the higher excited states. The \( C_{H_2^-} \) channel in the CR-model has dissociative recombination included and is dominantly populating the \( n=3-7 \) states. The \( C_H \)
channel consists of direct excitation and electron (de)-excitation processes which mainly populate the \( n=2 \) state. This channel is important when the electron temperature and atomic ground state density are high. The simulation results with the CR-model show that direct excitation from the ground state is the dominant population process for the first excited state \( n=2 \) in the entire red light emitting plasma region. Dissociative recombination of \( \text{H}_2^+ \) ions (included in the channel of \( \text{C}_2\text{H}_2^+ \)) is not an important population process for the first excited state \((n=2)\) in the red light emitting plasma region. The summation of the six channel contributions to the excited state densities is labeled by "Yacora" and it is compared with the experimentally determined excited states. The results from the CR-model show a good agreement with the experiments and it underpins the importance of molecular processes in the red light emitting plasma.

**The important reaction processes in the blue plasma region**

A constructed ASDF in the blue light emitting plasma at \( z=25 \) cm is shown in figure 5.11. Note that only ions play a role in the formation of the excited states. The population of excited states by atomic recombination processes is not important at all. The molecular mutual neutralization process, with the correct \( \Lambda^*\)-process/\( M^*\)-process ratio, is important to include in the CR-model to explain the observed population inversion of \( n=4-7 \) with respect to \( n=3 \) in the blue light emitting plasma region. For this process a low electron temperature is needed since then it can dominate dissociative recombination, \( n_{\text{H}_2^+} n_{\text{H}^-} k_{\text{mmr}} > n_{\text{H}_2^+} n_e k_{\text{dr}} \).

The molecular mutual neutralization process becomes dominant over dissociative recombination when the following condition in the plasma is met:

\[
\frac{n_e}{n_{\text{H}^-}} < \frac{k_{\text{mmr}}}{k_{\text{dr}}^\text{H}_2^+}.
\] (5.18)

In the blue light emitting plasma the following holds: \( n_e < 10^{19} \text{ m}^{-3} \), \( k_{\text{mmr}} = 10^{-13} \text{ m}^3/\text{s} \) (\( \Lambda^*\)-process) at an electron temperature of \( T_e=0.2 \) eV and \( k_{\text{dr}}^\text{H}_2^+ = 10^{-16} \text{ m}^3/\text{s} \). Therefore, the molecular mutual neutralization process is expected to be dominantly populating the excited states when \( n_e < 10^{19} \text{ m}^{-3} \) and \( n_{\text{H}^-} > 10^{17} \text{ m}^{-3} \) at \( T_e=0.2 \) eV. The simulation results show that these conditions are
Figure 5.11: The excited state densities of atomic hydrogen per statistical weight at $z=25$ cm in the blue light emitting plasma region. The following plasma parameters are used as input to the model: $n_H=1 \cdot 10^{20}$ m$^{-3}$, $n_{H_2}=7 \cdot 10^{20}$ m$^{-3}$, $n_{H^+}=2 \cdot 10^{16}$ m$^{-3}$, $n_{H^+_2}=2 \cdot 10^{16}$ m$^{-3}$, $n_{H^+_3}=3 \cdot 10^{18}$ m$^{-3}$, $n_{H^-}=1 \cdot 10^{17}$ m$^{-3}$ and $T_e=0.2$ eV. The lines between the data points are a guide to the eye.

met just after the transition from the red to blue light emitting plasma region. Since no other reaction process than the molecular mutual neutralization process can sufficiently populate the $n=4-7$ excited state densities to achieve population inversion with respect to $n=3$ we conclude that this is a key population process in the blue light emitting plasma. The $\text{C}_2\text{H}_2$ channel includes the dissociative excitation process of a hydrogen molecule, which is not important throughout the magnetized hydrogen plasma expansion due to the too low electron temperature ($T_e < 6$ eV) to excite the molecule. The dissociative recombination process of $\text{H}_3^+$ is dominantly populating the first excited state of atomic hydrogen in the blue light emitting plasma region. This clearly shows us that the presence of $\text{H}_3^+$ ions in the plasma are key in the formation of $n=2$ since the electron temperature is
too low for direct electron excitation from the ground state.

Due to large amounts of $\text{H}_3^+$ and $\text{H}^-$ ions present in the blue light emitting plasma, the mutual neutralization process

$$\text{H}_3^+ + \text{H}^- \rightarrow \text{H}_2 + \text{H} + \text{H}(n) \quad (5.19)$$

could populate the first excited state ($n=2$) significantly. However, there is no experimental and theoretical information of this process available and therefore not included in the model. Including this neutralization process in the CR-model could lower the simulation results of the $\text{H}_3^+$ density in the plasma.

There is still one issue to be resolved with respect to the input to $n=3$ in the blue light emitting plasma region as can be observed in figure 5.11. The main population processes to the $n=3$ state are dissociative recombination and both atomic and molecular mutual neutralization. Those three processes together populate the $n=3$ state by a factor of three too much. It was not possible to reduce the density of $n=3$ without reducing the input to the other excited states. One obvious reason could be an incorrect absolute calibration factor for the OES data, but a double-check showed us that the calibration was done correctly.

### 5.4.4 A sensitivity study on the density of the species

#### A sensitivity study in the red light emitting plasma region

A study about the sensitivity of the $\text{H}^-$ and $\text{H}_2^+$ densities to the excited states is started in the red light emitting plasma region at $z=13$ cm, see figure 5.12. Simulations show that the $\text{H}_2^+$ density at $z=13$ cm is $n_{\text{H}_2^+}=(1.0 \pm 0.5) \cdot 10^{17}$ m$^{-3}$. The proton density is $n_{\text{H}^+}=(2.4 \pm 0.1) \cdot 10^{19}$ m$^{-3}$ and close to the density of the electrons. The obtained densities have also been simulated with a one-dimensional flow model in which all of the relevant processes are included and agree with the same order of magnitude. In the left graph of figure 5.12 the sensitivity is investigated for the negative ion density while keeping the other densities fixed. A detailed study with the simulations show that a negative ion density of $n_{\text{H}^-}=1 \cdot 10^{16}$ m$^{-3}$ is needed to get the best agreement to the excited states of atomic hydrogen compared to the experimental data. The change of the negative
Figure 5.12: The sensitivity of the species is checked in the red light emitting plasma region at z=13 cm. In the left graph, the H\(^-\) density is changed while keeping the other densities fixed: \(n_{H^-} = 2.5 \cdot 10^{20} \text{ m}^{-3}\), \(n_{H^-} = 1.0 \cdot 10^{16} \text{ m}^{-3}\), \(n_{H+} = 2.1 \cdot 10^{21} \text{ m}^{-3}\), \(n_{H_2^+} = 1.0 \cdot 10^{16} \text{ m}^{-3}\), \(n_{H_3^+} = 1.0 \cdot 10^{17} \text{ m}^{-3}\) and \(n_{H+} \approx n_e = 2.4 \cdot 10^{19} \text{ m}^{-3}\). In the right graph, the variations to the excited states are investigated by changing the H\(_2^+\) density while keeping the other densities fixed.

The sensitivity study on the H\(_2^+\) ion is shown on the right graph of figure 5.12. The sensitivity to the excited states by changing the H\(_2^+\) density is less than changing the negative ion density. This is especially observed at lower H\(_2^+\) densities since the dissociative recombination process is not populating the excited states sufficiently. The sensitivity study shows that the uncertainty of the H\(_2^+\) ions is 50%.
5.4. Results

A sensitivity study in the blue light emitting plasma region

A study about the sensitivity of the H\(^-\) and H\(_2\)^+ densities to the excited states is started in the blue light emitting plasma region at \(z=25\) cm, see figure 5.13.

![Figure 5.13: A sensitivity study on the obtained species in the blue light emitting plasma region at \(z=25\) cm. In the left graph, the H\(^-\) density is changed while keeping the other densities fixed: \(n_{H^-}=9.8 \cdot 10^{19}\) m\(^{-3}\), \(n_{H^+}=6.1 \cdot 10^{20}\) m\(^{-3}\), \(n_{H_2}=1.5 \cdot 10^{16}\) m\(^{-3}\), \(n_{H_2^+}=3 \cdot 10^{18}\) m\(^{-3}\) and \(n_e=3 \cdot 10^{18}\) m\(^{-3}\). In the right graph, the variations to the excited states are investigated by changing the H\(_2\)^+ density while keeping the other densities fixed.

The results in the left graph of figure 5.13 show that the amount of negative ions is very sensitive to the excited state densities and is \(n_{H^-}=(1.5 \pm 0.5) \cdot 10^{17}\) m\(^{-3}\). This is more than one order of magnitude higher than in the red light emitting plasma region.

The results in the right graph of figure 5.13 show that for low H\(_2\)^+ densities the output to the excited states is not influenced much. The dissociative recombination process populates the excited states \(n=2-5\) strongly for H\(_2\)^+ densities higher...
than $2 \cdot 10^{16}$ m$^{-3}$ and therefore we observe that the H$_2^+$ ion cannot be the dominant positive ion in the red light emitting plasma region. The low sensitivity to the excited states by changing the amount of H$_2^+$ makes it difficult to determine the density accurately and therefore an uncertainty of at least 70\% is estimated: 

$$n_{H_2^+}=(1.5 \pm 1) \cdot 10^{16} \text{ m}^{-3}.$$ 

The contribution of the H$_3^+$ recombination process to the first excited state in the blue light emitting plasma region is important and simulated to be $n_{H_3^+}=(3 \pm 1) \cdot 10^{18} \text{ m}^{-3}$.
5.5 Conclusion

In the red light emitting plasma region a current from the plasma source is present because the charged particles within the plasma source cannot close the circuit due to their limited mobility across the magnetic field. The current heats the plasma expansion resulting in a high electron density \(10^{19}-10^{20} \text{ m}^{-3}\) and a relatively high electron temperature (1-2 eV), but after 18 cm of expansion the current density from the source is insufficient to sustain the "hot" plasma. As a result the chemistry in the plasma changes and a transition from a red light emitting plasma region to a blue light emitting plasma region is formed. The transition can be explained by the fast dropping electron temperature from 0.9 eV to 0.2 eV in 7 cm of expansion due to elastic collisions with neutrals and ions. The low electron temperature (0.15-0.75 eV) in the blue light emitting plasma region provides optimal conditions forming negative ions and producing highly excited states via the molecular mutual neutralization process of \(\text{H}_3^+\) and \(\text{H}^-\). For the latter process the cross-sectional data from Eerden et al is used. The molecular mutual neutralization process is essential to include in the CR-model for obtaining a good agreement of simulation with experiment for the excited states \(n=2\) up to 9 in the blue light emitting plasma region. The simulation results show a good agreement with experiment when about 84 % of the released energy by the molecular mutual neutralization process is populating the excited states \(n=2-9\). This indicates that the cross-sectional data, as calculated by Eerden et al, is too high or that about 16 % of the released energy is transferred to the excitation of a hydrogen molecule as mentioned by Janev et al. The new insights that are presented in this work could give valuable information in analyzing optical emission data obtained in negative ion sources.
Bibliography


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5.6 Appendix A

The simulated excited state densities of $n=2$ up to $n=9$ that are obtained with the CR-model are compared with the experimentally determined densities in figure 5.14.
Figure 5.14: The excited state densities $n=2$-$9$ of the CR-model (labeled as "Yacora") are compared with the experiments (labeled as "Experiments") as function of $z$. In the first couple of cm of the expansion self absorption of Lyman-$\alpha$ is present for $n=2$. This is shown in the transparent grey box.
5.7 Appendix B

In this appendix an explanation is given why a fast decreasing electron temperature is observed when the transition from red to blue light emission occurs.

5.7.1 Energy Conservation equation

Just before the transition from red to blue light emission a fast drop in electron temperature is observed while the electron density is conserved. In this appendix we calculate the distance in which the electron temperature drops from 0.9 eV to 0.2 eV from the energy conservation equation. The experiments show that the drop in temperature starts at \( z = 17 \, \text{cm} \) and ends at \( z = 24 \, \text{cm} \), see figure 5.15. In this distance the electron density drops about 40\% and the electron temperature 77\%. In this appendix it will be shown that the fast decrease in electron temperature and slower decrease in electron density is explained by elastic collisions of the electrons with ions and neutrals. This behavior of \( n_e \) and \( T_e \) at \( z = 17 \, \text{cm} \) to \( z = 24 \, \text{cm} \) is not unique but it is also measured with different nozzle sizes (see chapter

![Figure 5.15: The on-axis electron temperature and electron density at different axial positions from the plasma source.](image)

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3).

The Energy Conservation equation is given by [43]:

\[
\frac{\partial}{\partial t} \left( \frac{3}{2} p \right) + \frac{3}{2} \vec{\nabla} \cdot \left( p \vec{w}_e \right) + p \vec{\nabla} \cdot \vec{w}_e + \nabla \cdot \vec{q} = Q_{tot}. \tag{5.20}
\]

For simplifying this equation we assume that the plasma is in steady state, so the first term is zero. \( p \vec{w}_e \) is the macroscopic energy flux (W/m\(^2\)), \( \vec{\nabla} \cdot \vec{w}_e \) gives the heating or cooling of the plasma due to compression or expansion of its volume and \( q \) is the heat flow vector (W/m\(^2\)). The heating term \( Q_{tot} \) includes all heating processes due to ionization, elastic scattering, and Ohmic heating. This equation is usually closed by setting \( \nabla \cdot \vec{q} = 0 \). By assuming that \( \vec{\nabla} \cdot (n_e \vec{w}_e) = 0 \), using the ideal gas law \( p = n_e k_B T_e \) and

\[
\vec{\nabla} \cdot \vec{w}_e = -\vec{w}_e \cdot \vec{\nabla} \left( \frac{k_B T_e}{n_e} \right)
\]

the following simplified energy conservation equation is obtained:

\[
\frac{3}{2} n_e \vec{w}_e \cdot \vec{\nabla} (k_B T_e) + n_e \left( -\vec{w}_e \cdot \vec{\nabla} \frac{n_e}{n_e} \right) = Q_{tot}. \tag{5.21}
\]

This results in:

\[
\vec{w}_e \left( \frac{3}{2} n_e \vec{\nabla} (k_B T_e) - k_B T_e \vec{w}_e \cdot \vec{\nabla} \frac{n_e}{n_e} \right) = Q_{tot}. \tag{5.22}
\]

Figure 5.16 shows that the electron density does not change much when the electron temperature is changed. Furthermore, the following relation between \( T_e \) and \( n_e \) is obtained: \( n_e = c_1 T_e^\beta \), with \( \beta = 0.2 \) and \( c_1 = 6.4 \times 10^{17} \). Substituting \( n_e = c_1 T_e^\beta \) into equation (5.23) we obtain the following:

\[
\frac{3}{2} c_1 T_e^\beta \vec{w}_e \cdot \vec{\nabla} (k_B T_e) - k_B T_e \vec{w}_e \cdot \vec{\nabla} c_1 T_e^\beta = Q_{tot}. \tag{5.24}
\]

Since the observed problem is investigated on-axis, it is basically a 1-D problem:

\[
\frac{3}{2} c_1 T_e^\beta w_e \frac{\partial}{\partial z} (k_B T_e) - T_e w_e c_1 \frac{\partial}{\partial z} (k_B T_e^\beta) = Q_{tot}, \tag{5.25}
\]

with \( \frac{\partial}{\partial z} (k_B T_e^\beta) = \beta T_e^{\beta-1} \frac{\partial}{\partial z} (k_B T_e^\beta) \). This equation can be simplified into:

\[
\left( \frac{3}{2} - \beta \right) T_e^\beta w_e c_1 \frac{\partial}{\partial z} (k_B T_e^\beta) = Q_{tot}, \tag{5.26}
\]

where \( Q_{tot} = Q_{heating} - Q_{ea} - Q_{es} \):
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Figure 5.16: The linear fit with $n_e = c_1 T_e^\beta$ is used on the data points to obtain $c_1 = 6.4 \cdot 10^{17}$ and $\beta=0.2$.

- $Q_{heating} = \eta f^2$; Ohmic heating is dominantly present at the start of the plasma expansion due to the current from the source, but it is negligible after $z=17$ cm.

- $Q_{ea} = n_e n_a k_{ea} c(\hat{T}_e - \hat{T}_a)$; The cooling term of elastic electron collisions with neutrals.

- $Q_{ei} = \frac{3}{2} n_e^2 e \frac{T_e - T_i}{3 \cdot 10^{-14} T_e^{3/2} A_e} \ln \Lambda$; Elastic collisions of electrons with ions.

Here $\ln \Lambda$ is the Coulomb logarithm and $\hat{T}_e$, $\hat{T}_i$ and $\hat{T}_a$ is the temperature of the electrons, of the ions and of the neutrals [in eV], respectively. In an adiabatic expansion the heat input is zero, namely $Q_{tot} = 0$, which results in $\beta = 3/2$. The obtained $\beta$ in the plasma expansion is smaller than in an adiabatic expansion which indicates the cooling of electrons through elastic collisions with ions and neutrals.

The function $f(t = T_e/T_i) \approx 0.3$ remains constant within an error of 20% when $t$ is between 2 and 11. The cooling of electrons by ions $Q_{ei}$ is then estimated to be $2 \cdot 10^4$ W m$^{-2}$. The cooling of electrons by neutrals $Q_{ea}$ depends much more by varying the electron temperature and need to be integrated along $T_e$, see next subsection.
Calculation of $\Delta z$

At the positions of interest ($z=17-24 \text{ cm}$), Ohmic heating can be neglected $Q_{\text{tot}} = -(Q_{\text{ea}} + Q_{\text{ea}})$:

$$\frac{3}{2} - \beta)T_e^3 w_e c_1 \frac{\partial}{\partial z}T_e = Q_{\text{tot}} = -(Q_{\text{ea}} + Q_{\text{ea}}).$$

(5.27)

Then set:

$$(\frac{3}{2} - \beta)T_e^3 w_e c_1 k_B = \gamma,$$

(5.28)

with $\beta = 0.2$, $c_1 = 6.4 \cdot 10^{17}$ and $w_e = 5000 \text{ m/s}$. This results in $\gamma = 0.053$. When $\gamma$ is included we obtain:

$$\gamma T_e^3 \frac{\partial}{\partial z}T_e = Q_{\text{tot}}.$$

(5.29)

This equation needs to be integrated to get the distance over which the electron temperature has dropped from $10444 \text{ K}$ to $2321 \text{ K}$:

$$\int_{T_e=10444}^{T_e=2321} \frac{T_e^3}{132(T_e - T_a)} - 3.8 \cdot 10^5 dT_e = \int_0^{z'} dz.$$

(5.30)

The gas temperature $T_a = 900 \text{ K}$ is measured with TDLAS to be constant in the region of interest and the velocity of the electrons is estimated to be $w_e = 5000$
m/s. Integrating equation (5.30) from $T_e=0.9$ eV to $T_e=0.2$ eV gives as result $\Delta z=6.8$ cm. The calculated distance $\Delta z$ is in good agreement with distance that is obtained with the experimental diagnostics, see figure 5.15.
A novel diagnostic to study processes in a magnetized hydrogen expansion that involve negative hydrogen ions

Abstract In this chapter we will experimentally verify the presence of processes involving negative ions in a magnetized hydrogen plasma expansion. To study the role of these processes we have used a novel photo-detachment technique. This technique is based on the recording of the change in Balmer line emission after the injection of a laser pulse into the plasma. We will show that all the negative ions will be photo-detached by the laser so that the population to the excited states by processes involving negative ions is interrupted. With a detailed analysis we have determined a negative ion density of $10^{16}$ m$^{-3}$ in the red light emitting plasma which is in good agreement with simulation results in Chapter 5. Processes that involve negative ions and do not populate the excited states of atomic hydrogen are also indirectly detected in the blue light emitting plasma. These processes disturb the results of the photo-detachment in such a way that only an underestimation of the negative ion density can be determined in the blue light emitting plasma.
6.1 Introduction

The simulations results (from Chapter 5), that were obtained with a collisional radiative model [1], have shown us that molecular processes such as dissociative recombination of $\text{H}_2^+$ and $\text{H}_3^+$, and processes with negative hydrogen ions are key in explaining the detected Balmer line emission (visible light) from the magnetized hydrogen plasma expansion. In this chapter, we investigate the processes with negative ions by disturbing the negative ion density with a laser while monitoring at the same time the change in Balmer line emission. This chapter is therefore "the proof of the pudding" that processes which involve negative hydrogen ions are present in our plasma.

In the previous chapter we have seen that in the red light emitting plasma the $\text{H}^-$ density is $n_{\text{H}^-}=10^{15-16} \text{ m}^{-3}$ and that the atomic mutual neutralization process of $\text{H}^+$ with $\text{H}^-$ is the main process involving negative hydrogen ions:

$$\text{H}^+ + \text{H}^- \rightarrow \text{H}(n) + \text{H}, \quad \text{with } n = 3. \quad (6.1)$$

The cross-sectional data of this reaction has been calculated with a single-crossing Landau-Zener approximation by Bates et al [2] and Olsen et al [3] and shows a good agreement with experimental data. The excited states $n=2$ and $n=4$ in equation (6.1) are less populated than $n=3$, since the corresponding non-adiabatic couplings are weaker. The population to the excited states $n \geq 5$ do not exist at all because of energy constraints.

At the transition from the red light emitting plasma to the blue light emitting plasma a higher $\text{H}^-$ density is present ($n_{\text{H}^-}=10^{17} \text{ m}^{-3}$) than in the red light emitting plasma since the dissociative attachment process is more efficient due to optimal conditions: a low electron temperature ($T_e \approx 0.2 \text{ eV}$) in combination with a high ro-vibrational energy of $\text{H}_2^0$ molecules. Furthermore, we have determined in Chapter 5 from modeling that the $\text{H}^+$ ion density has decreased significantly from $n_{\text{H}^+}=10^{18-19} \text{ m}^{-3}$ to $n_{\text{H}^+}=2 \cdot 10^{16} \text{ m}^{-3}$ and the $\text{H}_3^+$ density has increased from $n_{\text{H}_3^+}=10^{16} \text{ m}^{-3}$ to $n_{\text{H}_3^+}=3 \cdot 10^{16} \text{ m}^{-3}$ in several cm of expansion. The $\text{H}_2^+$ density is pinned along the full plasma column ($n_{\text{H}_2^+}=2 \cdot 10^{16} \text{ m}^{-3}$). Although this density value is relatively low compared to other ion densities, it is still a...
very important ion since large amounts of $\text{H}_2^+$ are created by charge exchange and large amounts are destroyed by background collisions to create $\text{H}_2^+$ ions.

The excited states of $n=4$ and higher are mainly populated by the molecular mutual neutralization process of $\text{H}_2^+$ and $\text{H}^-$ in the blue light emitting plasma region, as described by Eerden et al [4]. (In Chapter 5 we have shown that about $\sim 84\%$ branches into excited atoms and $\sim 16\%$ in ro-vibrationally excited molecules):

$$\text{H}_2^+ + \text{H}^- \rightarrow \text{H}(n) + \text{H}_2, \quad \text{with } n = 2 - 9. \quad (6.2)$$

The ionization energy of $\text{H}_2$ is 15.42 eV and the binding energy of $\text{H}^-$ is 0.75 eV. This leaves 14.67 eV to excite the hydrogen atom. As the ionization energy of atomic hydrogen is only 13.6 eV, all states can be populated in this reaction leaving some energy for the ro-vibrational excitation of the resulting $\text{H}_2$ molecule. The cross sections of $n=2-9$ were calculated with a multi-crossing Laundau-Zener approximation valid at collision energies below 10 eV. There is a non-monotonic behavior of partial cross sections observed as function of $n$, with a maximum efficiency of excitation for the quantum states $n=4, 5$ and $6$. Simulation results with the collisional radiative model revealed that the measured excited state densities of $n=4-9$ in the blue light emitting plasma (see Chapter 3) can be explained with the molecular mutual neutralization process of $\text{H}_2^+$ and $\text{H}^-$. In Chapter 5 we have simulated that the $\text{H}_2^+$ and $\text{H}^-$ ion densities are dominantly present in the blue light emitting plasma (see Chapter 5, figure 5.8). Therefore, the molecular mutual neutralization process of $\text{H}_2^+$ and $\text{H}^-$ is expected to be present as well [5].

For the detection of negative hydrogen ions many diagnostics have been developed the last couple of decades. A well known diagnostic is the photo-detachment of a negative hydrogen ion with laser photons in combination with a double Langmuir probe [6]. To photo-detach the extra electron from the negative hydrogen ion a laser photon energy of 0.75 eV is necessary:

$$\text{H}^- + h\nu \rightarrow \text{H} + e^- . \quad (6.3)$$

The extra electrons that are detected by the double Langmuir probe is a measure of the negative ion density in the plasma.
Another method detecting negative hydrogen ions is the very sensitive absorption technique called Cavity Ring Down Spectroscopy (CRDS) [7]. This method is based on the injection of a laser pulse into a cavity with highly reflecting mirrors which contains the plasma under investigation. The CRDS setup measures how long it takes for the light to decay to $1/e$ of its initial intensity, and this "ringdown time" can be used to calculate the negative ion density in the cavity.

The negative ion density can also be determined with optical emission spectroscopy when the excited hydrogen atoms are populated by mutual neutralization processes. At the Max-Planck-Institut für Plasmaphysik (IPP) in Garching the line ratio of $H_\alpha/H_\beta$ emission in combination with a Collisional Radiative model (CR-model) has been used to determine the negative ion density in active plasmas (for fusion research) [8].

In this Chapter, a novel photo-detachment technique is applied to the plasma to experimentally verify the presence of processes involving negative ions, i.e. the atomic and molecular mutual neutralization process. The photo-detachment setup consists of a pulsed Nd:YAG laser to photo-detach all the present negative hydrogen ions in the detection volume and an optical detection setup is used to monitor time dependently the change in Balmer line emission. We will also show that the molecular mutual neutralization process of $H_3^+$ and $H^-$ is an important destruction channel for $H^-$ and that it influences the photo-detachment process in the blue light emitting plasma.

6.2 Experimental setup and diagnostics

6.2.1 Plasma source

For the creation of the hydrogen plasma a cascaded arc is used. The cascaded arc is a wall stabilized thermal plasma source and was first introduced by Maecker in 1956 [9]. The plasma source consists of three tungsten-lanthanum cathodes, four water-cooled copper plates that are separately insulated by PVC spacers and vacuum sealed by rubber O-rings, and a copper anode endplate, see figure 6.1.
6.2. EXPERIMENTAL SETUP AND DIAGNOSTICS

6.2. EXPERIMENTAL SETUP AND DIAGNOSTICS

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Figure 6.1: The wall-stabilized cascaded arc. The zero position (z=0 cm) starts at the end of the nozzle and is indicated by an asterisk (*).

Hydrogen flows at 3 standard liters per minute or 1.25·10²¹ H₂/s through the discharge channel (4 mm diameter). The partially ionized and nearly fully dissociated hydrogen plasma is produced with an input power of 6.8 kW at a pressure of 10⁴ Pa. At the anode endplate a copper nozzle can be mounted which size and geometry can be chosen. Due to significant losses of electrons, H⁺ ions and H atoms at the nozzle surface, a nozzle with a large diameter (open nozzle) is chosen to reduce the contact with the plasma and thereby minimizing the surface association processes [10]. The hydrogen plasma freely expands in a 3 meter long stainless steel cylindrical vessel at low pressure (typically 10 Pa in this work), which has a diameter of 30 cm. The pressure gradient between the cascaded arc and the expansion vessel forces the plasma to expand first supersonically and then, after the formation of a shock, subsonically into the background [11]. Four Helmholtz coils mounted around the vessel produce a parallel uniform magnetic field of 14 mT over a length of approximately 1.4 meter.

6.2.2 The photo-detachment setup

A part of the photo-detachment setup is shown in figure 6.2. The laser pulses that are used for the photo-detachment experiments are produced by a Q-switched Nd:YAG laser operating at 10 Hz with either a wavelength of 532 or 1064 nm. The two different wavelengths are used to distinguish photo-ionization from photo-
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Figure 6.2: Schematic representation of the photo-detachment setup. The scheme enables both 532- and 1064 nm pulses to be directed through the plasma expansion.

detachment. This was done because the cross-section of photo-ionization is a factor eight higher at a wavelength of 1064 nm than at 532 nm for all excited states of atomic hydrogen, while the cross-section of photo-detachment remains similar for both wavelengths, see figure 6.4. For both wavelengths the pulse length and pulse diameter is 10 ns and 1.4 cm respectively. The unfocussed laser pulses are directed to the expansion vessel of PLEXIS to investigate the photo-detachment process in the magnetized hydrogen plasma expansion. The cascaded arc is mounted on a movable arm inside the low pressure vessel which allows for spatial and axial measurements throughout the plasma expansion while keeping the laser path fixed at the window ports.

In figure 6.3 the cross beam experiment for photo-detachment is shown. An optical lens system is creating an 1:1 image of the plasma on a Photo Multiplier Tube (PMT) with a spatial resolution of 3 mm. The wavelength selection is done with an appropriate optical bandpass filter and the data-acquisition is realized by a fast (∼ns) oscilloscope, triggered by the Q-switch of the Nd:YAG. Note that we measure along the integrated Line Of Sight (LOS).

The effect of the laser pulse on the plasma is monitored by a time resolved measurement on the Balmer line emission, namely H\textsubscript{a}, H\textsubscript{β}, and H\textsubscript{γ}. This corresponds with emission from the upper state \(n=3, 4\) and 5 to the lower state \(n=2\).
6.2. Experimental Setup and Diagnostics

Figure 6.3: Experimental setup for detecting the Balmer line emission originating from the plasma expansion. The laser beam alignment is perpendicular to the axis of the plasma expansion. The laser pulses of 532- or 1064 nm are directed through the plasma expansion to a beam dump. The effect of the laser pulse is monitored by a PMT and an appropriate optical bandpass filter.

respectively. Due to the limited bandwidth of the used optical filters, the emission from the excited states $n \geq 6$ to $n=2$ are measured simultaneously.

We argue that processes which involve negative hydrogen ions are not present during the photo-detachment process (since all H$^-$ ions are photo-detached) and can therefore not populate the excited states of atomic hydrogen. This should result in a decreasing Balmer line emission. After the laser pulse has passed the plasma, negative hydrogen ions are created again by the dissociative attachment process and an increase in Balmer line emission is observed until steady state emission has been reached. The decreased Balmer line emission induced by the laser as well as the time-constant of populating the excited state is monitored.

The uncertainty in these measurements depends on whether the observed de-population of the Balmer line emission is due to photo-detachment or photo-ionization. The cross-section for photo-ionization $\sigma_{n^+}$ of level $n$ for hydrogen
6. PHOTO-DETACHMENT  6.2. EXPERIMENTAL SETUP AND DIAGNOSTICS

![Figure 6.4: The cross-sectional data of photo-ionization (PI) for the excited states \( n=3 \)-7 and photo-detachment (PD) at different wavelengths is shown. Note that the important cross sections in this work are at 532 nm and 1064 nm, indicated by the vertical dashed lines.](image)

The cross-sectional data of the photo-detachment and photo-ionization process is shown in figure 6.4.

Laser induced ionization could be present in the plasma when 
\[
F_{n^+} > \sum_{m<n} A_{nm}, \quad \text{where } m \text{ is a level lower than } n \text{ and } F_{n^+} = \frac{\sigma_{n^+} <I>}{h\nu} \quad \text{[in s\(^{-1}\)]}. \]

Here 
\[
<I> = \frac{E_{\text{pulse}}}{\tau_{\text{pulse}} A_{\text{laser}}}, \quad \text{with } \tau_{\text{pulse}} \text{ the laser pulse length [in s], } E_{\text{pulse}} \text{ the laser pulse energy [in J/pulse] and } A_{\text{laser}} \text{ the cross-section of the laser beam [in m}\(^2\)].
\]

The results are shown in table 6.1. As the energy of the photons at a wavelength of 1064 nm (1.15 eV) is lower than the ionization energy of the atoms in state \( n=3 \) (1.51 eV) photo-ionization can not be detected when looking at \( \text{H}_\alpha \) line emission. We exclude multi-photon ionization, since the rate for this process at our laser intensities is too small to play a significant role. When the response of the Balmer line emission of \( \text{H}_\beta \) and \( \text{H}_\gamma \) is monitored during the photo-detachment measure-
6.2. EXPERIMENTAL SETUP AND DIAGNOSTICS

Table 6.1: The laser induced ionization $F_{n+}$ [s$^{-1}$] and the spontaneous emission $A_{nm}$ [s$^{-1}$] for the states $n=3, 4$ and 5. The experimental conditions are: $E_{pulse} = 100$ mJ/pulse, $A_{laser} = 1.77 \cdot 10^{-4}$ m$^{-2}$ and $\tau_{pulse} = 10$ ns.

<table>
<thead>
<tr>
<th>$\sum_{m&lt;n} A_{nm}$</th>
<th>$n_{3}^{32}$ nm</th>
<th>$n_{4}^{1064}$ nm</th>
<th>$n_{3}^{32}$ nm</th>
<th>$n_{4}^{1064}$ nm</th>
<th>$n_{5}^{32}$ nm</th>
<th>$n_{5}^{1064}$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{n+}$</td>
<td>9.1 $\cdot$ 10$^7$</td>
<td>n/a</td>
<td>2.3 $\cdot$ 10$^7$</td>
<td>1.9 $\cdot$ 10$^8$</td>
<td>6.4 $\cdot$ 10$^6$</td>
<td>3.0 $\cdot$ 10$^7$</td>
</tr>
</tbody>
</table>

ments a small part of the decrease in emission might be due to photo-ionization (see table 6.1). The photo-detachment experiments are carried out along the full plasma column to determine how important the processes with negative ions are to the population of excited hydrogen atoms.

The balance equation of $H^-$ is given by:

$$\frac{\partial n_{H^-}}{\partial t} = n_{e} n_{H_{2}^{+}} k_{da}^{H_{2}^{+}} - n_{H^{+}} n_{H^-} k_{amr}^{H^{+}} - n_{H_{2}^{+}} n_{H^{+}} k_{mmr}^{H_{2}^{+}} - n_{H_{3}^{+}} n_{H^-} k_{mmr}^{H_{3}^{+}},$$

(6.5)

where $k_{da}^{H_{2}^{+}}$, $k_{amr}^{H^{+}}$, $k_{mmr}^{H_{2}^{+}}$ and $k_{mmr}^{H_{3}^{+}}$, are the rate coefficients [in m$^{3}$s$^{-1}$] of dissociative attachment, atomic mutual neutralization of $H^{+}$, molecular mutual neutralization of $H_{2}^{+}$ and molecular mutual neutralization of $H_{3}^{+}$ respectively. The production term $P_{H^-}$ of $H^-$ consists of the dissociative attachment process and the destruction term $D_{H^-}$ consists of the three mutual neutralization processes of $H^+$, $H_{2}^{+}$ and $H_{3}^{+}$ with $H^-$. When we define

$$n_{H^{+}} n_{H^-} k_{amr}^{H^{+}} + n_{H_{2}^{+}} n_{H^-} k_{mmr}^{H_{2}^{+}} + n_{H_{3}^{+}} n_{H^-} k_{mmr}^{H_{3}^{+}} = n_{H^-} \sum_{n=1}^{3} n_{H_{n}^{+}} k_{rec}^{H_{n}^{+}} = n_{H^-} \tau^{-1}$$

(6.6)

the balance equation for $H^-$ is given by:

$$\frac{\partial n_{H^-}}{\partial t} = P_{H^-} - n_{H^-} \tau^{-1}.$$ 

(6.7)

The following is assumed for the balance equation:
The $H_3^+ + H^-$ channel is an important loss channel for the $H^-$ ions. This channel does not lead to excited hydrogen atoms but it can influence the repopulation time constant $\tau$. Likewise, the $H_3^+ + H^- \rightarrow H_2^+ + H(n=1)$ also does not lead to excited hydrogen atoms.

During the photo-detachment process we assume a complete depletion of $H^-$ (saturation) in the detection volume. Therefore, the negative ion density just after the photo-detachment process is zero, $n_{H^-}(t = 0) = 0$.

The solution of equation (6.7) for the production of $H^-$ after the photo-detachment process is:

$$n_{H^-}(t) = P_{H^-}\tau [1 - \exp^{-t/\tau}] \quad (6.8)$$

with $1/\tau = \sum_{n=1}^{3} n_{H^+_n} k_{n}^{rec,-}$, $P_{H^-} = n_e n_{H^+_2} k^{da}$ and $n_{H^-}(t = 0) = 0$.

After the photo-detachment process the density of the excited states will increase. We obtain for $n=3$ the following mass balance during repopulation:

$$\frac{\partial n_3}{\partial t} = P_0 - n_3 D_0 + n_{H^-} \sum_{n=1}^{2} n_{H^+_n} k_{n}^{rec,-} = P_0 - n_3 D_0 + n_{H^-}/\tau_-. \quad (6.9)$$

Note that $\tau_-$ can be different from $\tau$ since the mutual neutralization process of $H_3^+ + H^-$ is not included in the former time constant $\tau$. In equation (6.9) the production term $P_0$ and destruction term $D_0$ are given by:

- $P_0 = \sum_{m>3} n_m A_{m3} + n_e \sum_{m \neq 3} k_{m3} n_m + n_e n_{H^+_2} k^{dr}_{n=3}$,
- $D_0 = \sum_{m=2,1} A_{3m} + n_e \sum_{m \neq 3} k_{3m}$,
- $\tau_-= \sum_{n=1}^{2} n_{H^+_n} k_{n}^{rec,-} = n_{H^+} n_{H^-} k_{n=3}^{amr} + n_{H^+_2} n_{H^-} k_{n=3}^{mmr}$.

Here $A_{3m}$ and $A_{m3}$ is spontaneous emission from and to the excited state $n=3$ respectively. $k_{3m}$ and $k_{n3}$ are the rate coefficients of electron (de)excitation from and to the excited state $n=3$ respectively.
To solve differential equation (6.9) we make the following ansatz:

$$n_3(t) = n_3^0 - \Delta n_3 \exp(-t/\tau).$$  \hspace{1cm} (6.10)

Here we assume that there is only one time constant $\tau$ that is related with H$^-$. A second time constant that could be observed is assumed to be caused by atomic processes such as photo-ionization. $\Delta n_3$ is the amount of $n=3$ that is destroyed by the photo-detachment process at $t=0$ (without photo-ionization) and $n_3^0$ is the steady state density of $n=3$ (see Chapter 3). The definitions of $t=0$, $\Delta n_3$, $\tau$ and $n_3^0$ are shown in figure 6.5.

**Figure 6.5**: The photo-detachment process induces a change in the excited state density of $n=3$. At $t = 0$ s the photo-detachment process has stopped and an increase of the excited state density of $n=3$ occurs.

The steady state density $n_3^0$ of $n=3$ follows from equation (6.9):

$$n_3^0 = \frac{P_0 - n_H^-/\tau_-}{D_0}$$  \hspace{1cm} (6.11)

and for $\Delta n_3$ we obtain:

$$\Delta n_3 = n_3^0 - \frac{P_0}{D_0} = \frac{n_H^-}{D_0\tau_-}.$$  \hspace{1cm} (6.12)

In the red light emitting plasma region we know (from Chapter 5) that:

$$n_{H^+} \gg n_{H_2^+}, n_{H_3^+}.$$  \hspace{1cm} (6.13)
Because the atomic mutual neutralization process is mainly present in the red light emitting plasma we obtain, when \( k_n^{rec} \) does not change much:

\[
\tau^{-1} = n_{H^+} k_{n=3}^{amr}. \tag{6.14}
\]

If we know the relation between \( \tau \) and \( \tau_\text{rec} \) we can determine the rate coefficient of \( k_{amr}^{rec} \) in the red light emitting plasma by plotting \( \tau^{-1} \) against \( n_{H^+} \). Note that \( \tau \) is measured with the photo-detachment measurements and not \( \tau_\text{rec} \). Since the molecular mutual neutralization process of \( \text{H}_3^+ \) is not present in the red light emitting plasma the assumption of \( \tau = \tau_\text{rec} \) is justified.

In the blue light emitting plasma region we know (from Chapter 5) that:

\[
n_{\text{H}_3^+} \gg n_{\text{H}_2^+}, n_{H^+}, \tag{6.15}
\]

so that

\[
\tau^{-1} = n_{\text{H}_3^+} k_{\text{mmr}}. \tag{6.16}
\]

With equation (6.16) we can determine the rate coefficient of the molecular mutual neutralization process of \( \text{H}_3^+ \) with \( \text{H}^- \).

As already discussed before we observe an increase of the Balmer line emission after the photo-detachment process. The densities that change after the photo-detachment process are \( n_3 \) and \( n_{H^-} \):

\[
\frac{\partial n_3}{\partial t} = P_0 - n_3 \left( D_0 + n_{H^-} / \tau_\text{rec} \right), \tag{6.17}
\]

with

\[
n_{H^-}(t) = P_{H^-}[1 - \exp(-t/\tau)] \tag{6.18}
\]

and

\[
n_3(t) = n_3^0 - \Delta n_3 \exp(-t/\tau). \tag{6.19}
\]

The change in density for \( n=3 \) in the plasma is given by:

\[
\Delta n_3 = P_{H^-}[D_0 - 1/\tau]^{-1} \frac{\tau}{\tau_\text{rec}}. \tag{6.20}
\]

The consequence of equation (6.20) for the interpretation of the photo-detachment results will be discussed in the next section.
6.3 Results and discussion

6.3.1 Time dependent photo-detachment measurements

Two typical oscilloscope recordings of time dependent photo-detachment measurements of Balmer line emission are shown in figure 6.6.

Figure 6.6: Two typical oscilloscope recordings of time dependent photo-detachment measurements are shown. At t=0 µs a decrease in the Balmer line emission of H\textalpha
top) and H\textbeta (bottom) is observed. a) A single repopulation time constant \( \tau \) of H\textalpha is observed in the red light emitting plasma region while b) two repopulation time constants (denoted by \( \tau_1 \) and \( \tau_2 \)) of H\textbeta are observed at the transition from red to blue light emission.
The data that is obtained in figure 6.6 is an average of 200 time-resolved measurements. On a fixed spatial position in the plasma expansion a constant amount of Balmer emission is observed. At $t=0 \mu$s a decrease in the Balmer line emission is observed as a result of photo-detachment of H$^-$ (the time of the photo-detachment process is 10 ns). After the sudden decrease in the Balmer line emission, an exponential increase is observed. Note that the process occurring first is denoted first process, and the processes observed secondly is called second process. When only one process is present no statement is made about whether the first or second process is present. Within these experiments the decrease in Balmer emission induced by the laser pulse is converted to absolute densities (in $m^{-3}$) as described in ref.[13]. Furthermore, the $1/e$ time constants ($\tau_1$ and/or $\tau_2$) of the increasing Balmer line emission after the photo-detachment process are determined. The criteria to decide whether the signal consists of one or two time constants is well defined since they differ one order of magnitude ($\tau_1 \approx 10^{-8} \text{ s}^{-1}$ and $\tau_2 \approx 10^{-7} \text{ s}^{-1}$). Immediately after the laser pulse the emission of H$\alpha$, H$\beta$ and H$\gamma$ exponentially increases back to the original value with a time constant ranging from 0.1 to 1 $\mu$s in the red light emitting plasma and 66 ns in the blue emitting plasma. The flow in the plasma is investigated by looking at the Balmer line.

Figure 6.7: The photo-detachment process for $n=3$ at different relative positions with respect to the laser pulse position $z=10$ cm.
6.3. RESULTS AND DISCUSSION

emission at different relative positions with the detection system while keeping the laser pulse fixed at a \( z = 10 \) cm, see figure 6.7. In the downstream direction of the plasma expansion no depopulation of \( n=3 \) is observed outside the cross-section of the laser pulse, indicating that the negative ions have a mean free path of several mm. Therefore, the flow of particles in the plasma can be neglected during the photo-detachment measurements.

6.3.2 The laser power dependence on the photo-detachment process

The influence of the laser pulse energy on the photo-detachment process is investigated in figure 6.8 and 6.9. In these figures the percentage of depopulation for \( n=3 \) and 4 with respect to the steady state density is given as function of the laser pulse energy.

![Graph](image.png)

**Figure 6.8:** The percentages of depopulation of \( n=3 \) and \( n=4 \) with respect to the steady state density in the red light emitting plasma region is given as function of the laser pulse energy. The uncertainty of the obtained data points due to the analysis method is 10%.

In figure 6.8 the percentage of depopulation for \( n=3 \) (\( n=4 \)) along the line of sight is shown when the energy of the laser pulse is varied. It is observed that there are three regions present when the energy of the laser pulse is varied.
The first region for \( n=3 \) is from 0 to 40 mJ/pulse: There are not sufficient laser photons present in the plasma to fully detach the negative ions. The second region is from 40 to 120 mJ/pulse: The percentages of depopulation of the excited states do not change when the energy of the laser pulses are increased. In this region it is assumed that saturation is reached, i.e. all negative ions are detached by the laser photons. When the energy of the laser pulse is more than 120 mJ/pulse the depopulation of the excited states increases even more, indicating depopulation by atomic processes such as photo-ionization.

\[
\begin{align*}
\text{Figure 6.9:} & \quad \text{The percentages of depopulation of } n=3 \text{ and } n=4 \text{ with respect to the steady state density in the blue light emitting plasma region is given as function of the laser pulse energy. The uncertainty of the obtained data points due to the analysis method is 10 \%.} \\
\end{align*}
\]

In figure 6.9 the percentages of depopulation for \( n=3 \) (\( n=4 \)) when the energy of the laser pulse is varied in the blue light emitting part of the plasma expansion is given. For \( n=4 \) saturation is reached at about 30-40 mJ/pulse and for \( n=3 \) no saturation is observed.

In this work we use 100 mJ/pulse for all the photo-detachment experiments since then the photo-detachment process saturates and the photo-ionization process is not significantly present. Note that when a laser wavelength of 1064 nm is used for \( n=3 \) no photo-ionization can occur.
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The characteristic time constant of the photo-detachment (PD) process is given by the following equation:

$$\tau_{PD} = \left( \frac{E_{\text{pulse}} \sigma_{PD}}{A_{\text{laser}} \tau h \nu} \right)^{-1}. \quad (6.21)$$

From this we calculate that the PD processes occur in 1-2 ns when a laser pulse energy of 100 mJ/pulse and a laser pulse diameter of 1.4 cm is used. Therefore, we expect that the laser pulse length of 10 ns is sufficiently long to detach all the negative ions. When we use the cross-sectional data of the photo-ionization process we calculate time constants of about 10 ns which are slower than that of the photo-detachment process.

6.3.3 The photo-detachment experiments along the full plasma column

In figure 6.10 and 6.11 the first data representation of the photo-detachment experiments are given at different axial positions in the plasma column. In the top row of the two figures, the maximum depopulation $\Delta N_n$ [in m$^{-2}$] of the excited states $n=3, 4$ and 5 for both 532 and 1064 nm laser pulses is shown. Here, $\Delta N_n$ is the line of sight density of state $n$ that is depopulated by the photo-detachment process. Furthermore, the time constants $\tau_n$ for repopulating the excited states $n=3, 4$ and 5, and $\Delta N_n/\tau_n$ [in m$^{-2}$s$^{-1}$] are shown.

The red light emitting plasma region

When we observe the maximum depopulation $\Delta N_n$ [in m$^{-2}$] of the excited states $n$ as a result of the photo-detachment process, a maximum for the excited state $n=3$ is reached. Since the depopulation $\Delta N_n$ by the photo-detachment process is decreasing with the quantum state $n$ the atomic mutual neutralization process is believed to be responsible (main input to $n=3$).

Because we ascribe the observed depopulation of the excited states by the atomic mutual neutralization process, the rate coefficient can be determined with equation (6.14) and compared with the known literature value [4, 5]. In the red part of the plasma expansion the time constant of repopulating the excited states $n=3$ increases from 0.1 to 1 $\mu$s along the plasma column, see the second row.
Figure 6.10: In the first row, the line of sight densities for $n=3$ (left) and $n=4$ (right) are determined with two different laser wavelengths at several positions along the expansion axis (z-axis). The two graphs in the middle row show the time constants for $n=3$ (left) and $n=4$ (right) and the lowest two graphs, show $\Delta N_n/\tau_n$ of $n=3$ (left) and $n=4$ (right).

of figure 6.10. For the higher excited states similar time constants are observed, because the excited states $n=4$ and 5 are in electron saturation balance with $n=3$. Therefore, it is not possible to determine the rate coefficients for the higher excited states.

Since we know that in the first 15 cm of expansion the electron density is
Figure 6.11: In the first row on the left the line of sight densities for \( n=5 \) is determined with two different laser wavelengths at several positions along the expansion axis (z-axis). In the first row on the right, the percentage of depopulation with respect to the steady state density for \( n=[6 - \infty] \) is given. The two graphs in the middle row show the time constants for \( n=5 \) (left) and \( n=[6 - \infty] \) (right) that are determined with two different laser wavelengths and the lowest graphs on the left shows \( \Delta N_5/\tau_5 \).

high, \( n_{H^+} \approx n_e \) and \( n_{H^+} \gg n_{H_2^+}, n_{H_3^+} \) we can determine the rate coefficient
6. PHOTO-DETACHMENT

6.3. RESULTS AND DISCUSSION

Figure 6.12: Here the inverse time constant $\tau_{-1}$ [in s$^{-1}$] is plotted as function of the electron density [in m$^{-3}$]. A linear fit is applied to the data points to determine the rate coefficient of the atomic mutual neutralization process $k_{amr}$ for $n=3$ in the red light emitting plasma ($z=1$-17 cm).

of $k_{amr}$ by plotting $\tau_{-1}$ as function of the electron density $n_e$:

$$\tau_{-1} = n_e \cdot k_{amr}^{n=3}.$$  (6.22)

The time constant consists of

$$\frac{1}{\tau} = \frac{1}{\tau_{amr}} + \frac{1}{\tau_{mmr2}} + \frac{1}{\tau_{mmr3}}.$$  (6.23)

Here $\tau_{amr}$, $\tau_{mmr2}$ and $\tau_{mmr3}$ are the time constants of the atomic mutual neutralization process, the molecular mutual neutralization process of H$_2^+$ and the molecular mutual neutralization process of H$_3^+$. In figure 6.12 the result is shown. In the first 15 cm of expansion $\tau = \tau_{amr}$ and the rate coefficient of the atomic mutual neutralization process is determined to be $k_{amr}^{n=3} = 5.7 \cdot 10^{-14}$ m$^3$s$^{-1}$. The obtained rate coefficient is in good agreement with the literature value of $k_{amr}^{n=3} = 5.0 \cdot 10^{-14}$ m$^3$s$^{-1}$ [2–4]. This proves that we are photo-detaching the
negative hydrogen ions and that the repopulation of $n=3$ is by the atomic mutual neutralization process and not by other processes or flow. For lower electron densities we can not say that $\tau = \tau_{amr}$ and corrections due to the molecular mutual neutralization processes are expected.

From equation (6.12) we can determine the negative ion density:

$$n_{H^-} = \Delta n_3 D_0 \tau_3.$$  \hspace{1cm} (6.24)

Here the depopulation of $n=3$ due to the photo-detachment process is $\Delta n_3 = 8.1 \cdot 10^{13} \text{ m}^{-3}$, the time constant $\tau = \tau_-$ changes from $0.1 \cdot 10^{-6}$ to $1.0 \cdot 10^{-6} \text{ s}$ and the destruction term is given by

$$D_0 = \sum_{m=2,1} A_{3m} + n_e \sum_{m \neq 3} k^{3m}. \hspace{1cm} (6.25)$$

For the destruction term we have

$$\sum_{m=2,1} A_{3m} = 10^8 \text{ s}^{-1} \hspace{1cm} (6.26)$$

and

$$\sum_{m \neq 3} k^{3m} = 10^{-12} \text{ m}^3 \text{ s}^{-1}. \hspace{1cm} (6.27)$$

The negative ion density can then be determined by plotting $\Delta n_3 D_0 / k_{amr}$ as function of the electron density $n_e$, see figure 6.13. Note that $\tau_3 = k_{amr} / n_{3n_H^+}$, with $n_{H^+} = n_e$. In the first part of the red light emitting plasma (where the electron density is highest) a negative ion density of $n_{H^-} \approx 5.7 \cdot 10^{15} \text{ m}^{-3}$ is determined and further downstream it increases to $n_{H^-} \approx 7.0 \cdot 10^{15} \text{ m}^{-3}$. In Chapter 5, we simulated a negative ion density of $n_{H^-} \approx 5.0 \cdot 10^{15} \text{ m}^{-3}$ close to the arc exit and $n_{H^-} \approx 1.0 \cdot 10^{16} \text{ m}^{-3}$ further downstream in the red light emitting plasma expansion. Therefore, the results of the model and experiment are in good agreement with each other.

In figure 6.10 and 6.11 we observe that photo-ionization is not present for $n=3$ at 1064 nm since the energy of the laser photons are insufficient to photo-ionize the hydrogen atom. Furthermore, no photo-ionization is observed for $n=3$ during the photo-detachment process when a laser pulse wavelength of 532 nm
6. PHOTO-DETACHMENT

6.3. RESULTS AND DISCUSSION

Figure 6.13: Here we plot $\Delta n_3 D_0 / k_{amr}^{\text{nm}}$ as function of the electron density $n_e$ [in m$^{-3}$] to determine the negative ion density. Two linear fits are applied to the data points in the red light emitting plasma.

is used because the laser pulse energy is too low. Note that the photo-ionization process has a minor contribution on the decreasing Balmer line emission and that the very fast time constants ($\sim$10 ns) are mainly caused by photo-ionization in the red light emitting plasma region for $n=4$, 5 and [6-$\infty$].

The blue light emitting plasma region

In the blue light emitting plasma expansion the time constants for repopulating the excited states $n=3$ and 4 are about 70 ns. The same time constants are also observed for $n=5$ and [6-$\infty$], see figure 6.11. The much faster time constants that are observed in the blue emitting plasma expansion (compared to the time constants of 0.1·10$^{-6}$ to 1.0·10$^{-6}$ s in the red light emitting plasma) must be caused by dominant mutual neutralization processes other than the atomic mutual neutralization process, see equation (6.23). The molecular mutual neutralization process of H$_3^+$ with H$^-$ is believed to be the reason for the fast time constant that is observed in the blue light emitting plasma since $n_{H_3^+} >> n_{H^+}, n_{H_2^+}$ (see
6.3. Results and Discussion

The maximum depopulation $\Delta N_n$ of the excited states by the photo-detachment process is observed for the excited states $n=4$ and $5$. This shows us that the processes involving negative ions have a larger influence on the higher excited states $n=4$ and $5$ than on $n=3$ in the blue light emitting plasma. Therefore, the molecular mutual neutralization process of $\text{H}_2^+\text{H}^-$ is believed to be the reason for the depopulation $\Delta N_n$ since the cross-sectional data of the molecular mutual neutralization process as given by Eerden et al [4] has a maximum for $n=4$, $5$ and $6$.

In Chapter 5 we have shown with a collisional radiative model that an increase of $\text{H}^-$ density from $10^{16}$ to $10^{17}$ m$^{-3}$ occurs at the red to blue light emitting plasma transition. This increase occurs because the efficiency of the dissociative attachment process is increasing significantly at this transition. To show this we plot $n_{\text{H}^-}n_{\text{e}}^{-1}\tau^{-1}$ as function of the axial distance from the arc $z$, see figure 6.14. Note that $n_{\text{H}^-}n_{\text{e}}^{-1}\tau^{-1} = n_{\text{H}^+}k_{da}$. In figure 6.14 we observe that the production of $\text{H}^-$ increases almost four orders of magnitude in the blue light.

![Figure 6.14: Here we plot $n_{\text{H}^-}n_{\text{e}}^{-1}\tau^{-1}$ as function of the axial distance from the arc $z$ [in cm].](image)
emitting plasma. The larger production term in the blue light emitting plasma region is accompanied with a larger destruction term due to the molecular mutual neutralization processes.

An estimation of the $H_{2}^{+}$ density can be made when a rate coefficient of dissociative attachment $k^{da} \approx 10^{-13} \text{ m}^{3}\text{s}^{-1}$ is assumed in the blue light emitting plasma: $n_{H_{2}^{+}} \approx 3 \times 10^{18} \text{ m}^{-3}$ (This is $\sim 0.3 \%$ of the total $n_{H_{2}}$ density).

### 6.3.4 The CR-model

The results of the photo-detachment experiments for the depopulation of $n=3$, 4 and 5, in percent of the steady state value, are compared with the simulation results (of Chapter 5) as function of $z$ in figure 6.15. The processes involving negative hydrogen ions that contribute to the production of excited states $n$ is simulated with a collisional radiative model [1]. This contribution is denoted by the $C_{H^{-}}$ channel (see Chapter 5, section 3). The $C_{H^{-}}$ channel consists of the atomic mutual neutralization process given by:

$$H^{+} + H^{-} \rightarrow H(n) + H, \quad \text{with } n = 3. \quad (6.28)$$

and molecular mutual neutralization process of $H_{2}^{+}$ with $H^{-}$ that populates $n=2$ up to 9 with a branching ratio of $\approx 0.84$:

$$H_{2}^{+} + H^{-} \rightarrow H(n) + H_{2}, \quad \text{with } n = 2 - 9. \quad (6.29)$$

The other $\approx 0.16$ branching ratio does not lead to excited states but it leads to ro-vibrationally excited molecules [5] (see Chapter 5):

$$H_{2}^{+} + H^{-} \rightarrow H(n) + H_{2}^{rv}, \quad \text{with } n = 1. \quad (6.30)$$

The molecular mutual neutralization process of $H_{3}^{+}$ with $H^{-}$ is also a process that consumes negative ions but does not populate the excited states $n$ of atomic hydrogen. This process branches into [5]:

$$H_{3}^{+} + H^{-} \rightarrow H_{2} + H_{2}, \quad (6.31)$$

and

$$H_{3}^{+} + H^{-} \rightarrow H_{2} + H + H. \quad (6.32)$$
In figure 6.15 we observe that in the red light emitting plasma region a good agreement between simulation and experiment for the excited states \( n = 3, 4 \) and 5 is obtained. The data show that the photo-detachment results are in good agreement with the CR-model in the red light emitting plasma region.

In the blue light emitting plasma region the recombination process of \( \text{H}_3^+ \) with \( \text{H}^- \) is present so that the time constant of \( \tau \) and \( \tau_- \) are not equal. The presence of this process results in a depopulation of \( n = 3, 4 \) and 5 which is lower (typically a factor 4 to 6 lower) than expected by the CR-model. The depopulation term \( \Delta n_3 \) is given by:

\[
\Delta n_3 = P_{\text{H}_3^-} [D_0 - 1/\tau]^{-1} \frac{\tau}{\tau_-}.
\]

Since \( \tau < \tau_- \), the depopulation of \( n = 3 \) due to the photo-detachment process is higher in reality than measured with the photo-detachment process. This indicates that the recombination term with \( \text{H}_3^+ \) must be large. This is one of the first measurements in which the molecular mutual neutralization process of \( \text{H}_3^+ \) and \( \text{H}^- \) is shown to be present in a plasma. Furthermore, the molecular mutual neutralization process of \( \text{H}_2^+ \) with \( \text{H}^- \) can also lower the dip \( \Delta n_3 \) because \( \approx 0.16 \) of the branching ratio does not lead to excited states, see reaction (6.30).

We know that the main population of \( \text{H}_2^+ + \text{H}^- \) is to the excited state \( n = 5 \). From figure 6.15 we observe that for \( n = 5 \) the ratio of \( \Delta n_5 \) from the CR-model (CR) and \( \Delta n_5 \) from the photo-detachment (PD) measurements is

\[
\frac{(\Delta n_5)_{\text{CR}}}{(\Delta n_5)_{\text{PD}}} \approx 5.
\]

This gives a relation between \( \tau \) and \( \tau_- \), and with equation (6.33) we then obtain

\[
\frac{\tau}{\tau_-} = \frac{n_{\text{H}_3^+} k_{\text{amr}} + n_{\text{H}_2^+} k_{\text{mmr}2} + n_{\text{H}_3^+} k_{\text{mmr}3}}{n_{\text{H}_3^+} k_{\text{amr}} + n_{\text{H}_2^+} k_{\text{mmr}2} + n_{\text{H}_3^+} k_{\text{mmr}3}} = \frac{1}{5}.
\]

The rate coefficient of molecular mutual neutralization process of \( \text{H}_3^+ \) with \( \text{H}^- \) is then \( k_{\text{mmr}3} \approx 10^{-14} \text{ m}^3 \text{ s}^{-1} \) in the blue light emitting plasma region with a factor of 5 uncertainty. This is the first time by our knowledge that the rate coefficient of the molecular mutual neutralization process of \( \text{H}_3^+ \) with \( \text{H}^- \) is experimentally estimated.
Figure 6.15: The photo-detachment results are compared with the modeling results for the excited states $n=3$, 4 and 5. The density change of $n=3$, 4 and 5 due to the photo-detachment laser is expressed in percent of steady state density.
As a summary the rate coefficient of mutual neutralization of H\(^+\) and H\(_3\)\(^+\) with H\(^-\) which were experimentally determined are given:

- \(k_{\text{amr}} \approx k_{\text{amr}}^{n=3} = 6 \cdot 10^{-14} \text{ m}^3 \text{ s}^{-1}\),
- \(k_{\text{mmr}}^{2} \approx 1 \cdot 10^{-14} \text{ m}^3 \text{ s}^{-1}\).

Furthermore, the rate coefficient of H\(_2\)\(^+\) with H\(^-\) is \(k_{\text{mmr}}^{2} \approx 4 \cdot 10^{-13} \text{ m}^3 \text{ s}^{-1}\).

An underestimation of the negative ion density can be made with:

\[
n_{H^-} = \Delta n_5 D_0 \tau_-. \tag{6.36}
\]

At \(z = 25 \text{ cm}\) we have: \(\tau_- \approx 4 \cdot 10^{-7} \text{ s}\), \(D_0 = 1.2 \cdot 10^7 \text{ s}^{-1}\) and \(\Delta n_5 = 5 \cdot 10^{14} \text{ m}^{-3}\). Then the negative ion density is estimated to be \(n_{H^-} \approx 3 \cdot 10^{15} \text{ m}^{-3}\). This is much lower than the modeled negative ion density with a collisional radiative model \((n_{H^-} = 10^{17} \text{ m}^{-3})\) and a one dimensional flow model \((n_{H^-} \approx 10^{17} \text{ m}^{-3})\).

An outlook for future photo-detachment experiments is to perform lateral measurements with the cross-beam setup. This gives us more insight at which lateral position the processes involving negative ions is maximum. This is especially interesting at the red to blue color transition where a hollow profile in Balmer line emission is observed.
6.4 Conclusion

A novel photo-detachment system is successfully applied to proof that both the atomic mutual neutralization process of H\(^+\) with H\(^-\) and the molecular mutual neutralization process of H\(_2\)\(^+\) with H\(^-\) populate the excited states of atomic hydrogen in the magnetized hydrogen plasma expansion. We have shown experimentally that for a certain laser pulse intensity photo-ionization is minimal and full photo-detachment of negative ions (saturation) occurs in the plasma. After the sudden decrease in the Balmer line emission due to the photo-detachment of negative ions by the laser, an exponential increase is observed. The amount of depopulation with respect to the steady state density and the time constant of repopulation depend strongly on the processes involving negative ions that are present in the detection volume. From the absolute amount of depopulation in the red light emitting plasma we have determined the negative ion density (\(n_{H^-} = 10^{16} \text{ m}^{-3}\)) which is in good agreement with the simulation results of a collisional radiative model. In the blue light emitting plasma region a much faster time constant of repopulation the excited states is observed after the photo-detachment process than when we compare it with the time constant in the red light emitting plasma. The much faster time constant that is observed in the blue light emitting plasma is because processes involving negative ions are present that do not lead to excited atoms: the molecular mutual neutralization process of H\(_3\)\(^+\) with H\(^-\) and a branching ratio of the molecular mutual neutralization process of H\(_2\)\(^+\) with H\(^-\). The presence of processes that do not lead to excited atoms weaken the depopulation of the excited states. By knowing the relative importance of \(n_{H^+}k^{amr}\), \(n_{H_2^+}k^{mmr2}\) and \(n_{H_3^+}k^{mmr3}\) in the blue light emitting plasma region an underestimation of the negative ion density can be made \(n_{H^-} \approx 3 \cdot 10^{15} \text{ m}^{-3}\). The obtained negative ion density with the photo-detachment setup is much lower than the modeled negative ion density with a collisional radiative model (\(n_{H^-} = 10^{17} \text{ m}^{-3}\)) and a one dimensional flow model (\(n_{H^-} \approx 10^{17} \text{ m}^{-3}\)). Therefore, the photo-detachment technique works best for determining the negative ion density when only processes involving negative ions that lead to excited atoms are present in the detection volume.
Bibliography


Concluding Remarks

The magnetized hydrogen plasma expansion

In this general conclusion I will answer in an overview the research questions as mentioned in the introduction. The weakly magnetized expanding hydrogen plasma was investigated in a low pressure vessel (typically 10 Pa). When we applied a magnetic field parallel to the plasma expansion two distinct color regions were observed. In the first part of the expansion we observed a red light emitting plasma (dominated by H$_\alpha$ emission) and after a sharp transition a blue light emitting plasma region (dominated by H$_\beta$, H$_\gamma$, and H$_\delta$ emission).

The red light emitting plasma region

In the first part of the expansion, H$_\alpha$ line emission is dominantly present which is responsible for the distinct red color of the plasma. Furthermore, Fulcherband emission from the molecules is detected in the red light emitting plasma due to a relatively high electron temperature of 2 eV. The high electron temperature that is observed in the first several cm of expansion makes direct excitation from the ground state of atomic hydrogen an important population process for the excited states $n$=2 and 3.

The externally applied magnetic field creates a plasma current in the expansion vessel due to the limited mobility of the charged particles. The plasma current heats the particles in the plasma expansion which results in a slower decrease of electron temperature and electron density along the plasma column than when no magnetic field is applied. When the strength of the magnetic field is increased, a stronger confinement of the charged particles and a longer penetration length of...
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the plasma current into the expansion vessel occurs. This results in a longer red light emitting plasma region while the blue light emitting plasma region is less affected by the strength of the magnetic field.

Due to the plasma current in the vessel a more or less constant dissociation degree of 10% in the red light emitting plasma was determined. The dissociation degree that is determined in the plasma expansion is much lower than determined inside the plasma source (which is almost 100% [1]) due to wall association processes at the nozzle surface. The wall association processes was investigated in more detail by using different nozzle sizes that are mounted at the anode endplate of the cascaded arc. The penetration length and light emission of the magnetized hydrogen plasma expansion was significantly lowered by increasing the nozzle size indicating significant losses of hydrogen atoms at the surface of the nozzle.

Due to wall association processes at the nozzle surface, ro-vibrationally excited molecules H\textsubscript{2}v\textsubscript{x} are created [2, 3]. The ro-vibrationally excited molecule is an important precursor for the creation of negative ions via dissociative attachment and for the creation of H\textsubscript{2}+ via charge exchange. We have detected these negative ions indirectly by means of a novel photo-detachment technique by looking at processes involving negative ions. We have shown that the negative ions are locally produced and destroyed in the plasma expansion and that the negative ion density is \( n_{H^-} = 5.7 \cdot 10^{15} \text{ m}^{-3} \) close to the arc exit and \( n_{H^-} = 7.0 \cdot 10^{15} \text{ m}^{-3} \) further downstream in the red light emitting plasma region. Furthermore, the rate coefficient of atomic mutual neutralization has been determined to be \( k_{amr} \approx k_{amr}^{n_{H}\equiv3} = 6 \cdot 10^{-14} \text{ m}^3 \text{ s}^{-1} \) which is in very good agreement with the literature values [4–6].

The transition from the red to the blue light emitting plasma

After some distance from the source, the electron temperature drops sufficiently to make dissociative recombination of both H\textsubscript{2}+ and H\textsubscript{3}+ and mutual neutralization of H\textsuperscript{+} with H\textsuperscript{−} more dominant population processes than direct excitation from the ground state. The lower electron temperature that is observed after some distance from the source is caused by a decreasing plasma current. At larger dis-
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stances from the source the plasma current has returned completely and ohmic heating to the plasma stops. The absence of ohmic heating results in a fast dropping electron temperature from 0.9 eV to 0.2 eV over a distance of about 7 cm in the expansion. This fast dropping electron temperature changes the plasma chemistry completely and a sharp transition from the red light emitting plasma (dominated by H_α emission) to a blue light emitting plasma (dominated by H_β, H_γ and H_δ emission) occurs. Just before this transition large amounts of H^+ ions and H_2^+ molecules are converted via charge exchange to H_3^+ ions and H atoms. These H_3^+ ions collide with the background gas forming H_4^+ ions. The amount of H_2^+ ions is rather low \(n_{H_2} = 10^{16} \text{ m}^{-2}\) when we compare it with other species in the plasma but it is nonetheless a very important ion in the chemistry of the plasma. The H_3^+ ion density is pinned to a low absolute value because of significant losses by the molecular mutual neutralization process, the dissociative recombination process and H_3^+ generation:

\[
\frac{\partial n_{H_2^+}}{\partial t} = n_{H^+} n_{H_2^{\nu}} k_{ce} - n_{H_2^+} n_e k_{dr} - n_{H_2} n_{H^+} k_{mmr} - n_{H_2^+} n_{H_2} k_{H_3^+}.
\]  

(7.1)

The important reaction processes in the plasma are highlighted in figure 7.1.

The blue light emitting plasma region

Population inversion of the excited states \(n=4, 5, 6\) and 7 with respect to \(n=3\) is observed in the blue light emitting plasma with optical emission spectroscopy. Therefore, the Balmer line emission of H_β, H_γ and H_δ is stronger than the emission of H_α giving the plasma a blue color. The low electron temperature \((T_e=0.2 \text{ eV})\) in combination with the inflow of H_2^{\nu} from the background gives optimal conditions forming negative hydrogen ions \((H^-)\) via the dissociative attachment process. These negative hydrogen ions react with the H_2^+ ions via the molecular mutual neutralization process to populate \(n=2-9\):

\[
H_2^+ + H^- \rightarrow H(n) + H_2, \quad \text{with} \quad n = 2 - 9.
\]  

(7.2)

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The population of excited states by the molecular mutual neutralization process was first investigated by Eerden et al [6]. Detailed analysis with a collisional radiative model have shown us that the molecular mutual neutralization process of \( \text{H}_2^+ \) with \( \text{H}^- \) is dominantly populating the excited states of \( n=4-7 \) and can therefore explain the blue color. The presence of the molecular mutual neutralization process has been experimentally proven with the novel time dependent photodetachment technique. This technique showed evidence of the mutual neutralization process of \( \text{H}_2^+ \) and \( \text{H}_3^+ \) with \( \text{H}^- \) in the blue light emitting plasma expansion. Furthermore, we have estimated the rate coefficient of the mutual neutralization process of \( \text{H}_3^+ \) with \( \text{H}^- \) to be \( k_{\text{mmr}} \approx 1 \times 10^{-14} \text{ m}^3 \text{ s}^{-1} \). This is to our knowledge the first time that the mutual neutralization process of \( \text{H}_3^+ \) with \( \text{H}^- \) has been determined.

The blue light emission diminishes slowly when the pressure in the vessel increases from 10 Pa to 30 Pa. When the pressure in the expansion vessel is higher than 30 Pa the blue light emission diminishes fast. This because the negative ions are destroyed by background collisions and an efficient conversion of \( \text{H}_2^+ \) into \( \text{H}_3^+ \) occurs via:

\[
\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}. \tag{7.3}
\]
The important reaction processes in the magnetized hydrogen plasma

![Diagram showing reaction processes]

**Generation of H⁻**

\[
H^+ + e \rightarrow H + H^-
\]

\[
H^+ + H_{2n}^+ \rightarrow H_{2n}^+ + H
\]

\[
H_{2n}^+ + H_{2n}^+ \rightarrow H_{2n+1}^+ + H
\]

\[
H_{3n}^+ + H^- \rightarrow H_{2n}^+ + H + H
\]

**Population processes**

\[
H^+ + H^- \rightarrow H(n) + H
\]

\[
H_{2n}^+ + H^- \rightarrow H(n) + H_{2n}
\]

\[
H_{2n}^+ + e \rightarrow H(n) + H
\]

\[
H_{3n}^+ + e \rightarrow H(n) + H_{2n}
\]

main input to \( n = 2, 3 \)  
main input to \( n = 4, 5 \) and \( 6 \)

**Figure 7.1:** A summary of the important reaction processes in the magnetized hydrogen plasma expansion.
Bibliography


Dankwoord

Natuurlijk is dit proefschrift niet alleen het resultaat van mij alleen. Een dergelijk onderzoek omvat het werk van velen en een paar wil ik er even uitleichten. Allereerst wil ik Daan bedanken voor het delen van zijn kennis, ideeën en gedachtengoed waar ik erg veel van heb geleerd. De zeer inspirerende en enthousiaste manier van kennisoverdracht begreep ik meestal niet meteen maar na de nodige herhalingen begon meestal het belletje wel te rinkelen. Bedankt voor de zeer goede input die van cruciaal belang voor dit proefschrift is geweest. Ook wil ik Richard Engeln bedanken in het vertrouwen dat hij me de afgelopen jaren heeft geschenken om deze promotieplek te mogen vervullen en voor het corrigeren van mijn proefschrift. Onno wil ik bedanken voor het uitleggen van de PLEXIS opstelling. Ik heb veel geleerd van zijn experimentele vaardigheden en theoretische kennis. De resultaten in mijn proefschrift zijn voor een groot deel toe te schrijven aan de studenten die ik de afgelopen jaren heb mogen begeleiden: Baptiste (analyse), Soleiman, Rogier (TALIF), Rob (photo-detachment), Kees (OES en TDLAS) en Veerle (OES). Natuurlijk mag ik de technici Ries, Janneke en Joris niet vergeten. Ries stond altijd voor me klaar om de cascadeboog onderdelen snel te vervangen als deze het weer eens begaven. Herman wil ik bedanken voor de hulp bij het opzetten van de experimenten in de begin periode van mijn promotie. Ik weet niet hoe hij alles kan onthouden maar het is erg indrukwekkend.

Then I would like to thank Dirk Wünderlich, Ursel Fantz and all the people from the IPP in Garching for inviting me at the Max-Plank institute to do simulations with an advanced collisional radiative model. I learned a lot during the three months abroad in Germany and I am really impressed by all the accomplishments
you achieve with fusion research. Ten slotte wil ik Richard van de Sanden bedanken voor zijn enthousiasme en het kritisch doorlezen en corrigeren van mijn proefschrift.

Mijn promotie bij PMP was een stuk lastiger geweest zonder een paar bijzondere collega’s: Terje, ben je nu een Belg of een wannabe Noor? Jurgen de bierkoning, Srinath the punching bag :) and Ming Ma the kickboxer. Ook wil ik mijn kamergenoten in NL C1.07 bedanken voor de leuke tijd, Harm (ik praat graag zo hard mogelijk), Harald, Teo en Florian. I especially liked the number of nice chess games against Teo during working time! Verder zal ik de schaakwedstrijden tegen Arjeh Tal in de kantine tijdens de pauze niet snel vergeten. Ik wil de teamleden van het PEST team bedanken voor de leuke tijd met zaalvoetballen: Luc, Bas de keeper, dr. Gijs, Harm, Jan-Pieter en de rest die ik nu vergeet op te noemen.

Ik wil ook Wouter, Joost, Dion, René en de hardloopvrienden en vriendinnen bij AV Oss ’78 bedanken omdat jullie een belangrijke bijdrage hebben geleverd aan de oh-zo-nodige ontspanning naast het werk. Tenslotte wil ik natuurlijk ook mijn vader, moeder en mijn broer Noud bedanken voor hun geduld tijdens mijn promotie periode.
Summary

Plasma chemistry and kinetics in a magnetized hydrogen plasma expansion: A study of negative ions

Studying hydrogen plasmas is of great importance from a fundamental point of interest since hydrogen is the most abundant molecule in the known universe and from a theoretical point of view the simplest to work on. In industry, hydrogen containing plasmas are used for example in surface modification, thin film deposition and creating negative hydrogen ions in neutral beam injectors for future fusion devices.

In this work the hydrogen plasma is created by a cascaded arc plasma source which expands in a low pressure surrounding. When an external magnetic field is applied to this expansion a confined plasma column is created with two distinct color regions. At a specific distance from the source of expansion a sharp transition from a red light emitting plasma (dominated by Hα emission) to a blue light emitting plasma (dominated by Hβ, Hγ and Hδ emission) occurs. The main research question was to understand the kinetics in the plasma expansion. Since atomic processes alone cannot explain the distinct emissions observed in the two different regions, molecular processes such as dissociative recombination and processes involving negative hydrogen ions were suspected to be key in the understanding of the underlying mechanisms. Therefore, the relevance of this work was to underpin the importance of these molecular processes in atomic regimes of hydrogen containing plasmas both by simulation and experiment.

A Collisional Radiative model (CR-model), which includes molecular pro-
cesses, was used to simulate the spatially resolved excited state densities. This CR-model assumes quasi steady state and requires as input the temperature of the species (the heavy particle temperature $T_{\text{gas}}$ and the electron temperature $T_e$) and the density of the species (the electron density, the atomic hydrogen density, the molecular hydrogen density, the positive ion densities of H$^+$, H$_2^+$ and H$_3^+$ and the negative ion density). The output of the CR-model gives excited state densities of atomic hydrogen which are compared with the measured excited state densities as determined using two diagnostics: tunable diode laser absorption spectroscopy for the first excited state $n=2$ and absolute optical emission spectroscopy for $n=3$-9. Only when the two molecular mutual neutralization processes of H$_2^+$ and H$_3^+$ with H$^-$ are included in the CR-model, good agreement for all the investigated excited state densities of $n=2$ up to $n=9$ was obtained.

Since we suspected that the excited states of atomic hydrogen are mainly populated by processes involving negative hydrogen ions a novel photo-detachment technique was developed. This technique uses a laser to photo-detach all present negative hydrogen ions in the detection volume in combination with an optical detection setup to monitor time dependently the change of Balmer line emission. We have shown that the atomic mutual neutralization process of H$^+$ with H$^-$ mainly populates the excited state $n=3$ in the red light emitting plasma and that a branching ratio of the molecular mutual neutralization process of H$_3^+$ with H$^-$ mainly populates the excited state $n=3$ up to 9 in the blue light emitting plasma. We have also shown that there are processes involving negative ions that do not lead to the population of excited states, namely the molecular mutual neutralization process of H$_3^+$ and H$^-$ and a branching ratio of the molecular mutual neutralization process of H$_2^+$ and H$^-$. 

The main conclusion of all the presented work is that we now have a much better understanding of the kinetics of weakly magnetized expanding hydrogen plasmas. The two distinct color regions that are resulting from specific Balmer line emission can be explained by molecular processes populating excited atomic hydrogen states in the plasma, i.e. dissociative recombination and processes involving negative hydrogen ions.
Curriculum Vitae

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