Spectroscopic investigation of OH dynamics in transient atmospheric pressure plasmas

PROEFSCHRIFT

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Tiny Verreycken

geboren te Diest, België
Dit proefschrift is goedgekeurd door de promotoren:

prof.dr.ir.lic. P.J. Bruggeman
en
prof.dr.ir. G.M.W. Kroesen

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Summary

Spectroscopic investigation of OH dynamics in transient atmospheric pressure plasmas

Non-equilibrium cold atmospheric pressure plasmas (CAPPs) are characterized by a strong non-equilibrium between energetic electrons and heavy particles that remain close to room temperature. As a result, highly reactive species are created upon collisions with the energetic electrons at low gas temperatures, such as the free radical OH. The combination of moderate gas heating and the efficient energy transfer of the electrons to create a large density of oxidizing radicals, makes CAPPs ideally suited for a large variety of applications. These applications include the treatment of heat sensitive materials (e.g., polymers and biological tissue) and even large volume industrial processes like water or air cleaning. At high pressure, plasma instabilities may occur on time scales of about hundred nanoseconds, which lead to significant gas heating. In the field of air cleaning, mostly filamentary dielectric barrier discharges and nanosecond pulsed corona discharges are investigated to prevent this excessive heating.

The OH radical is ubiquitous in water containing air plasmas and is, due to its high oxidation potential, believed to be one of the most reactive radicals in plasmas used for air cleaning. The production and destruction mechanisms of the short living OH radical remain subject to several fundamental questions. In particular, for filamentary atmospheric pressure plasmas, limited quantitative data and knowledge on production mechanisms are available. Often OH formation in filamentary discharges is presumed to be caused by dissociation of water molecules by energetic electrons. However, there is no consensus on the OH production mechanisms for a large variety of plasma conditions. Many other OH production processes are possible, such as metastable induced dissociation of water, dissociative recombination of the water ion, ionic charge exchange reactions and vibrationally induced dissociation.

As plasma filaments are often randomly occurring in space and time, we have built a plasma reactor with a needle-needle geometry and a repetitive nanosecond pulsed voltage excitation, which allows us to create a highly reproducible
nanosecond pulsed plasma filament. With this setup, it is possible to study the OH dynamics in the plasma filament with a high resolution in space and time. A combination of the OH density measurements by laser induced fluorescence (LIF) with a detailed characterisation of the plasma properties (gas temperature, electron density, He metastable density, electron temperature) through absorption and optical emission spectroscopy measurements, allows us to thoroughly analyse the production and destruction mechanisms of OH for the first time. Because of its low complexity the discharge is operated in helium with a varying percentage of water vapour and oxygen. The discharge is also investigated in nitrogen-water vapour mixtures.

To obtain absolute OH densities, the LIF signal is calibrated using a Rayleigh scattering intensity calibration of the LIF setup and a LIF model. Since this LIF model strongly depends on the significant collisional transfer between different states at atmospheric pressure, this method is compared to two other calibration methods: (1) a chemical model of the OH decay in the afterglow, fitted to the relative LIF signal and (2) an independent time resolved UV absorption measurement in the plasma filament. The resulting densities of the three methods correspond within the experimental accuracy and validate the methods used in this research.

In helium-water vapour mixtures, two modes are observed depending on the applied voltage: a low- and high-density mode, in which the maximum electron density is of the order $10^{21} \text{ m}^{-3}$ and $10^{22} \text{ m}^{-3}$ respectively. By investigating the two modes, the influence of the electron density on the OH density is investigated. In the low-density mode the maximum OH density is in the centre of the discharge filament, while in the high density mode the largest OH density is observed at the edge of the discharge. It is found that, apart from electron dissociation and metastable induced dissociation of water, also dissociative recombination of the water ion and charge transfer of the water ion can be important production processes for OH under specific plasma conditions in transient atmospheric pressure plasma filaments.

When a small amount of oxygen is added to the discharge in helium with 0.1% water vapour, an increase in the measured OH density is observed in the far afterglow. The reactions responsible for this OH production are studied using a zero-dimensional chemical kinetics model, taking into account the main production and loss processes of OH. From the model, it is observed that the addition of oxygen leads to a strong quenching of OH by O. Due to the strong decrease in OH density, production of OH through HO$_2$ is temporarily more important, resulting in a recycling of OH in the far afterglow.

In the discharge in nitrogen with saturated water vapour, a pronounced increase in OH density is found in the far afterglow. In this case, the increase in OH density is attributed to similar processes which cause the pink splash or pink afterglow.
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Chapter 1

Introduction

Plasma is a (partly) ionized gas containing free electrons. As the presence of free electrons and charged species give plasmas distinctive properties compared to normal gases, plasmas are often referred to as the fourth state of matter. Plasmas occur in all kinds of shapes, magnitudes and conditions; man-made or created by nature. The ubiquitous plasma in our universe is contained in stars and interstellar clouds (more than 99\%), while the plasmas familiar to most people are located in plasma TV screens and light bulbs. Man-made plasmas are often produced between two metal electrodes, across which a high voltage is applied. The generated electric field accelerates the electrons in the gap, which leads to excitation, dissociation of molecules, and ionization. The latter is responsible for the sustenance of the plasma.

Because of the large variety of appearances, plasmas can be subdivided into different categories. Often a distinction is made between thermal (equilibrium) and non-thermal (non-equilibrium) plasmas. In non-equilibrium plasmas the temperature of the electrons is much higher than the temperature of the atoms, molecules and ions, while for a thermal plasma all species in the plasma are in equilibrium and have the same temperature. In non-equilibrium plasmas, at low gas temperatures, collisions with energetic electrons lead to the production of reactive species, which normally are only created at strongly elevated gas temperatures. Nowadays, a lot of research is conducted on technological applications of plasmas at atmospheric pressure. This dissertation deals with non-equilibrium plasmas.
1.1 Non-equilibrium plasmas at atmospheric pressure

At atmospheric pressure, the collision frequency is very high and gas heating is important in many plasmas. The high collision frequency of electrons with neutral particles lead to enhanced ionization and instabilities may occur in the plasma on time scales of tens to hundreds of nanoseconds. These instabilities normally coincide with strong heating ($T > 1000$ K). Since for many applications, a high gas temperature is to be avoided (e.g. treatment of heat sensitive surfaces), several approaches have been developed to stabilize non-equilibrium plasmas at atmospheric pressure. One of the possibilities to prevent that equilibrium is reached, is generating plasmas by nanosecond voltage pulses, as the heating in plasmas usually occurs on a time scale of 100 ns or more [11]. Based on the same principle, dielectrics are introduced between the metal electrodes (dielectric barrier discharges). The dielectric surfaces lead to self-limiting of the current of filamentary discharges due to charge deposition on the dielectric electrode, which causes a significant drop in the applied electric field on the time scale of a few nanoseconds. This approach allows producing very reactive non-equilibrium plasmas, without the necessity of complex power supplies.

Recently, atmospheric pressure plasmas are extensively studied in view of applications in the field of environmental remediation, biomedicine and material processing [6, 9, 32, 34, 45]. The wide range in applications is due to the rich and complex chemistry of atmospheric pressure plasmas, in which molecules are dissociated at a relatively low gas temperature, creating amongst others reactive species and radicals such as O$_3$, NO, O and OH. However, the knowledge of non-equilibrium plasma chemistry (e.g. accurate knowledge of radical densities and production mechanisms) is often far from complete. In addition, it is important to gain more understanding in view of optimizing plasma reactors for applications. Especially for plasmas in and in contact with water accurate knowledge on the plasma chemistry is currently lacking [60].

The goal of this thesis is to study the OH radical dynamics in water containing plasmas, to unravel the important production and destruction mechanisms of OH. The understanding of radical production is a pre-requisite to unravel the differences in treatment results for various applications when different plasma conditions are used. OH radicals belong to the most strongly oxidative species produced by water containing plasmas. This motivates why the OH radical is chosen in this work.

1.1.1 Filamentary nature of atmospheric pressure plasmas

While most low pressure plasmas are diffuse, atmospheric pressure plasmas are mostly filamentary in nature. The filamentation is due to the increased ionization rate which leads to constriction of diffuse glow discharges, and causes that the
1.2: OH in plasmas

Meek criterion for streamer formation in an avalanche is easily fulfilled. The existence of these filaments, with diameters of the order of 100 μm and lifetimes as small as 10 ns, is correlated with strong gradients in plasma properties in both space and time, which can significantly affect the plasma chemistry. The electron temperature in filamentary discharges is often high, while the gas temperature is usually relatively low [10]. This leads to an efficient production of radicals, as the energy applied is used for dissociation and ionization rather than for gas heating.

As filaments are often randomly appearing in space and time, stabilization of the filament is necessary to study the OH chemistry time and spatially resolved. This requires special geometries and/or nanosecond voltages pulses to control the position and creation of filaments accurately [8, 31, 63]. In addition, the small dimension of filamentary discharges makes it challenging to apply diagnostics [13]. In this work a nanosecond pulsed filamentary discharge is stabilized in space and time by applying a nanosecond pulsed voltage between two needle electrodes at a sufficient short distance (approximately 2 mm).

Filamentary discharges are often studied in the form of nanosecond repetitively pulsed (NRP) discharges. These discharges are created by repetitively applying a high voltage pulse across two electrodes. The high electrical field causes ionization and dissociation processes, and NRP discharges are thus a rich source of reactive species [63]. In spite the fact that the applied electrical field is short and often rather moderate compared to pulsed coronas, for which tens of kV are applied, the pre-ionization by the previous discharge helps to make the ignition of NRP discharges reproducible [58]. The short voltage duration prevents the transition to an arc and excessive heating [11].

1.2 OH in plasmas

In plasma applications such as environmental remediation [59, 71], biomedical treatment [36], plasma-enhanced combustion [1, 37, 57] and chemical synthesis [41], radicals are believed to play a key role. Since in these applications often water (vapour) is present, the hydroxyl radical, which is highly reactive, is involved.

In wound healing, for instance, the OH radical gains a lot of interest besides other important reactive species like NO and ozone [40]. OH is also an important oxidizer for e.g. volatile organic compounds (VOC’s), NO\textsubscript{x} and SO\textsubscript{x}, and plays a role in the destruction and removal of harmful components in exhaust gases [71]. Air pollution is a major problem of today’s society, and plasmas show the possibility to contribute to the remediation. Several groups around the world, including the electrical engineering department at the Eindhoven University of Technology, have industrial demonstrator systems based on corona discharge technology, which are effective in the removal of pollutants from air exhausts.

In the field of plasma-enhanced combustion, radicals produced by plasmas are
used to increase the combustion efficiency, or to lower the threshold for ignition of combustion processes [64]. Finally, OH is one of the building blocks of H₂O₂, which is considered as an important agent in the chemical reactivity of plasmas in and in contact with liquids [41].

A recent review paper by Malik shows that the energy efficiency of treatment of dyes in water by plasmas can vary up to 5 orders of magnitude for different plasma sources [43]. Unfortunately, these large differences are not fully explained at this time. This clearly shows the necessity of a thorough and in depth study of the plasma chemistry of water containing plasmas. The general trend for environmental remediation applications is however clear: highly transient streamer discharges in the gas phase are not only the most efficient for air purification, but also for water treatment [24].

1.2.1 OH production mechanisms

In literature, often thermal dissociation or electron-impact dissociation of H₂O is considered as the main reaction pathway to create OH [54, 61]. Nevertheless, many other reaction pathways exist and are possible in atmospheric pressure plasmas, as reported by Bruggeman and Schram [10]. In streamer discharges, the production of OH radicals inside the channel is attributed to dissociation of water molecules by energetic electrons [54, 56]. In addition OH can be produced by metastable induced dissociation, ionic recombination processes, charge transfer and vibrationally induced dissociation [10]. However, Bruggeman and Schram argued that vibrationally induced dissociation is not expected to be important for water, as the conditions necessary for important vibrationally induced dissociation coincide with plasma conditions where ionic processes are dominant. On the other hand, in atmospheric pressure arc discharges it is well known that the plasma in the core is close to LTE (local thermodynamic equilibrium) and water molecules are fully dissociated at temperatures above 4000 K, with a maximum in OH density at approximately 3000 K [22]. In table 1.1 (adapted from [10]), a summary is shown of the dominant reactions responsible for the production of OH, as obtained from literature. For every reaction a typical value of the reaction rate is given. As is clear from this table, OH radicals can be produced by a large number of reactions. The plasma conditions for which these typical rates are valid are indicated in the table.

The production of OH is found to strongly depend on:

- the gas temperature \( (T_g) \)
- the electron temperature \( (T_e) \)
- the ionization degree
- the electron density \( (n_e) \) and the negative ion density
Table 1.1: Summary of reactions involved in OH production in non-equilibrium plasmas at atmospheric pressure. The typical values of the rates as found in literature for the indicated plasma conditions are also given.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Typical rate $k$ (m$^{-1}$ s$^{-1}$)</th>
<th>Remark</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal dissociation</td>
<td>$H_2O + H^+ \rightarrow OH + H + H_2O$</td>
<td>$10^{-26} - 4 \cdot 10^{-20}$</td>
<td>$T_e = 2500 - 5000$ K</td>
</tr>
<tr>
<td>Electron dissociation</td>
<td>$e + H_2O \rightarrow OH + e$</td>
<td>$2.3 \cdot 10^{-18} - 1.8 \cdot 10^{-16}$</td>
<td>$T_e = 1 - 2$ eV</td>
</tr>
<tr>
<td>Electron-ion dissociative recombination</td>
<td>$e + H_2O^+ \rightarrow OH + H$</td>
<td>$2.6 \cdot 10^{-14}$</td>
<td>$T_e = 1$ eV</td>
</tr>
<tr>
<td></td>
<td>$e + H_2O^+ \rightarrow OH + H_2 + e$</td>
<td>$10^{-13}$</td>
<td>$T_e = 1$ eV</td>
</tr>
<tr>
<td></td>
<td>$e + H_2O^+ \rightarrow H_2O + OH + H$</td>
<td>$9.6 \cdot 10^{-13}$</td>
<td>$T_e = 1$ eV</td>
</tr>
<tr>
<td>Dissociative attachment</td>
<td>$e + H_2O \rightarrow OH + H^*$</td>
<td>$4.9 \cdot 10^{-18} - 4.7 \cdot 10^{-17}$</td>
<td>$T_e = 1 - 2$ eV</td>
</tr>
<tr>
<td>Water ion hydration</td>
<td>$H_2O^+ + H_2O \rightarrow H_2O_2^+ + OH$</td>
<td>$1.9 \cdot 10^{-15}$</td>
<td></td>
</tr>
<tr>
<td>Positive-negative ion recombination</td>
<td>$H^+ + H_2O^+ \rightarrow OH + H_2$</td>
<td>$2 \cdot 10^{-13}$</td>
<td>$T_e = 300$ K</td>
</tr>
<tr>
<td></td>
<td>$H^+ + H_2O^+ \rightarrow OH + H_2^+$</td>
<td>$2 \cdot 10^{-13}$</td>
<td>$T_e = 300$ K</td>
</tr>
<tr>
<td></td>
<td>$OH^+ + OH_2^+ + M \rightarrow H_2O_2 + OH + O_2 + M$</td>
<td>$2 \cdot 10^{-31}$</td>
<td>$T_e = 300$ K</td>
</tr>
<tr>
<td>Dissociation by metastables</td>
<td>$N_2(A) + H_2O \rightarrow OH + H + N_2$</td>
<td>$\approx 6 \cdot 10^{-20}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$N_2(D) + H_2O \rightarrow OH + H + NH$</td>
<td>$2 \cdot 10^{-16}$</td>
<td>$T_e = 300$ K</td>
</tr>
<tr>
<td></td>
<td>$N_2^*(P) + H_2O \rightarrow OH + NH + M$</td>
<td>$5 \cdot 10^{-19}$</td>
<td>$T_e = 300$ K</td>
</tr>
<tr>
<td></td>
<td>$O_2(1D) + H_2O \rightarrow OH + OH$</td>
<td>$2 \cdot 10^{-16}$</td>
<td>$T_e = 300$ K</td>
</tr>
<tr>
<td></td>
<td>$Ar_{in} + H_2O \rightarrow OH + H + Ar$</td>
<td>$4 \cdot 10^{-16}$</td>
<td>$T_e = 300$ K</td>
</tr>
<tr>
<td>Radical reactions</td>
<td>$H + HO_2 \rightarrow OH + OH$</td>
<td>$6 \cdot 10^{-17}$</td>
<td>$T_e = 300$ K</td>
</tr>
<tr>
<td></td>
<td>$H + HO_2 \rightarrow OH + H_2$</td>
<td>$4 \cdot 10^{-20}$</td>
<td>$T_e = 300$ K</td>
</tr>
<tr>
<td></td>
<td>$O + HO_2 \rightarrow OH + O_2$</td>
<td>$5 \cdot 10^{-17}$</td>
<td>$T_e = 300$ K</td>
</tr>
<tr>
<td></td>
<td>$O + HO_2 \rightarrow OH + HO_2$</td>
<td>$1 \cdot 10^{-21}$</td>
<td>$T_e = 300$ K</td>
</tr>
<tr>
<td></td>
<td>$O + H_2 \rightarrow OH + H$</td>
<td>$9 \cdot 10^{-24} - 5 \cdot 10^{-17}$</td>
<td>$T_e = 300 - 3000$ K</td>
</tr>
<tr>
<td></td>
<td>$H + O_2 \rightarrow OH + O$</td>
<td>$2 \cdot 10^{-27} - 1 \cdot 10^{-17}$</td>
<td>$T_e = 300 - 3000$ K</td>
</tr>
<tr>
<td></td>
<td>$H + O_2^<em>(M) \rightarrow OH_2^</em>(M)$</td>
<td>$\approx 10^{-20}$</td>
<td>$T_e = 1000 - 3000$ K</td>
</tr>
<tr>
<td>Dissociation by vibrational excitation</td>
<td>$H_2O + H_2O^+ \rightarrow OH + H + H_2O$</td>
<td>$10^{-20}$</td>
<td>$T_e = 0.5$ eV, $T_p = 300$ K</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>$Ar^+ + H_2O \rightarrow OH + ArH^+$</td>
<td>$0.5 \cdot 10^{-15}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$He^+_2 + H_2O \rightarrow OH + HeH^+ + He$</td>
<td>$10^{-16}$</td>
<td></td>
</tr>
</tbody>
</table>
the dominant positive and negative ionic species

- the gas composition when admixtures of water with other gases are used

Considering the large variety in plasma parameters, the knowledge of the OH density alone is not sufficient to explain the OH production mechanisms. Therefore, in this work, apart from the OH density, several plasma characteristics \( (n_e, T_g, T_e, n_{\text{He}_m}) \) are also investigated.

### 1.2.2 Diagnostics of OH densities

The measurement of (densities of) OH radicals has a long history, of which many important developments are made in the field of combustion \([15, 33, 64]\). In this field, the main emphasis has been on the laser induced fluorescence (LIF) technique. This is the preferred diagnostic due to its high sensitivity and spatial and temporal resolution (as determined by the laser beam dimensions and the laser pulse duration respectively).

One of the first LIF studies of a high-energy atmospheric pressure electrical pulsed discharge in air is performed by Ershov and Borysow \([21]\). They investigated the OH dynamics exciting the \( \text{OH}(\text{A}; \nu' = 1) \leftarrow \text{OH}(\text{X}; \nu'' = 0) \) transition around 282 nm. However, at that time, the lack of reliable information on rate coefficients concerning production and loss of OH radicals, did not allow the development of a quantitative model. Nowadays, due to the large effort of the combustion community, the OH radical is one of the most studied radicals, and many collisional transfer reactions are studied and cross sections or rates are reported.

LIF is in the past often only used to locate the OH and to measure relative densities \([30]\) or to measure the spatially averaged OH density in the entire plasma volume instead of in a single filament \([56]\). To absolutely determine the OH density in a plasma filament at atmospheric pressure, there are a few challenges. First, to probe a plasma filament, its position needs to be fixed and it needs to be reproducible in time, at least if no single shot saturation LIF is performed. Second, at atmospheric pressure, collisional induced processes are highly important and need to be considered in the LIF measurement interpretation. Third, the laser beam dimension needs to be of the same order or smaller than the typical plasma filament diameter (200 μm).

Laser induced predissociative fluorescence (LIPF), exciting OH radicals around 248 nm, is used to overcome the need to correct for collisional effects (see e.g. \([56]\)). In LIPF, the ground state is excited to a higher vibrational level of the OH(A) state that is short-lived, quenching of this level is negligible compared to its predissociation, even at high pressures. However, this method has some drawbacks \([49]\). The sensitivity of LIPF is low and the laser wavelength around 248 nm can induce ozone and \( \text{H}_2\text{O}_2 \) photodissociation, which can result in additional...
OH production by the laser. In saturation LIF, the laser power density is very high, so the absorption transition is saturated and the LIF signal is practically insensitive to the laser irradiance. Stimulated emission is in this case the dominant loss mechanism of the excited level population and collisional processes are less important [33]. The fluorescence signal is also very large and independent on variations of the laser power density, so it can be used in single shot measurements. However, for most molecules the excitation cannot be modeled with a simple 2-level model, which increases the experimental complexity since the fluorescence signal from each additional level needs to be recorded independently [14, 20]. Another aspect that needs to be considered is that uniform spatial saturation is experimentally difficult to achieve due to the Gaussian profile of the power density in the laser beam, which can significantly increase the experimental inaccuracies for saturation LIF.

Apart from modelling the collisional redistribution, which is a necessity for the excitation scheme used by Ershov and Borysow [21], the optical detection system needs to be calibrated as well. One possibility to overcome this, is calibration by simultaneously measuring LIF signals from the investigated molecule at known concentrations. However, OH is not a stable molecule, and this calibration method cannot be applied easily [42]. Another possibility to calibrate the optical system is using Raman or Rayleigh scattering of a known gas density [42, 52]. Since the Raman scattering cross sections are typically three orders of magnitude smaller than the Rayleigh cross-sections, Rayleigh scattering is used in this thesis to eliminate the optical detection factor. When a pulsed plasma is investigated, a correction for the optical detection system can also be overcome by applying a chemical model to predict the decay time of the LIF intensity [65]. Finally, Dilecce et al have shown that the OH density can be calibrated on-line and real-time by using a low-pressure, low-power pulsed RF discharge as a reference source [17]. They have used the fact that OH(A) and NO(A) have the same excitation precursor, N2(A). However, in their method, four quantities (the emission intensities of OH(A) and NO(A) and the LIF intensities of NO in the discharge and the reference cell) have to be measured, which increases the complexity of the method significantly.

Apart from LIF, the OH density can also be obtained using UV absorption. In this method, the accuracy only depends on the Einstein B coefficient of the transition and the (temperature dependent) line profile, and thus not on collisional processes. A disadvantage of the UV absorption is that it has a low sensitivity, especially for filamentary discharges with small optical depth. UV absorption is also line integrated, so an Abel inversion is necessary to obtain spatially resolved densities for cylindrically symmetric plasma filaments. Hibert et al applied a resonant absorption method, using a pulsed DBD as a UV probe source, resonant with OH(A−X) transitions, to measure the OH density [26]. However, resonant absorption spectroscopy suffers from uncertainties induced by the lack of information on the line profile of the light source, which can be altered by self-absorption in the plasma used as light source [48]. To overcome this problem, Bruggeman et al performed broadband UV absorption with a UV LED [12]. Another method to obtain absolute OH densities is cavity ring-down spectroscopy (CRD) [46, 70].
This method is more straightforward and less dependent on assumptions and on the stability of the light source, but is more difficult to implement, especially in the case of filamentary discharges. Again, CRD is a line-of-sight technique. Often line-of-sight techniques are combined with LIF to obtain both absolute and spatially resolved information (see e.g. [46]).

1.2.3 OH production in different non-equilibrium plasmas at atmospheric pressure

As mentioned above, OH density measurements have a long history. A (non-exhaustive) summary of OH densities measured in different atmospheric pressure plasmas, as obtained from literature, is shown in table 1.2. The typical plasma parameters and conditions are also included. From the table it can be concluded that a large range of OH densities is observed, from $10^{19}$ m$^{-3}$ to $10^{22}$ m$^{-3}$. The table also shows that several studies of similar discharges yield significantly different results, like the RF plasma jet. Many studies do not include all collisional transfer processes in the calibration of the LIF signal. From the above it is concluded that the available data in literature are dispersed, and that more information is needed on the effect of plasma properties on the OH production. A more systematic study is thus necessary.

1.3 Outline of the thesis

In this work, the OH production and loss mechanisms are investigated in various gas mixtures using LIF of the $P_{1}(2)$ transition of the OH [(A; $\nu' = 1$) $\leftarrow$ (X; $\nu'' = 0$)] band, including absolute calibration of the OH density. All experiments are performed in a nanosecond repetitively pulsed discharge in a pin-to-pin geometry, to obtain a filament which is stable in space and time. The study is performed in He, N$_2$ and He-O$_2$ mixtures with various water vapour concentrations. The results and discussions are organized as follows:

- The LIF calibration method to obtain absolute OH densities is introduced in chapter 2. The calibration of the LIF signal is performed using Rayleigh scattering and a 4-level and 6-level model, which includes laser pumping, spontaneous emission, quenching, vibrational (VET) and rotational (RET) energy transfer. This LIF calibration method is independently validated by comparison with two other methods applied for the same plasma conditions: calibration by broadband UV absorption and calibration of the relative LIF intensity in the afterglow as function of time using a chemical kinetic model. A sensitivity analysis of the absolute OH density to the parameters used in the LIF models is also performed.
Table 1.2: Overview of some typical atmospheric pressure plasmas with their relevant plasma parameters and measured OH densities. The dashes indicate that the property is not given in the reference and cannot be estimated from the data provided in the reference. For pulsed plasmas the discharge power is calculated as the energy per cycle or per pulse, times the repetition frequency.

<table>
<thead>
<tr>
<th>Plasma type</th>
<th>Gas</th>
<th>$T_e$ (eV)</th>
<th>$n_e$ ($m^{-3}$)</th>
<th>$T_g$ (K)</th>
<th>$n_e/n_g$</th>
<th>$n_{OH}$ ($m^{-3}$)</th>
<th>Power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gliding arc [5]</td>
<td>air (50% RH)</td>
<td>1</td>
<td>$10^{10}$-$10^{12}$</td>
<td>3000-5000</td>
<td>10$^{-3}$ - 10$^{-4}$</td>
<td>10$^{20}$ (OES)</td>
<td>$\approx$ 100-500</td>
</tr>
<tr>
<td>Pulsed arc [34]</td>
<td>air + 3% H$_2$O</td>
<td>1</td>
<td>$10^{10}$-$10^{12}$</td>
<td>3000-4000</td>
<td>10$^{-3}$ - 10$^{-4}$</td>
<td>10$^{24}$ (LIF)</td>
<td>-</td>
</tr>
<tr>
<td>AC arc [62]</td>
<td>air + $\approx$ 1% H$_2$O</td>
<td>1</td>
<td>$10^{10}$-$10^{12}$</td>
<td>3000-4000</td>
<td>10$^{-3}$ - 10$^{-4}$</td>
<td>10$^{24}$ (CRD)</td>
<td>-</td>
</tr>
<tr>
<td>Pulsed streamers [55]</td>
<td>air + 2.4% H$_2$O</td>
<td>1-10</td>
<td>$10^{21}$</td>
<td>300</td>
<td>10$^{-4}$ - 10$^{-5}$</td>
<td>10$^{24}$ (LIF)</td>
<td>$\approx$ 0.6 (0.3 $\mu$s, 5 Hz)</td>
</tr>
<tr>
<td>AC DBD [39]</td>
<td>He + $\approx$ 1% H$_2$O</td>
<td>1-2</td>
<td>$10^{20}$-$10^{21}$</td>
<td>300-400</td>
<td>10$^{-4}$ - 10$^{-5}$</td>
<td>10$^{19}$ (CRD)</td>
<td>$\approx$ 10-50</td>
</tr>
<tr>
<td>RF glow [12]</td>
<td>He + 0.05-1.5% H$_2$O</td>
<td>3</td>
<td>$10^{15}$-$10^{18}$</td>
<td>300-450</td>
<td>10$^{-7}$ - 10$^{-8}$</td>
<td>10$^{24}$-$10^{25}$ (ABS)</td>
<td>30-130</td>
</tr>
<tr>
<td>Pulsed DBD [26]</td>
<td>Ar + 1.35% H$_2$O</td>
<td>1-5</td>
<td>$10^{20}$-$10^{22}$</td>
<td>350</td>
<td>10$^{-8}$ - 10$^{-9}$</td>
<td>10$^{24}$ (ABS)</td>
<td>0.36 (50 ns, 10 Hz)</td>
</tr>
<tr>
<td>(sinusoidal) [16,18]</td>
<td>Ar + $\approx$ 1% H$_2$O</td>
<td>300-400</td>
<td>10$^{19}$ (LIF, ABS)</td>
<td>39 ($T_{ON}$ = 10 ms, 10 kHz)</td>
<td>2.57 ($T_{ON}$ = 10 ms, 10 kHz)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(sinusoidal) [19]</td>
<td>He + $\approx$ 0.1% H$_2$O</td>
<td>300-400</td>
<td>10$^{19}$ (LIF)</td>
<td>12 ($T_{ON}$ = 10 ms, 10 kHz)</td>
<td>120 ($T_{ON}$ = 10 ms, 10 kHz)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW jet [69, 70]</td>
<td>Ar</td>
<td>1-2</td>
<td>$10^{20}$-$10^{21}$</td>
<td>500-2000</td>
<td>10$^{-8}$ - 10$^{-9}$</td>
<td>10$^{22}$ (CRD)</td>
<td>12</td>
</tr>
<tr>
<td>RF jet [72]</td>
<td>Ar + 0.05-1% H$_2$O</td>
<td>-</td>
<td>$10^{19}$</td>
<td>500</td>
<td>10$^{-6}$</td>
<td>10$^{19}$ (LIF)</td>
<td>10</td>
</tr>
<tr>
<td>[68]</td>
<td>Ar + $\approx$ 1% H$_2$O</td>
<td>-</td>
<td>300-400</td>
<td>-</td>
<td>10$^{19}$ (LIF)</td>
<td>10$^{20}$-$10^{22}$ (ABS)</td>
<td>30-130</td>
</tr>
<tr>
<td>[67]</td>
<td>Ar + 0.2-6% H$_2$O</td>
<td>1-3</td>
<td>$10^{19}$-$10^{20}$</td>
<td>400</td>
<td>10$^{-5}$ - 10$^{-6}$</td>
<td>10$^{20}$-$10^{22}$ (ABS)</td>
<td>-</td>
</tr>
<tr>
<td>Pulsed jet [63]</td>
<td>He + 0.09% H$_2$O</td>
<td>-</td>
<td>300</td>
<td>-</td>
<td>10$^{19}$ (LIF)</td>
<td>2.5 (35 $\mu$s, 8.4 kHz)</td>
<td>-</td>
</tr>
<tr>
<td>Glow discharge [51]</td>
<td>humid air</td>
<td>1-2</td>
<td>3000</td>
<td>-</td>
<td>10$^{21}$-$10^{22}$ (LIF)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\mu$-flow DC plasma [38, 50]</td>
<td>Ar</td>
<td>1</td>
<td>$10^{20}$</td>
<td>1500-1800</td>
<td>10$^{-5}$</td>
<td>10$^{20}$ (LIF)</td>
<td>-</td>
</tr>
<tr>
<td>with liquid electrode</td>
<td>He</td>
<td>2</td>
<td>$10^{20}$</td>
<td>10$^{-5}$</td>
<td>10$^{21}$ (LIF)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
• **Chapter 3** describes the plasma properties \((n_e, T_g, T_e, n_{He})\) of the nanosecond pulsed discharge in He-H\(_2\)O mixtures, measured with time resolved imaging, optical emission spectroscopy and LIF. Two discharge modes are studied, which are created depending on the applied DC voltage, and which are characterized by a different electron density. Using the measured plasma parameters, the mechanisms responsible for the observed time and spatially resolved OH density are deduced. The influence of the water concentration is discussed, as well as the contribution of ionic processes to the production of OH.

• In **chapter 4** the influence of O\(_2\)-chemistry on the production of OH is investigated. The plasma parameters are reported and the observed OH dynamics are explained with a zero-dimensional chemical kinetic model.

• The same nanosecond pulsed discharge is investigated in N\(_2\)-H\(_2\)O mixtures in **chapter 5**, using time resolved imaging, optical emission spectroscopy, Rayleigh scattering and LIF. Particular effects of N\(_2\)-chemistry on OH production in the afterglow are presented.

• Finally, in **chapter 6** the main findings are summarized and conclusions are drawn.
References


References


S. Samukawa, M. Hori, S. Rauf, K. Tachibana, P. J. Bruggeman, G. M. W. Kroesen, J. C. Whitehead, A. B. Murphy, A. F. Gutsol, S. Starikovskaia,
References


Chapter 2

Absolute calibration of the OH density: comparison of independent calibration methods

Abstract

The absolute density of OH radicals generated in a nanosecond pulsed filamentary discharge in atmospheric pressure He + 0.84% H₂O, is measured independently by UV absorption and laser induced fluorescence (LIF) calibrated with Rayleigh scattering. For the calibration of LIF with Rayleigh scattering, two LIF models, a 6-level and 4-level model, are studied to investigate the influence of the rotational (RET) and vibrational (VET) energy transfers. In addition, a chemical model is used to deduce the OH density in the afterglow from the relative LIF intensity as a function of time. The different models show good correspondence, and by comparing these different methods the accuracy and the effect of assumptions on the obtained OH density is discussed in detail. An analysis of the sensitivity of the absolute OH density to the parameters used in the LIF models is also included.

Chapter 2: Absolute calibration of the OH density

2.1 Introduction

In this chapter, a plasma filament is used to compare different methods of OH density determination, and to evaluate their corresponding accuracies. As described in chapter 1, the position of the plasma filament is fixed in a pin-to-pin electrode geometry, and the filament generation by a nanosecond pulsed voltage is time aligned with the diagnostics. The details of the physics and chemistry of the plasma are presented in chapter 3, the current chapter only focuses on the calibration of the absolute OH density.

The OH radical density is probed using linear LIF with an excitation wavelength around 283 nm. Absolute calibration of the LIF signal is accomplished by Rayleigh scattering in nitrogen. The absolute OH density is then calculated with two LIF models that take into account the collisional transfer processes. The first model is a detailed 6-level model that takes into account both rotational (RET) and vibrational (VET) energy transfer reactions. The second model is a simplified 4-level model that takes into account VET and assumes that RET is infinitely fast, a very common assumption at atmospheric pressure (see e.g. [6]). Comparing these two models gives information on the importance of the RET on the OH density determination. Because of the inaccuracies of some input parameters, it is hard to assess the accuracy of the obtained OH density with this method. Therefore the absolute OH density is also obtained in this work by two other methods. The first method is broadband UV absorption, which only depends on the absorption coefficients, which are accurately known, and the gas temperature, of which the influence in the considered temperature range is low. The second method is based on the fact that the relative LIF intensity in the afterglow is a measure of the OH(X) decay after the plasma pulse. This allows to compare the relative decay with a chemical kinetic model, and to determine the initial OH density.

In section 2.2 an overview is given of the experimental setup that is used. Next, the broadband UV absorption measurement is presented in section 2.3. The chemical kinetic model to obtain the OH(X) density in the afterglow is introduced in section 2.4, and in section 2.5 the calibration method of the LIF signal using Rayleigh scattering is reported. The densities obtained using the three methods are compared in section 2.6 and conclusions are drawn on the accuracy of the LIF models.

2.2 Experimental setup

The discharge is created in a pin-to-pin electrode configuration in a vacuum vessel. The electrodes are made of tungsten and the distance between them is approximately 2 mm. High voltage pulses are applied with a width of 170 ns and an amplitude of 7 kV (high-density discharge mode, see chapter 3). A gas flow with a rate of 3 l min⁻¹ is constantly refreshing the gas in the vacuum vessel, which
2.2: Experimental setup

Figure 2.1: Experimental setup. The mass flow controllers and water admixing system are not shown.

has a volume of approximately 8 l. To have a gas mixture that contains 0.84 % H₂O, 11₈ min⁻¹ helium is led through a bubbler filled with distilled water. The water vapour concentration in the vessel is determined assuming that the helium flow passing through the bubbler is saturated with water vapour at room temperature. A sketch of the experimental setup is shown in figure 2.1. Further details about the setup can be found in chapter 3.

Laser induced fluorescence of OH is created with a frequency-doubled dye laser (Sirah CBR-LG-24-HRR), with Rhodamine 6G as the dye, pumped by a Nd:YAG laser (Edgewave Innoslab IS6II-E) at 532 nm. The laser pulses have a repetition frequency of 1 kHz and a width of 6 ns FWHM, as measured from the time resolved Rayleigh signal with a photomultiplier (Hamamatsu R636-10) and a 100-ps time digitizer (Ortec 9353). The photomultiplier is mounted on a Jobin Yvon THR 1000 monochromator, which allows obtaining time and spectrally resolved fluorescence signals. The spectral resolution, which is dependent on the slit width of the monochromator, is 0.3 nm. The LIF measurements are performed with fluorescence light created by exciting the f₁(2) rotational level of OH(X; ν'' = 0) at 282.58 nm to the F₁(1) rotational level in OH(A; ν' = 1); this is the P₁(2) transition. The f₁(2) level has the largest relative population of all rotational levels in the temperature range under investigation [18], and the P₁(2) transition is nicely separated from neighbouring lines. Further details about the LIF setup can be found in chapter 3. All measurements in this chapter are performed in the middle between the two electrodes. Rayleigh scattering measurements for the
calibration are performed with the same setup as for the LIF experiments, at 282.58 nm in pure nitrogen at room temperature and atmospheric pressure. For LIF and Rayleigh scattering measurements no filter is used to avoid additional corrections (and additional inaccuracies) for the transmission of the filter. The Rayleigh scattering signal in helium is negligible compared to the LIF signal.

The relative LIF intensity as a function of time (which equals the relative OH density as a function of time) is shown in figure 2.2, together with the gas temperature obtained from excitation LIF. Gas temperature measurements by LIF, and comparison with other techniques, are described in detail in chapter 3.

UV absorption spectra of OH are recorded with a UV light-emitting diode (LED, TF531C, Seoul Optodevice) with maximum intensity around 312 nm and a FWHM of 10 nm. A schematic drawing of the setup for UV absorption is shown in figure 2.3. The quartz Brewster windows of the vacuum vessel, used for LIF measurements, are replaced by flat quartz windows. Inside the vessel, the LED light is focused on the plasma filament with a quartz lens ($f = 9.0\, \text{mm}$), and collected again with an identical lens set at $f = 9.0\, \text{mm}$ from the filament. Emission and absorption spectra are recorded with a 2 m monochromator (SOPRA), equipped with a 1200 grooves/mm grating and working in the 4th diffraction order. The light is focused on the detector with a lens. The monochromator is backed by a 12.8 μm pitch PIMAX3 (Roper Scientific) iCCD. The UV absorption measurements are performed with a gate width of the iCCD of 500 ns, the acquisition interval is indicated in figure 2.2. Around 308 nm, the spectral resolution of the system is about 5 pm FWHM. The UV absorption measurements were performed...
2.3 Broadband UV absorption

To measure the OH(X) density in the plasma filament by UV absorption, four spectra are recorded: the emission of the plasma and the transmitted light of the LED \( L_{\text{plasma+LED}}(\lambda) \), the emission of the plasma alone \( L_{\text{plasma}}(\lambda) \), the emission of the LED without the plasma \( L_{\text{LED}}(\lambda) \) and the background signal of the detector \( L_{\text{back}}(\lambda) \). The recorded spectra shown in figure 2.4 are obtained with a gate width of 500 ns close to the end of the discharge pulse, between 200 and 700 ns, as shown in figure 2.2. The fractional absorption \( A(\lambda) \) is defined as

\[
A(\lambda) = 1 - \frac{L_{\text{plasma+LED}}(\lambda) - L_{\text{plasma}}(\lambda)}{L_{\text{LED}}(\lambda) - L_{\text{back}}(\lambda)} = 1 - \frac{I(\lambda)}{I_0(\lambda)}.
\]  

(2.1)

The obtained fractional absorption spectrum is shown in figure 2.5. Since the spectral width of the measured rotational lines of OH(A–X)(0-0) is smaller than the instrumental resolution [5], the spectrally integrated fractional absorption is used to determine the absolute density. This approach is independent of the instrumental resolution [16]. Using the Beer-Lambert law, the spectrally integrated fractional absorption of a rotational line can be written as

\[
W = \int A(\lambda)d\lambda = \int (1 - \exp(-h\lambda B \phi(\lambda, T)n_i l))d\lambda,
\]

(2.2)

where \( h \) is the Planck constant, \( B \) the absorption coefficient of the line [18], \( \phi(\lambda, T) \) the normalized line profile of the investigated absorbed line, \( n_i \) the density in the lower rotational level of the transition in the ground state and \( l \) the absorption length. The latter is determined from the radially resolved LIF profiles as shown in figure 2.6. The chemical kinetics leading to this profile are discussed in chapter 3. The effective absorption length can be estimated by the sum of the FWHM of the two LIF peaks, which in the current case is 0.4 mm.

Figure 2.3: Schematic drawing of the setup used for broadband UV absorption.

in Grenoble, while the LIF measurements were performed in Eindhoven.
Chapter 2: Absolute calibration of the OH density

Figure 2.4: Spectra recorded with a 500 ns gate \((t = 200 - 700 \text{ ns})\) to obtain the OH(X) absorption spectrum.

Figure 2.5: Obtained fractional absorption spectrum deduced from the results shown in figure 2.4.
In equation 2.2, it is assumed that the line profile of the measured rotational lines ($P_1(2)$ and $Q_1(4−6)$) has a Voigt profile, whose Doppler and van der Waals widths are given by the following equations [13, 24]:

$$\Delta \lambda_G (\text{pm}) = 7.16 \cdot 10^{-7} \lambda \sqrt{\frac{T}{M}},$$ (2.3)

$$\Delta \lambda_L (\text{pm}) = \frac{\lambda^2}{c} 1.71 \cdot 10^{-3} \left(\frac{T}{296}\right)^{-0.7}.$$ (2.4)

The OH(X) $f_1(2, 4−6)$ densities are derived from the integrated fractional absorption obtained from spectra as shown in figure 2.4, compared to calculated values of $W$ at different densities (see figure 2.7). The temperature assumed in this calculation is 425 K, as measured by LIF. The total density of OH(X) is deduced by applying the Boltzmann factor of the $f_1(2, 4−6)$ levels to the above estimated densities. The maximum OH(X) density for the plasma filament, averaged over the densities obtained from the different rotational lines, is then $(1.5 \pm 0.3) \cdot 10^{22} \text{ m}^{-3}$. The accuracy is determined by weighted averaging of multiple measurements of the measured rotational lines, the inaccuracy of the LIF profile is not included in the error calculation.
2.4 Calibration of the relative LIF intensity decay in the afterglow by a chemical model

A second estimate of the absolute OH(X) density is obtained from the decay of the LIF intensity in the afterglow, using the known reaction rates of the most important loss processes of OH (see table 2.1). This approach has been successfully used in the past for pulsed discharges in e.g. [7, 27]. In [7], even a comparison is given between the calibration with a chemical model and the calibration by Rayleigh scattering with a LIF model, which shows excellent agreement. However, several estimates and assumptions have been made. In the current work, a quadratic dependence is assumed in \( n_{\text{OH}} \):

\[
\frac{dn_{\text{OH}}(t)}{dt} = -n_{\text{OH}}^2(t)(2k_1 + 2k_3) - n_{\text{OH}}(t)n_H(t)k_2 \approx -n_{\text{OH}}^2(t)k_{\text{loss}}, \tag{2.5}
\]

as the density of H is assumed to be equal to the density of OH. This is a reasonable assumption on time scales smaller than the diffusion time. In addition, H contributes to the total loss rate of OH for only 10\%. This total loss rate is defined as \( k_{\text{loss}} = 2k_1 + k_2 + 2k_3 \), and is obtained from the reactions listed in table 2.1. The following decay is then used to fit the decay of the LIF intensity

\[
\frac{n_{\text{OH}}}{n_{\text{OH}}^0} = \frac{1}{1 + k_{\text{loss}} n_{\text{OH}}^0 (t - t_0)}, \tag{2.6}
\]

where \( n_{\text{OH}}^0 \) is the OH density at \( t = t_0 \) and \( t_0 \) is taken between 0.5\,\mu s and 5\,\mu s. The decay is fitted for at least two different \( t_0 \), the obtained OH densities with

Figure 2.7: The integrated fractional absorption \( W \) as a function of the OH(X; \( f_1(2) \)) density. The temperature is set to 425 K as measured by LIF.
2.5: Absolute calibration of LIF with Rayleigh scattering

Table 2.1: Dominant reactions responsible for the loss of OH in the afterglow. The rates are calculated for a temperature of 400 K. Rate coefficients have units of m$^3$s$^{-1}$ for 2-body reactions and m$^6$s$^{-1}$ for 3-body reactions. Note: The prefactor of R1 is obtained from [10], while the temperature dependence is obtained from [27].

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate coefficient $k$</th>
<th>$k$ at 400 K (m$^3$s$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>OH + OH + He $\rightarrow$ H$_2$O$_2$ + He</td>
<td>$3.7 \times 10^{-4}(T_g/300)^{2/3}$</td>
<td>$5.29 \times 10^{-18}$</td>
<td>[10, 27]</td>
</tr>
<tr>
<td>R2</td>
<td>OH + OH $\rightarrow$ H$_2$O + O</td>
<td>$2.9 \times 10^{-26}T_g^{1/6}\exp(945/T_g)$</td>
<td>$1.79 \times 10^{-18}$</td>
<td>[27]</td>
</tr>
<tr>
<td>R3a</td>
<td>OH + H + He $\rightarrow$ H$_2$O + He</td>
<td>$1.56 \times 10^{-36}(T_g/300)^{-2/3}$</td>
<td>$1.09 \times 10^{-18}$</td>
<td>[17]</td>
</tr>
</tbody>
</table>

these different fits are then averaged. The decay is fitted until $t = 15$ μs. The typical time scales for diffusion of OH and H are 40 μs and 16 μs, respectively, for a plasma radius of 150 μm. This allows us to obtain a reasonable estimate from the decay fit. Furthermore this method can only be applied when the gas temperature is constant, which is in good approximation valid for $t > 0.4$ s (see figure 3.19). The calibrated OH density, together with the fit of the chemical model, is shown in figure 2.8.

To validate the fact that only 3 reactions need to be taken into account to calculate the absolute OH density, the obtained OH density is compared with an extended chemical model which takes into account the rate equations for OH, H, O, O$_2$, H$_2$, HO$_2$, H$_2$O$_2$ and H$_2$O. This extended model is identical to the model reported by Tochikubo et al [27], except that some of the reaction rates are adapted to the current experimental conditions. The reactions and their rates are shown in table 2.2. As initial conditions, it is assumed that the H density is equal to the OH density, and that the sum of the OH and H$_2$O density equals the admixed H$_2$O density. The initial densities of O, O$_2$, H$_2$, HO$_2$ and H$_2$O$_2$ are assumed to be 10 orders of magnitude lower than the H$_2$O density. The obtained time resolved OH density is compared to the above calibrated OH density in figure 2.8. A good agreement is found; the OH density calibrated using only 3 reactions does not differ by more than 10% compared to the OH density obtained from the extended model. This also validates the assumptions made for the OH quenching by H atoms.

2.5 Absolute calibration of LIF with Rayleigh scattering

In the previous section, an estimate of the maximum OH density is obtained through fitting the decay of the OH LIF intensity with a chemical model. In a He + H$_2$O discharge this method is straightforward, since there are not many
Figure 2.8: Time resolved OH density in the high-density mode at 0.84% H$_2$O, calibrated with a chemical model. The fit is shown for two different starting times. A comparison is made with the result of an extended chemical model.
Table 2.2: Additional reactions that are involved in the OH chemistry in He-H₂O discharges, and that are used in the extended chemical model. The rate coefficients have units of m³s⁻¹ for 2-body reactions and m⁶s⁻¹ for 3-body reactions, and are calculated for the same conditions as in table 2.1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate coefficient $k$</th>
<th>$k$ at 400 K (m³s⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R3b</td>
<td>OH + H + H₂O $\rightarrow$ 2H₂O</td>
<td>$2.46 \cdot 10^{-45}(T_g/300)^{-2}$</td>
<td>$2.18 \cdot 10^{-19}$</td>
<td>[17]</td>
</tr>
<tr>
<td>R4</td>
<td>OH + H $\rightarrow$ H₂ + O</td>
<td>$1.38 \cdot 10^{-20}T_g\exp(-3500/T_g)$</td>
<td>$8.75 \cdot 10^{-22}$</td>
<td>[28]</td>
</tr>
<tr>
<td>R5</td>
<td>OH + O $\rightarrow$ O₂ + H</td>
<td>$2.01 \cdot 10^{-17}\exp(112/T_g)$</td>
<td>$2.66 \cdot 10^{-17}$</td>
<td>[3]</td>
</tr>
<tr>
<td>R6</td>
<td>OH + H₂ $\rightarrow$ H₂O + H</td>
<td>$7.69 \cdot 10^{-18}\exp(-2000/T_g)$</td>
<td>$5.18 \cdot 10^{-20}$</td>
<td>[2]</td>
</tr>
<tr>
<td>R7</td>
<td>OH + HO₂ $\rightarrow$ H₂O + O₂</td>
<td>$4.8 \cdot 10^{-17}\exp(250/T_g)$</td>
<td>$8.97 \cdot 10^{-17}$</td>
<td>[2]</td>
</tr>
<tr>
<td>R8</td>
<td>OH + H₂O₂ $\rightarrow$ H₂O + HO₂</td>
<td>$2.91 \cdot 10^{-18}\exp(-160/T_g)$</td>
<td>$1.95 \cdot 10^{-18}$</td>
<td>[2]</td>
</tr>
<tr>
<td>R9</td>
<td>H + H + M $\rightarrow$ H₂ + M</td>
<td>$2.7 \cdot 10^{-43}T_g^{-0.6}$</td>
<td>$1.39 \cdot 10^{-19}$</td>
<td>[3]</td>
</tr>
<tr>
<td>R10</td>
<td>H + H₂O $\rightarrow$ OH + H₂</td>
<td>$7.6 \cdot 10^{-22}T_g^{1.6}\exp(-9281/T_g)$</td>
<td>$9.28 \cdot 10^{-18}$</td>
<td>[30]</td>
</tr>
<tr>
<td>R11</td>
<td>H + HO₂ $\rightarrow$ H₂ + O₂</td>
<td>$7.11 \cdot 10^{-17}\exp(-710/T_g)$</td>
<td>$1.21 \cdot 10^{-17}$</td>
<td>[3]</td>
</tr>
<tr>
<td>R12</td>
<td>H + HO₂ $\rightarrow$ OH + OH</td>
<td>$2.81 \cdot 10^{-16}\exp(-440.2/T_g)$</td>
<td>$9.35 \cdot 10^{-17}$</td>
<td>[3]</td>
</tr>
<tr>
<td>R13</td>
<td>H + HO₂ $\rightarrow$ H₂O + O</td>
<td>$5 \cdot 10^{-17}\exp(-866/T_g)$</td>
<td>$5.74 \cdot 10^{-18}$</td>
<td>[3]</td>
</tr>
<tr>
<td>R14</td>
<td>H + HO₂ $\rightarrow$ H₂O + OH</td>
<td>$1.69 \cdot 10^{-17}\exp(-1780/T_g)$</td>
<td>$1.97 \cdot 10^{-19}$</td>
<td>[3]</td>
</tr>
<tr>
<td>R15</td>
<td>H + HO₂ $\rightarrow$ HO₂ + H₂</td>
<td>$2.81 \cdot 10^{-18}\exp(-1890/T_g)$</td>
<td>$2.49 \cdot 10^{-20}$</td>
<td>[3]</td>
</tr>
<tr>
<td>R16</td>
<td>H + O₂ + M $\rightarrow$ HO₂ + M</td>
<td>$5.4 \cdot 10^{-44}(298/T_g)^{1.8}$</td>
<td>$5.96 \cdot 10^{-19}$</td>
<td>[2]</td>
</tr>
<tr>
<td>R17</td>
<td>O + H₂ $\rightarrow$ OH + H</td>
<td>$3.44 \cdot 10^{-19}(T_g/298)^{2.67}\exp(-3162/T_g)$</td>
<td>$2.78 \cdot 10^{-22}$</td>
<td>[3]</td>
</tr>
<tr>
<td>R18</td>
<td>O + HO₂ $\rightarrow$ OH + O₂</td>
<td>$2.91 \cdot 10^{-17}\exp(200/T_g)$</td>
<td>$4.80 \cdot 10^{-17}$</td>
<td>[28]</td>
</tr>
<tr>
<td>R19</td>
<td>O + HO₂ $\rightarrow$ OH + HO₂</td>
<td>$1.4 \cdot 10^{-18}\exp(-2000/T_g)$</td>
<td>$9.43 \cdot 10^{-21}$</td>
<td>[2]</td>
</tr>
<tr>
<td>R20</td>
<td>HO₂ + HO₂ $\rightarrow$ H₂O₂ + O₂</td>
<td>$8.05 \cdot 10^{-17}(T_g/300)^{-1}$</td>
<td>$6.04 \cdot 10^{-17}$</td>
<td>[17]</td>
</tr>
<tr>
<td>R21</td>
<td>HO₂ + HO₂ + M $\rightarrow$ H₂O₂ + O₃ + M</td>
<td>$1.9 \cdot 10^{-45}\exp(980/T_g)$</td>
<td>$4.13 \cdot 10^{-19}$</td>
<td>[2]</td>
</tr>
</tbody>
</table>
reaction partners of OH. However, when helium is replaced by a molecular gas, the number of reaction partners of OH, of which the density has to be known, increases. As many of the species that react most with OH are produced in the plasma by dissociation reactions, their unknown densities introduce several parameters which need to be determined to calculate the quenching of the OH radicals in the afterglow. In molecular gases, calibration with Rayleigh scattering can therefore be more reliable. In this section a LIF model for He + 0.84% H₂O is developed.

2.5.1 Rayleigh scattering

The measured Rayleigh scattering intensity (counts) can be written as

\[ S_{\text{Ray}} = \eta N_n \frac{\partial^3 \sigma_0}{\partial \Omega} V_{\text{Ray}} I_L t_L, \]  

(2.7)

where \( \eta \) is a calibration constant that depends on the solid angle and the efficiency of the detector (counts sr⁻¹), \( N_n \) the density of scattering particles (m⁻³), \( \frac{\partial^3 \sigma_0}{\partial \Omega} \) the differential cross section for Rayleigh scattering (m² sr⁻¹), \( V_{\text{Ray}} \) the volume from which Rayleigh scattering is collected (m³), \( I_L \) the laser irradiance (W m⁻²) and \( t_L \) the temporal length of the laser pulse (s). At room temperature (300 K) \( N_n = p/k_B T_g = 2.5 \cdot 10^{25} \text{ m}^{-3} \).

The cross section in equation 2.7 is the differential cross section for linearly polarized (along z-axis) incident light propagating along the x-axis (parallel to the laser beam) and the scattered light is observed along the y-axis, perpendicular to both the laser beam and polarization. The detection system is polarization insensitive as the calibration is performed with an iCCD [19]. The cross section to consider for this geometrical configuration is [19]

\[ \frac{\partial^3 \sigma_0}{\partial \Omega} = \frac{3\sigma}{8\pi 2 + \rho_0^2}, \]  

(2.8)

where \( \sigma \) is the total cross section for Rayleigh scattering (m²) [19]

\[ \sigma = \frac{8\pi^3 (4\pi)^2 a_{\text{pol}}^2}{3\lambda_{\text{Ray}}^4} \left( \frac{6 + 3\rho_0}{6 - 7\rho_0} \right), \]  

(2.9)

where \( a_{\text{pol}} \) is the mean polarizability of the scattering species (10⁻³⁰ m⁴) and \( \rho_0 \) the ratio of the horizontally-to-vertically polarized light scattered at 90° for unpolarized (natural) incident light propagating along the x-axis. Both \( a_{\text{pol}} \) and \( \rho_0 \) are wavelength dependent. \( \lambda_{\text{Ray}} \) is the wavelength of the laser (m). The equation for the differential cross section then becomes

\[ \frac{\partial^3 \sigma_0}{\partial \Omega} = \frac{32a_{\text{pol}}^2}{2 + \rho_0} \left( \frac{\pi}{\lambda} \right)^4 \left( \frac{6 + 3\rho_0}{6 - 7\rho_0} \right). \]  

(2.10)
For $N_2$ at $\lambda = 282.58$ nm, $\rho_0 = 0.013$ and $a_{\text{pol}} = 1.9 \cdot 10^{-30}$ m$^3$ the differential cross section is $8.8 \cdot 10^{-31}$ m$^2$ sr$^{-1}$. $\rho_0$ and $a_{\text{pol}}$ are obtained for this wavelength by interpolation of the literature values given in [1, 4, 9, 21, 23, 26].

The laser irradiance is defined as

$$I_L = \frac{E_L}{\tau_L \Delta s^2},$$

(2.11)

where $E_L$ is the laser energy per pulse (J), $\tau_L$ the temporal FWHM of the laser pulse (s) and $\Delta s^2$ the square of the spatial FWHM of the laser beam at the observation point (m$^2$). To take into account the non-uniformity in space, it is assumed that the energy density has a Voigt distribution $f_s(y, z)$ (as obtained by a fit from the Rayleigh signal), which is normalized to $\Delta s^2$. The time variation of the laser energy $f_t(t)$ is measured with a photodiode and is also normalized to the FWHM $\tau_L$. The laser irradiance as a function of space and time is then

$$I_L(y, z, t) = \frac{E_L}{\tau_L \Delta s^2} f_s(y, z) f_t(t).$$

(2.12)

After taking into account the non-uniformity of the laser energy density, equation 2.7 becomes

$$S_{\text{Ray}} = \eta N_n \left. \frac{\partial \beta=0 \sigma_0}{\partial \Omega} \right|_{\Delta x} \frac{E_L}{\tau_L \Delta s^2} \int_{0}^{\Delta x} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f_s(y, z) f_t(t) \, dy \, dz \, dt$$

$$= \eta n \left. \frac{\partial \beta=0 \sigma_0}{\partial \Omega} \right|_{\Delta x} E_L \Delta x,$$

(2.13) (2.14)

where $\Delta x$ is the length of the detection volume (m).

The calibration constant $\eta$ can then be determined from the slope $\alpha$ of the measured Rayleigh intensity as a function of the laser energy per pulse times the pressure

$$\eta = \alpha k_B T \left( \left. \frac{\partial \beta=0 \sigma_0}{\partial \Omega} \right|_{\Delta x} \right)^{-1}.$$

(2.15)

To obtain the Rayleigh intensity $S_{\text{Ray}}$ from the images, the FWHM of the Rayleigh signal $\Delta s$ is determined. The Rayleigh intensity within an area $\Delta s \cdot \Delta x$ is summed and plotted as a function of energy times pressure to determine the calibration constant $\eta$ (figure 2.9).
Chapter 2: Absolute calibration of the OH density

2.5.2 LIF calibration

The measured intensity of the laser induced fluorescence (#counts) can be expressed as

\[ S_{\text{LIF}} = \frac{1}{4\pi} \int \eta \frac{hc}{\lambda} n_{\text{exc}}(x,y,z,t)A dx dy dz dt, \]

where \( n_{\text{exc}}(x,y,z,t) \) is the density of OH radicals in the excited state \( (\text{m}^{-3}) \) and \( \lambda \) and \( A \) are the wavelength \( (\text{m}) \) and Einstein emission coefficient \( (\text{s}^{-1}) \) of the observed transitions respectively. \( n_{\text{exc}}(x,y,z,t) \) is normalized to the density of OH radicals in the ground state \( n_{\text{exc}}/n_{\text{OH}} = N \). The normalized densities for different levels are calculated with a 6- or 4-level model.

The LIF signal \( S_{\text{LIF}} \) is determined from images recorded with the iCCD by averaging the intensity in ellipses around the maximum intensity. The radius in the \( z \) direction of the ellipses is the same as the FWHM of the Rayleigh scattering signal of the laser. This FWHM LIF intensity of the \( z \) radius is then used to determine the radius in the \( x \) direction. When necessary, the images of the LIF signal are corrected for the optical emission of the plasma, by subtracting the laser-off images from the laser-on images. The OH density determined in this way is thus averaged over the FWHM of the laser beam. It is estimated that the maximum OH density is not more than 20% higher, which is within the experimental accuracy of the method (see also further).
2.5: Absolute calibration of LIF with Rayleigh scattering

In the models the laser spectral irradiance \( I_s \) (Wm\(^{-1}\)) is used:
\[
I_s = \frac{E_L \Gamma}{\Delta \nu_L \tau_L A_L}, \quad (2.17)
\]
where \( \Gamma \) is the dimensionless overlap integral (see below), \( \Delta \nu_L \) the laser linewidth (m\(^{-1}\)) and \( A_L \) the area of the laser beam at the observation point (m\(^2\)).

**Overlap integral**

The common dimensional overlap integral \((1/\text{m}^{-1})\) is defined as
\[
g = \int_{-\infty}^{+\infty} Y_A(\nu) L_L(\nu) d\nu, \quad (2.18)
\]
where \( Y_A(\nu) \) is the spectral profile of the absorption transition \((1/\text{m}^{-1})\) and \( L_L(\nu) \) the spectral profile of the laser \((1/\text{m}^{-1})\), both functions in this formulation are normalized to unity \([20]\). When the laser spectral profile is normalized to its FWHM, the dimensional overlap integral in equation 2.18 is multiplied with the linewidth of the laser \( \Delta \nu_L \) \([20]\), and a dimensionless parameter is obtained
\[
\Gamma = \Delta \nu_L g. \quad (2.19)
\]

According to the specifications of the dye laser, the linewidth of the laser is 1.8 pm (FWHM). After frequency doubling the width is diminished by a factor \(2\sqrt{2}\), so the linewidth \( \Delta \lambda_L \) to consider is 0.64 pm. For the bandwidth of the laser in units of wavenumber this results in \( \Delta \nu_L = \Delta \lambda_L / \lambda_L^2 = 8 \text{ m}^{-1} \) at \( \lambda_L = 282.58 \text{ nm} \).

An estimate of the linewidth of the laser is also obtained by measuring the fluorescence signal when scanning the laser wavelength around the \( P1(2) \) transition of OH (figure 2.10). From a Voigt fit of the recorded profile, the Lorentzian \((\Delta \lambda^L)\) and Gaussian \((\Delta \lambda^G)\) widths are determined for different laser energies. The result is shown in figure 2.11, \( \Delta \lambda^L \) increases with increasing laser energy. This increase is due to the saturation broadening, even at pulse energies below 2 \( \mu \text{J} \), for which no saturation effects are observed in the measured LIF signal intensities (figure 2.16). For the calculation of the laser linewidth the widths corresponding to the lowest measured laser energy are used. These widths \((\Delta \lambda^{tot})\) result from the width of the absorption line and of the laser width. The Doppler and van der Waals linewidths of the absorption line can be calculated using equations 2.3 and 2.4. At 282.58 nm (the wavelength of the absorption line), at atmospheric pressure and a temperature of 350 K (the measured gas temperature) and \( M = 17 \text{ amu} \) for OH, the calculated widths (FWHM) of the absorption line are \( \Delta \lambda^{G,P1(2)} = 0.9 \text{ pm} \) and \( \Delta \lambda^{L,P1(2)} = 0.4 \text{ pm} \). The linewidth of the laser can now be calculated using
\[
\Delta \lambda^{L,laser} = \Delta \lambda^{L,tot} - \Delta \lambda^{L,P1(2)}, \quad (2.20)
\]
\[
\Delta \lambda^{G,laser} = \sqrt{(\Delta \lambda^{G,tot})^2 - (\Delta \lambda^{G,P1(2)})^2}, \quad (2.21)
\]
the combined FWHM of the laser follows from
\[
\Delta \lambda = \frac{\Delta \lambda^G}{2} + \sqrt{\frac{(\Delta \lambda^L)^2}{4} + (\Delta \lambda^G)^2}.
\]
(2.22)
The measured Gaussian and Lorentzian widths of the laser in the low energy limit are \(\Delta \lambda^G,\text{laser} = (0.8 \pm 0.3)\) pm and \(\Delta \lambda^L,\text{laser} = (0.9 \pm 0.1)\) pm respectively, and the total width \(\Delta \lambda,\text{laser} = (1.4 \pm 0.3)\) pm. The experimentally measured linewidth in units of wavenumber is then 17 m\(^{-1}\), about twice the value obtained from the specifications of the dye laser. The dimensionless overlap integral calculated with the theoretical absorption linewidth and the experimental, (respectively theoretical) laser width is 0.23, (respectively 0.28), which differs by 22 \%.

**Detailed 6-level LIF model**

In order to determine the number of laser excited OH(A) radicals as a function of the OH(X) density in equation 2.16, we use a 6-level LIF model including collisional processes. The detailed 6-level model simulates, apart from the laser excitation from the ground level and stimulated emission, also rotational (RET), vibrational (VET) and electronic (Q) energy transfer reactions. A detailed description of the 6-level model can be found in [8], the numbering of the levels and the dominant energy transfer reactions are schematically shown in figure 2.12. The accompanying set of partial differential equations is given by

\[
\frac{dN_1}{dt} = -f_t(t)I_0 B_{12} N_1 + (f_t(t)I_0 B_{21} + f_B^{'''''=0,J''''=2.5} A_{10}) N_2 \\
+ f_B^{''''=0,J''''=2.5} A_{10} N_3 + f_B^{''''=0,J''''=2.5} (Q_{00} + A_{00}) N_4 \\
+ f_B^{''''=0,J''''=2.5} V_X N_5 + TR_{61},
\]
(2.23)
\[
\frac{dN_2}{dt} = f_t(t)I_0 B_{12} N_1 - (f_t(t)I_0 B_{21} + A_{10} + A_{11} + Q_{11} + V_A) N_2 \\
- TR_{23},
\]
(2.24)
\[
\frac{dN_3}{dt} = TR_{23} - (A_{10} + A_{11} + Q_{11} + V_A) N_3,
\]
(2.25)
\[
\frac{dN_4}{dt} = V_A N_2 + V_A N_3 - (Q_{00} + A_{00}) N_4,
\]
(2.26)
\[
\frac{dN_5}{dt} = (Q_{11} + A_{11}) N_2 + (Q_{11} + A_{11}) N_3 - V_X N_5,
\]
(2.27)
\[
\frac{dN_6}{dt} = (1 - f_B^{''''=0,J''''=2.5}) A_{10} N_2 + (1 - f_B^{''''=0,J''''=2.5}) A_{10} N_3 \\
+ (1 - f_B^{''''=0,J''''=2.5}) (Q_{00} + A_{00}) N_4 \\
+ (1 - f_B^{''''=0,J''''=2.5}) V_X N_5 - TR_{61},
\]
(2.28)
\[
TR_{61} = 2R_{61}(N_1 + N_6 - N_1/f_B^{''''=0,J''''=2.5}),
\]
(2.29)
\[
TR_{23} = 2R_{23}(N_2 + N_3 - N_2/f_B^{''''=1,J''''=1.5}).
\]
(2.30)
2.5: Absolute calibration of LIF with Rayleigh scattering

---

Figure 2.10: Upper figure: Voigt fit of the recorded profile of the $P_1(2)$ transition of OH in He + 0.05% H$_2$O (1.4 kV) at a laser energy of 0.08 µJ/pulse. $\Delta \lambda^G = (1.2 \pm 0.2)$ pm, $\Delta \lambda^L = (1.3 \pm 0.1)$ pm. Lower figure: Absorption profile of the $P_1(2)$ transition in helium, compared with the theoretical and measured laser profiles. The intensities are normalized.
Chapter 2: Absolute calibration of the OH density

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Figure 2.11: Lorentzian and Gaussian FWHM as a function of the laser energy per pulse, measured in the afterglow of a He + 0.05% H$_2$O (1.4 kV) plasma. $T_g = 350$ K.

$N_i$ is the population of level $i$ (m$^{-3}$), $B_{ij}$ is the Einstein $B$ coefficient from level $i$ to level $j$ (mJ$^{-1}$), $j_{B_i}^{\nu,J}$ is the temperature dependent Boltzmann factor of the level with vibrational level $\nu$ and total angular momentum $J$. $V_A$ and $V_X$ are the vibrational energy transfer rates (m$^3$s$^{-1}$) in the excited and ground state respectively. $A_{ij}$ and $Q_{ij}$ are the quenching rate (m$^3$s$^{-1}$) and Einstein $A$ coefficient (s$^{-1}$) from vibrational level $i$ in the excited state to vibrational level $j$ in the ground state.

The initial condition of the set of partial differential equations is the equilibrium, governed by detailed balance. In the differential equations the Boltzmann factor is taken into account in the loss processes to the $(X; \nu'' = 0)$ state, which is split

Figure 2.12: Radiative and collisional schemes for the detailed 6-level model.
2.5: Absolute calibration of LIF with Rayleigh scattering

up in \( N_6 \) and \( N_1 \). The gas temperature during the laser pulse is assumed to be constant. In collisional quenching it is assumed that both the vibrational and rotational number are conserved and no other spontaneous emission than \( A_{11}, A_{10} \) and \( A_{00} \) is modelled since the rates for other spontaneous emissions (e.g. \( A_{01} \) and \( A_{12} \)) are more than two orders of magnitude smaller [18].

Considering the 3 excited state (lumped) levels in the detailed 6-level model, equation 2.16 becomes

\[
S_{\text{LIF}} = \frac{1}{4\pi} \eta \hbar c \Delta x \Delta y \Delta s_{\text{OH}} \int \left( (N_2(t) + N_3(t)) \left( \frac{A_{11}}{\lambda_{11}} + \frac{A_{10}}{\lambda_{10}} \right) + N_4(t) \frac{A_{00}}{\lambda_{00}} \right) dt. \tag{2.31}
\]

In table 2.3 the parameters of the model are summarized. The total RET rates for inelastic collisions of OH(A; \( \nu' = 1 \)) with H\(_2\)O and He following excitation of the \( F_1(1) \) level are not published in literature, but can be deduced as follows. In [14] the total RET rates are given for OH(A; \( \nu' = 1, F_2(5) \)) at 300 K in collisions with H\(_2\)O and He, the total RET rates for the other doublet component \( F_1(5) \) are assumed to be equal [12]. The rates are then interpolated to \( F_1(1) \) [15]. The rates for RET in the ground level are estimated assuming that the dependences on spin and rotational quantum number are the same as in the excited state. As will be shown later, the OH density is not strongly dependent on RET, which justifies this estimation in this case. The RET rates are shown in table 2.4, together with the rates for total quenching (electronic + vibrational relaxation) of OH(A; \( \nu' = 0, 1 \)) and vibrational relaxation. The rate for vibrational relaxation in the ground state \( V_X \) is assumed to be 2 orders of magnitude smaller than the rate for vibrational relaxation in the excited state \( V_A \) [22].

4-level model

The transitions in the 4-level model are shown in figure 2.13. In this model it is assumed that the RET is infinitely fast compared to quenching, emission and VET. As a consequence the quenching, emission and VET rates are not rotationally resolved. The vibrational levels considered are \( \nu = 0 \) and \( \nu = 1 \), so only VET from \( \nu = 1 \) to \( \nu = 0 \) is taken into account. The Boltzmann factor \( f_B^{\nu' = 1, \nu = 1.5} \) is used only for the stimulated emission originating from the \( F_1(1) \) level.

The densities of the 4 levels can be modelled with the following differential equa-
Chapter 2: Absolute calibration of the OH density

Table 2.3: Total rate constants and parameters of the 6- and 4-level model. The total rates for quenching, VET and RET are calculated as $k^{\text{He}} N^\text{He} + k^{\text{H}_2\text{O}} N^\text{H}_2\text{O}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{00}$ (nm)</td>
<td>308.900</td>
<td>[18]</td>
</tr>
<tr>
<td>$\lambda_{A1}$ (nm)</td>
<td>314.535</td>
<td>[18]</td>
</tr>
<tr>
<td>$\lambda_{A10}$ (nm)</td>
<td>282.792</td>
<td>[18]</td>
</tr>
<tr>
<td>$A_{00}$ (s$^{-1}$)</td>
<td>$1.451 \cdot 10^6$</td>
<td>[18]</td>
</tr>
<tr>
<td>$A_{11}$ (s$^{-1}$)</td>
<td>$8.678 \cdot 10^5$</td>
<td>[18]</td>
</tr>
<tr>
<td>$A_{10}$ (s$^{-1}$)</td>
<td>$4.606 \cdot 10^5$</td>
<td>[18]</td>
</tr>
<tr>
<td>$B_{12}$ (mJ$^{-1}$)</td>
<td>1.8</td>
<td>[18]</td>
</tr>
<tr>
<td>$B_{21}$ (mJ$^{-1}$)</td>
<td>2.8</td>
<td>[18]</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>425</td>
<td></td>
</tr>
<tr>
<td>$f^\nu_{B}^{\nu'}=0,J'=2.5$</td>
<td>0.153</td>
<td>[18]</td>
</tr>
<tr>
<td>$f^\nu_{B}^{\nu'}=1,J'=1.5$</td>
<td>0.1</td>
<td>[18]</td>
</tr>
<tr>
<td>$\Delta \tau$ (ns)</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>$\Delta s$ (nm)</td>
<td>290</td>
<td></td>
</tr>
<tr>
<td>$Q_{00}$ (s$^{-1}$)</td>
<td>$1.1 \cdot 10^8$</td>
<td>[6, 11]</td>
</tr>
<tr>
<td>$Q_{11}$ (s$^{-1}$)</td>
<td>$1.0 \cdot 10^5$</td>
<td>[6]</td>
</tr>
<tr>
<td>$V_{1} (s^{-1})$</td>
<td>$1.1 \cdot 10^5$</td>
<td>[22]</td>
</tr>
<tr>
<td>$V_{X} (s^{-1})$</td>
<td>$1.1 \cdot 10^5$</td>
<td>[22]</td>
</tr>
<tr>
<td>$R_{61}$ (s$^{-1}$)</td>
<td>$4.3 \cdot 10^8$</td>
<td>[12, 14, 15]</td>
</tr>
<tr>
<td>$R_{23}$ (s$^{-1}$)</td>
<td>$6.6 \cdot 10^9$</td>
<td>[12, 14, 15]</td>
</tr>
</tbody>
</table>

Table 2.4: Total RET rate coefficients estimated at 300 K, total quenching (electronic + vibrational relaxation) rate coefficients for OH(A; $\nu' = 0, 1$) and vibrational relaxation rate coefficients for inelastic collisions of OH with He and H$_2$O. (For an explanation of the RET rate coefficients, see text.) The quenching rate by He is neglected [11], the VET rate for He is estimated from the experimental results in this work.

<table>
<thead>
<tr>
<th>Collisional process</th>
<th>Initial level</th>
<th>He (10$^{-17}$ m$^3$ s$^{-1}$)</th>
<th>H$_2$O (10$^{-17}$ m$^3$ s$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RET (A; $\nu' = 1$, $P_{1}(11)$)</td>
<td>35.2</td>
<td>131</td>
<td></td>
<td>[12, 14, 15]</td>
</tr>
<tr>
<td>RET (X; $\nu' = 0$, $f_{1}(2)$)</td>
<td>23.2</td>
<td>98</td>
<td></td>
<td>[12, 14, 15]</td>
</tr>
<tr>
<td>Q (A; $\nu' = 0$)</td>
<td>0</td>
<td>68</td>
<td></td>
<td>[6, 11]</td>
</tr>
<tr>
<td>Q (A; $\nu' = 1$)</td>
<td>0.0002</td>
<td>66</td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td>VET (A; $\nu' = 1 \rightarrow \nu' = 0$)</td>
<td>0.0002</td>
<td>7.3</td>
<td></td>
<td>[6]</td>
</tr>
</tbody>
</table>
Radiative and collisional schemes for the 4-level model. 

\[
\frac{dN_1}{dt} = f(t)I_0 \left( -B_{12} f^{\nu''=0, J''=2.5} f^{\nu'=1, J'=1.5} N_1 + B_{21} f^{\nu'=1, J'=1.5} N_2 \right) + A_{10} N_2 + L_0 N_3 + V_X N_4, \tag{2.32}
\]

\[
\frac{dN_2}{dt} = f(t)I_0 \left( B_{12} f^{\nu''=0, J''=2.5} N_1 - B_{21} f^{\nu'=1, J'=1.5} N_2 \right) - L_1 N_2, \tag{2.33}
\]

\[
\frac{dN_3}{dt} = V_A N_2 - L_0 N_3, \tag{2.34}
\]

\[
\frac{dN_4}{dt} = (A_{11} + Q_{11}) N_2 - V_X N_4. \tag{2.35}
\]

\( L_{\nu} \) is the sum of all the loss processes of the vibrational level \( \nu \) (\( L_0 = Q_{00} + A_{00} \) and \( L_1 = Q_{11} + A_{11} + A_{10} + V_A \)).

For the 4-level model, equation 2.16 for the LIF signal becomes

\[
S_{\text{LIF}} = \frac{1}{4\pi} \eta \frac{hc}{\Delta x \Delta y \Delta n_{\text{OH}}} \int \left( N_2(t) \left( \frac{A_{11}}{\lambda_{11}} + \frac{A_{10}}{\lambda_{10}} \right) + N_3(t) \frac{A_{00}}{\lambda_{00}} \right) dt. \tag{2.36}
\]

### 2.5.3 LIF results and sensitivity analysis

In figure 2.14 the simulated level population fractions are shown for the 6- and 4-level model. Since the LIF measurements are performed in the linear regime, only a small amount of the ground level is pumped by the laser. Furthermore it can be seen in figure 2.14 that the populations of the \( \Lambda \) states decay slowly compared to the laser pulse. This is because the total quenching in He \( + 0.84\% \) \( \text{H}_2\text{O} \) is rather low.
Figure 2.14: Simulated population fractions over time, obtained from the 6- (upper figure) and 4-level (lower figure) model.
2.5: Absolute calibration of LIF with Rayleigh scattering

The measured and modelled time resolved fluorescence intensities of the \((\nu'' = 1 - \nu' = 1)\) and \((\nu'' = 0 - \nu' = 0)\) fluorescence are shown in figure 2.15. The relative intensity of the fluorescence is scaled to the ratio of the fluorescence of \((\nu'' = 1 - \nu' = 1)\) and \((\nu'' = 0 - \nu' = 0)\) obtained from a recorded LIF spectrum. The \((\nu'' = 1 - \nu' = 1)\) fluorescence obtained from the 6-level model seems to describe the measured fluorescence decay more accurately, although the difference is minor.

In figure 2.16, the measured total LIF intensity is shown as a function of the laser energy, together with the modelled LIF intensities. At \(E_L < 2.5 \mu\text{J}\) (first 7 data points) a laser energy averaged density is calculated from the measured LIF intensities calibrated by the model. At higher energy saturation starts. The resulting averaged density between 200 and 700 ns is \(8.4 \times 10^{21} \text{m}^{-3}\) for respectively the 6- and 4-level model when the experimental overlap function is used. When the theoretical overlap function is used, this density is \(3.6 \times 10^{21} \text{m}^{-3}\) and \(3.2 \times 10^{21} \text{m}^{-3}\) respectively. This means that the calculated OH density differs with more than a factor of 2 depending on whether the overlap function is determined experimentally or from the specifications of the dye laser manual. As a result, the knowledge of the laser profile is important for the accurate determination of the absolute OH density.

An error analysis of the obtained OH density is performed with the inaccuracies of the input parameters as a starting point, the results are shown in table 2.5. In this analysis the measured laser linewidth is used.

The laser energy is reproducible within 15%. Considering the accuracy of the
experimentally obtained laser linewidth, the laser spectral irradiance $I_s$ yields an accuracy of up to a factor 2 in the upper limit of the OH density. The measured gas temperature is $425 \pm 60$ K, which means the accuracy is 15%. The inaccuracy of the gas temperature can influence the OH density by 20%. The added water concentration depends on the temperature in the lab, which could change between 20.5 °C and 22.5 °C. The corresponding change in water concentration is small and has a minor effect on the obtained OH density, even though the water concentration strongly influences the rates for quenching and VET since these rates are much higher for H$_2$O than for He. The rates for quenching, RET and VET are taken from literature and although these values might have a considerable variation in the literature, the error analysis shows that the accuracy of these rates have only a minor influence on the calculated OH density. The influence of the VET rate is, just as the RET rate, small. To assess potential non-linear effects, the OH density is calculated for different laser energies up to 2.5 $\mu$J/pulse, yielding an effect of 10%.

### 2.6 Comparison of calibration methods

The maximum OH densities in He + 0.84% H$_2$O obtained with the 3 calibration methods are summarized in figure 2.17. The accuracy in the OH density determination using a chemical model is estimated to be a factor 2, which is mainly determined by the inaccuracy of the rates of the OH loss processes [29]. The main
Table 2.5: Sensitivity analysis of parameters used in the absolute calibration of the OH density. For the laser spectral irradiance $I_s$ the cumulative accuracy is calculated, it includes the contributions of $E_L$, $\Gamma$, $\Delta\nu$, $\tau_L$ and $A_L$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Accuracy</th>
<th>Effect on $n_{OH}(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_s$</td>
<td>67%</td>
<td>190%</td>
</tr>
<tr>
<td>$E_L$</td>
<td>15%</td>
<td></td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>11%</td>
<td></td>
</tr>
<tr>
<td>$\Delta\nu$</td>
<td>25%</td>
<td></td>
</tr>
<tr>
<td>$\tau_L$</td>
<td>9%</td>
<td></td>
</tr>
<tr>
<td>$A_L$</td>
<td>8%</td>
<td></td>
</tr>
<tr>
<td>$T_g$</td>
<td>15%</td>
<td>20%</td>
</tr>
<tr>
<td>$n_{H_2O}$</td>
<td>6%</td>
<td>7%</td>
</tr>
<tr>
<td>$V_A$</td>
<td>25%</td>
<td>$\leq 3%$</td>
</tr>
<tr>
<td>$Q_1$</td>
<td>2%</td>
<td>2%</td>
</tr>
<tr>
<td>$Q_0$</td>
<td>1%</td>
<td>1%</td>
</tr>
<tr>
<td>$R_1$</td>
<td>100%</td>
<td>$&lt; 0.1%$</td>
</tr>
<tr>
<td>$R_1 = 0$</td>
<td></td>
<td>3%</td>
</tr>
<tr>
<td>$R_2$</td>
<td>100%</td>
<td>$&lt; 0.1%$</td>
</tr>
<tr>
<td>$R_2 = 0$</td>
<td></td>
<td>4%</td>
</tr>
<tr>
<td>non-linear effects</td>
<td>10%</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.17: Calculated OH density for the three calibration methods, averaged over the time interval used for the UV absorption measurement.
inaccuracy for the LIF calibration with Rayleigh is due to the laser linewidth. All 3 independent methods provide comparable OH densities. The agreement also validates the 6- and 4-level models used in this work, as well as the assumptions made in the models. In the He-H$_2$O discharge, it seems that the RET can be assumed to be infinitely fast without a large effect on the calculated OH density.

2.7 Conclusion

For the first time, 3 independent methods (broadband UV absorption, LIF calibration with Rayleigh scattering and relative calibration with a chemical model of the OH LIF decay after the plasma pulse) are applied to measure the absolute OH density in a He-H$_2$O discharge at atmospheric pressure. The densities obtained with all 3 methods correspond within the experimental accuracy. Comparison between the 6- and 4-level models shows that RET can be assumed to be infinitely fast in an atmospheric pressure He-H$_2$O discharge. The LIF models applied in this work are validated, and can thus be used in pulsed discharges with other gas mixtures or other discharges where OH density calibration by UV absorption and/or relative calibration of the LIF decay are not possible. In the calibration of the LIF signal with Rayleigh scattering, it is clear that the knowledge of the laser profile is of great importance, since it can significantly alter the obtained OH density.
References


References


Chapter 3

He-H$_2$O mixtures

Abstract

The production of OH in a nanosecond pulsed filamentary discharge, generated in a pin-pin geometry, is studied in He-H$_2$O mixtures by time and spatially resolved laser induced fluorescence (LIF). Apart from the OH density also the gas temperature, the electron density and the He $^3$S$_1$ metastable density are measured. Depending on the applied voltage the discharge is in a different mode. The maximum electron density in the low- and high-density mode is of the order $10^{21}$ m$^{-3}$ and $10^{22}$ m$^{-3}$ respectively. The gas temperature does not exceed 500 and 1600 K respectively. In the low-density mode the maximum OH density is in the centre of the discharge filament, while in the high density mode the largest OH density is observed on the edge of the discharge. The chemical kinetics in the discharge are discussed in the case of the high-density mode, to explain the OH production mechanism, in particular the depletion of the OH(X) density observed in the core of the discharge. It is shown that charge transfer processes and dissociative recombination play a key role in the OH production.

Chapter 3: He-H$_2$O mixtures

3.1 Introduction

In this chapter, time and spatially resolved LIF of OH is applied on a nanosecond pulsed filamentary discharge in He-H$_2$O mixtures to investigate the OH production mechanisms. The dynamics of OH radical densities in pulsed discharges are already extensively studied in the past using LIF [22, 36, 37]. In these studies, however, there is often no complete description of other important plasma parameters like the electron density ($n_e$), the gas temperature ($T_g$), the electron temperature ($T_e$) and the metastables density. In the current work the aforementioned plasma parameters are obtained as well (although only an estimate of $T_e$). Additionally, compared to previous studies, a much higher spatial resolution is obtained for the LIF measurements. The circular cross-section of the laser beam in this work has a FWHM of 250 $\mu$m, this diameter is approximately equal to the diameter of the plasma filament. LIF is also performed both during and after the discharge. This allows us to investigate the OH production mechanisms in more detail.

The experimental setup and methods are shown in section 3.2. Next, the discharge morphology and properties of the discharge modes, obtained from imaging, electrical measurements and optical emission spectroscopy, are described in sections 3.3 and 3.4 respectively. The density of helium metastables, and its effect on the OH kinetics, are assessed in section 3.5, followed by a discussion of the general discharge kinetics deduced from time resolved optical emission measurements (section 3.6). Section 3.7 is devoted to the time and spatially resolved OH density, and finally general conclusions are drawn (section 3.8).

3.2 Experimental setup and methods

The discharge is created in a pin-to-pin electrode configuration, which is enclosed in a vacuum vessel (see figure 2.1). The electrodes are made of tungsten and the distance between them is approximately 2 mm. High voltage pulses are applied using a DEI PVX-4110 HV pulser. The DC high voltage for the high voltage pulses is delivered by a Spellman DC power supply (10 kV, 15 mA), and the repetition frequency and pulse width are set with a function generator (Agilent 33220A). In this work, positive high voltage pulses are applied to the upper electrode with a repetition frequency of 1 kHz and a pulse duration of 170 ns. A delay generator (BNC, model 575) is synchronized with the function generator that controls the high voltage pulses to adjust the delay of the laser and the diagnostics (iCCD cameras) relative to the voltage pulse. The precision of the time alignment is 7 ns, as this is the smallest gate width of the iCCD camera. The jitter on the current and voltage compared to the trigger signal is 2 ns.

A resistor of 1 k$\Omega$ is placed in series with the discharge gap to limit the current. A second resistor of 6 M$\Omega$ is placed in parallel to the electrodes to remove the
3.2: Experimental setup and methods

Charge on the driven electrode when the system is operated and no breakdown occurred, this is implemented for the safety of the operator. Voltage and current are obtained with a high voltage probe (Tektronix P6015) and a current monitor (Pearson 2877) just before the high voltage enters the vacuum vessel.

The discharges are generated in helium with admixtures of 0.05, 0.1, 0.3, 0.84 and 2.6% H₂O. A total flow of 3l min⁻¹ is constantly refreshing the gas in the vacuum vessel which has a volume of approximately 8l. Water admixtures of 0.05 and 0.1% are added to a flow of 3l min⁻¹ helium using a Bronkhorst High-Tech B. V. “CEM”-system (Controlled Evaporation Mixing). In this system, distilled water is drawn from a container and measured by a liquid flow meter (μ-FLOW series L01, 250 mg/h H₂O). A determined amount of water is mixed with helium and led into the evaporator to achieve total evaporation at a certain temperature. Water admixtures higher than 0.1% are obtained using two mass flow meters (Bronkhorst EL-FLOW Select, 0.08 to 4l min⁻¹), one operating at a flow rate F₁ for dry gas and the other one (operating at flow rate F₂) for gas passing through a bubbler filled with distilled water. The water vapour concentration in the vessel is determined assuming that the helium flow which passed through the bubbler is saturated with water vapour at room temperature. The percentage of water in the mixture (C) is then determined by the ratio of the saturated water vapour pressure in the gas (P_{sat}H₂O) to the total vapour pressure in the vessel (P_{total})

\[ C = \frac{P_{sat}H₂O}{P_{total}} \cdot \frac{F₁}{F₁ + F₂} \]  

(3.1)

3.2.1 Diagnostics

Time dependent spatially averaged optical emission spectra of the discharge are obtained with an iCCD camera (4 Quik E SR) coupled to a 27.5 cm monochromator (ACTON). To collect as much light as possible, an optical fiber was introduced into the vessel through a vacuum coupling, and placed close to the filament. To obtain time resolved intensities a grating with 150 grooves/mm is used and 1000 accumulations are taken. For the high resolution spectra of OH and Hβ (which are used for gas temperature and electron density determination) the intensity is accumulated over 15000 pulses using a grating with 1200 grooves/mm. The time resolution is 10 ns for the emission spectra recorded with the 150 grooves/mm grating, and 30 ns for the emission spectra of OH and Hβ (recorded with the 1200 grooves/mm grating).

The evolution of the discharge morphology as a function of the added water concentration is studied by current-voltage measurements and by taking time resolved images with an iCCD (Andor DH534). The combined system of the Andor iCCD camera and a Nikkor 105 mm f/4.5 UV lens is sensitive in a spectral range between 250 and 800 nm.

Fluorescence of OH is induced with a frequency doubled dye laser (Sirah CBR-LG-
Chapter 3: He-H₂O mixtures

24-HRR), with Rhodamine 6G as the dye, pumped by a Nd:YAG laser (Edgewave Innoslab IS6II-E) at 532 nm. The P₁(2) transition of the OH[(A; ν′ = 1) ←(X; ν′′ = 0)] system at 282.6 nm is used to study time and spatially resolved LIF. This transition is nicely separated from neighbouring lines and no overlap occurs during excitation. Additionally, the ground level f₁(2) has the largest relative population of all rotational levels in the temperature range under investigation [29].

The laser pulse has a repetition frequency of 1 kHz and a pulse width of about 6 ns FWHM, as measured with a photomultiplier (Hamamatsu R636-10) operating in photon counting mode. The photomultiplier is coupled to a Jobin Yvon THR 1000 monochromator, which operates as a 0.3 nm bandwidth filter. The individual photon signal from the photomultiplier is processed by a discriminator and is read out by an Ortec 9353 time digitizer card, which counts the pulses with a time resolution of up to 2 ns, limited by the response time of the photomultiplier. This same setup is also used to measure the time resolved fluorescence intensities originating from different vibrational bands.

LIF measurements are performed in the linear regime, the corresponding laser energy ranges between 0.1 and 1 μJ per pulse as measured with a power meter (Quantel 3A-P-CAL, S/N 107785). The measurements are averaged over 500 to 1000 laser pulses. A quartz lens (f = 500 mm) is used to focus the laser beam. Two diaphragms are used to create a circular beam profile (before the lens) and to reduce stray light (after the lens). The diameter of the laser beam at the position of the plasma is about 250 μm, as measured from the FWHM of the Rayleigh intensity of the beam in air at atmospheric pressure obtained by the same detection system as used for the emission and LIF measurements. The discharge chamber has two Brewster windows to allow the laser beam to pass through the chamber. The laser is synchronized to the voltage pulse using a fast photodiode. The jitter of the laser beam compared to the voltage pulse is less than 7 ns.

The fluorescence signal at the centre of the discharge is detected through a quartz window of the vacuum vessel under an angle of 90 degrees with the laser beam. Time and spatially resolved images of the plasma emission and fluorescence are taken with an iCCD camera (4 Quik E HR and Andor DH534) and the Nikkor UV lens. The spatial resolution of the cameras is approximately 60 μm (3 pixels). The exposure time of the images is 10 ns. To obtain the LIF images, a bandpass filter with a central wavelength of 313 nm and FWHM of 10 nm is used to filter out most of the optical emission. Any plasma light that is still present during the LIF measurement is corrected for by subtracting a background plasma emission image obtained at the same conditions. Each measurement is an accumulation of 1000 pulses.

A cross-sectional distribution of the LIF signal at a fixed axial position is obtained by measuring the spatially resolved LIF-signal for different positions of the y-coordinate (as defined in figure 2.1). The cross-section is obtained by moving the
discharge compared to the fixed laser beam by steps of 100µm. We stress that no planar LIF is performed.

**Gas temperature**

To determine the gas temperature 3 methods are used. First, the gas temperature is obtained by excitation LIF. With this method, the rotational temperature of the ground state of OH is measured. Different rotational levels of the ground state are excited and from the obtained (broadband) LIF intensities a Boltzmann plot is made (see also [37]). The intensities $I_i$ that are obtained after exciting different levels $i$ are related to the rotational temperature according to

$$I_i \propto (2J_i + 1)B_i \exp\left(-\frac{E_i}{k_B T_{rot}}\right),$$

where $J_i$ is the total angular momentum of level $i$, $B_i$ is the Einstein $B$ coefficient of the transition taken from [8], $E_i$ is the energy of rotational level $i$ taken from [10], $k_B$ is the Boltzmann constant and $T_{rot}$ is the rotational temperature. The transitions that are excited in this work are $P_1(1)$ to $P_1(6)$ (see figure 3.1). As this method can suffer from transition dependent Einstein coefficients and collisional transfer rates, as is explained in [30] and [44], we verify this method with the gas temperature obtained from the rotational temperature of the OH(A; $\nu' = 1$) state. This temperature is determined from the spectrally resolved fluorescence signal of the OH(A-X) (1-1) and (0-0) transitions, when the ground state is excited using the $P_1(2)$ transition. An example of a spectrally resolved fluorescence signal is shown in figure 3.1. The measured spectrum is compared to a synthetic spectrum obtained using LIFBASE [29], assuming that the rotational lines are distributed according to a Boltzmann distribution with a temperature of 400 K. In this method, the rotational temperature is determined from the excited state and this temperature is only equal to the gas temperature when the characteristic time for rotational energy transfer is significantly shorter than the lifetime of OH(A; $\nu' = 0, 1$). From the total RET and quenching rate for $F_1(1)$ in He + 0.84% H$_2$O in table 2.3, it can be seen that this is the case. The same method for OH fluorescence spectra to measure the gas temperature was recently applied by Dilecce et al on a DBD in atmospheric pressure He-H$_2$O [12]. The temperatures obtained in both aforementioned methods correspond within the experimental accuracy, and thus confirm that a realistic estimate of the gas temperature is obtained by excitation LIF.

In addition, the gas temperature is also obtained from optical emission spectra of OH(A–X). These measurements are performed in Grenoble with the same 2m monochromator (SOPRA) as used in chapter 2 for the UV absorption measurements, equipped with a 1200 grooves/mm grating working in the 4th diffraction order, and backed by a 12.8 µm pitch PIMAX3 (Roper Scientific) iCCD. The optical emission spectra were recorded between 308 and 309 nm. The gas temperature is calculated from the Boltzmann plot of the $Q_1(5-6)$ and $P_1(2)$ lines. For each
Figure 3.1: Gas temperature obtained using excitation LIF and fluorescence spectra in the high density mode in He + 0.84% H₂O at t = 1 μs. Upper figure: Boltzmann plot of the excitation LIF signal (coming from the surrounding of the plasma filament). Lower figure: spectrally resolved fluorescence signal, the simulation is obtained with LIFBASE [29].
of the lines the intensity is integrated. An example of a Boltzmann plot obtained from optical emission of OH(A−X) is shown in figure 3.2 for the same conditions as in figure 3.1. The discrepancy of the gas temperatures obtained from LIF and optical emission of OH(A−X) are due to the different locations of the OH(A) and OH(X) maximum densities and will be discussed in section 3.4.2.

**Electron density**

The electron density is determined from Stark broadening of the H$_3^+$ Balmer line. This method is also used in [5]. Other line broadening mechanisms that are taken into account are instrumental broadening and van der Waals broadening. As the gas temperatures are rather low (<1600 K, see further) Doppler broadening is negligible [25]. The instrumental broadening is determined with a low pressure Hg/Ar lamp and has a FWHM of 0.13 ± 0.03 nm. The van der Waals broadening (in nm) is determined from

$$\Delta \lambda_{vdW} = \frac{2.4}{T_0^{0.7}},$$

(3.3)

where the constant 2.4 is calculated for helium in the same way as the constant is calculated for air in [25]. A gas temperature of 350 K is assumed during the entire pulse, resulting in a lower estimate of the electron density. The gas temperature dependence can be estimated by comparing the calculated van der Waals broadening with the measured broadening of H$_3^+$ (see figure 3.3). For the case of He +
0.84% H$_2$O, the van der Waals broadening is about 10 times lower than the measured broadening, and remains smaller than the instrumental broadening. The influence of the gas temperature on the obtained electron density is thus small.

To calculate the Stark broadening, the Stark broadening profiles of H$_\beta$ in [17] are used for an effective emitter-perturber reduced mass $\mu^*$ of 10 and an electron temperature of 1 eV. Gigosos uses this reduced mass, $\mu^*$, which simulates a plasma which is not in thermal equilibrium ($T_e \neq T_g$):

$$\mu^* = \mu \cdot \frac{T_e}{T_g}$$  \hspace{1cm} (3.4)

where $\mu = 0.8$ is the reduced mass for H-He. For several electron densities between $5 \cdot 10^{20}$ m$^{-3}$ and $1 \cdot 10^{23}$ m$^{-3}$, a convolution is performed of the Stark, van der Waals and instrumental profiles. The FWHM of these convoluted lines is then plotted as a function of the electron density, from which we obtain a FWHM correlation for our specific conditions. With a Voigt fit the FWHM of the measured line profiles are obtained and the FWHM of the correlation is used to determine the electron density.
The density of helium ($^3S_1$) metastables is measured using tunable diode laser absorption spectroscopy. A DL DFB system (Toptica) with a wavelength tunable around 1083 nm is used to measure the time-dependent absorption at different frequencies around 1083 nm. A scheme of the setup used is given in figure 3.4. The laser, of which the light is horizontally polarized, is placed under an angle of 45° to obtain light that is equally horizontally and vertically polarized. To avoid any saturation effects, a filter with 10% transmittance is placed in front of the laser. The laser beam is then separated in two beams by a beam splitter. One beam is directed into the plasma, while the other beam is guided to a reference system. A polarizer is put in the beam path to the discharge to transmit only the horizontally, or only the vertically polarized light. However, it is found that the polarization does not have a significant influence on the measured metastable density, so no static Stark broadening component is present. The laser beam is focused on the plasma filament with a lens ($f = 20$ cm), the laser beam diameter obtained in this way is about 140 μm. After the beam passes the discharge vessel through Brewster windows, it is focused with a lens ($f=10$ cm) on a photodiode with a diameter of 1 cm and a sensitivity of 0.05 V/(μW). The reference system consists of a Fabry-Pérot interferometer and a low pressure helium lamp to calibrate the laser frequency. The photodiodes detecting the light that passes through the reference system have an area of $3 \times 3$ mm$^2$ and a sensitivity of 0.5 V/(μW). Frequency-resolved profiles of the absorption were obtained by scanning the narrow bandwidth laser around the line centre frequency, by taking steps of about 1 GHz.

**Figure 3.4:** Scheme of the setup to measure the density of helium ($^3S_1$) metastables. F: filter, BS: beam splitter, P: polarizer, DP: diaphragm, L: lens, M: mirror, D: detector, FP: Fabry-Pérot interferometer.

**Helium metastable density**
Chapter 3: He-H₂O mixtures

The measured profile includes two transitions which overlap due to pressure broadening, \( 2^3S_1 \rightarrow 2^3P_1 \) (1083.025 nm) and \( 2^3S_1 \rightarrow 2^3P_2 \) (1083.034 nm). The \( 2^3S_1 \rightarrow 2^3P \) transition includes also the \( 2^3S_1 \rightarrow 2^3P_0 \) transition (1082.909 nm). The latter transition is well separated from the other two lines and has a lower oscillator strength. The \( 2^3S_1 \) metastable density is estimated from the surface of the absorption line (GHz), given by

\[
S = \int_0^\infty \ln \left( \frac{I_0(\nu)}{I(\nu)} \right) d\nu = h\nu_0 B_{ik} l \langle N_i \rangle ,
\]  

where \( I_0(\nu) \) and \( I(\nu) \) are the measured background and absorbed intensities as a function of frequency \( \nu \), \( h \) Planck’s constant (Js), \( \nu_0 \) the centre frequency (GHz), \( B_{ik} \) the absorption coefficient of the transition (m\(^2\)s\(^{-1}\))J\(^{-1}\)), \( l \) the absorption length (m), and \( \langle N_i \rangle \) the mean absolute density of absorbing atoms (m\(^{-3}\)). The latter can be calculated from

\[
\langle N_i \rangle = \frac{1}{h\nu_0 B_{ik} S} = \frac{4\epsilon_0 m_e c}{e^2 f_{ik} l} S = \frac{1}{lf_{ik}} 3.8 \cdot 10^{14} S ,
\]  

where \( \epsilon_0 \) is the vacuum permittivity (Fm\(^{-1}\)), \( m_e \) the mass of an electron (kg), \( c \) the speed of light (m/s\(^{-1}\)), \( e \) the elementary charge (C) and \( f_{ik} \) the oscillator strength of the lines [23];

\[
f_{ik} = 0.060 \quad 2^3S_1 \rightarrow 2^3P_0 ,
\]  

\[
f_{ik} = 0.18 \quad 2^3S_1 \rightarrow 2^3P_1 ,
\]  

\[
f_{ik} = 0.30 \quad 2^3S_1 \rightarrow 2^3P_2 .
\]

When the two most intense lines are not resolved, the oscillator values must be added and the relation becomes,

\[
\langle N_i \rangle (m^{-3}) = 7.92 \cdot 10^{14} \times \frac{S}{l} .
\]  

From the widths of the absorption line profile the temperature of the absorbing species, and thus an estimate of the gas temperature, can also be obtained. In the investigated nanosecond pulsed atmospheric discharge, the dominant broadening mechanisms are Doppler broadening, van der Waals broadening and Stark broadening. The latter is, in the case of the He 1083 nm line, only known in literature for thermal plasmas at temperatures higher than 2000 K. Therefore, to be able to neglect Stark broadening, the gas temperature is estimated several s after the discharge is switched off. In this case no external electric field is present. The Doppler FWHM is (in GHz) [45]

\[
\Delta \nu_{\text{Doppler}} = 7.06 \cdot 10^{-7} (e/\lambda)(T_g/M)^{0.5} ,
\]  

where \( M \) is the mass of the absorbing species. For an individual He 1083 nm line at 300 K, \( \Delta \nu_{\text{Doppler}} = 1.78 \) GHz. The equation for the van der Waals broadening
3.2: Experimental setup and methods

Figure 3.5: Pressure broadened absorption line profile of the $^3S_1 \rightarrow ^3P_J (J = 0, 1, 2)$ transitions measured in He + 0.84% H$_2$O at $t = 5 \mu$s, $V = 7$ kV. The profile is fitted with a superposition of 3 Voigt profiles. The obtained gas temperature is 450 K.

$\Delta \nu_{vdW} = 14 \frac{T_0}{g}$, \hspace{1cm} (3.12)

where the experimental value of 14 GHz is taken from [48]. However, the pressure-broadening coefficients determined from experiments and theory are scattered. In [54] a theoretical coefficient of 18.35 GHz at 300 K is reported. In [48] the gas temperature in the experiment is likely to be 100 K higher, which could partially explain the difference compared to the theoretical value of [54]. In later work of the same group of Tachibana, a coefficient of 19.5 GHz at 300 K is experimentally determined [53]. Finally Niemann et al reported a pressure-broadening coefficient of 11.2 GHz [35]. Published results obtained by Sadeghi indicate that the value of 14 GHz is recommendable [1].

An example of a measured line profile is shown in figure 3.5. The profile is fitted with a superposition of 3 Voigt profiles. The separation between the lines of $J = 1$ and $J = 2$ is 2.3 GHz, and the separation between the lines of $J = 1$ and $J = 0$ is 32 GHz. Compared to the peak intensity of the $J = 1$ line, the peak intensity ratios are 3/5 and 1/5 for the $J = 2$ and $J = 0$ lines respectively. The absorption length in the case of figure 3.5 is 350 µm. This value is obtained from measuring the absorption signal at different off axis positions with an increment of 100 µm. The accuracy of the absorption length is about 50 µm, which leads to an accuracy of the average helium ($^3S_1$) metastable density of 15%. As there are
strong temporal and spatial gas temperature gradients in the plasma filament, a
detailed analysis of the line profile is not performed.

**OH absolute density calibration**

Absolute calibration of the OH LIF signal is performed using Rayleigh scattering
and using a chemical model. These methods are explained in detail in chapter 2.

### 3.3 Discharge modes and morphology

Two discharge modes occur in the setup, a low- (applied DC voltage < 3 kV)
and high-density (applied DC voltage > 3 kV) mode. The names low- and high-
density mode are related to the strong difference in the electron density or current
density (see later). A picture of each mode is shown in figure 3.6, these two modes
will be discussed separately.

#### 3.3.1 Low-density mode

The low-density mode is studied at an applied voltage between 1.3 and 1.5 kV. A
higher voltage (up to 2 kV) is applied for helium without and with 0.05 % water
addition, to increase the stability of the discharge. The current and voltage as a
function of time for different water concentrations are shown in figure 3.7. The
capacitive current is subtracted from the measured current. As the discharge
draws a significant current, the voltage starts to decrease before the voltage is
switched off by the pulser. A current peak is observed at the end of the pulse.
The dissipated energy per pulse in the low-density mode is about 30 μJ as obtained
from the current and voltage waveforms.

Images of the initial phase of the low-density discharge are shown in figure 3.8. The
discharge starts at the upper electrode (anode) with the development of a cloud
of light, which moves towards the cathode. This behaviour is observed as well in
corona discharges by e.g. Briels (at reduced pressures) [4], in low pressure pulsed
argon discharges [55, 56], and in nanosecond repetitively pulsed air discharges by
e.g. Pai and Celestin et al [7, 13, 39, 40, 51]. This cloud of light near the anode is
created as follows [39, 55]. First, an electron avalanche is initiated by application
of a high-voltage pulse, and then moves towards the anode (upper electrode).
The electrons needed for the first electron avalanche can come from previous
discharges or from cosmic rays in the natural background radiation. Because of
the avalanches a space-charge layer is build up, which, when it complies Meek’s
criterion, causes the development of a streamer. This streamer moves towards the
cathode, and when it reaches the cathode, secondary electron emission processes
Figure 3.6: Images (in false colours) of the low ($V \approx 1.3 \, \text{kV}$) and high ($V \approx 3 \, \text{kV}$) density mode during the current pulse in He + 0.84\% H_2O (1000 accumulations, exposure time = 10 ns). The plasma diameter is obtained from the FWHM of the intensity.

Figure 3.7: Current and voltage waveforms of the low-density mode for He with no, 0.1 and 0.84\% H_2O admixture.
Figure 3.8: Discharge formation in He + 0.84% H₂O at 1.3 kV. The time indicated in the images corresponds to the current and voltage waveforms in figure 3.7. The false colour images are recorded with the Andor camera with a gate width of 10 ns and 1000 accumulations. The gain for the images is 255.

When the streamer reaches the cathode (at $t = 140$ ns), a strong emission is observed at the cathode, which is consistent with the formation of a negative glow region, and thus the transition to a glow discharge. Note that the conduction current (in figure 3.7) starts to rise at the moment the streamer connects with the cathode. Also in [38] it is described how the streamer head transforms into the cathode fall region of a glow discharge, causing a return wave of potential redistribution to propagate from the cathode to the anode. However, in this case the applied electric field is turned off before the glow discharge is fully developed.

In [51], images of the optical emission recorded by Pai et al are compared to the calculated spatial distributions of emission of the second positive system of N₂. At the onset of the pulse, corona discharges are observed on both electrodes in this case, with more intense emission on the anode. However, in [39], for other conditions of the discharge, a two-step behaviour is observed where emission of N₂(C) and N₂⁺(B) is first generated at the anode. In the model results presented in [7], it appears that the intensity of the negative streamer is low. In the current work also no emission is observed near the cathode at the start of the discharge.

The discharge emission as a function of water concentration is shown in figure 3.9. A change in the discharge morphology is observed when varying the water admixture. For low water concentrations, the discharge emission covers the cathode to a large extent. The covering of the cathode by the discharge is also observed by Wagenaaars et al at reduced pressures [56], who ascribed it to secondary electron emission. Furthermore, figure 3.9 shows that for low water concentration there is a strong emission in the afterglow (220-230 ns), while for 0.84% H₂O the emission has its maximum during the current pulse (see also later). In the latter
3.3: Discharge modes and morphology

The high-density mode in this chapter is studied at an applied DC voltage to the pulser of 7.0 kV. The current and voltage waveforms for different water concentrations are shown in figure 3.10. The maximum value of the high voltage pulse is between 3 and 4 kV, since the voltage drops when the discharge current increases up to a few Amperes at \( t = 60 \text{ ns} \), in spite the fact that a 170 ns is applied. The current is corrected for the capacitive current only during the rising slope of the voltage. The large increase in current indicates the formation of a spark (see also further). The energy dissipated per pulse is estimated to be 300 \( \mu \text{J} \), which is in the range where also the spark discharge is observed by Pai et al in nanosecond repetitively pulsed discharges in air [40].

The images of the high-density discharge, corresponding to figure 3.10, are shown in figure 3.11. Like in the low-density mode, the discharge starts at the anode, but the propagation to the cathode is at least 3 times faster. This is in line with the (3 times) larger voltage, and thus a larger electric field in the gap. In [55], it is observed that the time between the start of the voltage rise and the time when the light front reaches the middle of the discharge gap, increases when the afterglow period between the pulses is increased. Wagenaars et al estimated the loss of charged particles by volume recombination and diffusion as a function of time, and came to the conclusion that the light front crossing the gap occurs faster when the density of charged particles, remaining from previous pulses, is higher. In the present study, since the electron (and ion) density is higher in the high-density mode, a different pre-ionization density could also contribute to the differences observed between the low- and high-density mode.

Between 45 and 55 ns, the discharge connects the two electrodes and a broad and intense, glow-like emission is observed. Around 60 ns the discharge contracts and a spark is formed, which corresponds with the increase in current in figure 3.10. During the formation of a glow-type of discharge in air, Tholin and Pai et al observed that the positive and negative corona discharges that are created near the electrodes, connect, followed by a similar intense emission [39, 51]. They have performed an extensive research on the conditions necessary for the creation of a glow regime, and for the appearance of the glow-to-spark transition [39, 40, 50]. In [40], the glow discharge is described in terms of two phases, a streamer phase and a conduction phase, in which a uniform electric field is created in the gap. If the applied voltage is then maintained, the discharge heats the gas (when the electric field is above a threshold field), and a glow-to-spark transition occurs [50]. Also El-Koramy et al have investigated the formation of a spark channel in self-sustained discharges initiated by pre-ionization in helium [15]. They found that for DC applied voltages, the critical current density for the glow-to-spark
Figure 3.9: Discharge emission profiles obtained for various times as a function of water concentration in the low-density mode. The time indicated in the images corresponds to the time axis of the current and voltage waveforms in figure 3.7. The images (in false colours) are recorded with the Andor camera with a gate width of 7 ns and 1000 accumulations. The gain is different for every water concentration.
transition already occurs at a current of $40 \text{ A cm}^{-2}$ and at consumed energy in the range $0.1 - 0.2 \text{ J cm}^{-3}$. For a diameter of 400 $\mu$m in the glow phase, this would correspond to a current of about 50 mA and an energy of $25 - 50 \mu\text{J}$. In the present case this means that the pulse duration determines if the glow-to-spark transition will occur or not, due to the finite time necessary for the transition. A glow-to-spark transition is also observed in a similar discharge (but in a pin-water electrode geometry) in [57]. In this reference, when the pin is the anode, the constriction starts at the anode with an increase in emission intensity, and it grows on a time scale of 1 $\mu$s to the cathode (the gap distance in this work is 2.8 mm).

As illustrated by the images in figure 3.11 (and the corresponding current waveforms in figure 3.10), the discharge transitions start earlier when the water concentration increases. This can be explained by an increase in the gas temperature with increasing water concentration (see further), which results in an increase of the reduced electric field $E/N$ for the same applied electric field. As a result the voltage necessary for the transition to occur is lowered. This thermal effect has been described before by Pai et al [40]. They refer to it in their publication as a thermal ionization instability, which determines the glow-to-spark transition in nanosecond repetitively pulsed discharges.

Figure 3.12 shows the plasma diameter as estimated from the FWHM of the emission intensities in figure 3.11. After the spark formation, around $t = 100 \text{ ns}$, the plasma diameter strongly increases until the end of the current pulse. The speed of the expansion is calculated from a linear fit to the time resolved diameter, and summarized for various water concentrations in table 3.1. The velocities
Figure 3.11: Time resolved images of the high-density discharge for the addition of no, 0.1 and 0.84% H\textsubscript{2}O. The time indicated in the images corresponds to the time axis of the current and voltage waveforms in figure 3.10. The images (in false colours) are recorded with the Andor camera with a gate width of 7 ns and 1000 accumulations. The intensities of the images at 40 and 50 ns, which were recorded at maximum gain, are normalized to the maximum intensities, to clearly show the discharge morphology. The image at \( t = 50 \text{ ns} \) for 0.84% H\textsubscript{2}O is overexposed. No gain is used for the other images.
Electron properties and gas temperature

3.4: Electron properties and gas temperature

seem to decrease for increasing H₂O concentration, and range between 1.15 and 1.45 · 10⁴ m s⁻¹. This corresponds to the speed of sound in helium between 382 and 607 K (the speed of sound in helium is 1019 m s⁻¹ at 300 K). Assuming that the increase in emission radius corresponds with the expansion of a shock-wave, the temperature and pressure behind the shock-wave can be calculated from the Rankine-Hugoniot relations

\[
\frac{p_2}{p_1} = \frac{2\gamma}{\gamma + 1} \left( \frac{u_s}{u_1} \right)^2 - \left( \frac{\gamma - 1}{\gamma + 1} \right), \quad (3.13)
\]

\[
\frac{T_2}{T_1} = \left( \frac{p_2}{p_1} \right) \frac{(\gamma + 1) + (\gamma - 1)(p_2/p_1)}{(\gamma - 1) + (\gamma + 1)(p_2/p_1)}, \quad (3.14)
\]

where subscript 1 is used for the condition ahead of the shock-wave (initial condition), subscript 2 the condition behind the shock-wave, \(u_s\) the velocity of the shock-wave, \(u_1\) the acoustic velocity and \(\gamma\) the adiabatic exponent. For the case of 0.84 % H₂O, assuming \(T_1 = 750\) K at \(t = 0.1\) μs (see figure 3.19), \(p_2 = 1360\) hPa and \(T_2 = 844\) K are found. As a result, if the expansion is a shock-wave, it is induced by a small increase in gas temperature. Note as well that during the expansion, energy is still deposited in the gas by the plasma. Qualitatively similar results have been found in nanosecond pulsed discharges in air investigated by Schlieren images, by Xu et al [58] (\(\Delta T_{\text{max}} < 200\) K), and in argon and air by Liu et al [27].

During the discharge, the plasma emission diameter doesn’t change significantly as a function of water concentration (see figure 3.12). Only in the case of 0.84 % H₂O, the constriction and subsequent broadening of the plasma channel seems to occur at later times. A possible reason for this could be the slower rise in electron density in this case (see section 3.4.2), and thus the energy input which lasts longer. After the discharge is switched off, the plasma emission diameter seems to decrease faster when the water concentration is increased. Note that the emission intensity decreases with increasing water concentration, which makes it more difficult to determine the FWHM. In addition, inhomogeneous collisional quenching of excited states could also influence the measured FWHM of the emission profile.

3.4 Electron properties and gas temperature

3.4.1 Low-density mode

Overview emission spectra between 300 and 850 nm, measured during and immediately after the current pulse in the low-density mode for 0.05 and 0.84 % H₂O, are shown in figure 3.13. The spectra are corrected for the wavelength dependent sensitivity of the detection system. For He + 0.84 % H₂O, no emission is observed after the current pulse. For both water concentrations, He lines dominate the overview spectra. The main differences between the overview spectra for
Figure 3.12: Diameter of the plasma, obtained from the FWHM of the emission intensities in figure 3.11, in the high-density mode as a function of time for no, 0.1 and 0.84 % H₂O admixture.

Table 3.1: Expansion velocity of the plasma radius for different water admixtures, calculated from data as shown in figure 3.12.

<table>
<thead>
<tr>
<th>w (\text{H}_2\text{O})</th>
<th>expansion speed ((10^3 \text{ m s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.45 ± 0.10</td>
</tr>
<tr>
<td>0.05</td>
<td>1.35 ± 0.15</td>
</tr>
<tr>
<td>0.1</td>
<td>1.30 ± 0.10</td>
</tr>
<tr>
<td>0.3</td>
<td>1.15 ± 0.05</td>
</tr>
<tr>
<td>0.84</td>
<td>1.15 ± 0.05</td>
</tr>
</tbody>
</table>
0.05 and 0.84% is that no OH is detected in the case of 0.05% H₂O, and that in this case significant emission of He₂ is observed. When the discharge is switched off, the emission of He₂ strongly increases. This confirms that the excimers are formed in 3-body electron ion recombination processes like [9]

\[
\begin{align*}
2e + He^{+}_2 & \rightarrow He^{*}_2 + e, \\
e + He^{+}_2 + He & \rightarrow He^{*}_2 + He.
\end{align*}
\] (3.15) (3.16)

The electron density obtained from the line broadening of H₃ is shown in figure 3.14. The electron density has its maximum at the current peak. The maximum electron density is \(7.6 \cdot 10^{21} \text{ m}^{-3}\) and \(1.9 \cdot 10^{21} \text{ m}^{-3}\) for 0.05 and 0.84% H₂O, respectively. The higher electron density in the case of 0.05% H₂O can be explained by the higher applied voltage compared to the case of 0.84% H₂O (see section 3.3.1). The electron densities for the two cases are also measured in a different measurement campaign.

During the current pulse the electron density increases in time. As the dissociative attachment rate (calculated assuming a Boltzmann distribution of the electrons with the cross-section from [21]) equals the ionization rate at \(T_e \approx 4\text{ eV}\), the electron temperature will be larger than this value during the pulse. The dominant processes will then be electron induced excitation, ionization and dissociation.

The gas temperatures as obtained by excitation LIF and optical emission of OH(A−X) are shown in figure 3.15 as a function of time. The gas temperatures obtained with both methods are in agreement within the experimental accuracy, and do not exceed 500 K. At the end of the current pulse the gas temperature is around 350 K, it then slowly decreases to about room temperature. No significant difference in gas temperature is observed for the different water concentrations investigated in the low-density mode.

### 3.4.2 High-density mode

In figure 3.16, overview spectra between 300 and 850 nm, measured during and immediately after the current pulse in the high-density mode, are shown for 0.05 and 0.84% H₂O. The spectra are corrected for the wavelength dependent sensitivity of the detection system. Similar to the low-density mode, the spectra are mostly dominated by He lines. Only in the afterglow of the high-density discharge in He + 0.84% H₂O, H and O lines show a much higher intensity. In the high-density mode the emission from He₂ is less pronounced than in the low-density mode. The large broadening of the He (492 nm) and H₃ lines at the start of the current pulse (\(t = 65\text{ ns}\)) is shown in the inset of figure 3.16.

The time resolved electron densities in the high-density mode, obtained by H₃ broadening measurements, are shown in figure 3.17 for different water concentra-
Figure 3.13: Overview spectra measured in the low-density mode for 0.05\% H$_2$O, at 170 ns and immediately after the current pulse at 230 ns, and for 0.84\% H$_2$O at 200 ns. The corresponding current and voltage waveforms are shown in figure 3.23. The spectra are recorded using a gate width of 10 ns.
3.4: Electron properties and gas temperature

Figure 3.14: Time resolved electron density for 0.05 and 0.84\% H$_2$O in the low-density mode.

Figure 3.15: Time resolved gas temperature for 0.05 and 0.84\% H$_2$O in the low-density mode, as obtained from excitation LIF and OES.
Figure 3.16: Overview spectra measured in the high-density mode at 65 ns and immediately after the current pulse (215 ns) for 0.05 (upper figure) and 0.84% (lower figure) H$_2$O. The corresponding current and voltage waveforms are shown in figure 3.24. The spectra are recorded using a gate width of 10 ns.
The electron density measured in the high-density mode is about 1 order of magnitude larger than the electron density measured in the low-density mode. A maximum in the electron density is obtained during the current pulse, this maximum occurs with a delay for 0.84% H₂O. The electron density decay is also slower in this case compared to 0.1% H₂O. The decreasing electron density, and the drop in applied voltage during the current peak, suggest a recombining plasma with a low electron temperature. The rate at which the electron density decays, is obtained by fitting the results in figure 3.17 assuming that the electron density decays like

\[
\frac{dn_e(t)}{dt} = -k_{dr}n_e^2(t),
\]

(3.17)

where \(k_{dr}\) is a rate for (2-body) dissociative recombination. Integrating this relation results in a function for \(n_e\) of the form

\[
n_e(t) = \frac{n_e^0}{1 + n_e^0k(t-t_0)},
\]

(3.18)

which is fitted to the measured electron densities, with the starting point \(t_0\) at 245 ns, when the discharge is switched off. The resulting decay rates are shown in figure 3.18 as a function of the added water concentration. The comparison of the decay rates of about \(10^{-15}\) m³ s⁻¹ with the dissociative recombination rate of water and its clusters, which is approximately \(10^{-13}\) m³ s⁻¹, suggests that there is a significant production of electrons in the afterglow, or that the main ions are He⁺ or water fragments (OH⁺, H⁺, O⁺). The latter processes have an electron-ion recombination rate equal to, or even slower than the measured rates.
Chapter 3: He-H₂O mixtures

In figure 3.19, the time-dependent gas temperature of the high-density mode, determined by excitation LIF, is shown for different water concentrations. For 0.05 and 0.84% H₂O, the gas temperature of the plasma core is obtained from highly rotationally resolved emission of OH(A−X) (2 m monochromator). The optical emission spectra were recorded between 308 and 309 nm. The gas temperature is calculated from the Boltzmann plot of Q₁(5 − 6) and P₁(2) lines. When N₂ is added to the gas mixture by leading 1 l min⁻¹ N₂ through the bubbler, N₂(C−B) emission could be detected during the first 60 ns of the pulse. The N₂(C−B) optical emission spectra are recorded with a 27.5 cm monochromator (ACTON) and a grating with 1200 grooves/mm. The rotational temperatures of N₂(C) are determined using Specair [24], these temperatures are also shown in figure 3.19. In figure 3.20 the profiles of the wavelength integrated optical emission (as obtained by an iCCD as described above) and the OH LIF signal at t = 250 ns are shown. As the LIF signal is located on the edge of the discharge in the high-density mode (see also further), the temperature determined from LIF is thus the gas temperature in the outer region of the plasma filament, while the temperature obtained by OES is the gas temperature in the core of the filament. Hence the significant difference in the gas temperatures obtained by both techniques shown in figure 3.19.

The gas temperature obtained from excitation LIF (the temperature of OH(X)) was compared to the gas temperature obtained from spectrally resolved fluorescence (the temperature of OH(A)) for the case of the high density mode at V = 5 kV. As can be seen in figure 3.21, the gas temperatures obtained with
Figure 3.19: Time resolved gas temperature of the outer region of the plasma filament, obtained from excitation LIF for 0.05, 0.84 and 2.6 \% H\textsubscript{2}O. For 0.05 and 0.84 \% H\textsubscript{2}O the gas temperature in the plasma core, obtained from rotationally resolved emission of and OH(A−X), is also shown. In the case of 0.84 \% H\textsubscript{2}O, N\textsubscript{2} has been added to measure the rotational temperature of N\textsubscript{2}(C−B) in the pre-spark phase.

Figure 3.20: Radial profiles of the optical emission and LIF signal intensities at \( t = 250 \text{ ns} \) in He + 0.84 \% H\textsubscript{2}O at 7 kV, with \( x = 0 \text{ mm} \) the middle of the plasma filament.
Figure 3.21: Time resolved gas temperature in the high-density mode in 0.84% H₂O at 5 kV, obtained from excitation LIF and spectrally resolved fluorescence.

both methods correspond. It is then assumed that the temperature obtained from excitation LIF is correct, both during plasma on and off phase.

At the start of the pulse the measured temperature is about room temperature, as can be deduced from the gas temperature measurement by N₂(C−B) shown in figure 3.19. During the discharge the gas is heating up, and after the plasma is switched off, the gas temperature determined from OES increases further. This temperature corresponds to the gas temperature in the core of the discharge. On the other hand the gas temperature measured by LIF initially decreases. The increase of the gas temperature in the core in the recombining plasma is potentially due to the kinetic energy release in the dissociative e−-ion recombination processes, which was previously also observed in air discharges [32, 37]. After about 1 μs, the gas temperature measured in the outer region increases as well, which suggests that a heat source is present in the afterglow.

From the plasma volume and the dissipated power, the maximum gas temperature in the core can be estimated using the heat capacity of the gas. The total dissipated energy during the pulse (170 ns) is estimated to be 300 μJ. Considering the heat capacity of the gas in the plasma volume, for a plasma radius of 0.2 mm, the calculated maximum temperature change is 1300 K. This is consistent with the observed maximum in gas temperature of 1600 K. Nonetheless, the possibility exists that the rotational population distribution of OH(A) is strongly influenced by the production mechanism in the afterglow, e.g. [46]

\[ e + \text{H}_2\text{O}^+ \rightarrow \text{H} + \text{OH}(A). \]  

However, the RET should be fast enough to thermalize the rotational population
3.5: 

He metastable densities

The measured He (3S1) metastable density is shown in figure 3.22 for the two modes for various water concentrations. In the case of the low-density mode in He + 0.84 % H2O, the metastable density is too low to detect. As a reference also the metastable density in the low-density mode, when no water is added, is shown in figure 3.22. Because of the strong emission of the discharge, and the limited time resolution of the detector, the metastable density is only calculated 2 μs after the start of the voltage pulse. The metastable density decay can be fitted with a single exponential decay, the obtained decay constants are shown in table 3.2.

The main loss processes of helium metastables are shown in table 3.3. If helium metastables are mainly quenched by helium (M6), the lifetime would be of the order 10 μs. For 0.84% H2O the lifetime is between 10 and 100 μs for reactions M3-M5. However, the measured decay time is about 5 μs for all cases, and no significant influence is measured as a function of water concentration. If H2O would be the main quencher of helium metastables, in the case of 0.05% H2O a decay time of about 10 times faster than in the case of 0.84% H2O would be

Table 3.2: Decay times of the measured He (3S1) metastable density in the two modes in He with various water concentrations. The He (3S1) metastable density at \( t = 2.5 \mu s \) is compared with the estimated electron density at that time.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Decay time (μs)</th>
<th>( n_{He} ) ( \times 10^{18} ) m(^{-3} )</th>
<th>( n_{e} ) ( \times 10^{20} ) m(^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% H2O, low ne</td>
<td>5.1 ± 0.4</td>
<td>21 ± 2</td>
<td>-</td>
</tr>
<tr>
<td>0.05% H2O, low ne</td>
<td>5.3 ± 0.6</td>
<td>2.5 ± 0.3</td>
<td>2</td>
</tr>
<tr>
<td>0.05% H2O, high ne</td>
<td>4.1 ± 0.4</td>
<td>4.5 ± 0.1</td>
<td>5</td>
</tr>
<tr>
<td>0.84% H2O, high ne</td>
<td>6.7 ± 0.5</td>
<td>0.70 ± 0.05</td>
<td>4</td>
</tr>
</tbody>
</table>
Chapter 3: He-H$_2$O mixtures

Figure 3.22: He ($^3S_1$) metastable density in the low- and high-density mode in He with various water concentrations added. An exponential decay is fitted to the data in the case of the high-density mode in He + 0.84% H$_2$O. The corresponding decay constants of the He ($^3S_1$) densities are shown in table 3.2.

expected. Note that in the case of the high-density discharge, the core, where the metastable density is the highest, is highly dissociated (see also below). Thus, O and H atoms might be more important quenchers of helium metastables (M1-M2) than H$_2$O molecules. In addition, the gas heating will reduce the quenching by He atoms.

The measured He ($^3S_1$) metastable densities for the conditions studied in this work are about 2 orders of magnitude lower than the electron densities (see table 3.2). As a result, ionic processes will dominate over He ($^3S_1$) metastables in the production of OH radicals.

The question remains if molecular metastable states will have a higher density

Table 3.3: Main loss processes of helium metastables.

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
<th>Rate coefficient $k$ (m$^3$ s$^{-1}$, m$^6$ s$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>He$_{m}^+$ + H → H$_2$ + He + e</td>
<td>1.1 $\cdot$ 10$^{-17}$</td>
<td>[26]</td>
</tr>
<tr>
<td>M2</td>
<td>He$_{m}^+$ + O → O$^+$ + He + e</td>
<td>3.96 $\cdot$ 10$^{-16}$($T_g/300)^{0.17}$</td>
<td>[26]</td>
</tr>
<tr>
<td>M3</td>
<td>He$_{m}^+$ + H$_2$O → He + H$_2$O$^+$ + e</td>
<td>6.6 $\cdot$ 10$^{-16}$</td>
<td>[26]</td>
</tr>
<tr>
<td>M4</td>
<td>He$_{m}^+$ + H$_2$O → He + OH$^+$ + H + e</td>
<td>1.5 $\cdot$ 10$^{-16}$</td>
<td>[26]</td>
</tr>
<tr>
<td>M5</td>
<td>He$_{m}^+$ + H$_2$O → He + OH + H$^+$ + e</td>
<td>2.6 $\cdot$ 10$^{-17}$</td>
<td>[26]</td>
</tr>
<tr>
<td>M6</td>
<td>He$<em>{m}^+$ + 2 He → He$</em>{2m}^+$ + He</td>
<td>2.0 $\cdot$ 10$^{-46}$</td>
<td>[3]</td>
</tr>
</tbody>
</table>
than the density of atomic metastable states. Molecular helium metastables are created for instance by M6. We now make an estimate of the possible impact of these molecular metastables. Stevefelt et al [47] studied a 6 ns pulsed discharge in atmospheric helium, and found that the density of the lowest molecular metastable state \((a^3\Sigma_u^+)\) is 1 order of magnitude lower compared to the density of He \((^3S_1)\), which is, in their experiment, of the same order as the electron density \((10^{21} \text{ m}^{-3})\). It is suggested in the work of Stevefelt et al that this low density is potentially due to a collisional coupling to the radiating \(A^{1\Sigma_u^+}\) state. In addition, Liu et al studied He-H\(_2\)O mixtures by a global model for different H\(_2\)O concentrations, for discharges with an electron density of \(10^{17} - 10^{18} \text{ m}^{-3}\), and found a molecular metastable density which is consistently smaller compared to the atomic metastable density [26]. Finally, in microwave discharges at elevated temperatures (2500 K) it is also assumed that the dissociation of the dimer in collisions with a ground state helium atom is very fast, leading to a small molecular metastable density [3]. The above motivates why the total metastable density can be well estimated from the measured density of He \((^3S_1)\) metastables, and no significant contribution of He metastables is expected on the OH kinetics in the afterglow.

### 3.6 Discharge kinetics

#### 3.6.1 Low-density mode

The time resolved optical emission intensities of He, O, H\(_a\) and OH in the low-density mode are shown in figure 3.23 for 0.05 and 0.84 % H\(_2\)O. To obtain the time resolved intensities of He (667 nm) and H\(_a\) (656 nm), the emission lines measured with a resolution of about 0.2 nm are integrated over the entire line profile to avoid an influence of the change in broadening of the lines on the obtained intensities. The time resolved emission of OH in the case of 0.84 % H\(_2\)O is integrated over the entire \((0, 0)\) vibrational band, and rescaled to the peak intensity of OH measured at 309 nm in the low-resolution overview spectrum. In the case of 0.05 % H\(_2\)O, the time resolved intensity of OH is obtained with the same high-resolution monochromator as used to measure OH absorption. Therefore, the intensity of OH in figure 3.23 does not scale with the intensities of the other emission lines. The emission of OH is in this case obtained from the area of the \(P_1(2)\) line.

In the case of 0.05 % H\(_2\)O, there is a sharp increase in He emission before the maximum of the current. The He emission then decreases and when the plasma is switched off, an increase is found again. In contrast, O and H\(_a\) have a maximum in emission intensity in the recombination phase. The decay times measured from the decay of O (777 nm) and H\(_a\) in the case of 0.05 % H\(_2\)O are 230 ± 20 ns and 290 ± 20 ns respectively, which is an order of magnitude larger than the radiative lifetime of H\(_a\) and O (777 nm) (23 ns and 27 ns respectively, without considering quenching) [23]. Although only a few data points are available for the emission
of OH(A−X), the decay of the OH(A−X) emission seems to be similar to the decay of the intensities of O and Hα. The increase in the P1(2) emission in the afterglow for low water concentrations is consistent with the production of OH(A) by e-ion dissociative recombination. This production mechanism is also proposed by Ricard et al, to explain a similar dependence in the OH(A−X) emission in a helium DBD [43].

In the low-density mode in He + 0.84 % H₂O, optical emission is only observed during the current pulse. The emission follows the current, although the maximum in He-emission seems to precede the maximum in Hα and OH emission. The He-emission intensity follows the dependence of the electron temperature as a function of time.

### 3.6.2 High-density mode

In figure 3.24 the time resolved optical emission of He, O, Hα and OH in the high-density mode is shown for 0.05 and 0.84 % H₂O. Two maxima are observed in the time resolved emission, the first one at the start of the current peak, and the second one when the discharge is switched off.

The two maxima in emission in figure 3.24 are observed before in studies on helium pulsed discharges at low pressure [20, 34]. The first maximum corresponds to the production of excited states by direct electron excitation, while the second maximum, in the early afterglow, is due to ionic recombination processes. In figure 3.24, a clear dependence of the emission intensities on the added water concentration is observed. For low water concentration He emission is dominant, while for high water concentration, emission from O and H is dominant (see also 3.16). The He emission also seems to start before the emission from O and H.

The emission intensities of Hα and O in figure 3.24 show a maximum at the plasma onset, when the electric field and the electron temperature are high. Between 100 and 200 ns the emission decreases, indicating a decrease in Tₑ. Finally, when the discharge is switched off, the Hα and O emission shows a sharp increase, especially in the case of 0.84 % water. This significant emission during the recombination phase can be explained by a very fast drop in Tₑ, and a 3-body electron-ion recombination reaction like

\[
2e + H^+ \rightarrow e + H^*,
\]  

(3.20)

which has a rate coefficient \(k_{3BR} = 8.8 \cdot 10^{-39}T_e^{-4.5} \text{ m}^6 \text{s}^{-1}\) [26]. This conclusion is consistent with the measured decay time of Hα (345 ± 6 ns), which is an order of magnitude larger than the radiative lifetime of Hα (23 ns [23]). Other processes that can additionally produce H(n = 3) in the afterglow are positive-negative ion recombination and three-body ion-ion recombination of H⁻, H⁺ and potentially other molecular ions [6]. As the energy needed to produce H(n = 3) (12.09 eV) and O(5P) (13.62 eV) is higher than the energy which becomes available in dis-
3.6: Discharge kinetics

Figure 3.23: Time resolved optical emission of He (667 nm), O (777 nm), H\textsubscript{\textalpha} (656 nm) and OH(A–X) (309 nm) for 0.05 (upper figure) and 0.84\% (lower figure) H\textsubscript{2}O in the low-density mode. Current and voltage waveforms are shown as a reference. The intensities of O, and of H\textsubscript{\textalpha} in the case of low water concentration, are multiplied for clarity. The OH(A–X) (\textit{P}\textsubscript{1}(2)) intensity is measured independently and is not scaled to the other time resolved intensities.
Figure 3.24: Time resolved optical emission of He (667 nm), O (777 nm), Hα (656 nm) and OH(A−X) (309 nm) for 0.05 (upper figure) and 0.84 % (lower figure) H₂O in the high-density mode. Current and voltage waveforms are shown as a reference.
3.6: Discharge kinetics

Figure 3.25: Time resolved images of the discharge with 0.84% H₂O without (upper images) and with (lower images) bandpass filter of 313 nm. The time indicated in the images corresponds to the time axis in figure 3.10. The images are recorded with the Andor camera with a gate width of 7 ns and 1000 accumulations. The intensities of the images are normalized to the maximum intensity of each image to show the morphology.

Sociative recombination of an electron with water ions, atomic ion recombination is necessary to explain both H(\(n = 3\)) and O(\(^5\)P) emission (see also [6]).

To see where the emission of OH originates, images of the discharge are recorded using a bandpass filter with a central wavelength of 313 nm and a FWHM of 10 nm. From these images, shown in figure 3.25, it is clear that most of the OH emission is coming from the bulk of the discharges. The total emission, however, has its maximum emission close to the electrodes, especially at the time of the spark formation. Near the electrodes the electric field is higher, resulting in more excitation (and ionization), and thus more emission. After the spark is formed, the electric field becomes more homogeneous in the gap, which is also observed in the axial emission profile for \(t = 80\) ns. As is clear from figure 3.16, the dominant emission is due to He, H and O lines. In addition, the OH emission is broader, which might indicate that the core of the discharge is atomic, while the outer area of the filament is molecular, or potentially direct electron excitation from ground state OH contributes to the OH(A) production at the edge of the filament.

The maximum in OH emission at the start of the discharge indicates that OH(A) is (partly) produced by electron dissociation of H₂O or by electron excitation of OH(X). When the electron temperature decreases during the pulse, OH(A) is created from dissociative electron recombination of H₂O⁺ or H₃O⁺.

In figure 3.26 the ionization rates of He (\(E_i = 24.6\) eV) and H₂O (\(E_i = 12.6\) eV [14]) are shown as a function of the reduced electric field, multiplied by the density.
Chapter 3: He-H\textsubscript{2}O mixtures

Figure 3.26: Ionization rates for He and H\textsubscript{2}O as a function of the reduced electric field, multiplied by their respective densities. The ionization rates are obtained by Bolsig [19], using the cross sections for H\textsubscript{2}O from [21]. For H\textsubscript{2}O, the ionization energy $E_i$ is obtained from [14].

of He and H\textsubscript{2}O respectively. For a voltage of about 3 kV (see figure 3.24) and an inter-electrode distance of 2 mm, the reduced electric field is estimated to be about 60 Td at room temperature. According to the rates in figure 3.26, at this $E/N$ value, ionization of He is faster than ionization of H\textsubscript{2}O. Initially, for a high $E/N$ value, the dominant ion will be He\textsuperscript{+}. These helium ions will be lost, apart from electron-ion recombination reactions, in the following charge transfer reactions [26]:

\begin{align*}
\text{He}^+ + 2 \text{He} &\rightarrow \text{He}_2^+ + \text{He} & 1.4 \cdot 10^{-43} \text{ m}^6 \text{ s}^{-1} , \\
\text{He}^+ + \text{H}_2\text{O} &\rightarrow \text{H}^+ + \text{OH} + \text{He} & 2.04 \cdot 10^{-16} \text{ m}^3 \text{ s}^{-1} , \\
\text{He}^+ + \text{H}_2\text{O} &\rightarrow \text{OH}^+ + \text{H} + \text{He} & 2.86 \cdot 10^{-16} \text{ m}^3 \text{ s}^{-1} , \\
\text{He}^+ + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{O}^+ + \text{He} & 6.05 \cdot 10^{-17} \text{ m}^3 \text{ s}^{-1} , \\
\text{He}^+ + \text{H}_2\text{O} &\rightarrow \text{H}^+ + \text{OH(A)} + \text{He} & 5 \cdot 10^{-19} \text{ m}^3 \text{ s}^{-1} .
\end{align*}

The rates for these reactions (Compiled from [26]) suggest that the production of H\textsuperscript{+} and OH\textsuperscript{+} is more likely than the production of H\textsubscript{2}O\textsuperscript{+}. As seen in section 3.5, the density of helium metastables is about 2 orders of magnitude lower than the electron density, so it is assumed that Penning ionization is not important in the production of H\textsuperscript{+}, OH\textsuperscript{+} and H\textsubscript{2}O\textsuperscript{+}.
3.7 Time and spatially resolved OH density

3.7.1 Radial and axial OH profiles

In figure 3.27, a cross-section of the LIF signal in the middle of the discharge gap, obtained after the discharge is switched off (at $t = 430$ ns), is shown for both the low- and high-density mode in He + 0.84% H$_2$O. The results are qualitatively similar for all water concentrations. In the low-density mode the maximum LIF intensity is located in the centre of the discharge channel. In the high-density mode, however, the fluorescence signal in the centre of the discharge is extremely low (see also figure 3.20). The maximum LIF intensity is in this case located at the edge of the discharge channel.

The time resolved LIF profiles of the two modes are shown in figure 3.28. The inner diameter of the LIF signal in the high-density mode becomes visible at around 100 ns, and increases accordingly with the plasma diameter. Before 100 ns the plasma emission is too strong to obtain the LIF signal, even when a bandpass filter is used. In the recombination phase, on the time scale of $\mu$s, the inner diameter (the zone of low OH density) expands further (see figure 3.28). At this time scale the expansion is related to diffusion of species.

As can be seen in figure 3.19, at $t = 430$ ns the gas temperature measured in the core of the discharge is only a factor of 2 higher than the gas temperature measured in the outer region of the discharge. This leads to a decrease in the Boltzmann factor of the $f_1(2)$ level of maximum a factor 1.8, which is much smaller than the observed ratio in LIF intensities at the edge and in the core of the filament (see figure 3.27). The higher gas temperature in the core of the discharge will not cause an increase in the destruction of OH, since the rates of the main destruction processes of OH are inversely proportional to the gas temperature (see e.g. [52]).

As the depleted zone of OH is also present after the discharge, electron induced quenching, such as

$$\text{OH}(A) + e \rightarrow \text{OH}(B) + e,$$  \hspace{1cm} (3.26)

with $k \sim 10^{-16}$ m$^3$ s$^{-1}$ at 1 eV [42], cannot be the origin of the dip of LIF signal in the centre of the discharge. A change in the composition of the gas (e.g. H$_2$O is replaced by OH, H, O) is also not likely to contribute to a strong effect in spatial variations in collisional quenching, as the rates for quenching of OH(A) by OH, H and O are lower than for quenching by H$_2$O [41, 49]. An increase in collisional quenching can only be expected if the dissociation degree is large and the number of species increases significantly due to fragmentation of the water molecules. The depleted zone in OH can also have a plasma chemical origin.

The appearance of a central dip in the LIF signal after the discharge is also observed by Ono and Oda for a 100 torr and a 760 torr discharge [36]. They
Figure 3.27: Radial cross-sections of the LIF signal obtained by scanning through the discharge with the laser beam at different $y$-coordinates. The cross-sections shown are measured in He + 0.84% H$_2$O at a fixed axial position in the middle between the two electrodes in the low- (upper figure) and high-density (lower figure) mode measured at $t = 430$ ns.
3.7: Time and spatially resolved OH density

Figure 3.28: Time resolved radial profile of the LIF signal of OH for 0.84% H$_2$O in the low- (upper figure) and high- (lower figure) density mode at a fixed axial position in the middle of the gap.
observed an expansion of the LIF signal on a time scale of tens of $\mu$s, and this was solely attributed to diffusion effects. However, on a time scale of 100 ns, as observed in this work, diffusion (typically $\tau_{\text{diffusion}} > 10 \mu$s) is not very important at atmospheric pressure. As a result, the cause of the dip in the LIF signal in our case has clearly a different reason.

Ono and Oda also observed a difference in the OH density in high and low gas temperature regions in a pulsed corona discharge in an atmospheric $\text{N}_2$-$\text{H}_2\text{O}$-$\text{O}_2$ mixture [37]. They saw that the OH density shows a faster decay in the low gas temperature region than in the high gas temperature region. This behaviour was explained by OH production through atomic oxygen in the high temperature region.

Recently Miura and Hopwood [33] found a depletion of the Ar metastable state in the core of a microplasma. Although the exact reason is not clear from the article, it is most likely due to depletion reactions. In our case not only production mechanisms of OH, but also depletion reactions could contribute to the low OH density that is found in the core. A possible reason is ionization of the OH that is produced in the core of the discharge.

To have more insight in the processes that occur on time scales of the first expansion of the LIF signal ($t < 1 \mu$s), in figure 3.29 the plasma emission radius is plotted as a function of time, together with the inner radius of the LIF signal (calculated by subtracting the HWHM of the LIF signal from the distance of the LIF maximum to the core). For comparison, the distance of the LIF maximum to the centre and the FWHM of the LIF signal are also shown. Note that the FWHM of the LIF profile decreases between 130 and 250 ns, and increases again on longer time scales. The decrease in FWHM of the LIF profile indicates a compression.

From the data in figure 3.29, the speed of the increase in plasma radius and LIF radius can be calculated. As mentioned in section 3.3.2, the plasma radius expands with a speed of 1150 m s$^{-1}$. The inner radius of the LIF signal in figure 3.29 is of the same magnitude as the plasma radius, but increases with a smaller velocity (820 m s$^{-1}$ from 130 to 250 ns). In figure 3.29 the plasma radius measured without filter stops increasing around 200 ns, while the inner radius of the LIF signal keeps on increasing up to about 300 ns. A slight difference in time and radius between the plasma radius and inner radius of LIF is possible since these measurements are performed during a different measurement campaign. The plasma radius is also obtained from the plasma emission images that are used to correct the images of LIF for plasma emission. However, for these images a filter with a central wavelength of 313 nm is used, and, as is shown in figure 3.25, the radius (FWHM) of the OH($A-X$) emission is larger than the radius (FWHM) of the total plasma emission. The increase of the radius of the OH($A-X$) emission seems to level off at about the same time as the increase of the inner LIF radius.

The LIF profile depends quantitatively on the water concentration. It is found that the distance between the LIF peaks decreases when the water concentration
Figure 3.29: Plasma emission radius (measured without and with filter of 313 nm) and inner radius of the LIF signal, measured in the high-density mode in He + 0.84% H₂O, together with the distance of the LIF maximum to the centre and the FWHM of the LIF signal. The measurement of the plasma radius from imaging, without using a filter, occurred on a different time.

In conclusion, a clear correlation between the OH(X) dip and the expansion of the discharge emission is found, indicating the importance of the plasma edge on the OH density distribution and production.

Finally, the spatially resolved LIF signal of OH, measured in He + 0.84% H₂O at t = 500 ns at different positions of the laser beam between the two electrodes, is shown in figure 3.31. In the case of the low-density mode, the maximum LIF signal is observed near the electrodes, especially near the anode. On the contrary, in the high-density mode the maximum LIF signal is observed in the middle between the two electrodes. The signal close to the anode in the case of the high-density mode is due to scattering. The high electric field region influences the OH density in the low-density mode, but not in the high-density mode.
Figure 3.30: Distance between the two LIF maxima in the high-density mode for different water concentrations.

3.7.2 Time resolved OH density

In figure 3.32 the time dependent LIF intensity, and density of OH calibrated with Rayleigh scattering, is shown for the low- and high-density mode. Details about the calibration using Rayleigh scattering can be found in chapter 2. Since it is found that the decay time of the LIF signal after excitation with the laser (and thus the collisional quenching) is not constant throughout the entire discharge, the measured LIF intensity needs to be corrected for this. The origin of a different decay time of the LIF signal is discussed in a separate section (section 3.7.2). Both uncorrected and corrected time resolved LIF intensities (and OH densities) are shown in figure 3.32. The obtained LIF intensities are also corrected with the temperature dependent Boltzmann factor of the level that is excited, to obtain the total OH(X) density. The gas temperatures used for this correction are obtained from figures 3.15 and 3.19. However, this correction shows only a minor effect. In the high-density mode the correction for quenching has a significant effect on the measured LIF intensity at $t < 400$ ns. In this case, after correction, the LIF intensity shows a monotone decrease up to 30 $\mu$s. The decrease is faster for 2.6% H$_2$O, in which case a considerably higher OH density is measured. The faster decrease is caused by the ‘self-destruction’ processes of OH

\[
\begin{align*}
\text{OH} + \text{OH} + \text{M} & \rightarrow \text{H}_2\text{O}_2 + \text{M}, \\
\text{OH} + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{O}.
\end{align*}
\]

For 0.05% H$_2$O the time resolved OH density shows a slight increase in the early afterglow, and thus a production of OH, even after correction for quenching. In
3.7: Time and spatially resolved OH density

Figure 3.31: Spatially resolved LIF intensity composed of different measurements for different positions of the laser (beam waist $\approx 250 \, \mu m$) between the two electrodes, measured in the low- (upper figure) and high- (lower figure) density mode in He + 0.84% H$_2$O at $t = 500$ ns. The measurements are performed with a gate width of 40 ns and 1000 accumulations. $E_L = 0.73 \pm 0.03 \, \mu J/pulse$. The colour scale is in arbitrary units.
Chapter 3: He-H$_2$O mixtures

Table 3.4: Most important ionic reactions involved in the production of OH in recombining plasmas. The rates are obtained from [26].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient $k$ (m$^3$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$ + H$_2$O → H$_2$O$^+$ + H</td>
<td>$6.9 \cdot 10^{-15}$</td>
</tr>
<tr>
<td>O$^+$ + H$_2$O → H$_2$O$^+$ + O</td>
<td>$2.6 \cdot 10^{-15}$</td>
</tr>
<tr>
<td>OH$^+$ + H$_2$O → H$_2$O$^+$ + OH</td>
<td>$1.5 \cdot 10^{-15}$</td>
</tr>
<tr>
<td>OH$^+$ + H$_2$O → H$_2$O$^+$ + O</td>
<td>$1.3 \cdot 10^{-15}$</td>
</tr>
<tr>
<td>H$_2$O$^+$ + OH → H$_3$O$^+$ + O</td>
<td>$6.9 \cdot 10^{-15}$</td>
</tr>
<tr>
<td>H$_2$O$^+$ + H$_2$O → H$_3$O$^+$ + OH</td>
<td>$1.9 \cdot 10^{-15}$</td>
</tr>
<tr>
<td>He$^+$ + H$_2$O → H$_3$O$^+$ + He</td>
<td>$6.05 \cdot 10^{-17}$</td>
</tr>
<tr>
<td>H$_2$O$^+$ + e → OH + H</td>
<td>$5.1 \cdot 10^{-14}T_e^{-0.5}$</td>
</tr>
<tr>
<td>H$_3$O$^+$ + e → OH + 2 H</td>
<td>$1.1 \cdot 10^{-13}T_e^{-0.5}$</td>
</tr>
</tbody>
</table>

Since for the case of the low-density mode with 0.05% H$_2$O both the time resolved electron density and OH density are known at the same position (the core of the plasma), a basic chemical model is developed to simulate the observed temporal behaviour. The measured electron density decays with a rate of $2.5 \cdot 10^{-15}$ m$^3$s$^{-1}$, which is too slow to be explained by dissociative recombination with water ions ($k_{dr} \sim 10^{-13}$ m$^3$s$^{-1}$ at 350 K [16]). The slow electron density decay can be explained by dissociative recombination of OH$^+$ ($6 \cdot 10^{-15}$ m$^3$s$^{-1}$ at $T_e = T_g = 350$ K [18]), or by charge transfer processes of atomic ions (H$^+$, O$^+$, He$^+$) with water ($k_{ce} \sim 10^{-15}$ m$^3$s$^{-1}$) followed by dissociative recombination of water ions (see table 3.4). Note that the time determining reaction in the two-step charge transfer and dissociative recombination reaction is the charge transfer reaction.

To explain the production of OH, it is assumed that charge transfer of H$^+$, O$^+$, OH$^+$ and He$^+$ with water will be the rate limiting step in the OH formation process. The temporal behaviour of the OH density can thus be modelled as follows (see section 2.4 for the OH decay):

$$\frac{dn_{OH}(t)}{dt} = k_{ce}n_{H2O}n_e(t) - k_{loss}n_{OH}^2(t).$$  (3.29)

Since the electron density in the case of 0.05% H$_2$O is measured in a different measurement campaign for a slightly higher applied voltage (1.6 kV instead of 1.3 kV) than the OH density shown in figure 3.32, the OH density measured in the same measurement campaign is used in figure 3.33 to fit the model. Note that the OH density calibrated with Rayleigh is in this case about 3 times larger. The fitting parameters to obtain the fit shown in figure 3.33 are $k_{ce} = 5 \cdot 10^{-16}$ m$^3$s$^{-1}$, $n_{OH}(t = 200 \text{ns}) = 1 \cdot 10^{20}$ m$^{-3}$. The gas temperature is kept constant at 300 K, as measured in figure 3.15. To obtain agreement with the measurement and the
Figure 3.32: Time resolved OH density in the low- (upper figure) and high-density (lower figure) mode for different water concentrations. The densities are calibrated using Rayleigh scattering.
Chapter 3: He-H₂O mixtures

Figure 3.33: Time resolved OH and electron density measured, together with the calculated OH density for the low-density mode in He + 0.05% H₂O. The fitting parameters are \( k_{ce} = 5 \times 10^{-16} \text{ m}^3 \text{ s}^{-1} \), \( n_{\text{OH}}(t = 200 \text{ ns}) = 1 \times 10^{20} \text{ m}^{-3} \). The gas temperature is kept constant at 300 K as measured in figure 3.15.

fit, the OH density calibrated using Rayleigh scattering is increased by a factor 1.85. This is within the experimental accuracy as determined in chapter 2.

Similar reaction processes can explain the dip in the OH density in the core of the plasma filament in the case of the high-density mode, considering that the water density is similar to the electron density and that water will be fully dissociated and ionized. A schematic drawing of the charge transfer and subsequent dissociative recombination processes for the high-density mode is shown in figure 3.34. The dissociation of H₂O in the core and the charge transfer reactions causing the OH production can explain the observed spatial profile.

In the high-density mode, for 0.84 and 2.6% H₂O, an increase in the OH density is observed around 50 μs. Using the model with 22 reactions including OH, H, O, HO₂, H₂O₂, O₂, H₂ and H₂O (as described in chapter 2), a fit is made of the time resolved OH density in the far afterglow for the case of 0.84% H₂O (see figure 3.35). The OH density which is simulated in the model is the density calibrated using the decay. The modelled time resolved OH density deviates from the measured time resolved OH density in the far afterglow. As shown in figure 3.35 this can not be explained by a different gas temperature. Another possible explanation for the measured increase in OH density is production of OH by photodissociation of H₂O₂ [12]. The species densities of OH and its by-products for the model at \( T_e = 400 \text{ K} \) are shown in figure 3.36. From the maximum density of H₂O₂ (≈ 10^{22} \text{ m}^{-3}), the laser fluence and the absorption cross section given in [2], the estimated amount of photons absorbed is 10^{18}. The measured
Figure 3.34: Schematic drawing of the mechanisms that are assumed to be responsible for the observed spatial profile of OH(X) in the high-density mode.
Figure 3.35: Measured and modelled time resolved OH density in the far afterglow, for the case of the high-density mode in He + 0.84% H$_2$O. The modelled OH density is calculated with the extended chemical model for $T_g = 350$ K, 400 K, and 450 K. The initial conditions are $n_{OH}^0 = n_H^0 = 4.6 \cdot 10^{21}$ m$^{-3}$.

OH density is thus not influenced by photodissociation of H$_2$O$_2$. To explain the increase in the OH density in the far afterglow a more detailed, 2-dimensional model is necessary.

The maximum OH densities for the low- and high-density mode, calibrated using Rayleigh scattering and using a chemical model (for details see chapter 2), are shown in table 3.5. A good agreement is found between the densities obtained with the two methods. Only in the case of the high-density mode with 0.05% H$_2$O the discrepancy is larger than the experimental accuracy. This could be due to the short time range where the reduced chemical model could be applied, increasing the inaccuracy in this case. For low water concentration, when the electron density is approximately equal to the OH density in the afterglow, the initial decay of the OH density can also be enhanced by processes such as [26]

\[
\begin{align*}
    H^+ + OH &\rightarrow OH^+ + H & k = 2.1 \cdot 10^{-15} \text{ m}^3 \text{ s}^{-1}, \\
    O^+ + OH &\rightarrow OH^+ + O & k = 3.3 \cdot 10^{-16} \text{ m}^3 \text{ s}^{-1}, \\
    H_2O^+ + OH &\rightarrow H_3O^+ + O & k = 6.9 \cdot 10^{-16} \text{ m}^3 \text{ s}^{-1}, \\
    He^+ + OH &\rightarrow O^+ + H + He & k = 1.1 \cdot 10^{-15} \text{ m}^3 \text{ s}^{-1}.
\end{align*}
\]

As a result, the chemical model including only neutral chemistry will overestimate the OH density.
Figure 3.36: Modelled species densities of OH and its by-products for the conditions of figure 3.35 at $T_g = 400$ K.

Table 3.5: Maximum OH densities for the low- and high-density mode in He with different water admixtures calibrated with a reduced chemical model ($n_{OH,CM}$) (see section 2.4) and using Rayleigh scattering ($n_{OH,R}$). $t_{\text{max}}$ is the time at which the maximum OH density is measured.

<table>
<thead>
<tr>
<th>Density mode</th>
<th>$n_{H_2O}$ (%)</th>
<th>$t_{\text{max}}$ (µs)</th>
<th>$n_{OH,CM}$ ($10^{22}$ m$^{-3}$)</th>
<th>$n_{OH,R}$ ($10^{22}$ m$^{-3}$)</th>
<th>Accuracy $n_{OH,R}$ ($10^{22}$ m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>0.05</td>
<td>2.57</td>
<td>0.3</td>
<td>0.11</td>
<td>+0.21; -0.04</td>
</tr>
<tr>
<td>Low</td>
<td>0.84</td>
<td>0.25</td>
<td>0.7</td>
<td>0.3</td>
<td>+0.6; -0.1</td>
</tr>
<tr>
<td>High</td>
<td>0.05</td>
<td>1.57</td>
<td>1.0</td>
<td>0.16</td>
<td>+0.36; -0.06</td>
</tr>
<tr>
<td>High</td>
<td>0.84</td>
<td>0.16</td>
<td>5.1</td>
<td>1.0</td>
<td>+1.9; -0.4</td>
</tr>
<tr>
<td>High</td>
<td>2.6</td>
<td>0.25</td>
<td>11</td>
<td>10</td>
<td>+18; -4</td>
</tr>
</tbody>
</table>
Chapter 3: He-H₂O mixtures

Time resolved collisional quenching

The fluorescence decay time, after excitation by the laser at different times during the plasma pulse, is shown in figure 3.37 for the low- and high-density mode. The measured quenching time in the case of the high-density mode with 0.84% H₂O is compared with the temperature dependent quenching in figure 3.38. At 300 K the quenching time obtained from the quenching rate in [11] is 7.2 ns. At \( t = 400 \mu s \), the measured quenching time is 7.7 ns, which is close to the value at room temperature. Note that the measured quenching decay times are not corrected for spontaneous emission (Einstein A-coefficients), since the rate for this process is in this case more than 2 orders of magnitude lower than the rate for quenching (see also table 2.3), and can thus be neglected. The quenching time as a function of temperature can be estimated from the gas temperature measured by excitation LIF in figure 3.19 as

\[
\tau = \frac{1}{n_{H_2O}k_Q(T)}.
\] (3.34)

The dependence of the quenching constant \( k_Q \) on the gas temperature is obtained from the relation given in [41]. The decay time calculated from the gas temperature as a function of time is shown in figure 3.38. After \( t = 5 \mu s \) the calculated decay time shows approximately the same behaviour as the measured decay time, which means that it is determined by changes in gas temperature. Before \( t = 500 \, ns \) the calculated decay time is significantly higher than the measured decay time. For a higher gas temperature (which characterizes the plasma towards the end of the current pulse), quenching is reduced, so a longer decay time is expected. The measured short decay times of the LIF signal around \( t = 100 \, ns \) can then possibly be explained by an increase in pressure. To explain the measured decay time compared to the calculated decay time only by a pressure difference, the pressure should be about 4 times higher. This is much higher than what is expected from the expansion velocity obtained from figure 3.12 (see section 3.3.2). Another possibility that can explain the short decay times is a change in composition. OH(A) is quenched less by OH, H and O than by H₂O [41, 49], but when H₂O is highly dissociated, the density of quenchers increases. In addition, the high ion/electron density could increase the quenching by charge transfer reactions or by electron quenching. Teulet et al have reported rate coefficients for

\[
\text{OH(A) + e} \longrightarrow \text{OH(B) + e},
\] (3.35)

which has the largest rate for the possible electron quenching processes of OH(A). The rate \( k_e \) (calculated for \( T_e = T_g \)) is \( 9 \cdot 10^{-26}T^{2.76} \exp(-54911.4/T) \) [42].

Also in the case of the low-density mode, a shorter quenching decay time than expected, is observed. In this case, this will mainly be due to electron quenching as the dissociation degree is low. For the low-density mode with 0.84% H₂O, at \( T_g = 400 \, K \) (the gas temperature measured at \( t = 200 \, ns \)), the quenching time is expected to be 8.2 ns. For an electron density of \( 2 \cdot 10^{21} \, m^{-3} \) (as measured at
3.7: Time and spatially resolved OH density

Figure 3.37: Time resolved fluorescence decay time of OH(A−X) (1-1), obtained from measured time resolved fluorescence signals in the low- (upper figure) and high-density (lower figure) mode for different water concentrations.
200 ns), the time scale for electron quenching would be reduced to $3 - 4\,\text{ns}$ for $T_e \approx 3.5\,\text{eV}$, as obtained using the rate for reaction 3.35.

### 3.8 Conclusion

Time and spatially resolved laser induced fluorescence of OH with high resolution in space and time is performed on a nanosecond pulsed plasma filament in He-H$_2$O mixtures. The breakdown mechanism is a streamer-to-spark transition, of which the spark only occurs if the DC applied voltage is high enough at a constant pulse width. A low- and a high-density plasma mode are investigated which are characterized by a different electron density ($\approx 10^{21}\,\text{m}^{-3}$ and $\approx 10^{22}\,\text{m}^{-3}$ respectively). A significant amount of emission from these plasmas is shown to be due to recombination processes. In the high-density mode, after the spark formation, an expansion of the plasma channel is observed at a velocity close to the sound velocity.

LIF results show that the OH production depends strongly on the electron density. In the case of the low-density mode the LIF signal, and thus also the OH density, is the largest inside the discharge. On the other hand, in the case of the high-density mode the core is highly dissociated and OH is only observed at the edge of the discharge. The measured slow electron density decay in the high-density mode confirms that the core of the discharge should mainly consist
of atomic ions and OH$^+$. As the recombination rates of atomic ions and OH$^+$ are slower than or comparable to the rate of charge transfer, charge transfer and subsequent dissociative recombination will be an important ionic loss mechanism at the plasma boundary. The latter processes can explain the maximum OH density at the edge of the plasma filament.

A model is developed, consisting of the two-step process of charge transfer of atomic ions producing water ions, and subsequent dissociative recombination producing OH. Together with the self-quenching of OH, this model can explain the measured time resolved OH density. It is shown that He metastables do not contribute to the OH dynamics in the afterglow of the discharge. During the current pulse, electron quenching significantly contributes to the reduction of the effective (fluorescence) lifetime of OH(A).
Chapter 3: He-H$_2$O mixtures
References

[1] Personal communication with N. Sadeghi.


Chapter 4

He-H$_2$O-O$_2$ mixtures

Abstract

In this chapter the influence of the addition of O$_2$ on the OH production in the He + 0.1% H$_2$O discharge is investigated. The plasma properties ($T_e$, $n_e$) are reported and used to explain the observed time and spatially resolved OH density, which is absolutely calibrated using Rayleigh scattering. Compared to the case when only H$_2$O is added, an increase in the measured OH density is observed in the far afterglow. A zero-dimensional chemical kinetic model is constructed, which allows to determine the reactions responsible for the OH production in the far afterglow. The key reaction O + OH $\rightarrow$ O$_2$ + H causes the production of increased densities of H and HO$_2$, which lead to OH production occurring in the late afterglow.
4.1 Introduction

In literature, a production process of OH that is often suggested to be important, besides direct electron dissociation of water, is [13, 16]

\[ \text{O}_2 + e \rightarrow \text{O}(^{3}\text{P}) + \text{O}(^{1}\text{D}) + e, \]  
\[ \text{O}(^{1}\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{OH}. \]

In [16], it is observed in a DBD in atmospheric argon that the OH density increases when the O\(_2\) concentration increases. The OH density peaks at 3\% O\(_2\), and decreases with a further increasing O\(_2\) addition. The decrease in OH is ascribed to O\(_2\) being an attaching gas (and thus an increasing loss of electrons with increasing O\(_2\) concentration), and to destruction of OH by O\(_3\):

\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2. \]

Recently, modelling studies of the reactive species chemistry have been reported by the group at Loughborough University [8, 12], in which small additions of O\(_2\) to He-H\(_2\)O RF driven capacitively coupled glow discharges increase the OH production in the discharge. Previous modelling work on O\(_2\)-H\(_2\)O chemistry for a streamer discharge is reported by Peyrous et al [14]. In this work it is shown that in humid O\(_2\) the OH density increases up to about 1\,\mu s after the pulse. This is ascribed to the following reaction

\[ \text{O} + \text{H}_2\text{O} \rightarrow 2 \text{OH}. \]

However, at 600\,K the reported rate in [14] \((k = 1 \cdot 10^{-17} \exp(-550/T_{\text{g}}) \text{m}^3 \text{s}^{-1})\) is almost 5 orders of magnitude faster than the rate found in [11], which is \(1.84 \cdot 10^{-17}(T_{\text{g}}/300)^{0.85} \exp(-8571/T_{\text{g}}) \text{m}^3 \text{s}^{-1}\). This error is probably introduced by the fact that Peyrous et al did not consider O(1\,D) and O(1\,S) in their model, but only the ground state O(3\,P). In addition, in spite the high electron density of 5\,\cdot\,10^{21} \text{m}^{-3}, no ionic recombination reactions producing OH are considered in the early afterglow (which are shown to be important in chapter 3).

Recent work of Komuro et al [5] reports on the 3 main reaction processes of the OH kinetics in the afterglow of a pulsed discharge in humid air. The production process of OH is due to dissociation of water by O(1\,D) and N\(_2\)(A). The second process is a OH-recycle mechanism, in which mainly O(3\,P) is responsible for the destruction of OH to form O\(_2\) and H. H is converted further in HO\(_2\), which allows to recycle part of the lost OH through the following reactions

\[ \text{O}(^{3}\text{P}) + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2, \]  
\[ \text{H} + \text{HO}_2 \rightarrow 2 \text{OH}. \]
Finally, in the far afterglow the OH radicals are consumed by self quenching reactions.

In older reported work by the same group [13], it is shown for similar discharge conditions that reaction 4.4 is responsible for the observed increase in OH production in a high-temperature zone of the corona, compared to the OH density in the low-temperature zone.

The importance of the $O(^3P)$ radical and the remaining questions in the $O_2$-H$_2$O kinetics as outlined above, motivate the investigation of the He-$O_2$-H$_2$O chemistry in the current study. Spatially and time resolved LIF is applied on the discharge in He + 0.1% H$_2$O upon the addition of 0.05 to 2% O$_2$ (section 4.4). The experimental setup and the plasma properties ($T_e$, $n_e$) are reported in sections 4.2 and 4.3 respectively.

### 4.2 Experimental setup

The setup used in this chapter is identical to the setup used in chapter 3.

The effect of the addition of O$_2$ on the OH density is investigated in the high-density mode, with an applied voltage of 7kV. A water admixture of 0.1% is added to a total flow of 3 l/min using a Bronkhorst High-Tech B. V. “CEM”-system (Controlled Evaporation Mixing). O$_2$ admixtures between 0.05 and 2% are added with a 100 ml/min Ar mass flow meter (Bronkhorst EL-FLOW).

Time resolved optical emission spectra are recorded with an iCCD camera (4 Quik E SR) coupled to a 27.5 cm monochromator (ACTON). Line broadening of H$eta$ is used to obtain the electron density (see also section 3.2.1). The OH(X) density is obtained by LIF of the $P_1(2)$ transition. The LIF signal is detected with an iCCD camera (4 Quik E HR) and with a photomultiplier (Hamamatsu R636-10) operating in photon counting mode. The photomultiplier is coupled to a Jobin Yvon THR 1000 monochromator which operates as a 1.3 nm bandwidth filter. The slit width is larger for the He-H$_2$O-O$_2$ measurements than for the He-H$_2$O measurements, to capture more light. The individual photon signal from the photomultiplier is processed by a discriminator and is read out by an Ortec 9353 time digitizer card, which counts the pulses with a time resolution of up to 2 ns, limited by the response time of the photomultiplier. Gas temperatures are obtained from excitation LIF (see also section 3.2.1). More details about the experimental setup and methods used can be found in section 3.2.
4.3 Plasma properties

When adding up to 2% O₂ to He + 0.1% H₂O, the current and voltage as a function of time do not change significantly. The electron densities and gas temperatures for different O₂ admixtures are shown in figure 4.1 and figure 4.2, respectively. Although O₂ is an attaching gas, and it is expected that the electron density would decrease with an increasing amount of O₂, the measured electron densities for different O₂ admixtures are equal within the experimental accuracy during the pulse. In the afterglow a slightly higher electron density is measured for 1% O₂. The gas temperatures, as measured from excitation LIF (so the gas temperature at the edge of the filament), are also equal within the experimental accuracy, except at the end of the current pulse (around t = 150 ns), where the gas temperature measured for 2% O₂ is consistently larger than the gas temperature measured without O₂. In general, a maximum gas temperature between 400 and 600 K is measured towards the end of the current pulse. The gas temperature then decreases to about 300-350 K around t = 600 ns, followed by a slow increase up to about 400 K. For the case of 0.05% O₂ (in which case the fluorescence signal is the most intense, so it can be measured during the entire pulse), the temperature decreases again to about room temperature before the next voltage pulse is applied.

The time resolved optical emission of He, O and Hα are shown in figure 4.3 for no and 0.3% O₂ admixture. As explained in section 3.6, for a low water concentration initially mostly He will be ionized (and excited). For 0.3% O₂
admixture a maximum in He emission is observed before a maximum in O emission occurs. In addition to the charge transfer reactions discussed in section 3.6, helium ions can further produce $O^+$ and $O_2^+$ by the reactions [6]

$$\text{He}^+ + O_2 \rightarrow O^+ + O + \text{He} \quad 1.07 \cdot 10^{-15} (T_g/300)^{-0.5} \text{ m}^3 \text{s}^{-1}, \quad (4.7)$$

$$\text{He}^+ + O_2 \rightarrow O_2^+ + \text{He} \quad 3.3 \cdot 10^{-17} (T_g/300)^{-0.5} \text{ m}^3 \text{s}^{-1}. \quad (4.8)$$

Similar to chapter 3, $O(^5\text{P})$ and $H(n = 3)$ are likely to be produced by electron - atomic ion recombination. Note as well that $O^+$ production is favoured over $O_2^+$ production in $\text{He}^+$ charge transfer reactions, which will be important for small O$_2$ admixtures. This explains why the decay rate is similar as in the case of H$_2$O, where the dominant ions in the plasma core are atomic.

### 4.4 Time and spatially resolved OH density

#### 4.4.1 Radial and axial OH profiles

The spatially resolved LIF signal of OH in $\text{He} + 0.1\% \text{H}_2\text{O} + 2\% \text{O}_2$, measured at $t = 500 \text{ ns}$ for different positions between the two electrodes, is shown in figure 4.4. As in the high-density mode without an admixture of O$_2$ (see figure 3.31), the measured LIF signal has its maximum in the middle of the gap.
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Figure 4.3: Time resolved optical emission of He (667 nm), O (777 nm) and Hν (656 nm) for no O₂ admixture (upper figure) and for 0.3% O₂ (lower figure). The corresponding current and voltage waveforms are also shown.
4.4: Time and spatially resolved OH density

Figure 4.4: Spatially resolved LIF intensity graph composed of different measurements for different positions of the laser (beam waist ≈ 250 μm) between the two electrodes, in He + 0.1% H₂O + 2% O₂ at t = 500 ns. The measurements are performed with a gate width of 70 ns and 1000 accumulations. E_L = 0.73 ± 0.03 μJ/pulse. Scattering at the anode could not be completely subtracted and is responsible for the high intensity at the anode. The colour code is in arbitrary units.

The time variation of the radial profiles of the LIF signal is shown in figure 4.5. When O₂ is added significantly more fluorescence is observed in the afterglow (in spite of the increased quenching of OH(A) by O₂). A local maximum in OH fluorescence is found at the axis of symmetry around 100 μs after the plasma pulse.

4.4.2 Time resolved OH density

The time resolved LIF intensity is obtained from the profiles in figure 4.5 by taking the average of the maxima of the two LIF peaks, fitted with a multiple Gaussian peak fit (I_max), and by summing the total measured LIF signal (I_total). These two intensities are shown in figure 4.6. The total LIF signal includes the maximum at the axis of symmetry and shows a sharp increase at t = 40 μs, while the maximum LIF intensity shows a levelling off at this time. As for the discharge in He + H₂O mixtures (see section 3.7.2), the measured decay time of the LIF signal (by quenching) after the laser excitation is not constant during the entire plasma cycle. The time resolved LIF intensities are shown with and without correction for the different quenching measured and for the gas temperature dependent population of f₁(2). The gas temperature is obtained from the results presented in figure 4.2.
Figure 4.5: Time resolved radial profile of the LIF signal of OH for no (upper figure) and 0.1% (lower figure) O₂ admixture to He + 0.1% H₂O at a fixed axial position in the middle of the gap. In the case of 0.1% O₂ the profiles from 10 to 1000 µs are measured with a higher gain of the iCCD camera and rescaled.
4.4: Time and spatially resolved OH density

Figure 4.6: Maximum LIF intensity and total LIF intensity as a function of time for 0.1% O₂ admixture to He + 0.1% H₂O. Both intensities are shown with and without correction for quenching and the temperature dependent population of $f_1(2)$.

(The gas temperature for 0.1% O₂ is equal to the gas temperature for 0.05% O₂ within the experimental accuracy).

Absolute calibration using Rayleigh scattering

The time resolved absolute OH densities for various O₂ admixtures, calibrated using Rayleigh scattering (see chapter 2), are shown in figure 4.7. A significantly larger OH density is observed at 100μs when O₂ is added. The parameters and rates used for the calibration in the case of He + 0.1% H₂O + 0.1% O₂ are shown in tables 4.1 and 4.2. The measured and modelled time resolved fluorescence are shown in figure 4.8. More details about the calibration using Rayleigh scattering can be found in chapter 2.

Since quenching is not measured during the entire pulse for all O₂ concentrations, the time resolved OH density in figure 4.7 is only shown from $t = 1\mu$s onwards. In all cases the density at $t = 10\mu$s is calibrated. Because of the limitation in the dynamic range of the available detection system, the density could not be calibrated at an earlier time when the difference in OH density is larger as indicated in figure 4.7. The absolute OH density seems to reach its maximum when the added O₂ concentration is similar to the H₂O concentration.

The fluorescence decay time of the OH(A–X) (1-1) fluorescence (as shown in
Figure 4.7: Time resolved OH density (obtained from the maximum LIF intensities) for different O\textsubscript{2} admixtures. The densities are calibrated at \( t = 10 \) \( \mu \)s using Rayleigh scattering. Since quenching is not measured during the entire pulse for all conditions, the time resolved OH density is only shown in the time interval 1-1000 \( \mu \)s.

Table 4.1: Total rate constants and parameters of the 4-level model for the absolute calibration of the OH density in He + 0.1\% H\textsubscript{2}O + 0.1\% O\textsubscript{2} at \( t = 10 \) \( \mu \)s. The total rates for quenching, VET and RET are calculated as \( k^{\text{He-}N} + k^{H_{2}O-NH_{2}O} + k^{O_{2}-NO_{2}} \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T ) (K)</td>
<td>350</td>
<td></td>
</tr>
<tr>
<td>( f_{0''''=0,J''''=2.5}^{0'''} )</td>
<td>0.177</td>
<td>[9]</td>
</tr>
<tr>
<td>( f_{0''''=1,J''''=1.5}^{0'''} )</td>
<td>0.1</td>
<td>[9]</td>
</tr>
<tr>
<td>( \Delta \tau ) (ns)</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>( \Delta s ) (( \mu )m)</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>( Q_{00} ) (s(^{-1}))</td>
<td>( 1.6 \times 10^{7} )</td>
<td>[1]</td>
</tr>
<tr>
<td>( Q_{11} ) (s(^{-1}))</td>
<td>( 1.7 \times 10^{7} )</td>
<td>[1]</td>
</tr>
<tr>
<td>( V_{A} ) (s(^{-1}))</td>
<td>( 2.0 \times 10^{6} )</td>
<td>[1]</td>
</tr>
<tr>
<td>( V_{X} ) (s(^{-1}))</td>
<td>( 2.0 \times 10^{4} )</td>
<td>[15]</td>
</tr>
<tr>
<td>( R_{61} ) (s(^{-1}))</td>
<td>( 4.8 \times 10^{9} )</td>
<td>[2-4]</td>
</tr>
<tr>
<td>( R_{23} ) (s(^{-1}))</td>
<td>( 7.3 \times 10^{9} )</td>
<td>[2-4]</td>
</tr>
</tbody>
</table>
Table 4.2: Total RET rate coefficients estimated at 300 K, total quenching (electronic + vibrational relaxation) rate coefficients for OH(A; $\nu' = 0, 1$) and vibrational relaxation rate coefficients for inelastic collisions of OH with O$_2$. The rates for quenching obtained from [17] are for $N' = 2$. (For an explanation of the RET rate coefficients see section 2.5.2.)

<table>
<thead>
<tr>
<th>Collisional process</th>
<th>Initial level</th>
<th>$O_2$ (10$^{-17}$ m$^3$ s$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RET (A; $\nu' = 1$, $F_1(1)$)</td>
<td>20</td>
<td>2-4</td>
<td></td>
</tr>
<tr>
<td>RET (X; $\nu' = 0$, $f_1(2)$)</td>
<td>50</td>
<td>2-4</td>
<td></td>
</tr>
<tr>
<td>Q (A; $\nu' = 0$)</td>
<td>9.3</td>
<td>[17]</td>
<td></td>
</tr>
<tr>
<td>Q (A; $\nu' = 1$)</td>
<td>20.2</td>
<td>[17]</td>
<td></td>
</tr>
<tr>
<td>VET (A; $\nu' = 1 \rightarrow \nu' = 0$)</td>
<td>2</td>
<td>[17]</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.8: Experimental and modelled time resolved fluorescence intensity of $(\nu'' = 1 - \nu' = 1)$ and $(\nu'' = 1 - \nu' = 1)$ for He + 0.1\% H$_2$O + 0.1\% O$_2$ at 7kV, $E_L = 0.76 \pm 0.02$ μJ. The temporal laser profile $f_l$, obtained by Rayleigh scattering, is also shown.
figure 4.8) is measured at different times for an admixture of 0.05 and 0.1 % O\textsubscript{2} to He + 0.1 % H\textsubscript{2}O, and shown in figure 4.9. As in the case when no O\textsubscript{2} is admixed (see section 3.7.2), the quenching time is significantly reduced at the end of the current pulse (around t = 200 ns), presumably because of a higher pressure. After 2 \mu s there is a slow increase in the quenching time, which can be related to the temperature (see also figure 4.2). The measured quenching times before the next voltage pulse starts are about 45 and 39 ns for 0.05 and 0.1 % O\textsubscript{2} respectively. The temperature at this time is close to room temperature, so from the quenching rates for H\textsubscript{2}O and O\textsubscript{2} at 300 K [1, 17], the calculated decay times by quenching are 55 and 49 ns respectively. This is about 25 % more than measured. As shown in [1, 17], the uncertainty in quenching rate coefficients can be quite high, which could explain the result.

Zero-dimensional kinetic model

In order to explain the increased OH density in the far afterglow when O\textsubscript{2} is added, a zero-dimensional model is constructed to model the maximum in OH density in the far afterglow. The case He + 0.1 % H\textsubscript{2}O + 0.1 % O\textsubscript{2} is treated. The model includes the relevant H\textsubscript{2}O and O\textsubscript{2} related neutral chemistry. The reactions included in this model are summarized in table 2.2 (H\textsubscript{2}O chemistry) and in table 4.3 (O, O(\textsuperscript{1}D) and O\textsubscript{2} chemistry). As we are only interested in the far afterglow, the time resolved OH density is calculated from t = 0.9 \mu s onwards. The known concentrations of H\textsubscript{2}O and O\textsubscript{2} are included (corrected for potentially important dissociation). As initial condition for the OH density, the OH density
calibrated with Rayleigh scattering (see figure 4.7) is used \((1.5 \cdot 10^{21} \text{ m}^{-3})\). Further it is assumed that the H density is equal to the OH density at \(t = 0.9 \mu\text{s}\), and that the initial densities of other species are negligible. The gas temperature used in the model is estimated from the gas temperature measured by excitation LIF (figure 4.2), an optimal fit to the measured LIF intensity is found by eye.

The modelled OH density is compared to the OH density measured in \(\text{He} + 0.1\% \text{H}_2\text{O} + 0.1\% \text{O}_2\) in figure 4.10. When no \(\text{O}_2\) is added, no local maximum is observed in the OH density around \(t = 100 \mu\text{s}\), as also experimentally observed. However, when assuming an admixture of 0.1\% \(\text{O}_2\), a local maximum is observed. The optimum fit at \(T_g = 350 \text{ K}\) is obtained for an initial O density of \(1 \cdot 10^{22} \text{ m}^{-3}\), which means that the dissociation degree of \(\text{O}_2\) is 30\%, while the dissociation degree of \(\text{H}_2\text{O}\) in the fit is 7\%. For both \(\text{H}_2\text{O}\) and \(\text{O}_2\) the dissociation energy is about 5 eV, so it is expected that the dissociation degree would be similar. A lower O density compared to the OH density might also be found if the initial OH density is increased. This adjustment is not investigated in detail, since it would increase the number of degrees of freedom and the OH density is a measured quantity. Note that when the OH density is low, the chemical model, which only considers neutral reactive chemistry, does not allow to accurately predict the OH density obtained by Rayleigh scattering and overestimates the OH density (see chapter 3).

In figure 4.10 the calculated OH density is also shown when the initial dissociation
Table 4.3: O and O(1D) related reactions in the production and loss of OH in a He-H₂O-O₂ discharge. Rate coefficients have units of m³ s⁻¹ for 2-body reactions and m⁶ s⁻¹ for 3-body reactions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>k at 400 K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>O(1D) + O₂ → O + O₂</td>
<td>3.20 · 10⁻¹⁸ exp(67/Tₖ)</td>
<td>3.78 · 10⁻¹⁸</td>
<td>7</td>
</tr>
<tr>
<td>O2</td>
<td>O(1D) + He → O + He</td>
<td>1 · 10⁻¹⁹</td>
<td>1 · 10⁻¹⁹</td>
<td>7</td>
</tr>
<tr>
<td>O3</td>
<td>O(1D) + H₂O → O + H₂O</td>
<td>1.22 · 10⁻¹⁷</td>
<td>1.22 · 10⁻¹⁷</td>
<td>6</td>
</tr>
<tr>
<td>O4</td>
<td>O(1D) + H₂O → 2OH</td>
<td>1.62 · 10⁻¹⁶ exp(64.95/Tₖ)</td>
<td>6.34 · 10⁻¹⁸</td>
<td>6</td>
</tr>
<tr>
<td>O5</td>
<td>H + HO₂ → H₂O + O(1D)</td>
<td>4.8 · 10⁻²²(Tₖ/300)⁴ + (80.58/Tₖ)</td>
<td>1.91 · 10⁻¹⁶</td>
<td>6</td>
</tr>
<tr>
<td>O6</td>
<td>3O → O + O₂</td>
<td>9.90 · 10⁻⁴⁶(Tₖ/300) (1 - 0.63)</td>
<td>8.26 · 10⁻⁴⁶</td>
<td>7</td>
</tr>
<tr>
<td>O7</td>
<td>2O + O₂ → 2O₂</td>
<td>2.75 · 10⁻⁴⁶(Tₖ/300) (1 - 0.63)</td>
<td>2.30 · 10⁻⁴⁶</td>
<td>7</td>
</tr>
<tr>
<td>O8</td>
<td>2O + O₂ → O₃ + O</td>
<td>3.4 · 10⁻⁴⁶ exp(345/Tₖ)</td>
<td>8.05 · 10⁻⁴⁶</td>
<td>7</td>
</tr>
<tr>
<td>O9</td>
<td>2O + He → O₂ + He</td>
<td>1.3 · 10⁻⁴⁴(Tₖ/300)⁴ (1 - 1) exp(-170/Tₖ) + 9.88 · 10⁻⁴⁷</td>
<td>1.08 · 10⁻¹⁹</td>
<td>7</td>
</tr>
<tr>
<td>O10</td>
<td>O + 2O₂ → O₃ + O₂</td>
<td>6 · 10⁻⁴⁶(Tₖ/300)⁴ (1 - 2.8)</td>
<td>2.68 · 10⁻⁴⁶</td>
<td>7</td>
</tr>
<tr>
<td>O11</td>
<td>O + O₂ + He → O₃ + He</td>
<td>1.1 · 10⁻⁴⁶ exp(510/Tₖ)</td>
<td>6.56 · 10⁻⁻²¹</td>
<td>7</td>
</tr>
<tr>
<td>O12</td>
<td>O + O₂ + O₃ → 2O₃</td>
<td>1.5 · 10⁻⁴⁶ exp(710/Tₖ)</td>
<td>8.85 · 10⁻⁴⁶</td>
<td>7</td>
</tr>
<tr>
<td>O13</td>
<td>O₃ + OH → HO₂ + O₂</td>
<td>1.6 · 10⁻¹⁸ exp(-1000/Tₖ)</td>
<td>1.31 · 10⁻¹⁹</td>
<td>16</td>
</tr>
<tr>
<td>O14</td>
<td>O(1D) + O₃ → 2O + O₂</td>
<td>1.2 · 10⁻¹⁶</td>
<td>1.2 · 10⁻¹⁶</td>
<td>7</td>
</tr>
<tr>
<td>O15</td>
<td>O(1D) + O₃ → 2O₂</td>
<td>1.2 · 10⁻¹⁶</td>
<td>1.2 · 10⁻¹⁶</td>
<td>7</td>
</tr>
</tbody>
</table>
of O₂ matches the initial dissociation of H₂O, and when reaction R5,
\[ \text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}, \]
is not taken into account. When reaction R5 is removed, the local maximum is no longer present, which means that this reaction is (directly or indirectly) causing the observed phenomenon. For a more detailed observation, the modelled species densities and total rates of the modelled production and loss processes of OH are plotted in figures 4.11 and 4.12 for the 2 cases shown above (with and without O₂). For both cases \( n^0_{\text{OH}} = n^0_{\text{H}} = 1.5 \cdot 10^{21} \text{m}^{-3} \) and in the case of 0.1% O₂ \( n^0_{\text{O}} = 1 \cdot 10^{22} \text{m}^{-3} \).

In the case with high O density, an increase in H density is observed. OH is actually strongly quenched by O and converted in H. This H is in its own a strong quencher of OH, which causes a reduction in the OH density at 10 μs. Due to the large drop in OH density, the destruction of OH significantly reduces. On the other hand the H atoms produce HO₂. The reaction of H and O with HO₂ is an important production mechanism of OH. For a few tens of μs, this then causes the total production of OH (due to reactions R12 and R18) to be larger than the total destruction of OH (see figure 4.12). Note that these are the reactions suggested by Komuro et al [5] to cause a recycling of the lost OH in the afterglow of a streamer discharge in air as mentioned in the introduction. In addition Magne et al [10] have shown that O, H and HO₂ play an important role in the production of OH in a nanosecond pulsed discharge in a N₂-O₂ mixture (5% O₂) containing ethane or ethene.

To illustrate the effect of O(^1)D, its initial density is assumed to be 1 order of magnitude smaller than the initial O density (see figure 4.10). The influence of O(^1)D is shown in figures 4.10 and 4.13. When the O(^1)D) density is increased, the OH density is reduced towards the end of the plasma cycle. As follows from reactions O1-O3, O is produced by O(^1)D), which increases the quenching of OH on longer time scales. Since the lifetime of O(^1)D) is approximately 1 μs, the O(^1)D) is not directly responsible for the observed increase in production of OH in the far afterglow.

Note that long lived molecular metastables such as O₂(a) are not included in the model, as their internal energy is not sufficient to play a role in H₂O dissociation. No other indirect reactions of molecular metastables involved with OH production are reported in literature.

As the key reaction R5 is strongly temperature dependent, figure 4.14 illustrates the sensitivity of the increase in OH density in the late afterglow on the gas temperature. Note that in the calculations the temperature is assumed to be constant during the afterglow. As temperature gradients in both time and space are present as experimentally observed, one indeed expects different maxima during different times at different locations (see figure 4.5). The presented zero-dimensional model captures the main chemistry which can explain the increase in OH, but a detailed
Chapter 4: He-H₂O-O₂ mixtures

Figure 4.11: Modelled species densities of OH and its by-products for the case of He + 0.1% H₂O without (upper figure) and with (lower figure) 0.1% O₂ at T = 350 K. The initial conditions are n⁰_{OH} = n⁰_H = 1.5 \cdot 10^{21} \text{ m}^{-3} and in the case of 0.1% O₂, n⁰_O = 1 \cdot 10^{22} \text{ m}^{-3}.
Figure 4.12: Total rates of the modelled production and loss processes of OH for the case of He + 0.1% H₂O without (upper figure) and with (lower figure) 0.1% O₂. The conditions are the same as in figure 4.11.
2-dimensional self-consistent model is necessary to capture all the details. It is not possible to fit the spatially averaged OH density (the total LIF intensity in figure 4.6), as it is affected by density gradients and diffusion, which are not included in the zero-dimensional model.

### 4.5 Conclusion

The high-density mode in He + 0.1% H₂O is investigated for various additions of O₂ ranging from 0.05 to 2%. The gas temperature and electron density are found not to depend significantly on the added O₂ concentration in the investigated range. In the early afterglow the time and spatially resolved OH density are qualitatively the same as when no O₂ is added, with maximum OH densities on the edge of the plasma filament. In the far afterglow, however, a substantial increase is observed in the total OH density. The time resolved OH density is simulated with a zero-dimensional model taking into account the main production and loss processes of OH, including O and O(¹D) related processes. It is found in the model that OH is strongly quenched by O (by a reaction which creates H and O₂). This causes a temporary reduction in the destruction of OH and production of H, HO₂ and H₂O₂. The higher HO₂ concentration leads to production of OH in reactions R12 and R18.

The zero-dimensional model allows to capture the key chemistry, but as temper-
Figure 4.14: Measured and modelled time resolved OH density in the far afterglow, calculated for different gas temperatures. The initial conditions are $n_{\text{OH}}^0 = n_H^0 = 1.5 \times 10^{21} \text{ m}^{-3}$, $n_O^0 = 1 \times 10^{22} \text{ m}^{-3}$.

Temperature gradients, species density gradients and diffusion are not included in the zero-dimensional model, a 2-dimensional self-consistent model is necessary to explain the observed behaviour in full detail. This is however outside the scope of this work.
Chapter 4: He-H$_2$O-O$_2$ mixtures
References


Chapter 5

N₂ and N₂-H₂O mixtures

Abstract

In this chapter, nanosecond pulsed discharges in N₂ and N₂ with small additions of H₂O at atmospheric pressure are studied with time resolved imaging, optical emission spectroscopy, Rayleigh scattering and LIF on OH. A 170 ns high voltage pulse is applied across two pin-shaped electrodes at a repetition frequency of 1 kHz. The discharge consists of three phases: an ignition phase, a spark phase and a recombination phase. During the ignition phase the emission is mainly caused by molecular nitrogen (N₂(C−B)). In the spark phase N and N⁺ emission is observed, while during the recombination phase mainly N emission is observed. The emission when H₂O is added is very similar, except for the small contribution of H₂ and the intensity of the molecular N₂(C−B) emission is less.

The gas temperature during the ignition phase, obtained from N₂(C−B) emission, is about 350 K. During the discharge the gas temperature increases and is equal to 750 K 1 μs after ignition. The temperature obtained from LIF is lower, since the maximum LIF intensity is located outside the core of the plasma channel. The electron density is obtained by the broadening of the N emission line at 746 nm and, if water is added, the H₂ line. The electron density reaches densities up to 4 \cdot 10^{24} \text{ m}^{-3}. Addition of water has no significant influence on the measured gas temperature and electron density.

OH densities are determined with LIF and studied for N₂ discharges with varying water concentration. A remarkable increase in OH density is found in the far afterglow and is discussed in analogy with the pink splash or pink afterglow.

Chapter 5: \( \text{N}_2 \) and \( \text{N}_2-\text{H}_2\text{O} \) mixtures

5.1 Introduction

Various properties of NRP discharges have already been reported in literature. The electron density in a NRP discharge (spark regime) in preheated air at atmospheric pressure has been studied by e.g. Pai et al [49] with spatially and time resolved OES. They produced the discharge by applying short voltage pulses (7-8 kV) of 10 ns with a repetition frequency of 30 kHz across two pin electrodes. They found that the spark generates a spatially homogeneous emission of \( \text{N}_2 \) (C-B) and \( \text{N}_2^+ \) (B-X). Further it was demonstrated that a spark can form without a streamer if repetitive pulsing is used. They reported electron densities, obtained from the conduction current, between \( 10^{21} \) and \( 10^{22} \) m\(^{-3}\).

Janda et al [29] studied the electron density in a self-pulsing DC transient spark discharge in atmospheric pressure air. The activity of this transient spark discharge is comparable to NRP discharges. Using a detailed analysis of the electrical circuit they found a maximum electron density of \( 10^{22} \) m\(^{-3}\). From Stark broadening of \( \text{H}_\alpha \) an electron density of \( 10^{24} \) m\(^{-3}\) is found. A reason for this discrepancy is not reported.

In [56, 57] the densities of atomic oxygen, metastable \( \text{N}_2 \) (A), \( \text{N}_2 \) (B) and \( \text{N}_2 \) (C) determined by LIF, cavity ring down spectroscopy (CRDS) and OES are reported in a similar NRP discharge as in [49]. They found densities of the order \( 10^{24} \) m\(^{-3}\) for O, \( 10^{21} \) m\(^{-3}\) for \( \text{N}_2 \) (A), and \( 10^{23} \) m\(^{-3}\) for \( \text{N}_2 \) (B) and \( \text{N}_2 \) (C). However getting a complete understanding of the radical production in this discharges is difficult as the electron density, electron temperature and gas temperature are not accurately known.

The goal of this chapter is to gain insight in the plasma parameters (such as the electron density and the gas temperature) of a NRP spark discharge in \( \text{N}_2 \) as a first step towards understanding the plasma kinetics and \( \text{OH} \) radical formation. The experiments are performed in room temperature \( \text{N}_2 \) and \( \text{N}_2-\text{H}_2\text{O} \) mixtures. The addition of \( \text{H}_2\text{O} \) also allows to investigate the line broadening of the hydrogen Balmer lines. In applications, the plasma will often be in an air environment. However, for reducing the complexity, the experiments in this chapter are conducted in \( \text{N}_2 \) without the addition of \( \text{O}_2 \). Chapter 4 deals with the effects of \( \text{O}_2 \)-chemistry on \( \text{OH} \) formation. Time resolved optical emission spectroscopy and Rayleigh scattering are used to obtain the electron density and gas temperature in the discharge. Significantly higher electron densities are found than in similar studies on this type of discharge [2, 29, 39, 48, 49, 56, 57, 59]. The discrepancies and the different methods used will be discussed in detail.

In the next section the experimental setup is described and the methods to determine the gas temperature and electron density are explained. In section 5.3 the experimental results are presented, which include imaging, Rayleigh scattering, line broadening and \( \text{OH} \) LIF. A more detailed analysis of the plasma kinetics is given by the analysis of the time resolved emission intensities (section 5.3.4).
Section 5.4 deals with the LIF results and the analysis of the OH kinetics.

## 5.2 Experimental methods

The discharge is created between two needle electrodes made of tungsten. The distance between the needles is approximately 2 mm. To ensure the purity of the introduced gas the electrodes are placed in a vacuum vessel (the volume is about 8 l), see figure 5.1. The vessel is pumped down and filled with the investigated gas mixture (two times) before starting the experiment to reduce impurities. During the experiment we have a continuous flow of 2.1 l min$^{-1}$. Water vapour is added by bubbling part of the N$_2$ flow through water. To calculate the water concentration it is assumed that the N$_2$ is saturated with water at the laboratory temperature.

High voltage pulses with a width of 170 ns and a repetition frequency of 1 kHz are applied to the upper electrode. The pulses are created with a DEI PVX-4110 pulser triggered by a signal generator and fed with a DC voltage of 9 kV. The signal generator also triggers a delay generator which is used to time align the laser pulse, the iCCD camera and the plasma. The rise time of the HV pulse is about 80 ns (from 10-90%), this is a bit larger than given by the manufacturer (60 ns). The drop in the voltage is significantly faster and is about 25 ns. This is because the decay time is determined by the impedance of the plasma, basically the plasma produces a shortcut. The time alignment can be as good as the minimum gate width of the iCCD camera (1.2 ns according to the manual) if the plasma has no jitter. The jitter of the plasma breakdown compared to the trigger pulse is 15 ns and determines the timing accuracy of the setup. The same setup is used in chapters 3 and 4 to perform LIF with a 6 ns laser pulse, and accurate time alignment was achieved on this time scale due to the significantly smaller jitter for
the He-plasma ignition compared to the N\textsubscript{2}-plasma. The resistor of 6 M\textOmega is used to remove the charge from the charged electrode if no discharge occurs and the resistor of 1 k\textOmega in series with the discharge is used to limit the current through the discharge. The voltage across the electrodes and the current are measured with a voltage probe (Tektronix P6015) and current probe (Pearson 2877) as close as possible to the plasma just outside the vessel. The measured current is corrected for the capacitive current during the raising flank of the voltage pulse. To account for the difference in response time of the current (2 ns) and voltage probe (10 ns) the boxcar average of 10 ns is taken of the measured current waveform. The maximum energy delivered to the plasma is estimated by the energy which is stored in the capacity of the system. This capacity is estimated from the capacitive current and is about 25 pF, which results in a maximum input energy of the order of 1 mJ per pulse. The energy input estimated from the voltage and current waveforms is of the same order of magnitude.

To study the emission of the discharge, photos are taken with an iCCD camera (4 Quik E HR camera from Stanford Computer Optics and an Andor DH534 iCCD camera, both with a Nikkor 105 mm f/4.5 UV lens). Optical emission spectroscopy is used to determine the spectrum of the emission. The light of the discharge is collected with an optical fibre, which is placed close the plasma. The collected light is mainly coming from the bulk of the discharge, however some emission could be from the region near the electrodes. To measure time resolved emission spectra an iCCD camera (Stanford Computer Optics 4 Quik E SR) is connected to a spectrometer (27.5 cm Acton SpectraPro275). The background noise is reduced by cooling the camera with a Peltier element. Unless stated differently a gate time of 10 ns is used and a spectrum consists of 1000 accumulations. The spectra are corrected for the wavelength dependent sensitivity of the detection system by a calibrated continuum lamp (Oriel Quartz Tungsten Halogen Lamp and Ocean Optics LS-1-CAL-220).

The laser system used to perform LIF on OH is described in chapters 3 and 4. As the linear relation of the LIF signal as a function of laser energy is valid up to a higher laser energy compared to the case of He-H\textsubscript{2}O mixtures, the laser energy used for LIF measurements in N\textsubscript{2}-H\textsubscript{2}O mixtures is higher, about 2.5 \mu J per pulse. The laser pulse duration is slighthly shorter at higher energy, since the laser pulse generated by the pump laser shows less jitter at higher applied laser current. In the case of N\textsubscript{2}-H\textsubscript{2}O, the measured laser pulse duration is about 5 ns.

5.2.1 Gas temperature

The rotational temperature from the N\textsubscript{2}(C-B)(0-0) band is determined by fitting experimental spectra with a program developed by Laux \textit{et al}, called Specair [38]. Due to the fast rotational energy transfer in atmospheric pressure discharges the rotational temperature is mostly equal to the gas temperature [39].

Another method which is used to determine the gas temperature is Rayleigh
scattering. An EdgeWave laser (IS6II-E) produces a beam with a wavelength of 532 nm. A diaphragm and a slit are inserted to reduce the amount of scattered light originating from the electrodes, see figure 5.1. A camera (4 Quik E SR) is used to detect the Rayleigh signal. In front of the lens of the camera a 532 nm interference filter (FWHM = 1 nm) is placed to remove most of the plasma emission during the Rayleigh measurements. The gas density is proportional to the intensity of the Rayleigh scattering. Assuming that the pressure is constant, this leads to an inversely proportional dependence of the gas temperature with the Rayleigh scattering intensity

\[
\frac{T_{\text{plasma}}}{T_{\text{reference}}} = \frac{n_{\text{plasma}}}{n_{\text{reference}}} = \frac{I^R_{\text{plasma}}}{I^R_{\text{reference}}}. \tag{5.1}
\]

As a reference the plasma off for room temperature N\textsubscript{2} at 1013 hPa is taken. In addition it is assumed that the gas composition is not drastically changed and that the N\textsubscript{2} molecules are the dominant species causing the Rayleigh signal.

A third method which is used to determine the gas temperature is excitation LIF. This method is described in chapter 3.

### 5.2.2 Electron density

The electron density is determined from the line broadening of spectral emission lines. In general the width of an emission line is influenced by Lorentzian (natural, resonance, van der Waals and Stark) and Gaussian (Doppler and instrumental) broadening.

**Stark broadening** For H\textsubscript{α} the Stark broadening is calculated by Gigosos *et al* [21]. Gigosos introduces a different reduced mass, \(\mu^*\), which simulates a plasma which is not in thermal equilibrium (\(T_e \neq T_g\)): 

\[
\mu^* = \mu \cdot \frac{T_e}{T_g}, \quad \mu \approx 1
\]

For an electron temperature of 10 000 K and \(\mu^* = 10\) (\(T_g = 1000\) K), the FWHM due to Stark broadening \(\Delta \lambda_{\text{Stark}}\) (nm) is:

\[
\Delta \lambda_{\text{Stark}} = 8.33 \cdot 10^{-3} \left( \frac{n_e}{10^{22}} \right)^{2/3}, \tag{5.2}
\]

where \(n_e\) is the electron density (m\(^{-3}\)). This formula is obtained from the results in the tables of [21]. The broadening is 0.8 mm for \(n_e = 10^{23}\) m\(^{-3}\), \(T_e = 10000\) K and \(T_g = 1000\) K. Since both the electron and gas temperature are not accurately known during the discharge, an error is induced on the electron density determined from Stark broadening. This error is estimated in section 5.3.3.

The quadratic Stark broadening for atomic (N) lines is given by Griem [24]:

\[
\Delta \lambda_{\text{Stark}} = \left[ 1 + 1.75a \left( \frac{n_e}{10^{22}} \right)^{1/4} (1 - 0.75r) \right] w \left( \frac{n_e}{10^{22}} \right), \tag{5.3}
\]
where \( a \) is the ion broadening parameter, \( w \) is the electron-impact width (m) and \( r \) is the Debye shielding parameter [24]. The \( a \) and \( w \) are tabulated in Griem [24] and are 0.035 and 4.75 pm respectively for the nitrogen line at 746 nm for an electron temperature of 10000 K. Konjević [37] has listed the ratio between the measured Stark broadening and the theoretical Stark broadening parameters listed by Griem. For the 746 nm line of N the ratio is:

\[
\frac{\Delta \lambda_{\text{meas}}^{\text{Stark}}}{\Delta \lambda_{\text{theory}}^{\text{Stark}}} = 1.197 - 2.97 \cdot 10^{-5} T_e. \tag{5.4}
\]

So the actual Stark broadening is:

\[
\Delta \lambda_{\text{Stark}}^{\text{meas}} = \left[ 1.197 - 2.97 \cdot 10^{-5} T_e \right] \cdot 
\left[ 1 + 1.75a \left( \frac{n_e}{10^{22}} \right)^{1/4} (1 - 0.75r) \right] w \left( \frac{n_e}{10^{22}} \right). \tag{5.5}
\]

For an electron density of \( 10^{23} \) m\(^{-3} \) and an electron temperature of 10000 K, the broadening is 0.09 nm.

**Van der Waals broadening**  In [15] an expression for van der Waals broadening \( \Delta \lambda_{\text{vdW}} \) (m) is given:

\[
\Delta \lambda_{\text{vdW}} = 2.06 \cdot 10^{-13} \lambda_0^2 \left( \alpha R^2 \right)^{2/5} \left( \frac{T_g}{\mu} \right)^{3/10} N_n, \tag{5.6}
\]

where \( \alpha \) is the polarizability of the perturber (1.8 \( \cdot \) 10\(^{-30} \) m\(^3 \) for nitrogen gas [7]), \( \mu \) is the reduced mass (kg), \( N_n \) is the neutral number density (m\(^{-3} \)) and \( R^2 \) is the difference between the values of the square radius of the emitting atom in the upper \( u \) and lower level \( l \). The van der Waals broadening (nm) of H\(_\alpha\) is:

\[
\Delta \lambda_{\text{vdW}} = 0.10 \cdot \frac{p}{(T_g/300)^{0.7}}, \tag{5.7}
\]

and for nitrogen at 746 nm:

\[
\Delta \lambda_{\text{vdW}} = 0.037 \cdot \frac{p}{(T_g/300)^{0.7}}, \tag{5.8}
\]

where \( p \) is the pressure (bar). At room temperature and atmospheric pressure this results in a broadening of 0.1 nm for H\(_\alpha\) and 0.04 nm for N.

The instrumental broadening Gaussian FWHM is measured with a low pressure mercury/argon Pen-Ray light source (linewidth \( \approx \) 1 pm) and is 0.19 nm.

Natural, resonance and Doppler broadening \( (T_g < 1000 \text{ K}, \text{ see further}) \) are smaller than 5 pm and can therefore be neglected in our conditions [39].
Fitting procedure  Since the width of the $H_n$ line is always larger than 1 nm and the line is well fitted by a Lorentzian profile, the electron density is obtained by $\Delta \lambda_{\text{Stark}} = \Delta \lambda_{\text{meas}} - \Delta \lambda_{\text{vdW}}$.

The broadening of $N$ is smaller and the instrumental broadening becomes significant in the recombination phase. In this case the deconvolution to obtain the Stark FWHM is made by the following approximative formula [11]:

$$\Delta \lambda_{\text{meas}} = \frac{\Delta \lambda_{\text{Stark}} + \Delta \lambda_{\text{vdW}}}{2} + \sqrt{\frac{(\Delta \lambda_{\text{Stark}} + \Delta \lambda_{\text{vdW}})^2}{4} + \Delta \lambda_{\text{instr}}^2}.$$  \hspace{1cm} (5.9)

### 5.2.3 Absolute OH density calibration

Absolute calibration measurements are performed with the Andor camera, without filter. The LIF signal of OH is calibrated using Rayleigh scattering and a collisional transfer model, this method is described in detail in chapter 2.

### 5.3 Results and Discussion

#### 5.3.1 Emission

The discharge can be divided into three phases. The voltage across the electrodes increases during the first 100 ns, while the current is small (see figure 5.3). This is the ignition phase of the discharge. In this phase an ionization channel is formed between the electrodes. If the conductivity of this channel is high enough, the voltage collapses and the current increases up to a few Amps and a spark is formed (spark phase). After 200 ns the current decreases as the power source is switched off and the plasma starts to recombine (recombination phase).

Time resolved images of the discharge are shown in figure 5.2. The images are an accumulation of 1000 discharges, except the figure at $t = 65$ ns, this is an accumulation of 2 discharges, which allows to observe the filamentation. Since the gate time (10 ns) is smaller than the plasma jitter (15 ns), an overlap between the images in figure 5.2 is not excluded. However, when looking at the images at 25 ns and 35 ns, the influence seems marginal since we do not see any emission of the (saturated) image at 35 ns in the image of 25 ns. Furthermore, the mentioned jitter is on the breakdown of the discharge, so before 100 ns the resolution is better than 15 ns. To be able to study the morphology of the discharge, the gain cannot be kept constant since the emission intensity changes more than 4 orders
Figure 5.2: Images (in false colours) of the emission of the nitrogen plasma at different delay times. The time indicated corresponds to the time axis in figure 5.3. The emission is accumulated over 1000 discharges, except for $t = 65$ ns only 2 discharges are accumulated. Note that the gain is not kept constant so no conclusion on relative intensities can be made from these images. The image at $t = 35$ ns is overexposed, however it clearly shows the increase in intensity of the discharge. The pictures are made with the 4 Quik E camera.

From figure 5.2 one can see that the discharge starts at the (upper) positive electrode. At the anode a cloud is formed which travels towards the cathode. This behaviour has also been observed previously by e.g. Briels [10] at reduced pressure. The emission of the discharge is still low at this point (see figure 5.3).

Experiments and simulations on the emission of a NRP streamer/glow discharge in a pin-to-pin electrode configuration are performed in [13, 55, 59]. Here it is also observed that the discharge starts at the anode and moves towards the cathode. Further they found that at the start of the discharge also some emission is present at the cathode, however it is less intense than at the anode. From the model, this emission is explained by the development of a weak negative streamer [13]. In our case this emission cannot be observed directly at the start of the discharge, however at 25 ns (just before the positive and negative streamers connect) we indeed observe emission at the cathode side.

After 35 ns filaments start to develop, at $t = 65$ ns multiple filaments are visible in figure 5.2. The filaments indicate that the discharge is constricted, which results in an increase in the current. This increase in the current cannot be seen in figure 5.3, probably because the increase is too small to be measured by the 8-bit digitizer of the oscilloscope. At this point the intensity of the discharge has increased by several orders of magnitude (figure 5.3).
5.3: Results and Discussion

Figure 5.3: Relative intensity of the emission obtained from images as shown in figure 5.2, which are all rescaled to a gain of 900.

Figure 5.4: Images (in false colours) of the emission of the nitrogen plasma at microsecond time scales. The emission is accumulated over 1000 discharges. The images are made with the Andor camera at maximum gain and a gate width of 30 ns.

The emission is homogeneously distributed during and after the current pulse (after 100 ns). To check whether this homogeneous distribution is caused by the accumulation of 1000 discharges, images were taken after 100 ns where only 2 discharges were accumulated (not shown in figure 5.2). These pictures also show a homogeneous distribution. The most intense emission is coming from the region near the cathode and this emission seems to spread during the afterglow on a time scale of tens of microseconds (see figure 5.4). This indicates that in the axial direction a gradient in the density of metastables or ions (and electrons) is present. The relative spatially integrated intensity of the images in figure 5.4 is shown in figure 5.5. Note the levelling off in the emission between 10 and 100 μs. This resembles the observation of increased emission in the far afterglow in a N₂ discharge by Akishev et al called pink splash [4], which shows similarities with the so-called pink afterglow found in low pressure plasmas (see also further). The images of the discharge in N₂ + 0.9% H₂O are very similar and therefore not presented.

The overview spectra of pure nitrogen are given in figure 5.6. Due to the relative low sensitivity of the spectrometer at shorter wavelengths, the noise between 300
and 400 nm is relatively large in the spark and recombination phase.

The spectra show clearly the emission from N₂(C-B), second positive system (SPS), in the range 300-450 nm and the N₂(B-A), first positive system (FPS), in the range of 600-850 nm. The N₂⁺(B-X), first negative system (FNS), has a spectral band at 391 nm, which is clearly visible in the spectrum recorded with a higher resolution. Other lines that are observed originate from excited N and N⁺. Emission from impurities (such as the O emission line at 777 nm) is not observed.

The emission is very similar when water is added, this is because the concentration of water (10²³ m⁻³) is smaller than or comparable to the electron density (see further). Therefore the plasma emission is still dominated by nitrogen. There are also some differences if water is added, of which the main differences are discussed below. First of all the emission of molecular nitrogen, compared to atomic emission, is less strong when water is added to the nitrogen gas. The addition of 0.9 % water increases the collisional quenching rate of N₂(C) by 30 % (so the lifetime of N₂(C) goes from 27 ns to 3.4 ns) [50]. Due to the quenching effect of water, the excited nitrogen states are more lost without radiation. This causes the decreased intensity of molecular nitrogen emission. The first positive system of nitrogen is not visible at all in this case.

Due to the addition of water, emission of hydrogen and NH(A-X) become visible. The H_β line is only visible during the ignition phase of the discharge. The wings of the H_α line are overlapping with the N⁺ lines, which is taken into account in the fitting procedure. During the ignition phase the N⁺ lines are too strong compared to the H_α line to discern the H_α line.

Figure 5.5: Relative intensity in the far afterglow, as obtained from images as shown in figure 5.4.
5.3: Results and Discussion

Figure 5.6: Overview emission spectra of the N\textsubscript{2} plasma during the ignition phase (upper figure), the spark phase (middle figure) and the recombination phase (bottom figure). Each spectrum consists of 1000 accumulations. The atomic emission lines are identified with the use of Lofthus [42] and the NIST database [52].
Chapter 5: \( \text{N}_2 \) and \( \text{N}_2\text{-H}_2\text{O} \) mixtures

5.3.2 Gas temperature

The gas temperature can be determined from the SPS of nitrogen only in the ignition phase, since only in this phase molecular nitrogen emission is visible. The measured gas temperature between 65 ns and 95 ns after the start of the voltage pulse is constant and is \((350 \pm 50)\) K in pure \( \text{N}_2 \). For the Rayleigh measurements no significant dip in the intensity is observed in the ignition phase, which indicates that the gas temperature is indeed close to room temperature.

After the discharge is switched off, the temperature is determined by Rayleigh scattering and excitation LIF (see figure 5.7). During the spark phase of the discharge the gas temperature could not be accurately measured since the emission intensity of the discharge is too high compared to the Rayleigh and LIF signal, in spite the fact that bandpass filters were used. During the recombination phase of the discharge the temperature measured from Rayleigh scattering is about 750 K. This could be due to heating of the gas when the plasma is on by elastic collisions between electrons and \( \text{N}_2 \). If all the energy of the applied voltage pulse (1 mJ) is converted into gas heating of the plasma volume, the gas temperature would be 1100 K. However, the impulse transfer rate of elastic collisions between electrons and neutrals is about \( k_{\text{elas}} = 6 \cdot 10^{-14} \text{ m}^3\text{s}^{-1} \) [26]. The rate of energy transfer is \( k_{\text{energy}} = 2m_e k_{\text{elas}}/m_{\text{neutrals}} \approx 2 \cdot 10^{-18} \text{ m}^3\text{s}^{-1} \). With an electron density of the order of \( 10^{24} \text{ m}^{-3} \) (see also further), the energy transfer time is about 0.5 \( \mu \)s. Note that at such high electron densities Coulomb collisions are dominant and elastic collisions between electrons and neutrals will contribute marginally to the plasma heating.

The rotational temperature determined from excitation LIF is almost a factor of 2 lower than the gas temperature determined from Rayleigh scattering. This can be explained by the fact that the Rayleigh temperature is determined in the centre of the plasma channel, while the temperature from excitation LIF is determined in the area where the LIF emission is maximal, which is outside the plasma channel. In figure 5.8 the temperature profile obtained from Rayleigh scattering and the LIF intensity profile are shown for \( t = 2 \mu \text{s} \). At the position where the LIF signal is at its maximum, the gas temperature obtained from Rayleigh scattering is about 550 K. This corresponds, within the margin of error, to the temperature obtained from excitation LIF, which is 500 K.

The elevated gas temperature in the core of the discharge channel at large time scales (10 \( \mu \text{s} \)) has also been observed by Ono and Oda [48] in pulsed corona discharges in a \( \text{N}_2\text{-O}_2\text{-H}_2\text{O} \) mixture. They explained the elevated gas temperature by energy transfer from vibrationally excited molecules to kinetic gas energy (vibrational to translational energy transfer V-T), which is fast if \( \text{O}_2 \) is present. The V-T rate for nitrogen and water is rather small and too slow to explain the heating in the current study [20].

Mintoussov \textit{et al.} [46] also observed an elevated temperature after the discharge. Their experiments have been performed in air at low pressure (10 mbar). They
5.3: Results and Discussion

Figure 5.7: The gas temperature of the discharge as function of time in pure N\textsubscript{2} and N\textsubscript{2} + 0.9\% H\textsubscript{2}O as obtained by OES, excitation LIF and Rayleigh scattering. The voltage and current waveforms are also shown.

explained the heating of the gas by quenching of excited molecular nitrogen and electron-ion recombination processes of N\textsuperscript{+}. The time scales for these processes are of the order of 10 ns. Via several collisions the energy is then transferred to kinetic energy. This can explain the elevated temperature in the current experiment, especially in view of the large electron density.

The gas temperature in a N\textsubscript{2}-H\textsubscript{2}O discharge is similar within the margin of error.

5.3.3 Electron density

The electron density is estimated from the linewidth of a N line at 746 nm and the H\textsubscript{α}-line as described in section 5.2.2. In figure 5.9, two examples of the line broadening of the N and H\textsubscript{α} lines at 125 ns are shown. The measured line is fitted with a Lorentzian line shape. The FWHM are indicated in the figures. The electron density as function of time is given in figure 5.10. A typical value of the electron temperature in a thermal atmospheric pressure plasma with a high electron density is 15 000 K \cite{9}. Due to reactions of electrons with vibrationally excited N\textsubscript{2} in the afterglow the electron temperature normally follows the vibrational temperature rather than dropping immediately to the gas temperature \cite{5, 22, 25}. Therefore an electron temperature of 10 000 K is assumed in the spark and recombination phase and since \( T_e > T_g \) 2500 K is taken as a lower estimate of \( T_e \). The gas temperature is about 1000 K, see section 5.3.2.
To estimate the error in the electron density determined from Hα due to the assumption that $T_e = 10000$ K, the electron density has also been determined for $T_e = 2500$ K ($T_g = 1000$ K) and $T_e = 20000$ K ($T_g = 2000$ K, as in [21] no data is reported for $T_g = 1000$ K). Also in the current experiment the gas temperature is not known in the time interval where the electron density is determined. To estimate the error including the uncertainty in $T_g$, the electron density is determined for $T_g = 2000$ K ($T_e = 10000$ K). Both effects result in a total error of not more than 25%. The same procedure has been used to estimate the error on the electron density determined for the N-line. The error due to $T_e$ is in this case 35%. There is no data available to estimate the error induced by the uncertainty in $T_g$ in this case.

The measured electron densities in a pure N$_2$ plasma and in a discharge in N$_2$ + 0.9 % H$_2$O are of the order of $10^{24}$ m$^{-3}$ and correspond within the margin of error. The highest electron density is found, within the margin of error due to the jitter, at the start of the current pulse. The obtained maximum electron density is $4 \times 10^{24}$ m$^{-3}$. The maximum ionization degree is 50%, assuming a gas temperature of 1000 K and a pressure of 1 bar in the spark phase. Due to the discharge the pressure in the plasma can increase to about 3 bar (no gas expansion), this results in a maximum ionization rate of 16%. So the ionization degree locally in the filament during a few tens of nanoseconds is 16-50%, which is unusually high.

To check the assumption that the broadening is mainly due to the Stark effect, the contribution of additional broadening mechanisms is estimated. First, the influence of an external electrical field is estimated. The broadening of Hα due to an external electrical field (assuming that the maximum E-field is 80 kV cm$^{-1}$)
5.3: Results and Discussion

(a) Line profile of the N (triplet) line at 746 nm in a pure nitrogen discharge at 125 ns after the start of the voltage pulse.

(b) Line profile of the H\textalpha{} line in a nitrogen with 0.9 % water vapour discharge at 122 ns after the start of the voltage pulse. The spectrum of N is subtracted from the spectrum of H\textalpha{} and N, to obtain only the H\textalpha{} line profile.

Figure 5.9: Examples of fits (Lorentzian profile) of the N- and H\textalpha{}-line spectra.

Figure 5.10: The electron density versus time in a discharge in N\textsubscript{2} and in N\textsubscript{2} with 0.9 % H\textsubscript{2}O.
is negligible compared to the observed line profile [1], it is assumed that this also holds for the atomic nitrogen line.

Another possible additional contribution to the broadening is that the van der Waals broadening is underestimated since it is assumed that the pressure remains constant at 1 bar. Due to the discharge the pressure in the plasma channel can increase for a short time, thereby increasing the van der Waals broadening. However to explain the observed broadening only by van der Waals broadening a pressure of 60 bar is needed. If the temperature increases from 350 K to 1000 K and if it is assumed that the density of neutral particles stays the same, the van der Waals broadening increases only by a factor 1.4, which is not significant. In case of significant dissociation the density can be increased with a maximum of a factor of 2, which leads to a van der Waals broadening which is maximum 3% of the experimentally obtained broadening.

A possible broadening mechanism which has not been taken into account is self-absorption. As the discharge has a diameter of only 0.2 mm, the effect of self-absorption on the electron density is less than 5% for N (assuming the N density equals \(2.5 \cdot 10^{25} \text{m}^{-3}\)). For H\(_{\alpha}\) the effect of self-absorption is even smaller.

As both H\(_{\alpha}\)-broadening and N-broadening yield comparable electron densities, it is unlikely that the formation processes of H\((n = 2)\) and N\((4S)\) will determine the broadening (e.g. in fragmentation processes in which a large kinetic energy is given to the fragments). In addition, the profile would likely be a Gaussian profile, and Czarnetzki et al [16] and Pu et al [63] have found similar large electron densities for comparable plasma conditions.

From the electron density \(n_e (\text{m}^{-3})\) and current density \(J (\text{A m}^{-2})\), the electric field during the spark phase can be estimated. The current density is:

\[
J = \frac{I}{A} = \sigma E = \frac{n_e e^2}{m_e} \nu_c E, \quad (5.10)
\]

where \(I\) is the current (A), \(A\) is the area through which the current flows (m\(^2\)), \(\sigma\) is the conductivity (\(\Omega^{-1} \text{m}^{-1}\)), \(\nu_c\) is the collision frequency (s\(^{-1}\)) and \(E\) is the electric field (V m\(^{-1}\)). In a plasma with a high ionization rate the collisions are dominated by electron-ion collisions and the collision frequency is then [8]:

\[
\nu_c = \nu_{ei} = \frac{n_e e^4 \ln \Lambda}{18\sqrt{2\pi} \varepsilon_0 \sqrt{m_e (k_B T_e)^3/2}}, \quad (5.11)
\]

where \(\ln \Lambda\) is the Coulomb integral [8]:

\[
\ln \Lambda = \ln \left(\frac{12\pi (c_0 k_B T_e)^{3/2}}{n_e^{1/2} e^3}\right). \quad (5.12)
\]

The current at \(t = 140\ \text{ns}\) is approximately 8 A, the plasma width is about 0.2 mm and the electron density is of the order of \(10^{24} \text{m}^{-3}\). The electric field obtained
from the above formula is about $30 \text{kV m}^{-1}$, corresponding to a voltage across the electrodes of approximately 65 V. This is consistent with the measurement, which indicates that the voltage is smaller than 100 V (see figure 5.11). To check the sensitivity of the electron density to the voltage, we assume that the electron density is 100 times lower. The voltage across the electrodes is then approximately 100 V, which is still consistent with the measurement (see figure 5.11). If the electron density is high, it is only present in equation 5.10 in the logarithm ($\ln\left(\frac{n_e - 1}{2}\right)$), so the current density is rather insensitive to changes in the electron density. Hence we can conclude that, at high electron densities, current density measurements are not accurate enough to determine the electron density.

From all of the above, we can conclude that the measured broadening is dominated by Stark broadening.

The obtained electron densities are significantly larger than found in literature by conductivity (current) measurements of very similar discharges [30, 49]. Pai et al [49] determined the electron density from the plasma current. In their calculations only electron-atom collisions are taken into account. Not including electron-ion collisions could result in an underestimation of the electron density. However it must be noted that the plasma on-time is smaller in the case of Pai et al, and as a consequence the electron density most likely does not reach the large values as in the current study. The line broadening of $H_a$ reported by Janda et al [30] is very similar to the one observed in the discharge presented in the current chapter. Janda et al [30] also determined the electron density from the conductivity $\sigma_p$ of the plasma:

$$n_e \propto \sigma_p \cdot \nu_c,$$

where $\nu_c$ is the collision frequency. They however used the collision frequency for discharges with a small ionization degree [28], which for an ionization degree larger than $10^{-3}$ leads to an underestimation of the collision frequency, and thus of the electron density as outlined above.

Note that, when estimating the energy necessary to obtain this large electron density with the plasma volume calculated from the FWHM of the plasma (200 µm), an energy of the same order of magnitude as the estimate of input energy is obtained. However the filamentation of the discharge (see figure 5.2) causes that the effective volume in which the discharge reaches this large electron density is significantly smaller than computed from this estimate of the volume. This allows for the additional losses in energy by (vibrational) excitation and dissociation.

### 5.3.4 Plasma kinetics as obtained from OES

To study the plasma kinetics the peak intensity of the most intense spectral lines as function of time is shown in figure 5.11. In the ignition phase of the discharge the emission is coming from the FPS, SPS and FNS of nitrogen. Due to the high
electron temperature, the excited states $N_2$(C), $N_2$(B) and $N_2^+$(B) are created by direct electron impact. Note that $N_2$(C) can also be created via a pooling reaction if the metastable density is large [3]:

$$N_2(A) + N_2(A) \rightarrow N_2(X) + N_2(C), \quad (5.14)$$

and $N_2^+$(B) can also be created by vibrational pumping [40]:

$$N_2^+(X) + N_2(X, \nu \geq 12) \rightarrow N_2^+(B) + N_2(X, \nu < 12), \quad (5.15)$$

however, the time scale for these reactions are $> 0.5 \mu s$ if the ion and metastable densities are smaller than $10^{22} \text{ m}^{-3}$ [3, 12]. Shortly (30 ns) after the start of the emission of the FPS, the emission of atomic and ionic nitrogen lines starts to emerge and the emission of molecular nitrogen collapses. The excitation energy of $N$ is larger than of $N_2$, so a drop in the electron temperature cannot explain this behaviour. Clearly, the concentration of atomic nitrogen needs to increase due to dissociation processes, since dissociative recombination of $N_2^+$ yields only 5.8 eV excess energy and can therefore not produce the excited nitrogen atoms responsible for the emission (see table 5.1). A large dissociation degree is consistent with the large electron density (figure 5.10).

During the spark phase of the discharge there is no significant molecular emission. In figure 5.11 it seems that there is emission of the FPS of nitrogen in the spark phase, however this could be partly caused by an overlap between the band of the FPS and atomic nitrogen lines. In the recombination phase only emission of atomic nitrogen lines is visible. This clearly shows that these excited states are produced by recombination processes.

From figure 5.11 the decay time of $N$ in the recombination phase can be determined
Table 5.1: Processes which can create atomic nitrogen in the ground state. The reaction rates and the excess energy of the reactions are obtained from [3], except for the rate for reaction N1, which is obtained from [20].

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
<th>Rate coefficient $k$ (m$^3$ s$^{-1}$, m$^6$ s$^{-1}$)</th>
<th>Excess energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>$N^+ + e \rightarrow N + h\nu$</td>
<td>$3.4 \cdot 10^{-16} T_e^{-3/4}$</td>
<td>$&lt;14.5$</td>
</tr>
<tr>
<td>N2</td>
<td>$N^+ + 2e \rightarrow N + e$</td>
<td>$7 \cdot 10^{-32} (300/T_e)^4.5$</td>
<td>14.5</td>
</tr>
<tr>
<td>N3</td>
<td>$N^+ + N_2 \rightarrow N + N_2$</td>
<td>$6 \cdot 10^{-30} (300/T_e)^{1.5}$</td>
<td>14.5</td>
</tr>
<tr>
<td>N4</td>
<td>$N^+_2 + e \rightarrow 2N$</td>
<td>$1.8 \cdot 10^{-13} (300/T_e)^{0.4}$</td>
<td>5.8</td>
</tr>
<tr>
<td>N5</td>
<td>$N^+_3 + e \rightarrow N_2 + N$</td>
<td>$1.2 \cdot 10^{-12} (300/T_e)^{0.5}$</td>
<td>11.1</td>
</tr>
</tbody>
</table>

by fitting the decay with an exponential function starting at the time when the discharge is switched off. The experimental decay times of N emission at 746 nm and 822 nm are, respectively, $92 \pm 3$ ns and $82 \pm 3$ ns. According to the NIST database [52], the effective lifetimes of the excited states are, respectively, 51 ns and 44 ns. These lifetimes will be even shorter due to collisional quenching. So, even considering the 15 ns jitter, there is a significant production of excited atomic nitrogen after the discharge is switched off. There are several processes which can create atomic nitrogen in the recombination phase when $T_e$ is low. The reactions are listed in table 5.1. The reactions should have enough energy to create an excited N atom in the upper level of the 746 nm and 822 nm transition, which is 12 eV and 11.8 eV, respectively [52]. Only reactions N1 till N3 have enough excess energy.

Assuming that the electron temperature in the afterglow is $T_e = 10000$ K (see section 5.3.3), the rate constants for reactions N1, N2 and N3 are $3.4 \cdot 10^{-19}$ m$^3$ s$^{-1}$, $9.8 \cdot 10^{-30}$ m$^6$ s$^{-1}$ and $3.1 \cdot 10^{-41}$ m$^6$ s$^{-1}$, respectively [3]. To compare the rates of N2 and N3 with the rate of equation N1, the rates are multiplied by the electron density and nitrogen density, respectively. The electron density is of the order of $10^{24}$ m$^{-3}$, see section 5.3.3. The nitrogen density at 750 K and 1 atm is $9.8 \cdot 10^{19}$ m$^{-3}$. This results in rate coefficients of $9.8 \cdot 10^{-15}$ m$^3$ s$^{-1}$ and $3.0 \cdot 10^{-16}$ m$^3$ s$^{-1}$ for N2 and N3, respectively. Therefore reaction N2 is dominant.

Note that the rates for charge transfer:

$$N^+ + 2N_2 \rightarrow N^+_2 + N_2,$$

(5.16)

$$N^+ + N_2 \rightarrow N^+_2 + N$$

(5.17)

(respectively $2.5 \cdot 10^{-16}$ m$^3$ s$^{-1}$ and $10^{-18}$ m$^3$ s$^{-1}$ [3]) and subsequent dissociative recombination (N4 and N5 in table 5.1) are too slow to compete with reaction N2 to cause the $n_e$ decay. As the 3-body electron-N$^+$ recombination reaction is dominant, atomic nitrogen is still produced in the recombination phase.

The measured decay time of the N emission (line at 746 nm) if water is added to the gas mixture is $(120 \pm 3)$ ns. So the decay time is about $30\%$ larger than.
in pure nitrogen. Therefore the source term should be faster if water is added. The reaction N2 in table 5.1 is the dominant source term for excited N atoms, as mentioned before. The gas temperature does not seem to be affected when water is added (see section 5.3.2). A reason could be that the electron density is slightly larger when water is added than in pure nitrogen (see figure 5.10). This will increase the production of N via reaction N2.

The decay of the electron density can be determined from figure 5.10. It can be seen that the decay is linear on the logarithmic scale, so the electron density is governed by the following differential equation:

$$\frac{dn_e(t)}{dt} = -kn_e(t) \Rightarrow n_e = n_e^0 \exp[-k_1(t-t_0)]. \quad (5.18)$$

where \(k_1\) is an effective rate (s\(^{-1}\)). This results in a rate constant \(k_1 = (1.49 \pm 0.08) \times 10^7\) s\(^{-1}\) in a pure N\(_2\) discharge. The time scale for diffusion \(\tau = (R/2.4)^2/D_a\), where \(R = 0.1\) mm is the radius of the plasma channel and \(D_a \approx (1 + T_e/T_i)D_i\) the ambipolar diffusion coefficient. The electron temperature is at maximum 20 times the ion temperature \(T_i\). The ion diffusion coefficient \(D_i\) can be calculated from the ion mobility \(\mu_i\) which can be found in [18] for the N\(^{+}\) ion in N\(_2\), \(D_i = k_B T_i \mu_i/e = 2.5 \times 10^{-5}\) m\(^2\)s\(^{-1}\). So the fastest possible time scale for ambipolar diffusion is 3.5\(\mu\)s, which is 2 orders of magnitude slower than the decay time of the electron density.

Based on the reaction rates (see table 5.1), one would expect that the electron density decays due to electron-ion recombination, which gives the following decay curve (assuming that the ion density is equal to the electron density):

$$\frac{dn_e(t)}{dt} = -k_2n_e^n(t) \Rightarrow n_e(t) = \frac{n_e^0}{\sqrt{1 + 2k_2(n_e^0)^2(t-t_0)}}. \quad (5.19)$$

where \(k_2\) is the reaction rate for electron-ion recombination (m\(^6\)s\(^{-1}\)). The experimental decay could however not be fitted with this decay curve. According to literature \(k_2 = 9.8 \times 10^{-39}\) m\(^6\)s\(^{-1}\) at \(T_e = 10\,000\) K [3]. At the end of the voltage pulse the decay rate would then be \(2 \times 10^9\) s\(^{-1}\) (\(n_e = 5 \times 10^{23}\) m\(^{-3}\)), which is more than 2 orders of magnitude faster than the measured rate. As mentioned above, the jitter is about 15 ns. This results in an error in the decay time of maximum a factor 10, so this cannot explain the slow decay time of the electron density. Another possible explanation is that the electron temperature remains large in the afterglow, which reduces the recombination rate. In order to explain the difference, the electron temperature should be 2.3 eV. This value is however large for a recombining plasma. In conclusion, there is a significant production of electrons during the recombination phase. One hypothesis is that electrons are created by Penning and associative ionization reactions [3, 40, 58], see table 5.2. These ionization processes should take place on a time scale of the order of 100 ns. This means that the density of N\(_2\)(a') should be, considering the different rates as found in literature (see table 5.2), of the order of \(5 \times 10^{22} - 10^{24}\) m\(^{-3}\) and the density of N(\(^2\)P) should be larger than \(2 \times 10^{24}\) m\(^{-3}\), which is of the same order of
5.4: OH radical density

Table 5.2: Penning and associative ionization reactions and their reaction rates.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate coefficient $k$ (m$^{-3}$ s$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N6</td>
<td>$N_2(a') + N_2(a') \rightarrow N_2(X) + N_2^+(X) + e$</td>
<td>$5 \cdot 10^{-17}$</td>
<td>[58]</td>
</tr>
<tr>
<td>N7</td>
<td>$N_2(a') + N_2(a') \rightarrow N_2^+ + e$</td>
<td>$10^{-17}$, $5 \cdot 10^{-17}$, $2 \cdot 10^{-16}$</td>
<td>[3], [4], [42]</td>
</tr>
<tr>
<td>N8</td>
<td>$N(2D) + N(2P) \rightarrow N_2^+(X) + e$</td>
<td>$1 \cdot 10^{-18}$, $10^{-19}$</td>
<td>[4], [58]</td>
</tr>
<tr>
<td>N9</td>
<td>$N(2P) + N(2P) \rightarrow N_2^+(X) + e$</td>
<td>$5 \cdot 10^{-18}$</td>
<td>[58]</td>
</tr>
</tbody>
</table>

magnitude as the electron density, so possible. $N_2(a')$ can for instance be created by recombination of two $N(2D)$ metastables [42]. The slow decrease in $n_e$ and emission intensity after the discharge pulse clearly indicates the large amount of energy which is stored in dissociated N and nitrogen metastables.

5.4 OH radical density

Absolute calibration using Rayleigh scattering

The absolute calibration is performed using Rayleigh scattering, by the same procedure as in chapter 2. The calibration is performed at $t = 2 \mu s$. The conditions for the case of 0.9% H$_2$O are summarized in table 5.3. The used rates for quenching, RET and VET obtained from literature, to calculate the total quenching, RET and VET, are shown in table 5.4. The pumping rate used is approximately $5 \cdot 10^7$ s$^{-1}$. Since the rate for VET in the $\nu' = 1$ level is of the same order of magnitude as the rate for RET (see table 5.3), the latter is taken into account in the LIF model and the 6-level model is used.

To determine the overlap integral, the pressure broadening constant 1.71 for He in equation 2.4 for the collisional broadening of the $P_1(2)$ absorption line is replaced by 6.5 for N$_2$ [32]. The measured laser line profile used for calculation of $\Gamma$ and $\Delta\nu_L$ is the measured laser line profile in He + H$_2$O, since the broadening of the $P_1(2)$ line is less in the case of He, so the accuracy of the laser line profile determination is higher. The overlap function $\Gamma$, calculated from the measured and theoretical laser linewidth, are 0.16 and 0.19 respectively.

The simulated level population fractions are shown in figure 5.12. In this figure the population of the OH(A; $\nu' = 1$) levels decays quickly because of the high total quenching (especially the high VET of N$_2$), the decay is following the laser pulse (see also figure 5.14).
Table 5.3: Total rate constants and parameters used in the 6-level model for the absolute calibration of the OH density in N$_2$ + 0.9 % H$_2$O at $t = 2 \mu$s. The total rates for quenching, VET and RET are calculated as $k^N$ N$_2$ + $k^H$ H$_2$O N$_2$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (K)</td>
<td>450</td>
<td></td>
</tr>
<tr>
<td>$j_B^{\nu'=0,J'=2.5}$</td>
<td>0.147</td>
<td>[44]</td>
</tr>
<tr>
<td>$j_B^{\nu'=1,J'=1.5}$</td>
<td>0.03</td>
<td>[44]</td>
</tr>
<tr>
<td>$\Delta r$ (ns)</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>$\Delta s$ (\mu m)</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>$Q_{00}$ (s$^{-1}$)</td>
<td>5.8 $10^8$</td>
<td>[14]</td>
</tr>
<tr>
<td>$Q_{11}$ (s$^{-1}$)</td>
<td>3.9 $10^9$</td>
<td>[14]</td>
</tr>
<tr>
<td>$V_A$ (s$^{-1}$)</td>
<td>2.3 $10^9$</td>
<td>[14]</td>
</tr>
<tr>
<td>$V_X$ (s$^{-1}$)</td>
<td>2.3 $10^7$</td>
<td>[53]</td>
</tr>
<tr>
<td>$R_{61}$ (s$^{-1}$)</td>
<td>5.2 $10^9$</td>
<td>[31, 33, 34]</td>
</tr>
<tr>
<td>$R_{23}$ (s$^{-1}$)</td>
<td>6.1 $10^9$</td>
<td>[31, 33, 34]</td>
</tr>
</tbody>
</table>

Table 5.4: Total RET rate coefficients estimated at 300 K, total quenching (electronic + vibrational relaxation) rate coefficients for OH(A; $\nu'$ = 0, 1) and vibrational relaxation rate coefficients for inelastic collisions of OH with N$_2$. (For an explanation of the RET rate coefficients see section 2.5.2.)

<table>
<thead>
<tr>
<th>Collisional process</th>
<th>Initial level</th>
<th>N$_2$ (10$^{-17}$ m$^3$ s$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RET</td>
<td>(A; $\nu'$ = 1, $F_1(1)$)</td>
<td>13</td>
<td>[31, 33, 34]</td>
</tr>
<tr>
<td>RET</td>
<td>(X; $\nu'$ = 0, $f_1(2)$)</td>
<td>37</td>
<td>[31, 33, 34]</td>
</tr>
<tr>
<td>Q</td>
<td>(A; $\nu'$ = 0)</td>
<td>2.8</td>
<td>[14]</td>
</tr>
<tr>
<td>Q</td>
<td>(A; $\nu'$ = 1)</td>
<td>23.6</td>
<td>[14]</td>
</tr>
<tr>
<td>VET</td>
<td>(A; $\nu'$ = 1 $\rightarrow$ $\nu'$ = 0)</td>
<td>14</td>
<td>[14]</td>
</tr>
</tbody>
</table>
5.4: OH radical density

Figure 5.12: Simulated population fractions over time, obtained from the 6-level model for \( \text{N}_2 + 0.9\% \text{H}_2\text{O} \).

The measured Rayleigh and LIF intensity as a function of the laser energy per pulse are shown in figure 5.13. When the latter is compared to the LIF intensity as a function of laser energy per pulse in the case of He + 0.84\% \text{H}_2\text{O} (figure 2.16), it is seen that the linear regime in the case of \( \text{N}_2 + 0.9\% \text{H}_2\text{O} \) is valid up to a higher laser energy. This can possibly be explained by a difference in pumping rate \( BI_s \) in He and \( \text{N}_2 \). The experimental overlap integral in He is 0.23, while the experimental overlap integral in \( \text{N}_2 \) is 0.16.

The time resolved fluorescence intensity calculated with the 6-level model is shown in figure 5.14, together with the measured fluorescence. In the case of \( \text{N}_2 \) the fluorescence was too low to record a spectrum of the fluorescence with the Acton spectrometer. The maximum slit width of the Jobin Yvon THR 1000 monochromator is used to measure the time resolved fluorescence of the two vibrational bands of \( \text{OH(A)} \). The spectral resolution of the Jobin Yvon monochromator is in this case 1.3 nm. An OH spectrum with this resolution is simulated with LIFBASE [44] and shown in figure 5.15, the spectral region in which the fluorescence is measured is indicated. The figure shows that the ratio of the measured (1-1) fluorescence to the measured (0-0) fluorescence can be used to scale the total time resolved fluorescence in figure 5.14. Since in \( \text{N}_2 \) VET is fast, most of the measured fluorescence originates from the \( \nu' = 0 \) level. The density obtained in \( \text{N}_2 + 0.9\% \text{H}_2\text{O} \) at \( t = 2\mu\text{s} \) using Rayleigh scattering is \( 4.7 \cdot 10^{20} \text{ m}^{-3} \).
Figure 5.13: Upper figure: Linear fit of the Rayleigh intensity as a function of the energy per pulse times pressure. The inserted image is the recorded Rayleigh signal in N₂ at 300 K and atmospheric pressure. Lower figure: Experimental and calculated LIF intensity as a function of the laser energy per pulse. The inserted image is the recorded LIF signal in N₂ + 0.9% H₂O at t = 2 μs.
Figure 5.14: Experimental and modeled time resolved fluorescence intensity of $(\nu'' = 1 - \nu' = 1)$ and $(\nu'' = 1 - \nu' = 1)$ for $N_2 + 0.9\% H_2O$, $E_L = 6 \mu J$.

Figure 5.15: Spectrum of OH(A−X) simulated with LIFBASE [44] for an instrumental resolution of 1.3 nm and a ratio of (1-1) to (0-0) emission of 0.2 (population OH(A; $\nu' = 1$)=0.27) as obtained from the measured fluorescence. The regions where the time resolved fluorescence in figure 5.14 is measured, are indicated.
Chapter 5: \( \text{N}_2 \) and \( \text{N}_2\text{-H}_2\text{O} \) mixtures

5.4.1 Time and spatially resolved OH density

The OH fluorescence intensity measured in \( \text{N}_2\text{-H}_2\text{O} \) mixtures is much lower compared to the OH fluorescence intensity measured in \( \text{He-H}_2\text{O} \) mixtures. This can be explained by the collisional quenching of OH(A) with \( \text{N}_2 \), which is much more effective than quenching of OH(A) by He. The spatial profile of the LIF signal measured in \( \text{N}_2\text{-H}_2\text{O} \) mixtures shows a dip in the core of the discharge channel, as is also observed in the high density mode in \( \text{He-H}_2\text{O} \) mixtures. In the following sections, the time and spatially resolved OH density is discussed in detail for the discharge in \( \text{N}_2 + 0.9\% \text{H}_2\text{O} \). Finally the effect of the water concentration on the OH density and kinetics is presented.

5.4.2 \( \text{N}_2 + 0.9\% \text{H}_2\text{O} \)

The spatially resolved LIF signal measured at different delay times in \( \text{N}_2 + 0.9\% \text{H}_2\text{O} \) is shown in figure 5.16. Because of the strong light emission of the plasma compared to the LIF signal, the latter could not be obtained before \( t = 350\text{ ns} \), even when using a bandpass filter (313 nm, FWHM = 10 nm). At \( t = 0.52\mu\text{s} \) a broad, more or less Gaussian LIF profile is observed. As the time delay after the pulse increases, a clear dip is observed in the centre.

By summation of 6 pixel rows around the centre line of the laser beam in the images in figure 5.16, radial LIF profiles are obtained as a function of time (see figure 5.17). To lower the noise in these profiles, the profiles are smoothed using the adjacent-averaging method with a moving window of 5 data points (120 \( \mu\text{m} \)). From figure 5.17 it is clear that with increasing time the maxima shift outwards and the width of the peaks gets larger. Note that the laser beam width is about 250 \( \mu\text{m} \), which does not allow to resolve the peaks found in the OH LIF intensity completely. This can cause a partial fill up of the observed LIF intensity in the core due to the spatial convolution of the OH(X) profile and the laser beam. The dip in the LIF profiles is about a factor of 2 smaller than the LIF maxima. Since the population of the \( f_1(2) \) rotational level decreases by a factor of 1.6 when the temperature increases from 450 K to 800 K (the gas temperatures corresponding to \( T_g \) at the maximum of the OH density and in the core of the plasma as obtained by Rayleigh scattering, see figure 5.8) [44], the temperature gradient contributes significantly to the dip observed in the LIF profiles in this particular case. In addition, a lower OH density in the core could also be explained by a higher concentration of N (and N\(^{+}\)) in the core compared to the edge. This would lead to the faster destruction of OH by the reactions [17, 45]

\[
\begin{align*}
\text{N} + \text{OH} & \rightarrow \text{NO} + \text{H} \quad k = 6.9 \cdot 10^{-17} \text{ m}^3 \text{ s}^{-1}, \\
\text{N}^+ + \text{OH} & \rightarrow \text{OH}^+ + \text{N} \quad k = 3.4 \cdot 10^{-16} \text{ m}^3 \text{ s}^{-1}, \\
\text{N}^+ + \text{OH} & \rightarrow \text{NO}^+ + \text{H} \quad k = 3.4 \cdot 10^{-16} \text{ m}^3 \text{ s}^{-1}.
\end{align*}
\]
Figure 5.16: Images of the LIF signal (in false colours) in the plasma filament in \(\text{N}_2 + 0.9\% \text{ H}_2\text{O}\) at different time delays. The width of the images corresponds to a length of 2.7 mm. The images are recorded with the Andor camera with a gate width of 40 ns and 1000 accumulations. The Rayleigh scattering signal is filtered out using a bandpass filter (313 nm, FWHM = 10 nm). \(E_L = (2.5 \pm 0.1) \mu J/pulse.\)
Figure 5.17: Time resolved radial profile of the LIF signal of OH in N$_2$ + 0.9\% H$_2$O at a fixed axial position in the middle of the gap. The profiles are obtained from the images shown in figure 5.16 by summation of 6 pixel rows around the centre line of the laser beam. The zero-level is indicated with a dashed line.

The density of N$^+$ in the core can be estimated from the electron density measured in the core. Around $t = 1$\,µs the measured electron density is of the order $10^{22}$\,m$^{-3}$ (see section 5.3.3). This would result in an N$^+$ density of the same order of magnitude as the OH density measured outside the core (see further), and the OH lifetime would be reduced to 300\,ns or less by this N$^+$ density. A more detailed analysis of the observed depletion of the LIF signal in the core would require a higher spatial resolution.

In figure 5.17, a background of OH fluorescence is present, which slowly decreases with increasing distance from the plasma filament. Since a bandpass filter is used for the LIF signal, no Rayleigh scattering signal is present here. A small asymmetry in the background LIF signal is due to incomplete correction for the inclination of the laser beam in the image. As the diffusion time of OH in N$_2$ for a distance of 2\,mm is longer than the time between two pulses (1\,ms), and this background LIF signal is constant during 1\,ms, the background is due to the OH density which is built up and which reached steady state over many cycles.

The distance from the position of the LIF maximum to the symmetry axis is obtained from the profiles in figure 5.17 as a function of time, and shown in figure 5.18. Because of the low signal-to-noise ratio, the profiles obtained from the images are fitted with a multiple Gaussian peak fit (two profiles for the LIF maxima, and one for the background). Note that also when no dip is observed, the profile is fitted using 3 peaks, since the peak is too broad at the top to be fitted with a Gaussian function for the background and a single Gaussian function.
Figure 5.18: Distance from the position of the LIF maximum to the symmetry axis as a function of time. The experimental conditions are the same as in figure 5.16. The data is fitted with a two-dimensional diffusion relation.

for the LIF maximum. From a linear fit of the distances of the LIF maximum to the centre, obtained between 370 and 770 ns, the speed at which the two LIF maxima move outwards can be calculated. It is found that this speed is 125 m s\(^{-1}\), which is much slower than in the case of helium. Note that the speed of sound in \(\text{N}_2\) at 500 K (the temperature measured by excitation LIF, see figure 5.7) is 456 m s\(^{-1}\). Note that the plasma emission radius measured as a function of time is approximately constant. In addition, in \(\text{N}_2\)-H\(_2\)O mixtures the discharge consists of multiple filaments (see figure 5.2).

The distance from the position of the LIF maximum to the symmetry axis as a function of time shows in first approximation a square dependence. For a 2-dimensional system this can be related to a diffusion process with the relation

\[ \Delta r \approx 2\sqrt{Dt}, \]

(5.23)

where \(\Delta r\) is the radial distance traveled by the maximum. This would lead to an effective diffusion constant of 15 cm\(^2\) s\(^{-1}\). The obtained diffusion constant is large compared to the diffusion of N in \(\text{N}_2\) (0.37 cm\(^2\) s\(^{-1}\) [62]), but is similar to the ambipolar diffusion constant, although at elevated \(T_e\). In addition, turbulence can enhance diffusion of species [3] and turbulent structures are observed in similar discharges by Xu et al [61] and Liu et al [41] using Schlieren measurements.

The maximum LIF peak intensities are also obtained from the multiple peak fit of the LIF profile. Since the LIF profile consists of two peaks (and the background fluorescence), the average of these two peaks is obtained, and plotted as
Figure 5.19: Relative maximum LIF peak intensity compared with the relative total LIF intensity as a function of time. The experimental conditions are the same as in figure 5.16.

a function of time in figure 5.19. This time resolved LIF intensity is corrected for the temperature dependent population of the $f_1(2)$ rotational level, using the temperature measured by excitation LIF. The measured LIF intensity increases slightly up to 0.77 µs and then decreases. Around 30 µs the LIF peaks decrease very quickly and it is no longer possible to fit the profile with a 3-peak fit. From about 70 µs onwards two broad peaks are visible, with a depletion at the symmetry axis. Around 100 µs the measured LIF intensity is approximately constant, which corresponds to the background OH density which is created by the buildup of OH density from previous discharges.

Since in the case of N$_2$-H$_2$O the background LIF intensity can not be neglected compared to the peak intensity (as is the case for He-H$_2$O mixtures), also the time resolved total LIF intensity is shown in figure 5.19. The decay of the total LIF intensity is slower than the decay of the peak intensity, which is consistent with the fact that self-quenching is an important loss mechanism of OH.

To investigate the OH density dependence on the position in between the electrodes, the electrode system is moved upward across the inter-electrode gap by distance intervals of 0.25 mm (only 0.15 mm close to the electrodes), while the laser beam position is kept fixed. The LIF signals measured at different laser positions is shown in figure 5.20. The LIF intensity is higher close to the cathode, where the observed optical emission is also higher (see section 5.3.1).
5.4: OH radical density

Figure 5.20: LIF signals measured at different positions of the laser beam between the electrodes, put together in one graph. The measurements are performed at $t = 1.07 \mu$s with a gate width of 40 ns and 2000 accumulations. $E_L = 2.6 \pm 0.2 \mu$J/pulse. The colour code is in arbitrary units.

5.4.3 Effect of water concentration on the OH kinetics

The time resolved calibrated OH density for various added water concentrations is shown in figure 5.21. These data series are not corrected for a potential change in quenching, since the LIF signal was too low to measure the quenching times as in figure 5.14 for all conditions. However the data series are corrected for the time resolved gas temperature as measured by excitation LIF. The gas temperature measured in the different N$_2$-H$_2$O mixtures, using excitation LIF, is shown in figure 5.22. There is no significant difference measured in the gas temperature for the different water concentrations (see also figure 5.7). As the water concentration decreases, LIF of OH is more difficult to observe. Therefore for N$_2 + 0.3$%H$_2$O the LIF signal could only be measured up to 30 $\mu$s.

In the case of N$_2 + 2.6$% H$_2$O, a significant increase is observed in the OH density around 20 $\mu$s, and a smaller increase around 200 $\mu$s. The profiles of the LIF signal at various times are shown in figure 5.23. In figure 5.24, the mean LIF peak intensity is compared with the total LIF intensity. The increase in OH density around 200 $\mu$s is pronounced less for the LIF peak intensity. This difference is due to the important effects of diffusion of OH in N$_2$ at a time scale of 200 $\mu$s. Note that in the afterglow, at the time of increase of OH ($\approx 20 \mu$s), also the gas temperature increases by about 60% (see figure 5.22).

Due to the uncertainty in the N density it is not possible to obtain the OH density
Chapter 5: \( N_2 \) and \( N_2-H_2O \) mixtures

Figure 5.21: Time resolved OH densities for different water admixtures, corrected for the temperature dependent population of the \( f_1(2) \) level and absolutely calibrated using Rayleigh scattering.

Figure 5.22: Time resolved gas temperature measured by excitation LIF for different water admixtures.
Figure 5.23: Time resolved radial profiles of the LIF signal of OH in N\textsubscript{2} + 2.6\% H\textsubscript{2}O at a fixed axial position in the middle of the gap. The profiles are obtained from images of the LIF signal by summation of 4 pixel rows around the centre line of the laser beam.

Figure 5.24: Maximum LIF peak intensity and total LIF intensity as a function of time for N\textsubscript{2} + 2.6\% H\textsubscript{2}O, corrected for the temperature dependent population of the \(f_1(2)\) level.
Figure 5.25: Measured and modelled OH density decay in the case of 2.6% H$_2$O. The initial conditions of the model are $n_{\text{OH}}^0 = n_{\text{H}}^0 = 2.1 \cdot 10^{21}$ m$^{-3}$ and the model is calculated at $T_g = 500$ K. The fit is obtained with an initial N density of $12 \cdot 10^{21}$ m$^{-3}$.

from a fit of the OH decay in the far afterglow, as the decay is strongly influenced by the collisional quenching of OH with N. In figure 5.25, a fit of the OH decay by a chemical model is shown. The reactions that are included in the model are given in tables 2.1, 2.2 and 5.5. The reactions R1 and R3a taken from table 2.2 are now calculated for N$_2$ as a third collision partner instead of He. When using the OH density as obtained from the Rayleigh calibration as the initial OH density, a necessary N density at $t = 0.7$ $\mu$s of about $1.2 \cdot 10^{22}$ m$^{-3}$ is estimated to allow to fit the initial decay of the OH density. Note that this density is 10 times larger than the OH density, hence the importance of collisional quenching of OH by N.

The reactions used for the chemical kinetic model include only ground state neutral species. As a consequence the observed increase in OH density for the case of 2.6% H$_2$O cannot be explained by radical chemistry. Note that the electron density obtained from the H$_\alpha$ line (see figure 5.10) yields similar densities as the obtained N density from the chemical model. Both are larger than the measured OH density. A significant contribution to the production of OH by ionic species cannot be excluded. The reaction pathways could include charge transfer reactions such as

$$N_2^+ + H_2O \rightarrow H_2O^+ + N_2,$$

and

$$N^+ + H_2O \rightarrow H_2O^+ + N,$$

followed by electron ion dissociative recombination reactions of the water ion or
Table 5.5: Main reactions in the production and loss of OH in a N₂-H₂O discharge. Rate coefficients have units of m³ s⁻¹ for 2-body reactions and m⁶ s⁻¹ for 3-body reactions. The rates are calculated for a gas temperature of 500 K.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate coefficient $k$</th>
<th>$k$ at 500 K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1a</td>
<td>OH + OH + N₂ $\rightarrow$ H₂O₂ + N₂</td>
<td>$1.05 \cdot 10^{-44}(T_g/298)^{-0.76}$</td>
<td>$1.01 \cdot 10^{-19}$</td>
<td>[45]</td>
</tr>
<tr>
<td>R1b</td>
<td>OH + OH + H₂O $\rightarrow$ H₂O₂ + H₂O</td>
<td>$6.9 \cdot 10^{-43}(T_g/300)^{-0.8}$</td>
<td>$1.8 \cdot 10^{-19}$</td>
<td>[6]</td>
</tr>
<tr>
<td>R3a</td>
<td>OH + H + N₂ $\rightarrow$ H₂O + N₂</td>
<td>$6.87 \cdot 10^{-43}(T_g/298)^{-2}$</td>
<td>$3.49 \cdot 10^{-18}$</td>
<td>[45]</td>
</tr>
<tr>
<td>N10</td>
<td>OH + N $\rightarrow$ NO + H</td>
<td>$3.80 \cdot 10^{-17}\exp(85/T_g)$</td>
<td>$4.50 \cdot 10^{-17}$</td>
<td>[45]</td>
</tr>
<tr>
<td>N11</td>
<td>OH + N $\rightarrow$ NH + O</td>
<td>$1.88 \cdot 10^{-17}(T_g/298)^{0.1} \exp(-10700/T_g)$</td>
<td>$1.01 \cdot 10^{-26}$</td>
<td>[45]</td>
</tr>
<tr>
<td>N12</td>
<td>N + H₂O $\rightarrow$ OH + NH</td>
<td>$6.03 \cdot 10^{-17}(T_g/298)^{1.2} \exp(-19245/T_g)$</td>
<td>$2.16 \cdot 10^{-33}$</td>
<td>[45]</td>
</tr>
<tr>
<td>N13</td>
<td>3N $\rightarrow$ N₂ + N</td>
<td>$1.25 \cdot 10^{-44}[N]$</td>
<td>$1.25 \cdot 10^{-44}[N]$</td>
<td>[45]</td>
</tr>
<tr>
<td>N14</td>
<td>2N + N₂ $\rightarrow$ 2N₂</td>
<td>$1.38 \cdot 10^{-45} \exp(503/T_g)[N₂]$</td>
<td>$3.77 \cdot 10^{-45}[N₂]$</td>
<td>[45]</td>
</tr>
<tr>
<td>N15</td>
<td>N₂ + H( + M) $\rightarrow$ N₃H( + M)</td>
<td>$3 \cdot 10^{-17}(T_g/298)^{-0.6} \exp(-7765/T_g)$</td>
<td>$4 \cdot 10^{-24}$</td>
<td>[45]</td>
</tr>
</tbody>
</table>
its clusters

\begin{align}
  H_2O^+ + e & \rightarrow OH + H + e, \\
  H_3O^+ + e & \rightarrow OH + \text{products},
\end{align}

and OH production. However, an extrapolation of the electron density with the measured decay time yields an electron density below $10^{20}$ m$^{-3}$ at 1 µs. This is well below the measured OH density and thus it can be concluded that not only charged species will be able to explain the significant increase in OH found at 20 µs.

The recombination of atomic N releases an energy of 9.8 eV, leading to a significant production of nitrogen metastables and vibrationally excited states. As the atomic nitrogen density is significantly larger than the OH density (as estimated from the fit in figure 5.25), this could be of importance for the OH production in the far afterglow.

In the remainder of this section a qualitative motivation similar to the mechanism of the pink afterglow is given to explain the increase in OH density in the far afterglow. This phenomenon has been observed by many groups, when nitrogen is appreciably dissociated and when its vibrational temperature differs substantially from the translational temperature. In this case, in a flowing afterglow, the emission reduces with increasing distance until a strong 'pink' emission is found at a significant distance from the active plasma. Hence the name 'pink afterglow'.

For instance, Sadeghi et al [54] measured several plasma parameters and species densities in the afterglow of a flowing N$_2$ microwave discharge at 440 Pa. After the end of the discharge zone, in the flowing afterglow, they observed a decrease in the emission, and in the density of N$_3$(A) metastables and electrons, followed by a sudden increase at longer distance. A similar behaviour is reported for the N(2P) metastable density in a subsequent publication [19]. The processes responsible for this pink afterglow are recombination processes of nitrogen atoms, which, due to the dissociation energy of N$_2$ (9.8 eV), release a large amount of energy when they recombine. In addition, the build up of metastables in the afterglow can be enhanced by reactions of vibrationally excited nitrogen molecules with nitrogen atoms [25]. Recombination processes of atomic nitrogen are also given as a main source of the pink splash observed by Akishev et al [4] in the afterglow of a pulsed nitrogen discharge.

At atmospheric pressure, it is shown for a nitrogen streamer discharge that the density of N$_2$(A) metastables is decaying, while the densities of N($^{14}$S) and N($^2$P) are still significant on a time scale of 100 µs [47]. The lifetime of the N density exceeds the N$_2$(A) density. Note that the levelling off of the emission between 10 and 60 µs in the pure N$_2$ discharge, as shown in figure 5.5, illustrates that the above mechanism is important also in the plasma reported in the current work.

A similar mechanism as for the pink afterglow is proposed to be responsible for
the generation of OH at the timescale of tens of μs. The recombination of atomic ground state nitrogen N(4S) leads to the production of vibrationally excited nitrogen and molecular nitrogen metastables N2(A) (see e.g. [54])

\[ \text{N}(4S) + \text{N}(4S) + \text{M} \rightarrow \text{N}_2(\text{B}), \nu \text{ high} + \text{M}, \]  

where M can be N2 or N, followed by radiative and collisional cascade of N2(B) to N2(A). Vibrationally excited states can also lead to additional metastable production by e.g. [23]

\[ 2\text{N}_2(\nu \geq 12) \rightarrow \text{N}_2(\text{A}) + \text{N}_2(\text{X}) \quad k = 1 \cdot 10^{-22} \text{m}^3\text{s}^{-1}. \]  

It is known that V-T transfer is very fast in H2O, and that V-V transfer from N2 to H2O is an important quenching process of the vibrationally excited states of N2 (see e.g. [35]). Therefore vibrational processes will be less important in N2-H2O discharges compared to pure N2 discharges. A depletion of vibrationally excited states of N2 also occurs when O2 is added to a N2 gas (see e.g. [43] for a low pressure discharge).

N2(A) is lost by e.g. the following reactions [36, 51]

\[ \text{N}_2(\text{A}) + \text{N}_2(\text{X}) \rightarrow 2\text{N}_2(\text{X}) \quad k = 3 \cdot 10^{-24} \text{m}^3\text{s}^{-1}, \]  

\[ 2\text{N}_2(\text{A}) \rightarrow \text{N}_2(\text{C}) + \text{N}_2(\text{X}) \quad k = 1.6 \cdot 10^{-16} \text{m}^3\text{s}^{-1}, \]  

\[ \text{N}_2(\text{A}) + \text{N}(4S) \rightarrow \text{N}(4\text{P}) + \text{N}_2(\text{X}, \nu) \quad k = 4 \cdot 10^{-17} \text{m}^3\text{s}^{-1}, \]  

\[ \text{N}_2(\text{A}) + \text{H}_2\text{O} \rightarrow \text{OH}(\text{X}) + \text{H} + \text{N}_2(\text{X}) \quad k = 5 \cdot 10^{-20} \text{m}^3\text{s}^{-1}, \]  

\[ \text{N}_2(\text{A}) + \text{OH}(\text{X}) \rightarrow \text{OH}(\text{A}) + \text{N}_2(\text{X}) \quad k = 1 \cdot 10^{-16} \text{m}^3\text{s}^{-1}, \]  

\[ \text{N}_2(\text{A}) + \text{H} \rightarrow \text{products} \quad k = 2.1 \cdot 10^{-16} \text{m}^3\text{s}^{-1}. \]  

As the dissociation degree of N2 is larger than 10^{-7}, the quenching of N2(A) with N2(X) will be negligible. Considering that the atomic nitrogen density estimated from the kinetic model is of the order 10^{22} m^{-3}, and thus larger than the OH density (< 5 \cdot 10^{20} m^{-3} at t = 10 \mu s), the majority of the losses of N2(A) will lead to the production of N2P. The N2(C) state will also be recycled to N2(B) and eventually N2(A) so the pooling reaction is not a significant loss of N2(A). As metastable nitrogen atoms are even more efficient in the dissociation of water compared to N2(A) through the reaction [27]

\[ \text{N}(4\text{P}) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{NH} \quad k = 5.7 \cdot 10^{-19} \text{m}^3\text{s}^{-1}, \]  

the quenching of N2(A) by atomic nitrogen does not lead to a reduction of the OH production. Moreover, if quenching of N(4P) leads to production of N(4D), OH will be produced in a reaction which has a rate that is 3 orders of magnitude
faster than production of OH from N(²P) [47]:

\[
N(²P) + N(⁴S) \rightarrow N(²D) + N(⁴S) \quad k = 1.8 \cdot 10^{-18} \text{ m}^3 \text{ s}^{-1},
\]

\[
N(²D) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{NH} \quad k = 2.5 \cdot 10^{-16} \text{ m}^3 \text{ s}^{-1}.
\]

As the expected large amount of nitrogen atoms \((n \propto 10^{22} \text{ m}^{-3})\) is quenching the OH radicals by reaction N10 (see table 5.5), the density of water molecules will have to be large enough compared to the atomic nitrogen density to allow for an increase in OH density by the proposed reactions. Hence, the OH production in the far afterglow is not expected for small water concentrations as observed in the experiment.

Several rates of reactions (and their gas temperature dependences) in N₂ and N₂-H₂O are not reported in literature. Therefore a quantitative calculation of the OH production at a µs time scale is not possible without a significant amount of measurements of the metastable and excited species densities of N₂. This is however outside the scope of this work.

### 5.5 Conclusion

Nanosecond pulsed discharges in N₂ and N₂-H₂O mixtures are studied with time resolved optical emission spectroscopy, Rayleigh scattering and LIF. The evolution of the discharge consists of three phases, the ignition phase (raising voltage, no current), the spark phase (low voltage, high current) and the recombination phase. From time resolved imaging it is observed that the discharge starts at the positive electrode during the ignition phase. At the end of the ignition phase multiple filaments are visible. When the spark phase starts, a homogeneous plasma channel is visible. Significant emission is found up to 60 µs after the discharge.

During the ignition phase the emission is mainly coming from molecular nitrogen. This emission of molecular nitrogen collapses at the end of this phase and the emission of atomic and ionic nitrogen increases. At the start of the spark phase only atomic nitrogen emission is visible. Due to the quenching of molecular nitrogen by water the emission of molecular nitrogen is weaker in the discharge with added water vapour. The atomic emission is largely caused by recombination reactions.

From the spectrum of molecular nitrogen the temperature during the ignition phase is estimated to be 350 K. In the recombination phase (1 µs after the start of the discharge) the temperature has been estimated with Rayleigh scattering and is about 750 K. The addition of 0.9% water has no significant influence on the gas temperature.

The electron density has been determined with the broadening of an atomic ni-
trogen line and Hα in the N₂/H₂O mixture. Electron densities up to 4 · 10²⁴ m⁻³ have been measured in a pure N₂ and N₂/H₂O discharge. During the recombination phase the electron density decreases with a rate constant of the order of 10⁷ s⁻¹ for both nₑ obtained from N and Hα. This is much slower than expected from electron-ion recombination rates, which indicates that there is a significant production of electrons in the recombination phase. Additionally the decay of the N emission is significant longer than the lifetime of the excited states which means that highly excited N atoms are produced after the discharge. Both effects illustrate the importance of the energy stored in metastables, atomic nitrogen and vibrationally excited nitrogen molecules.

In the measured LIF signal of OH generally a dip is observed in the centre of the OH LIF profile which, in the case of N₂, could be due to a difference in the gas temperature in the core and the surroundings, and by a higher N and N⁺ density in the core, leading to a locally larger rate for destruction of OH. A background OH density is observed in the LIF signal of OH, which is due to the accumulation of OH over several pulses. The calibrated OH density increases with increasing added water concentration. In the case of N₂ + 2.6 % H₂O, a strong increase in OH density is observed at a microsecond time scale, which is proposed to be caused by a similar mechanism as is responsible for the pink splash and pink afterglow observed in pure N₂ discharges.
References


References


Chapter 6

General conclusions

The aim of this work has been to investigate the OH kinetics in an atmospheric pressure plasma. All measurements and analyses have been performed for a single plasma filament, as for atmospheric pressure applications filamentary (pulsed) discharges have been proven to be very efficient. In addition most atmospheric pressure plasmas are also filamentary in nature. To be able to apply time and spatially resolved diagnostics with reproducible results, the plasma filament has been stabilized in both space and time. More specifically, a pin-to-pin electrode with an inter-electrode gap of 2 mm has been used, and 170 ns nanosecond pulses have been applied with a repetition frequency of 1 kHz. The power supply used, is a solid state nanosecond switch, which allowed to reduce the jitter of the voltage pulse down to 2 ns. As a result it was possible to investigate the plasma with a nanosecond time resolution.

The OH density was obtained by laser induced fluorescence, which has a high sensitivity compared to e.g. absorption. With this technique not only a high temporal resolution can be achieved, but also a high resolution in space. The laser beam diameter was about 250 μm, which was of the same magnitude as the diameter of the plasma filament, and determined the spatial resolution of the measurement. To obtain absolute OH densities from the OH LIF signals, Rayleigh scattering has been used together with a LIF model which included collisional transfer processes for the OH(A) state, which are very important at high pressures. This calibration method has been validated by two other methods, broadband UV absorption and a chemical model of the relative OH density as a function of time in the afterglow. For the first time, a significant drop in the effective lifetime of OH(A) has been found during the discharge, which is shown to be due to electron quenching of OH(A). This motivates why both time and spatially resolved LIF, as used in this study, are necessary to study OH kinetics in nanosecond pulsed discharges.
The OH production has been investigated for different gas mixtures. An extended study has been performed in He-H$_2$O mixtures because of its relative simplicity compared to the OH kinetics in (a mixture of) molecular carrier gases. Since in literature O($^1$D) is often held responsible for the production of OH in corona discharges in air, the effect of the addition of O$_2$ to He-H$_2$O mixtures has been examined. In addition, the production of OH has also been studied in N$_2$, a molecular gas which is the main component of air.

To unravel the OH kinetics, the discharge has been investigated with various other diagnostics. First of all, the discharge has been electrically characterized by current and voltage measurements. Fast imaging has been used to study the time resolved discharge morphology. By time resolved optical emission the plasma kinetics have been studied. Electron densities were deduced from Stark broadening of atomic lines. Gas temperatures were measured using excitation LIF and Rayleigh scattering, and diode laser absorption has been performed to examine the density of helium metastables. All these parameters allowed to perform a quantitative analysis of the production and loss mechanisms of OH for several plasma conditions.

The key experimental results giving novel insights in the discharge kinetics and OH dynamics are summarized below.

- Depending on the applied DC voltage, two different modes are observed in He-H$_2$O discharges. These modes are characterized by an electron density which differs by about a factor of 10, and are therefore named low- and high-density mode in this work. The discharge morphologies correspond to a glow and spark discharge.

- A large part of the emission observed in the discharge is due to electron-ion recombination processes, even though the discharge is nanosecond pulsed and an instantaneously high electric field is applied, and thus high electron temperatures occur. A delayed gas heating in the early afterglow is also observed, which can be attributed to recombination processes.

- In the high-density mode of the He-H$_2$O(-O$_2$) discharge, depletion of OH(X) has been observed at the location of the plasma filament. This effect is due to the fact that the water in the plasma core is fully ionized and that the core mainly consists of ionized water fragments (H$^+$, O$^+$, OH$^+$). The production of OH by charge transfer and subsequent dissociative recombination of the water ion requires water, which is found at the edge of the plasma filament, hence the maximum in OH density at this location.

- In the He-H$_2$O low-density mode, charge transfer and subsequent dissociative recombination of water ions are able to quantitatively explain the time resolved OH density in the early afterglow.

- An unexpected increase in the OH density has been observed in the far afterglow of He-H$_2$O-O$_2$ discharges. A zero-dimensional chemical kinetic
model has been used to qualitatively explain this observation. It was shown that in an oxygen rich environment OH is strongly quenched by O, upon which H is created, which is also a strong quencher of OH. Due to the induced strong decrease in the OH density, production processes of OH through HO$_2$ and H$_2$O$_2$ (which have a higher density when O$_2$ is added compared to pure H$_2$O discharges) will temporarily become more important. This then results in a temporally increased production of OH in the far afterglow.

- In the N$_2$(-H$_2$O) discharges an ionization degree of up to 50% has been measured. This indicates that the plasma is very reactive, even in the afterglow. The strong emission up to 100μs after the discharge pulse illustrates the reactivity, and has similarities with the pink afterglow. The energy release, which sustained this emission, is similarly to the pink afterglow most likely due to the recombination of atomic nitrogen.

- An unexpected creation of OH in the far afterglow has also been observed in the N$_2$ discharge with saturated water vapour concentration. This is qualitatively explained by mechanisms of energy storage in nitrogen atoms, which release their energy in the far afterglow by processes similar as in the pink splash/afterglow.

In conclusion, we have constructed a nanosecond pulsed discharge, stable in space and time, which allowed to study the OH kinetics in an atmospheric pressure plasma filament with a temporal and spatial resolution of 30 ns and 250 μm, respectively. It has been found that ionic processes can be a rich source of OH radicals. The results lead to new insights in the OH kinetics, which are useful for the further optimization of OH radical production in plasma sources used for applications. Finally the reliability and accuracy of the absolute calibration of the OH density in non-equilibrium atmospheric pressure discharges is analyzed, and yields valuable information for comparison with plasma models.
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Curriculum Vitae

11 March 1986
Born in Diest, Belgium.

1998–2004
Sancta Maria Instituut, Aarschot, Belgium.

2004–2009
MSc in Physics and Astronomy at Ghent University, Belgium (magna cum laude).
Subject of the Master thesis: Plasmas in contact with liquids.

One month research stay at Loughborough University (Plasma and Pulsed Power Group, professor Kong), UK, within the framework of the master thesis (18/01/2009-13/02/2009).

2009–2010
Member of the assisting academic staff of the department of Applied Physics, faculty of Engineering and Architecture, Ghent University, Belgium.

2010–2013