OH production in
a low-temperature atmospheric pressure
plasma jet
in the context of tooth whitening

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Abstract

Low-temperature atmospheric pressure plasmas (LTAPPs) have been receiving an increasing interest for biomedical applications and are studied intensively nowadays. The oxidative and bactericidal effects of these LTAPPs are investigated in the context of wound healing and even cosmetic applications such as tooth whitening are investigated. LTAPPs generate a mixture of highly reactive radicals and molecules, of which the most important ones are ozone, atomic oxygen, nitric oxide and the hydroxyl radical. From this group, the hydroxyl radical is the strongest oxidizer and is shown in preliminary studies to be the responsible agent for the tooth whitening effect. However, a direct correlation between the OH radical density produced in the plasma and the tooth whitening effect has not been reported. Hence, investigating this correlation is the goal of this graduation work. In this work the tooth whitening studies are performed with an LTAPP operating in Ar. By varying the water concentration in the argon flow, the hydroxyl density is changed. Both ground state and excited state of the OH radical are investigated. In order to determine the hydroxyl ground state density, laser induced fluorescence is used. A model has been developed and a calibration has been performed to deduce the absolute hydroxyl density in the plasma. A range in OH densities between $9 \cdot 10^{19}$ m$^{-3}$ and $3 \cdot 10^{21}$ m$^{-3}$ have been found, the maximum concentration corresponding to 1.3% of water. It is shown that the relative dependence of the OH ground state density is not well represented by optical emission originating from the electronically excited state of OH(A), in spite the fact that it is often used in literature for this purpose. The performed tooth whitening experiments yielded a colour change $\Delta E = 5 \pm 1$ a.u. for a treatment of 20 mins. This is a factor five higher than in case of a treatment with the mere Ar gas flow and it is three times smaller reported in literature for a helium plasma combined with hydrogen peroxide. It is to be expected that the OH density in this later case can be significantly increased by the dissociation of hydrogen peroxide by the plasma.
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Chapter 1

Introduction

Plasmas have practical applications in various areas such as material processing and display devices. Several of the largest manufacturing industries in the world use plasma processing technology in their ultra large scale integration (ULSI) processes, placing over 1 million circuit elements on a single chip [1]. Additionally, plasmas have applications in high-intensity discharge lamps, reduce ignition temperature in combustion processes, remove volatile organic compounds in polluted air, are used for coatings and arc plasmas are even used in welding and cutting[2].

Nowadays, atmospheric pressure plasmas are increasingly of great attention both in fundamental studies and in technological applications. Atmospheric pressure discharges fall into two main categories: thermal plasmas, with a gas temperature of the order of the electron temperature, so 8000 K or more, and non-equilibrium discharges, where the electron temperature is typically an order of magnitude higher than the gas temperature [3]. Thermal plasmas can only be used in treating temperature-insensitive surfaces, or should be used for processes like cutting and welding. Non-equilibrium plasmas on the other hand, can be designed to operate at temperatures close to room temperature.

These low-temperature atmospheric pressure plasmas (LTAPPs) are the focus of this thesis and have a rich area of applications, one of which is the interaction of plasma with biomaterials [4]. The foundation for these applications is due to the high electron temperature, typically 1-10eV, which is produced at ambient pressure and temperature, which leads to an enhanced radical chemistry, surrounded by neutral gas species. Before elaborating on the technical specifications, the applications are discussed.

Applications started in the second half of the 1990s by sterilization experiments by Laroussi et al. [4], and have resulted in cell manipulation for adhesion control, the surgical removal of body tissue, blood coagulation, wound healing and apoptosis\(^1\) induction on cancer cells [6, 7]. Goree et al.

\(^1\)Programmed cell death [5].
Chapter 1 Introduction

Figure 1.1 Cross section of the human tooth [9]. The hydrocarbon stains will attach to the enamel, causing the discolouration of the tooth.

[8] proved the killing of S. mutans bacteria using a plasma needle at atmospheric pressure. Another application is tooth whitening, which is the main application of the present work. Stains on teeth are formed by organic molecules, which can be oxidated and then removed from the tooth enamel, see figure 1.1.

Lee et al. [6], have shown that the combination of the conventional bleacher hydrogen peroxide (H$_2$O$_2$) with an LTAPP improved the bleaching efficacy by a factor 3 with respect to using H$_2$O$_2$ alone. In conventional tooth whitening, H$_2$O$_2$ is often used as bleaching media. H$_2$O$_2$ has a maximum redox potential of H$_2$O$_2$ [10], while OH is as high as 2.72 eV [11]. This fact suggests that applying OH, instead of H$_2$O$_2$, would be able to increase the whitening effects and probably shorten the treatment time. The OH radical has a lifetime which is too short (lifetime is of the order of μs [12, 13]) to be able to collect OH and store it, so that is why LTAPPs are used to continuously create new OH radicals out of the water of for instance the ambient air. The stronger oxidative potential together with the fact that no chemical feedstock is needed make OH interesting compared to H$_2$O$_2$.

The LTAPPs exist in various forms. The most common forms of LTAPPs for biomedical applications are a plasma needle, a dielectric barrier discharge (DBD) and a plasma jet. The latter will be investigated in more detail in this thesis and a simple version of this geometry is visualized in figure 1.2.

As mentioned before, a main characteristic of the LTAPPs is that the gas temperature is at least an order of magnitude smaller than the electron temperature. Two other characteristics of LTAPPs are the small size of the

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2The exact geometry of the jet used in this thesis are discussed in chapter 2.
Figure 1.2 Schematics of a plasma jet. The high voltage source ignites the discharge by creating a high electric field over the gas flow, resulting in a plasma flowing out into the open air at the downside [4].

plasmas (mm-cm range)\(^3\) and the low input power (1-100W).

The range of driving frequencies is broad [14]:

1. pulsed direct current (dc);
2. alternating current (ac): kHz range;
3. radio frequency (RF): MHz range;
4. microwave (MW): GHz range.

Apart from the frequency range, the type of gas fed into the plasma is crucial. Noble gases, mostly He and Ar\(^4\), are commonly used as a neutral gas, because of their advantages in both the generation and the sustenance of discharges at atmospheric pressure, since Ar and He have larger effective ionization rates with respect to air in the range of the electric fields used for operation. The additional advantage of He and Ar are that it produces diffuse discharges and its gas temperature is lower compared to molecular gases. Advantages of Ar with respect to He include:

1. Price is lower compared to He.

\(^3\)Dielectric barrier discharges could have large electrode plates, but the gap distance is usually of the order of millimeters [4].

\(^4\)Xenon is suitable as well, though the price is high compared to He and especially Ar.
2. In Ar more reactive oxygen species are produced with respect to He, when exposed to the ambient environment or when oxygen is added to the gas stream [4].

3. Gas temperature is lower than in He, which is important for biomedical applications.

However, a drawback of Ar is the possibility of making a glow-to-arc transition [15, 16], an undesired transition to an unstable thermal plasma. This can be prevented by maintaining the power and hence the electron density low.

LTAPPs are often produced either in liquids or in contact with liquids, since water vapour is naturally present in atmospheric air and most biological tissue contains water. Low-temperature water containing plasmas typically generate intense UV radiation and many active radicals like OH, O, and H$_2$O$_2$ [17].

The LTAPP experiments nowadays have been achieved mostly in empirical ways, because of the inherent complexities of both plasma and biological systems. Usually, an LTAPP is smaller than a low-temperature plasma generated in a vacuum chamber at reduced pressures and the plasma itself is highly collisional. This is why the use of direct contact probes is a no-go, since these would interfere with the plasma and falsify the results. Therefore, both Optical Emission Spectroscopy (OES) and Laser Induced Fluorescence (LIF) have become popular methods for characterizing these LTAPPs. Xiong et al. [18], have performed high-speed dispersed photographing of an Ar plasma jet with a grating ICCD camera system. It is found that OH emissions decayed immediately as soon as the plasma traveled out from the nozzle. Since OES is detecting the light which is being emitted by the plasma itself, it provides a measure of excited state OH(A), not of the ground state OH(X). On the other hand, LIF probes the ground state OH(X). The laser is exciting OH(X) to OH(A) and this fluorescence is detected. By using both diagnostic tools, the behavior of the excited state can be compared to the ground state.

LIF measurements are performed by Dilece et al. [19, 20], who found that the OH radical density is of the order of $10^{19}$ m$^{-3}$ in both an Ar-H$_2$O and a He-H$_2$O atmospheric pressure dielectric double-barrier He-H$_2$O discharge, with flow ranges from 0.1 slm to 1 slm. Bruggeman et al. [21], have investigated a radio frequency He-H$_2$O plasma and found densities of the order of $10^{20}$ m$^{-3}$.

In the present work, LIF and OES will be used to find out how the OH density varies for different conditions. This information can be used to test for a plasma-induced tooth whitening effect.

Before elaborating on the OES and LIF diagnostics, the LTAPP used for these experiments is described and a literature review is given of the characterization of this source. Subsequently, the diagnostic tools are discussed
alongside with the models needed to assess the diagnostic results. Next, the results of OES, LIF and tooth whitening are discussed. Finally, a conclusion and outlook is given.
Chapter 1 Introduction
Chapter 2

Plasma source: the kINPen 09

In this chapter, the plasma source under investigation is described. After discussing the technical specifications, a summary of the results of the characterization of the kINPen is presented.

The plasma source used in this work is the kINPen 09, developed by INP Greifswald [22]. An image of the kINPen is found in figure 2.1.

The kINPen is a plasma jet, of which the design is shown in figure 2.2. Inside the cylinder an electric field is created between the grounded outer electrode and the inner coaxial electrode, resulting in a breakdown of the gas, creating a plasma inside. The Ar flow transfers the plasma outside, the so-called effluent. In this effluent, the gas temperature and electron density are lower than inside the cylinder. The kINPen consists of a hand-held unit (170 mm length, 20 mm diameter, 170 g weight), a gas supply unit with an inlet pressure of 1.5 bar [23] and a DC power supply (8 W - 10 W at 230 V, 50/60 Hz). In the centre of a quartz capillary (inner radius = 0.8 mm) a pin-type electrode (0.5 mm radius) is mounted [24]. The flowmeter on the control unit is capable of providing a flow between 3 and 8 slm. The whole system works with all rare gases (especially Ar) with gas flow rates between 5 and 10 slm. Small admixtures of molecular gases to the feed gas are possible. At maximal input DC the electric power of 3.5 W to the hand-held unit, the ignited plasma jet has a length of up to 12 mm [7, 22]. The schematic setup of the kINPen is shown in figure 2.2. The electrode head is optimised for noble gasses. In the continuous working mode, the frequency...

1The device got the CE marking which certifies that the product has met EU consumer safety, health and environmental requirements.
2Contrary to previous versions of the kINPen, it is not possible to measure the power in the kINPen 09 used for the present work. For the literature review presented in this chapter, previous versions of the kINPen are used, where it is possible to measure the power.
3Specifications about the flow or type of gas are not given.
of 1.1 MHz and a peak-to-peak voltage range of 2-6 kV is coupled to the pin-type electrode. The plasma is generated from the top of this electrode and is expanding to the air outside the ceramic nozzle.

There is a variety of active components in the kINPen, visualized in figure 2.3. It comprises (V)UV radiation, visible light, electromagnetic fields, thermal radiation, electrons and ions, and radicals and other reactive chemical products, which are discussed in the next sections.

### 2.1 (V)UV Radiation and visible light

The kINPen generates (V)UV radiation as shown by Weltmann et al. [7]. In table 2.1, the types of UV and their respective are values are written.

Between 350 nm and 400 nm (within the UV-A range), bands of nitrogen have been observed. These bands arise because of the mixing of the excited Ar species with the ambient air. The values of this emission are not specified. The kINPen has UV-B irradiance of 5 mW cm$^{-2}$. UV-C (200 nm - 280 nm) is not quantified by Weltmann et al. [7]). The plasma jet emits significant
2.1 (V)UV Radiation and visible light

**Figure 2.2** Schematic setup of the kINPen plasma jet [24]. Because of the electric field caused by the peak-to-peak voltage range of 2-6 kV, the noble gas breaks down and a plasma is created which flows out towards open air.

<table>
<thead>
<tr>
<th>type</th>
<th>wavelength range (nm)</th>
<th>irradianace</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-A</td>
<td>350-400</td>
<td>N2 emission, no values specified.</td>
</tr>
<tr>
<td>UV-B</td>
<td>280-350</td>
<td>5mW cm(^{-2})</td>
</tr>
<tr>
<td>UV-C</td>
<td>200-280</td>
<td>NO(A-X) emission, no values specified.</td>
</tr>
<tr>
<td>VUV</td>
<td>120-135(^{1})</td>
<td>2.2 mW mm(^{-2}) sr(^{-1})</td>
</tr>
</tbody>
</table>

\(^{1}\) VUV is generally presented as the electromagnetic waves with a wavelength below 200 nm [26], in the case of Weltmann et al., the intensity has only been measured for the range between 120 nm and 135 nm.

amounts of VUV, mainly due to the second continuum of the Ar excimer\(^{4}\) \(\text{Ar}_2^{*}\): i.e., between 120 nm and 135 nm. Excimer emission will be significantly quenched when air or water is added to the Ar flow. In the present work, water will be added, so that this emission will not be relevant [27]. The irradiance in the 260-360 nm range is approximately 5 mW cm\(^{-2}\) at the minimal distance of 5 mm and maximum input power of 6 W [7].

Daeschlein *et al.* [28], investigated the 5 slm Ar flow through the kINPen by optical emission spectroscopy. The molecular nitrogen bands measured between 300 nm and 400 nm, increase along the length of the plasma jet, because of the increased intermixing with air. In the VIS/NIR region between 700 nm and 1000 nm, mainly emission lines of atomic Ar are found.

A spectrum has been taken by Weltmann *et al.* [22] (figure 2.4), where OH, N\(_2\) and Ar can be seen.

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\(^{4}\)An excimer is an unstable excited molecule which is formed by the combination of two smaller molecules and quickly dissociates with emission of radiation [5].
2.2 Electromagnetic fields

Scardino et al. [29] have shown an enhanced wound healing in dogs due to the electric field. No papers have been found on the measurements of the electromagnetic fields induced by the kINPen.

2.3 Thermal radiation

The plasma is heated by the energy induced by the high electric field. The Ar gas flow then lowers the gas temperature $T_g$ of the plasma again. The resulting $T_g$ is investigated by few authors. Daeschlein et al. [28] measured a temperature-dependent fluorescent signal of luminescent magnesium fluorogermanate which is excited with a xenon flash lamp. The temperature at the tip of the plasma ranges between 311 K and 313 K for a 5 slm Ar flow. The temperature profile is depicted in figure 2.5a.

According to Weltmann et al. [22], who used the same method as Daeschlein et al., the axial temperature at the plasma tip ranges between 319 K and 325 K, for a power range of 1.9W-3.2W. This is displayed in figure 2.5b. Comparing both figures in 2.5, a difference of 3% (in units of K) with respect to the work of Daeschlein et al.
2.4 Electrons and ions

The electron density is an important parameter that is related to the chemical reactivity of the plasma [14]. According to Chen et al. [30], the electron density $n_e$ of the kINPen in an Ar jet increases with the applied voltage and is in the following range: $9.0 \cdot 10^{17} \text{ m}^{-3} \leq n_e \leq 2.3 \cdot 10^{18} \text{ m}^{-3}$. Zhu et al. [31] calculated the electron density by evaluating the intensity ratio of the atomic Ar lines with the help of a collisional-radiative model. The calculated $n_e$ are said to be in agreement with those determined by the Stark broadening method and the electric model over a wide electron density range $10^{17} \text{ m}^{-3} - 10^{18} \text{ m}^{-3}$. These results are in contradiction with the detection limit of Stark broadening, which is $10^{19} - 10^{20} \text{ m}^{-3}$ [13, 32]. Hofmann et al. [14] found that the electron density is of the order of $10^{20} \text{ m}^{-3}$ in a 1 slm Ar plasma jet. The detection limit is $10^{19} \text{ m}^{-3}$. The diagnostical tool is the linebroadening of the H$_\alpha$ and H$_\beta$ line.

2.5 Radicals and chemicals

Various radicals and chemical products are created within the plasma plume. Special attention is laid on the NO (-0.68V [33]), O ($V_{ox}=2.42$ V[34]), O$_3$ ($V_{ox}=2.07$ V [34]) and OH radical ($V_{ox}=2.72$ V[11]). The OH radical is the main suspected radical for tooth whitening, and OH together with O, NO and H$_2$O$_2$ are predicted to have effects on killing of bacteria and wound
Chapter 2 Plasma source: the kINPen

(a) Temperature profile of the kINPen with a 5 slm Ar flow by Daeschlein et al. [28]. It is not specified how the voltage is determined.

(b) Temperature profile of the kINPen with a 5 slm Ar flow by Weltmann et al. [22]. It is not specified how the power is measured.

Figure 2.5 Comparison of the temperature profiles of Daeschlein et al. [28] and Weltmann et al. [22], the temperature difference in K is 3%.

2.5.1 OH

No information about absolute OH densities for RF Ar plasma jets are known, hence the goal of this thesis is to find an absolute value for this OH density.

2.5.2 O$_3$

Reuter et al. [35], measured the ozone density by two different diagnostics which show good agreement. The first method — UV absorption spectroscopy in the Hartley band — determines the spatial-resolved distribution of the ozone concentration in the jet effluent. The second method — quantum cascade laser-absorption spectroscopy in the mid-infrared spectral region — yields high sensitivity results of the average ozone concentration in a multipass cell, in which the effluent is directed. The result is a density of 100 ppm at 6 mm distance from the nozzle for an admixture of 1% O$_2$.

2.5.3 Atomic oxygen

Reuter et al. [24] measured atomic oxygen by means of TALIF spectroscopy.$^5$

$^5$TALIF stands for two-photon absorption laser induced fluorescence. Ground-state oxygen atoms ($2p^4 \; ^3P_2$) are excited by two UV-photons (225.65 nm) into the $3p \; ^3P_1$ state and the resulting fluorescence radiation proportional to the ground-state densities is detected in the infrared (844.87 nm de-excitation to $3s \; ^3S_1$).
2.5 Radicals and chemicals

For 5 slm Ar and 1% oxygen admixture, the atomic oxygen density is of the order of 100 ppm. It decreases with the distance to the nozzle (until 7 mm) by up to an order of magnitude. The atomic oxygen density is higher than for comparable conditions in atmospheric pressure plasma jets operated in He [24]. This might be explained by the fact that the electric field geometry in the kINPen is different than in common jets, resulting in a higher charged species density in the jet effluent. For Ar no sources have been found.

2.5.4 H$_2$O$_2$

As discussed before, H$_2$O$_2$, is common in tooth whitening [4]. No information about H$_2$O$_2$ densities in the kINPen are known.

2.5.5 NO

NO is known to be mediating wound healing, skin cell development and division or cell signalling [36]. Pipa et al. [37], have investigated the production of NO radicals of the kINPen by means of absorption spectroscopy in the mid-infrared region. A small addition of water vapour significantly affects the production of NO radicals, especially at air mixtures greater than 0.2%. Up to 1.0 ppm NO is detected for 0.1% of added air, measured by the absorption method. This holds for both 10 slm pure Ar, as well as an additional 580 ppm of water.
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Chapter 3

Diagnostics and experimental setup

In this chapter the diagnostic techniques used in this thesis are discussed along with the experimental setup. Three types of experiments have been performed: Optical Emission Spectroscopy (OES), Laser Induced Fluorescence (LIF) and tooth whitening.

3.1 Optical Emission Spectroscopy

This section starts with presenting the principle of OES, whereafter the experimental setup is described.

3.1.1 Principle

OES is a passive diagnostics, i.e. the plasma is not influenced by the diagnostic system. The OES is measured from three different species with the help of a grating monochromator. The atomic Ar line is detected at 696.5 nm, molecular N\textsubscript{2} bands around 337.0 nm and OH bands around 310.0 nm. Because OH and N\textsubscript{2} are molecules, the energy pumped into the plasma is not only going to be translational, but also rotational and vibrational, see figure 3.1. Because of the vibrational and rotational energy levels which exist in OH and N\textsubscript{2}, their spectra exist of several lines, contrary to the atomic Ar, which has only one line for each electronic transition\textsuperscript{1}. Two parameters could be determined with the help of OES: relative OH(A-X) emission and the rotational temperature. The temperature can be determined from the OH and the N\textsubscript{2} spectrum, assuming a Boltzmann distribution. With the help of the Specair software [39], the rotational temperature $T_{\text{rot}}$ can be

\textsuperscript{1}The fact that Ar gas can only absorb energy in a translational degree of freedom, $T_{g}$ is lower for Ar than for OH and N\textsubscript{2}, which can also absorb energy in vibrational and rotational energy levels.
determined. \( T_{\text{rot}} \) is a measure for the energy stored in rotational motion. When an equilibrium is assumed between \( T_{\text{rot}} \) and \( T_k \), the aforementioned method can be used for determining \( T_k \). Specair is based on the following equation for calculating the rotational temperature:

\[
I \propto (2J_i + 1)A_{ij}\exp\left(-\frac{E_i}{k_B T_{\text{rot}}}\right),
\]

where \( I \) is the OES signal, \( J_i \) is the rotational number, \( A_{ij} \) is the spontaneous emission rate in s\(^{-1}\) and \( E_i \) is the energy of the level \( i \).

In figure 3.2, the theoretical OH spectrum can be seen for a distribution between the first 2 vibrational levels, obtained with database LIFBASE [40]. The smaller features are due to different rotational levels. During the OES experiment, there is a maximum range of 9.7 nm. The chosen range is from 305.15 nm to 314.85 nm. This means the focus is on the OH(\( \nu = 0 \)) level, since this has the strongest emission.

### 3.1.2 Experimental Setup

The experimental setup is shown in figure 3.3. Ar gas flow from a gas cylinder is split into two gas lines: in one line the Ar gas is flushed into two bottles filled with water (bubbler) to humidify the Ar gas flow with water, the other line remains pure. Both lines get together in a supply unit which leads to the kINPen plasma source. The light which is emitted by the kINPen is collected by a quartz lens and projected by a second quartz lens on the entrance slit of the Jobin Yvon grating monochromator.

The following components are used in the setup.

- Ar bottle, 5.0 purity\(^2\).

\(^2\) > 99.999% purity.
3.1 Optical Emission Spectroscopy

- Three mass flows:
  1. MASS-STREAM MFC:D - 5111, M+W instruments, (range is 50 slm, calibrated for air) [41]. This mass flow is used for the pure Ar branch.
  2. Brooks 5850E/B1A1B7D mass flow controllers (range from 0-3 slm calibrated for He) water concentration over 400 ppm.
  3. Brooks 5850E/B1A1B7D mass flow controllers (range from 0-200 sccm calibrated for air) for water concentration of 400 ppm.

- Two 250 mL bubblers from Drechsel (Lenz) with a filter of sintered glass.

- kINPen see chapter 2, it is positioned in such a way that it is height-adjustable.

- Two 110 mm quartz lenses. The lens material is quartz, because UV light should be transmitted and UV transmission for glass lenses is poor.

- High Resolution Monochromator Jobin Yvon, HR 1000 [43].
  - Focal length: 1000 mm.
  - Plane grating: 1200 grooves/mm (blazed at 200 nm), 120 mm height, 140 mm width, 20 mm.
  - Dispersion 8 Å/mm for 1200 grooves/mm grating (at 200 nm).
  - CCD ST - 2000 XMI-UV, Santa Barbara instrument group. 1600x1200 pixels. Pixel size 7.4 x 7.4 µm, so 12.16 mm x 9.12 mm CCD area [44].

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3 The position of the kINPen is movable. This is necessary because of the correction for chromatic aberration. This is the effect that the refractive index depends on the wavelength hence also the focal length depends on the wavelength [42]. When measuring other lines at different wavelengths, the kINPen needs to be moved to be in its focal point for that specific wavelength. For instance, when investigating the Ar line at 696.5 nm, the difference in focal length with respect to the OH measurement at 310.0 nm due to chromatic aberration is 3.5 cm.
Figure 3.2 OH(A-X) spectrum containing two different vibrational bands: OH(A-X)(1-1) in green and OH(A-X)(0-0) in red, calculated for a population distribution where 50% is in vibrational level $\nu = 1$ and 50% in level $\nu = 0$. The smaller features within the same vibrational transition are due to different rotational levels.
Figure 3.3 Experimental setup OES. Ar flows through both a water branch and a pure Ar branch. Both flows come together in the supply unit which leads to the kINPen. With the help of two quartz lenses the UV light is transmitted and focussed on the slit of the computer controlled CCD spectrometer.
3.1.3 Water concentration

H₂O is the feedstock for the creation of the OH radical. The formation mechanism of the OH radical in atmospheric plasmas is strongly influenced by the water concentration in the feeding gas, electron temperature, electron density, ionization degree, and presence of ionic species [45].

The water concentration in the gas flow is being varied to analyze its effect on the OH density. In order to determine how much of the water is absorbed in the gas flow, the Antoine equation is used [46–48], which describes the relation between vapour pressure and temperature for pure components:

\[ p_{\text{part}} = 10^{A - \frac{B}{C + T}}, \]

(3.2)

where \( p_{\text{part}} \) is the partial vapour pressure in mmHg, \( A = 8.07 \text{ mmHg}, B = 1730 \text{ mmHg}, \) and \( C = 233^\circ \text{C} \) in the temperature range of 1°C - 100°C. This assumes a temperature-independent heat of vaporization. The temperature range in the lab is in between 21°C and 23°C, which results in a relative partial pressure between 2.45% and 2.76%. For calculations the average value of 2.6% is used for maximum saturation. In order to cover the range from 2.6% till hundreds of ppms\(^4\), the water line is admixed with a pure Ar branch. By varying what part of the total of 4 slm flow is flowing through the water branch, the water concentration is varied.

3.2 Laser Induced Fluorescence

This section starts with explaining the principle behind LIF. It is followed up by discussing the experimental setup and the calculation of the OH density, including the model which is used for this calculation.

3.2.1 Principle

LIF is an active diagnostics as a laser irradiates the plasma, so actively interacting with the plasma. A tunable laser centred at 282.6 nm excites the OH molecule from the ground state OH(X) to the excited state OH(A). Because of the small width of the laser line (approximately 1 pm), a single rotational line is excited [49].

The ground state is described by OH(X, \( \nu'' \)) and the excited state by OH(A, \( \nu' \)). For simplicity reasons, the primes in the notation will be left out, since it can be seen from the ‘X’ or ‘A’ whether it considers a ground state or excited state. Additional information is given by adding \( f_1(N) \) for

\(^4\)The percentage is given as volume percent, since it is calculated as a partial pressure. When changing the flow which goes through the water branch, the number of molecules does not change, only the volume changes and therefore the partial pressure of the water changes.
3.2 Laser Induced Fluorescence

Figure 3.4 A simple schematic of the transitions involved in LIF, from Joosten et al. [49]. The linewidth of the laser is around 1 pm, so the single rotational line \( N=2 \) of the OH(X, \( \nu'' = 0 \)) is excited. Rotational energy transfer (RET) and vibrational energy transfer (VET) redistribute the population in both the ground state and excited state. In addition to fluorescence, quenching is another, non-radiative, process through which the energy transfer can occur. More detailed models are given in 3.2.3.4.

The electronic transition used for determining the OH radical density\(^5\) is that from \( \nu = 0, f_1(2) \) to \( \nu = 1, F_1(1) \) and is called \( P_1(2) \) [49], where \( P_1(N) = F_1(N - 1) - f_1(N) \) [50], where \( N \) is the rotational number of the ground state. When the OH radical is excited by the laser light to the electronically excited state, it relaxes to the ground state through both radiative and non-radiative processes. In subsection 3.2.3.4, this will be explained in more detail. The amount of fluorescent light is proportional to the OH ground state density [51]. In order to determine an absolute density, a model needs to be designed which accounts for the many collisional processes which could

\(^5\)For temperature measurements, other lines are probed as well, see 3.2.3.1.
Figure 3.5 Experimental LIF setup. The OH(X) produced by the kINPen plasma source is excited by the Sirah dye laser, fluorescence is detected in three ways, all gathered under the label ‘diagnostics’. First, the emission can be detected by the ICCD camera and second, the time resolved LIF is measured. Third, the wavelength resolved spectrum is measured with a grating monochromator.

significantly alter the fluorescence at atmospheric pressure. This is due to the fact that the absolute calibration of the OH radical with the help of a known amount of OH is not feasible, since the OH lifetime is in the order of µs, so too short to do a calibration with a gas containing a known OH density mixture [12, 13].

3.2.2 Experimental Setup

The experimental setup of the LIF experiment is shown in figure 3.5.

The OH(X,ν = 0) produced by the kINPen plasma source is excited by the Sirah dye laser into OH(A,ν = 1), of which the fluorescence is detected in three different ways. First, the emission can be detected by the ICCD camera and second, the time resolved LIF is measured by a photomultiplier tube (PMT), mounted on a 1 m monochromator. Third, the wavelength resolved spectrum is measured by an ICCD mounted on a 0.275 m monochromator. Specifically, the following components form part of the LIF setup:

- Edgewave-IS6II-E pumping laser at 1 kHz. Pumping occurred at 532 nm.
- Sirah dye laser, wavelength varies between 559 and 576 nm.
- Behind the dye laser is a resonant Frequency Doubler, which doubles the frequency of the laser light coming from the dye laser by second
3.2 Laser Induced Fluorescence

harmonic generation (SHG). Resulting wavelength is 282.6 nm\(^6\).

- 50 cm focal length quartz lens: for focusing the slightly divergent laser beam.

- Two diaphragms: The one before the lens to only transmit a small coherent laser beam. The one after the lens is to reduce scattered light. At the position of the kINPen, the spatial FWHM of the laser beam is 255 \(\mu\)m.

- Optical trap for laser light to prevent laser light from being scattered throughout the lab.

- Diagnostics

1. OH density measurement:
   (a) Andor ICCD camera (DU971N-UV-B), cooled until -11\(^\circ\)C, equipped with a Nikon UV-105 f4.5 lens\(^7\). Gate width 30 ns.
   (b) 4QuikE nanosecond high speed ICCD camera, equipped with a Nikon UV-105 f4.5 lens\(^8\).

2. Wavelength resolved measurement: 0.275 m Acton SpectraPro275 spectrometer. The Acton spectrometer is equipped with a 4QuikE camera.

3. Time resolved measurement: 1m Jobin Yvon spectrometer, 1200 grooves/mm grating, range is 175 nm to 1500 nm, which is equipped with a Multichannel Scaler (time regulation), and a photomultiplier tube (PMT) Hamamatsa R636. The gate width is 30 ns-250 ns\(^9\). Bin width (resolution in time dimensions) 0.4 - 0.8 ns. The wavelength range is 0.3 nm, a correction will have to be made for implementation in the model, since there is a variation of 8 nm \([40]\).

The LIF measurements have been performed in two series because of the limited availability of the LIF setup. In between the first and the second series of measurements three months have elapsed. In the first series, the following water concentrations have been measured: 400 ppm, 800 ppm, 1.3% of water, since that is a different series of measurements.

\(^6\)This is the LIFBASE value. For LIF intensity measurements, spectrum measurements, time resolved measurements, excitation wavelength have to be send to the laser with a setting between the 282.5756 nm and 282.5813 nm. This is since the computer is not sending an absolutely calibrated wavelength. Every experiment, a matching need to be made with the line transition. This is since the actual wavelength varies with temperature.

\(^7\)Used for the measurements on all concentrations except 1.3% of water, since that is a different series of measurements.

\(^8\)Used on the 1.3% measurement.

\(^9\)Gate width should not be too large to avoid capturing optical emission.
Chapter 3 Diagnostics and experimental setup

1600 ppm, 0.65% and 2.6%. This is done with the Andor camera and a laser energy of 6.55 µJ and the closest distance to the nozzle of the kINPen is 0.7 mm. For the second series of measurements, 1.3% of water has been measured with the help of the 4QuikE camera and the laser energy is 1.24 µJ. The laser energy has changed, because the dye of the dye laser changes over time. The distance closest to the nozzle is 1.2 mm. This disparity is caused because it is impossible to position the kINPen at exactly the same height for the second series of measurements as it is in the first series of measurements. Therefore, the distance measured closest to the nozzle is 1.2 mm for 1.3% of water and 0.7 mm for the other concentrations. In section 4.2.4 the effect of this 5 mm difference is discussed.

3.2.3 Influencing factors on LIF

The relation between the measured LIF signal and the OH density is going to be investigated. The measured LIF signal is proportional to the OH ground state density, where the size of the proportionality depends on the following six factors:

1. Gas temperature. As is shown next, $T_g$ affects both the density as well as the size of the fraction of the ground state which is excited.

2. Losses of light from the measurement system. With the help of Rayleigh scattering, the optical losses can be calibrated, see 3.2.3.2.

3. The energy of the laser pulse, which is discussed in 3.2.3.5.

4. The overlap between the width of the laser pulse and the molecular absorption linewidth. This is an effect of the laser bandwidth discussed in 3.2.3.3.

5. Transition rates between the different states.

6. The model including the factors above, which is discussed in 3.2.3.4.

3.2.3.1 Gas temperature by LIF

The gas temperature $T_g$ is an important parameter, for two reasons. First, as can be derived from the ideal gas law, the heavy particle density is inversely proportional to the gas temperature. Second, $T_g$ affects the fraction of OH(X) which is going to be excited. As can be seen from figure 3.4, only one rotational line is excited. The rotational line of the ground

---

10 The term ‘heavy particle density’ is more accurate than simply ‘density’, since this type of plasma is not in thermal equilibrium, i.e. the electron temperature is higher than the ion temperature. The ion temperature is equal to the neutral temperature. The ions and neutrals are called heavy particles and they are in thermal equilibrium and have the temperature $T_k$. 

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3.2 Laser Induced Fluorescence

state which overlaps with the laser line is a Boltzmann fraction $f_B$ of the entire ground state OH(X, $\nu = 0$), of which the values can be found in [40]. This $f_B$ is dependant on $T_g$. In order to calculate the OH density of the entire ground state, the density of the $N = 2$ state needs to be divided by the Boltzmann fraction $f_B^{\nu=0,N=2}$.

$T_g$ can be determined in three different ways. First, it could be deduced from the LIF spectrum. A higher gas temperature results in additional peaks for high rotational numbers. The sensitivity for this spectrum is low since the error is 50 K [40]. This is caused by the fact that the S/N for the Andor camera is too low.

Second, it could be determined with the help of OES, see section 3.1. Third, it could be determined by a so-called Boltzmann plot\(^{11}\). A detailed explanation of the Boltzmann plot is given in [52]. The principle is that the relative emission from different rotational levels is temperature dependent.

This Boltzmann plot is based on two assumptions: first, the ground state population is Boltzmann distributed and second, that the rotational temperature is equal to the gas temperature. Details underlying these assumptions can be found in the work of Joosten e.a. [49]. Both assumptions lead to equation 3.3:

$$n_i \propto (2J_i + 1) \exp\left(-\frac{E_i}{k_B T_{\text{rot}}}\right), \quad (3.3)$$

where $n_i$ is the density of level $i$, $J_i$ is the total angular momentum of level $i$ in dimensionless units, $E_i$ is the energy of level $i$ in Joule, $k_B$ is Boltzmann constant and $T_{\text{rot}}$ is the rotational temperature. Moreover, the following relationship holds between the measured LIF signal $S_{\text{LIF}}$ and the ground state density

$$S_{\text{LIF}} \propto n_i B_{12,i}, \quad (3.4)$$

where $B_{12,i}$ is the Einstein B absorption coefficient. The latter holds under the assumption that the decay of the pumped excited states is independent of the excited level, this is true within an error of 14\%\(^{12}\). At atmospheric pressure, the redistribution of the population over the entire rotational manifold is fast compared to the radiative decay time, regardless of the excited level, proving equation 3.4 is a fair assumption. The chosen transitions are displayed in table 3.1. These transitions are chosen because they show no overlap with other transitions.

Now the natural logarithm of the $\frac{S_{\text{LIF}}}{B_{12,i}(2J_i+1)}$ is plotted versus $E_i$, which is called the Boltzmann plot. This is shown in figure 3.6 for 1.3\% of water. The slope of the Boltzmann plot equals $-(k_B T_g)^{-1}$. From the slope it can

\(^{11}\)It is also possible to use OES in a Boltzmann plot, here only the LIF Boltzmann plot is presented since it has a higher S/N.

\(^{12}\)The calculation of this value will be made clear in table 3.4.
Chapter 3 Diagnostics and experimental setup

Table 3.1 Different transitions from OH(X, $\nu = 0$) to OH(A, $\nu = 1$) for determining $T_g$. $J_i = N_i + \frac{1}{2}$. Their corresponding parameters are indicated.

<table>
<thead>
<tr>
<th>transition</th>
<th>wavelength (nm)</th>
<th>$J_i$</th>
<th>$E_i$ ($10^{-21}$ J)</th>
<th>$B_{12,i}$($10^8$ m$^2$J$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_1(1)$</td>
<td>282.254</td>
<td>1.5</td>
<td>0</td>
<td>6.16</td>
</tr>
<tr>
<td>$P_1(2)$</td>
<td>282.663</td>
<td>2.5</td>
<td>1.7</td>
<td>5.53</td>
</tr>
<tr>
<td>$P_1(3)$</td>
<td>283.093</td>
<td>3.5</td>
<td>4.0</td>
<td>5.35</td>
</tr>
<tr>
<td>$P_1(4)$</td>
<td>283.546</td>
<td>4.5</td>
<td>7.1</td>
<td>5.29</td>
</tr>
<tr>
<td>$P_1(5)$</td>
<td>284.028</td>
<td>5.5</td>
<td>10.8</td>
<td>5.25</td>
</tr>
<tr>
<td>$P_1(6)$</td>
<td>284.542</td>
<td>6.5</td>
<td>15</td>
<td>5.23</td>
</tr>
</tbody>
</table>

Figure 3.6 Boltzmann plot for 1.3% of water for 4 slm Ar. The slope is $-1.95 \cdot 10^{20}$ J$^{-1}$, so $T_g = 371$ K. Upper and lower limits of the fit giving 364 K and 388 K, respectively. The presented error considers the error in the fit only.

It can be deduced that the resulting $T_g = 371$ K, with upper and lower limits of 364 K and 388 K. This is an accuracy of 5%. These limits come from a linear fit with the Origin software [53]. Origin provides the standard error, definition can be found in [54]. Since the reciprocal of the error in the slope is taken, the errors are asymmetric around the fitted value of 371 K.

$T_g$ is only measured at 1.2 mm from the nozzle, because of limited time for experiments. In order to determine $T_g$ along the plasma jet, an interpolation can be made between the Boltzmann plot temperature at 1.2 mm and $T_g$ at the tip of the jet by using the work of Daeschlein et al. [28] and Weltmann et al. [22]. Referring to section 2.3, $T_g$ at the tip of the jet is 324 K, when taking the average of the result of the works of Daeschlein et al. [28] and Weltmann et al. [22]. The deviation of the Boltzmann plot is
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Figure 3.7 $T_g$ and $f_B^{\nu=0,N=2}$ as a function of distance to the nozzle for 4 slm - 1.3% water at 1.2 mm from the nozzle. The end of the visible range of the plasma is 10.3 mm. Over the range of 1.2 mm to 10.3 mm, $T_g$ varies 14% and $f_B^{\nu=0,N=2}$ varies 11%.

approximately 15% with respect to literature values\textsuperscript{13}. For 1.3% of water, the emission in the UV has a length of 10.3 mm. This has been determined by taking an image with the UV sensitive 4QuikE camera, and the laser switched off. The temperature profile can be made assuming the temperature profile is the same as measured by Weltmann and Daeschlein, see figure 2.5. Their temperature profile is approximated by the assumption that the temperature is constant until 5 mm to the nozzle and the decay for larger distances is linear until the value of 324 K is reached. Linearly interpolating the temperature between 5 mm from the nozzle and the end of the jet at 10.3 mm from the nozzle. This results into a decay of 9.0 K per mm. $f_B^{\nu=0,N=2}$ changes for 10.3 mm to the jet to 0.19, so a change of 11%. In figure 3.7, both $T_g$ and $f_B^{\nu=0,N=2}$ can be seen as function of their distance to the nozzle.

3.2.3.2 Rayleigh calibration constant

With the help of Rayleigh scattering, the loss of light in the optics can be calibrated. Advantages of the Rayleigh calibration include:

1. accounting for the spatial non-uniformity of the laser;
2. explicitly defining the dimensions of the collection volume;
3. accounting for effects of the (optical) instruments.

\textsuperscript{13}Daeschlein measured without added water. As will turn out later, the measured $T_g$ in the present work does not vary for adding water, so the accuracy of 15\% is valid.
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The base for the Rayleigh calibration is that with the help of the detection of a known amount of light, the properties of the detection system can be calibrated [49]. This measurement is performed with the laser and the gas flow switched off. This is since the Rayleigh cross section of air is better defined than the mixture of an Ar flow with air. The measured Rayleigh signal $S_{\text{Ray}}$ (in #counts) is given by

$$S_{\text{Ray}} = \eta n \sigma \partial \Omega V_{\text{Ray}} I_L t_L,$$

where the parameters have the following meaning:

- $\eta$ (in counts·sr·J$^{-1}$) is the calibration constant which converts the photon energy in the dimension of photocounts on the detector, see 3.2.3.2.
- $n$ is the heavy particle density (in m$^{-3}$), which is assumed to follow the ideal gas law: $n = \frac{p}{k_B T_g}$.
- $\sigma$ (in m$^2$) is the integrated cross section for Rayleigh scattering for air at 282.6 nm. $\sigma = \frac{\partial \sigma}{\partial \Omega} \frac{1}{4\pi} \frac{3}{2}$, where $\frac{\partial \sigma}{\partial \Omega}$ is the differential Rayleigh cross section (in m$^2$sr$^{-1}$) [55, 56]. This correction factor is due to the fact that Rayleigh scattering is polarized in one plane.
- $V_{\text{Ray}} = n_{\text{pix}} d_{\text{pix}}^2 \Delta s$ (in m$^{-3}$) is the volume from which Rayleigh scattering is collected, where
  - $n_{\text{pix}}$ is the number of pixels in the $x$ direction.
  - $d_{\text{pix}}$ (in m) is the projected size of the image on each pixel, not to be confused with the size of the pixel itself. $d_{\text{pix}}$ is determined by measuring the pixel-mm-ratio by varying the height of the kINPen.
  - $\Delta s$ is the spatial FWHM of the laser beam.
- $t_L$ is the temporal length of the laser pulse (in s). This has been measured with the help of the time-resolved combination of the Multichannel Scale, photomultiplier and Jobin Yvon monochromator.
- $I_L = \frac{E_l}{\tau_L \Delta s^2}$ is the laser irradiance (in W m$^{-2}$), where $E_l$ is the laser energy per pulse (J), $\tau_L$ is the temporal FWHM of the laser pulse, and $\Delta s^2$ is the square of the spatial FWHM of the laser profile (in m$^2$).

The values can be found in table 3.2:

---

14So $t_L$ is the duration of the laser pulse, i.e. the time elapsed between the beginning of the end of the pulse, and $\tau_L$ is the FWHM of this laser function.
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Table 3.2 Values of the parameters involved in the calculation of the Rayleigh calibration constant \( \eta \), for 1.3% of water.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta )</td>
<td>( 2.53 \cdot 10^{18} ) counts-sr( J^{-1} )</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>( 1.4 \cdot 10^7 ) (J-Pa)(^{-1} )</td>
</tr>
<tr>
<td>( n_{\text{room}} ) (^1)</td>
<td>( 2.4 \cdot 10^{25} ) m(^{-3} )</td>
</tr>
<tr>
<td>( \frac{\partial \sigma}{\partial \Omega} ) (^2)</td>
<td>( 7.63 \cdot 10^{-30} ) m(^2)sr(^{-1} )</td>
</tr>
<tr>
<td>( V_{\text{Ray}} )</td>
<td>( 2.6 \cdot 10^{-11} ) m(^{-3} )</td>
</tr>
<tr>
<td>( n_{\text{pix}} )</td>
<td>160</td>
</tr>
<tr>
<td>( d_{\text{pix}} )</td>
<td>25.0 ( \mu )m (^3)</td>
</tr>
<tr>
<td>( \Delta s )</td>
<td>255.7 ( \mu )m</td>
</tr>
<tr>
<td>( t_L )</td>
<td>20 ( \text{ns} )</td>
</tr>
<tr>
<td>( I_L )</td>
<td>( 2.1 \cdot 10^9 ) W m(^{-2} )</td>
</tr>
<tr>
<td>( E_L )</td>
<td>1.24 ( \mu )J</td>
</tr>
<tr>
<td>( \tau_L )</td>
<td>7.05 ( \text{ns} )</td>
</tr>
</tbody>
</table>

\(^1\) For \( T_g=300 \) K and \( p = 10^5 \) Pa. The Rayleigh calibration is done in air at ambient temperature and pressure, since Rayleigh cross section for air is well known, contrary to an unknown admixture of air and Ar.

\(^2\) Träger et al. [57] give \( 7.31 \cdot 10^{-30} \) m\(^2\)sr\(^{-1} \). This is a 4\% error.

\(^3\) 20.5 \( \mu \)m for the other concentrations.

The laser energy \( E_L \) is neither constant over space nor time. In order to correct for the spatial dependence, it is assumed that the laser energy has a Gaussian spatial distribution\(^15\).

A two-dimensional Gaussian distribution function \( f_s(y, z) \) (the coordinates are defined in figure 3.8), with a spatial FWHM of \( \Delta s \) is given by:

\[
    f_s(y, z) = \frac{2}{\pi} \exp\left(-\frac{y^2 + z^2}{\Delta s^2}\right),
\]

\(^15\) Later, it will be seen that the profile is actually a convolution of a Gaussian and a Lorentzian. Since in the end, the integral over the distribution is taken anyway, this difference is negated. So for the sake of the argument, it is assumed here than it is a Gaussian profile.
where $f_s(y, z)$ is normalized to the square of its FWHM [58]:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_s(y, z) dy dz = \Delta s^2. \quad (3.7)$$

In order to correct for the temporal dependence, the temporal distribution of the Rayleigh signal has been measured by Verreycken [59] and its measured function $f_1(t)$ is normalised to the FWHM $\tau_L$. The two statements above result into a space and time dependent laser irradiance $I_L(y, z, t)$:

$$I_L(y, z, t) = \frac{E_L}{\tau_L \Delta s^2} f_s(y, z) f_1(t). \quad (3.8)$$

Since it is concluded from the above that the energy density is not constant over space and time, $V_{Ray} t_L$ from equation 3.5 has to be replaced by an integral over space and time of the laser energy irradiance, so equation 3.5 is converted into:

$$S_{Ray} = \eta \sigma E_L \tau_L \Delta s^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_s(y, z) dy dz \int_0^{\Delta t} f_1(t) dt, \quad (3.9)$$

where $\Delta x = n_{pix} d_{pix}=4.0$ mm is the length of the detection volume (in m).

In order to determine the Rayleigh calibration constant $\eta$, the Rayleigh signal is measured as function of the laser energy per pulse. With the help of the slope $\alpha$ of the Rayleigh signal versus the energy pressure product, $\eta$ is determined (see figure 3.9):

$$\eta = \alpha k_B T_{room} (\sigma \Delta x)^{-1}. \quad (3.11)$$

Reabsorption of light in the plasma jet is negligible, since it is 1% [13].

In Appendix A.1 the Rayleigh calibration for the measurements of the other water concentrations can be found.

### 3.2.3.3 Overlap integral

In equation 3.8, the irradiance of the laser is indicated. However, it is necessary to consider what amount of the laser energy is actually absorbed by the OH molecule, since both the laser and the probed OH line have a finite broadening.

The shape of both the laser and the line broadening contribute to the total broadening of the experimental line profile, which is displayed in figure 3.10, where an FWHM of 3.0 pm can be seen ($\Delta \lambda^G=1.65$ pm, $\Delta \lambda^L=1.75$ pm). In Appendix A.3, the broadening can be found for other concentrations.
Both in the laser spectrum and the line spectrum, a Lorentzian and a Gaussian broadening are determined. In case of the laser, the Lorentzian broadening is not due to the laser itself, but because of broadening mechanisms in the monochromator.

The Doppler broadening of the OH line is due to the distribution in velocities relative to the observer [60]. This Doppler broadening has a Gaussian shape and obeys to the following relation, when assuming the OH molecules follow a Maxwellian velocity distribution [61]:

$$\Delta \lambda^G = (7.16 \cdot 10^{-7}) \lambda \sqrt{\frac{T}{M}},$$  \hspace{1cm} (3.12)

where $\lambda=282.6$ nm is the wavelength of the absorption line (in this case $P_1(2)$), $T=371$ K is the temperature of the emitter, $M=17$ amu is the weight of the OH molecule.

There is a Lorentzian shaped Van der Waals broadening of the OH line in Ar. Presence of particles in the vicinity of the radiating OH molecule get influenced by Van der Waals Forces. This Van der Waals broadening for the OH molecule has been investigated by Kasyutich et al. [62] at 300 K. Since $T_g$ of the plasma is 371 K, a temperature correction needs to be done. According to [61], the broadening in pm is proportional to $T^{-\frac{5}{3}}$, so after doing the temperature correction, the broadening is 0.97 pm for
Figure 3.9 Rayleigh signal versus the product of the laser pulse energy and pressure. The calibration constant $\alpha$ can be determined from the slope of this graph: $\alpha = 1.4 \cdot 10^7 \pm 0.14 \cdot 10^6 \text{(J·Pa)}^{-1}$. Moreover, the fit is forced through the origin since for no Rayleigh signal, there must be 0 signal, because a background correction has been performed.

OH surrounded by Ar. The Gaussian and Lorentzian FWHM are added as follows [14, 63]:

$$\Delta \lambda = \frac{\Delta \lambda^L}{2} + \sqrt{\frac{\Delta \lambda^L^2}{4} + \Delta \lambda^G^2}. \quad (3.13)$$

For the laser broadening, a measurement performed by Verreycken [59] on the Sirah dye laser is used. It has been performed on a He parallel plate with 500 ppm water at $T_g = 290 \pm 20$ K, of which the profile with a FWHM of 2.1 pm is displayed in figure 3.11.

The Gaussian line broadening in helium is 0.84 pm. The Lorentzian broadening for He due to Van der Waals forces is 0.46 pm for $T_g=290$ K [62].

The disparity between the measured broadening in He and the line broadening of OH in He is caused by the laser broadening. So the deconvolution of the experimental profile and the He line profile are calculated using equation [64]:

$$\begin{align*}
\Delta \lambda^L_{\text{laser}} &= \Delta \lambda^L_{\text{tot}} - \Delta \lambda^L_{\text{line}} \quad (3.14) \\
\Delta \lambda^G_{\text{laser}} &= \sqrt{(\Delta \lambda^G_{\text{tot}})^2 - (\Delta \lambda^G_{\text{line}})^2} 
\end{align*}$$

where $\Delta \lambda^L_{\text{laser}} = 0.54$ pm and $\Delta \lambda^G_{\text{laser}} = 0.89$ pm, which adds up to a total
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![Figure 3.10](image)

**Figure 3.10** Experimental broadening in 4 slm Ar (1.3% water) jet in wavelength (nm). FWHM =3.0 nm, $\Delta \lambda^G=1.65$ pm, $\Delta \lambda^L=1.75$ pm.

The overlap term $g$ (in m) is defined as the integral of the laser profile $L_L(\nu)$ (in m) and the absorption profile $Y_A(\nu)$ (in m) [49]:

$$g = \int_{-\infty}^{\infty} Y_A(\nu) \cdot L_L(\nu) \, d\nu,$$

where $g=0.0024$ m, $\nu$ is the frequency in $(m^{-1})$ and $\int_{-\infty}^{\infty} Y_A(\nu) \, d\nu = 1$ and $\int_{-\infty}^{\infty} L_L(\nu) \, d\nu = 1$, both in dimensionless units. In figure 3.12, $Y_A(\nu)$ and $L_L(\nu)$ are plotted as function of the frequency.

Partridge & Laurendeau [58] defined a dimensionless overlap integral $\Gamma$ as

$$\Gamma = \Delta \nu_L \cdot g,$$

where $\Gamma = 0.222$ and $\Delta \nu_L$ (in $m^{-1}$) is the bandwidth of the laser:

$$\Delta \nu_L = 2\pi \frac{\Delta \lambda_{\text{tot}}^{\text{laser}}}{\lambda_{\text{tot}}^{\text{laser}}},$$

where $\Delta \nu_L=95$ m$^{-1}$. The factor 2 difference between the measured laser broadening and the value in the specifications results into $\Gamma=0.2711$, which is an increase of 22%.

The size of $\Gamma$ has the two effects. First, it affects the laser spectral irradiance. The irradiance mentioned in equation 3.8 referred to the laser irradiance only. When investigating the effect on the absorption of the
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Table 3.3 Broadening parameters. According the dye laser manual, the laser beam linewidth ($\Delta \lambda_L$) is 1.8 pm. After the dye laser, a Second Harmonic Generation Process takes place resulting in a decrease of the linewidth by a factor $2\sqrt{2}$, so 0.64 pm. This $\Delta \lambda_L$ has been experimentally verified by Verreycken [59]. The measured laser broadening is 1.20, so a factor 2 higher.

<table>
<thead>
<tr>
<th>type</th>
<th>Gaussian (pm)</th>
<th>Lorentzian (pm)</th>
<th>total (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>experimental</td>
<td>1.65</td>
<td>1.75</td>
<td>3.0</td>
</tr>
<tr>
<td>total</td>
<td>1.30</td>
<td>1.51</td>
<td>2.86</td>
</tr>
<tr>
<td>Ar line broadening</td>
<td>0.95</td>
<td>0.97</td>
<td>1.55</td>
</tr>
<tr>
<td>laser broadening</td>
<td>0.89</td>
<td>0.54</td>
<td>1.20</td>
</tr>
<tr>
<td>experimental He broadening</td>
<td>1.22</td>
<td>1.00</td>
<td>1.78</td>
</tr>
<tr>
<td>He line broadening</td>
<td>0.84</td>
<td>0.46</td>
<td>0.98</td>
</tr>
<tr>
<td>laser specification</td>
<td>0.64</td>
<td>0</td>
<td>0.64</td>
</tr>
</tbody>
</table>

laser by the OH molecules, $\Gamma$ needs to be incorporated. The laser spectral irradiance obeys to

$$I_s = \frac{E_L \Gamma}{\Delta \nu L \tau_L A_L} = I_L g, \quad (3.19)$$

where $A_L$ is the area of the laser beam. An underestimated $\Gamma$ gives a lower modeled fluorescence with respect to the measured signal, so a higher OH density. This would be the case when the lower, specifications value of the linewidth would have been used.

3.2.3.4 Models

Several different LIF models exist in literature [49]. Most LIF studies use a 2-level model with only a ground level and an excited level. There also exist extensive models such as LASKIN [66], which take into account every rotational state. At higher laser energies, the 2 level model is not valid anymore because of redistribution over other levels. The most common one is to consider the rotational manifold as a lumped single state. This is often allowed as the rotational energy transfer is much faster compared to all other processes at atmospheric pressure and instantaneous equilibrium within the level could be assumed. The other limit is to neglect rotational energy transfer in the OH(X) state, both approaches are discussed in the remainder of this section, hence the two models are:

1. 4 level model (infinitely fast RET in all states),
2. 4 level Dilecce model, an adaptation of the model described by Dilecce et al. [67]. Same model as the above, with the exception that RET=0 in OH(X,$\nu = 0$).
3.2 Laser Induced Fluorescence

![Experimental broadening of OH in a He parallel plate, FWHM is 2.1 pm. $\Delta \lambda^G=1.22$ pm, $\Delta \lambda^L=1.00$ pm.](image)

Both models are discussed, explaining their assumptions.

4 level model

In figure 3.13, the transitions between the four different energy levels are displayed.

The following assumptions are underlying the 4 level model:

1. Only the rotational level $f_1(2)$ is being excited by the laser (see $B_{12}$ in figure 3.13), so a fraction $f_B^{\nu=0,N=2} = 0.169$ of $n_X^{\nu=0}$ for $T_g = 371K$ [40].

2. RET is assumed infinitely fast with respect to all other processes, which is why RET is not incorporated in these equations. It is assumed that RET makes sure there is a Boltzmann distribution over the rotational manifold in all four levels. This means that the quenching and spontaneous emission come from all rotational levels from the thermally distributed state. For stimulated emission this is not the case, since only the transition from $F_1(1)$ to $f_1(2)$ corresponds to the laser energy, so a correction factor $f_B^{\nu=1,N=1}$ is introduced.

3. VET only occurs from $\nu = 1$ to $\nu = 0$. No other vibrational levels are considered.
Chapter 3 Diagnostics and experimental setup

4. Collisional quenching is assumed to only take place with conservation of both the vibrational and rotational number, hence only the collisional quenching processes $Q_{11}$ and $Q_{00}$ occur.

5. Spontaneous emission is limited to the following processes: $A_{11}$, $A_{00}$ and $A_{10}$. This assumption is made because other spontaneous emission processes are at least two orders of magnitude smaller [40].

The aforementioned assumptions and the transitions mentioned in figure 3.13 can be modeled in a set of differential equations, where $n_1$ is $n_{\nu=0}$, $n_2$ is $n_{\nu=1}$, $n_3$ is $n_{\nu=0}$ and $n_4$ is $n_{\nu=1}$, see figure 3.13:

$$
\frac{dn_1}{dt} = f_{i}(t) I_s \left( -B_{12}f_{B}^{\nu=0,N=2}n_1 + B_{21}f_{B}^{\nu=1,N=1}n_2 \right) + A_{10}n_2 + L_0n_3 + V_Xn_4,
$$
$$
\frac{dn_2}{dt} = f_{i}(t) I_s \left( B_{12}f_{B}^{\nu=0,N=2}n_1 - B_{21}f_{B}^{\nu=1,N=1}n_2 \right) - L_1n_2,
$$
$$
\frac{dn_3}{dt} = V_An_2 - L_0n_3,
$$
$$
\frac{dn_4}{dt} = (A_{11} + Q_{11})n_2 - V_Xn_4,
$$

(3.20)

where $L_1$ stands for loss processes in $n_2$, i.e. $L_1 = +A_{11} + A_{10} + Q_{11} + V_A$ which last during the entire duration of the filling of the $\nu = 1$ state. The stimulated emission only takes place during the duration of the laser pulse,
3.2 Laser Induced Fluorescence

Figure 3.13 Transitions between the different energy levels for the 4 level model. There is infinitely fast RET in all four levels.

where \( f(t) \) is a measured time dependent laser function with length \( t_L = 20 \) ns and FWHM \( \tau_L = 7.05 \) ns, which explains why it is stated separately. Moreover, \( L_0 = A_{00} + Q_{00} \), \( f_B^{\nu=0,N=2} = 0.17 \) and \( f_B^{\nu=1,N=1}=0.10 \) [40].

Initial values used in the equations are \( n_{\nu=0}^X=1, n_{\nu=1}^A=0, n_{\nu=0}^A=0 \) and \( n_{\nu=1}^A=0 \). The \( n_{\nu=1}^X \) (\( n_4 \)) state is mainly added for completing the picture, rather than its effect on the \( n_{\nu=0}^X \). \( V_X \) is two order of magnitude smaller than \( V_A \) [68]. So, the time scale of the filling of the \( n_{\nu=0}^X \) due to VET from \( n_{\nu=1}^A \) is \( 1/V_X \), so of the order of \( \mu s \). The laser is only pulsing for \( t_L = 20 \) ns [16], so the effect on the OH density of the filling of \( n_{\nu=0}^X \) by VET from \( n_4 \) is negligible. In table 3.4 all these rates are displayed. In Kienle et al. [69], total RET coefficients are given with \( F_2(5) \) as initial state. Total RET is for \( \nu = 0 \) and \( \nu = 1 \) the same size, within experimental limits [17]. In the present study, the RET for \( F_1(1) \) is studied rather than \( F_2(5) \). Since RET is the same for \( \nu = 0 \) and \( \nu = 1 \) and \( F_1(1) \approx F_1(2) \) (see Appendix), it is sufficient to estimate the total RET for \( F_1(1) \) for knowing the \( f_1(2) \) RET rates.

In table 3.5 the total RET rates for both Ar and H\(_2\)O can be found. In Appendix B, the estimation of the ratios between the different rotational levels can be found. The conclusion is that RET is an order of magnitude faster than the other decay rates.

In the work of Dilecce et al. [67], the VET rates for the transition from \( \nu = 1 \) to \( \nu = 0 \) can be found for both Ar and H\(_2\)O, as well as the quenching rates for both levels. In LIFBASE [40], the rates for the spontaneous emis-

\(^{16}\)Pulse duration \( t_L \), not to be confused with \( \tau_L \), which is the FWHM of the laser pulse.\(^{17}\)This fact is being confirmed by Luque et al. [70], since it is stated that the RET rate of the ground level is similar to the RET rate in the excited level.
Chapter 3 Diagnostics and experimental setup

...can be found. In table 3.6, the RET, VET, $Q_{11}$ and $Q_{00}$ rates can be found for Ar, H$_2$O, N$_2$ and O$_2$.

The LIF signal $S_{\text{LIF}}$ (in # counts) depends on the density of the OH radical in the excited states [49, 75]:

$$S_{\text{LIF}} = \frac{1}{4\pi} \int \eta \frac{hc}{\lambda_{\text{eff}}} n_{\text{OH}} n_{\text{sim}} A_{\text{eff}} dx dy dz dt,$$

(3.21)

where $n_{\text{OH}}$ is the OH density per pixel in m$^{-3}$, $n_{\text{sim}}$ is the normalised simulated effective state density (in dimensionless units), $A_{\text{eff}}$ is the effective Einstein emission coefficient (in s$^{-1}$, of which $\lambda_{\text{eff}}$ (in m) is the effective wavelength at which the emission takes place. Making equation 3.21 specific to the 4 level model yields

$$S_{\text{LIF}} = \frac{1}{4\pi} \int \eta h c n_{\text{OH}} \left( n_2(t) \left( \frac{A_{11}}{\lambda_{11}} + \frac{A_{10}}{\lambda_{10}} \right) + n_3(t) \frac{A_{00}}{\lambda_{00}} \right) dx dy dz dt,$$

(3.22)

$$S_{\text{LIF}} = \frac{1}{4\pi} \eta h c d^2 \Delta s n_{\text{OH}} \int \left( n_2(t) \left( \frac{A_{11}}{\lambda_{11}} + \frac{A_{10}}{\lambda_{10}} \right) + n_3(t) \frac{A_{00}}{\lambda_{00}} \right) dt.$$ (3.23)

Hence the formula for calculating $n_{\text{OH}}$ per pixel is the following [49, 75]:

$$n_{\text{OH}} = \left( 4\pi S_{\text{LIF}} \right) \left( \frac{hc \eta d^2 \Delta s}{\Delta \lambda_{\text{pix}}} \int \left( n_2(t) \left( \frac{A_{11}}{\lambda_{11}} + \frac{A_{10}}{\lambda_{10}} \right) + n_3(t) \frac{A_{00}}{\lambda_{00}} \right) dt \right)^{-1}.$$ (3.24)

The physical parameters have the following meaning:

- $n_{\text{OH}}$ is the absolute $n_{\text{OH}}$ (in m$^{-3}$) per pixel.
- The factor $4\pi$ incorporates the solid angle of $4\pi$ sr.
- $\frac{hc}{\lambda}$ is the laser photon energy:
  - $h$ is Planck's constant $6.63 \cdot 10^{-34}$ Js$^{-1}$.
  - $c$ is the speed of light: $3.00 \cdot 10^8$ ms$^{-1}$.
  - $\lambda$ is the wavelength of emission line. For $A_{00}$ this is 308.9 nm, for $A_{11}$ this is 314.6 nm and for $A_{10}$, this is 282.6 nm.$^{18}$
- $\eta$ stands for a Rayleigh calibration constant, which effectively is the transmission coefficient of the entire experimental setup for the wavelength of 282.6 nm.

$^{18}$Experimentally, the wavelengths 310.0 nm and 314.0 nm have been used, since when optimizing slit opening and wavelength, this provided the highest intensity.
3.2 Laser Induced Fluorescence

![Graph showing simulated densities over time for 1.3% of water and 1.2 mm to the nozzle. 'laser' and $n_1$ belong to the left axes, $n_2$, $n_3$, and $n_4$ belong to the right axes. The maximum of $n_3$ must remain below the maximum of $n_2$ since $n_3$ only gets filled by $n_2$. Emptying of $n_4$ gets two orders of magnitude slower than in case of the other states, so that explains why it raises to a high value and decays slowly.]

- $n_2$ and $n_3$ are the simulated density of two radiative states of the excited OH molecule (in dimensionless units). Three other aspects of OH need to be investigated to determine the OH density. First, in order to compare the OH(A-X)(1-1) and OH(A-X)(0-0) emission, a wavelength resolved spectrum is taken. OH(A-X)(1-1) is emitting around 314.0 nm and OH(A-X)(0-0) around 310.0 nm. Second, the time resolved emission needs to be measured to measure the decay rates of the states $\nu=1$ and $\nu=0$. Third, the LIF intensity will be measured as a function of the distance to the nozzle to see the variation of OH.

- $A_{xy}$ is the optical emission transition rate from vibrational level $x$ to vibrational level $y$ (in s$^{-1}$), values are found in table 3.4.

- $\Delta t$ is the time interval for which the system is relaxed back to its initial condition: $n_1=1$, $n_2=0$, $n_3=0$. 

---

**Figure 3.14** Simulated densities over time for 1.3% of water and 1.2 mm to the nozzle. ‘laser’ and $n_1$ belong to the left axes, $n_2$, $n_3$, and $n_4$ belong to the right axes. The maximum of $n_3$ must remain below the maximum of $n_2$ since $n_3$ only gets filled by $n_2$. Emptying of $n_4$ gets two orders of magnitude slower than in case of the other states, so that explains why it raises to a high value and decays slowly.
Chapter 3 Diagnostics and experimental setup

Figure 3.15 Transitions between the different energy levels for the 4 level Dilecce model. There is no RET in the $n_X^{\nu=0}$ state, there is infinitely fast RET in other three states.

4 level Dilecce model

In order to evaluate the effect of the RET in the ground state, the following model is developed, inspired by the Dilecce et al. [67]. In figure 3.15, it is displayed. The difference between the 4 level Dilecce model and the 4 level model is that the former has no RET at all in the $n_X^{\nu=0}$ state, while the latter has infinitely fast RET in the $n_X^{\nu=0}$ state. Knowing these extremes, yields an error estimate for the OH density.

Note that the assumption of no RET in the ground state $\nu=1$, but infinite RET in the other states is not consistent, since RET should have the same rate regardless of the vibrational level, ground state or excited state [71]. The reason why this approach is still used is to have a maximum estimate of the error which could be due to incomplete RET when the assumptions of the previous model turn out not to be valid.

Since there is no RET in the ground state, the $f_1(2)$ level is only being filled by a fraction $f_{B}^{\nu=0,N=1}$ by stimulated emission or a fraction $f_{B}^{\nu=0,N=2}$ of emission, quenching or VET coming from the other states. This smaller density of the $f_1(2)$ level is resulting in a lower simulated emission for the same experimental OH LIF signal. This results in an overestimate of the $n_{OH}$ with the 4 level Dilecce model with respect to the 4 level model. Together with the 4 level model, the lower and upper bounds for the OH density are provided.

Contrary to the 4 level model, not the entire ground state is modeled, but only the $f_1(2)$ level. After the simulations have been performed, the density of $f_1(2)$ is divided by $f_{B}^{\nu=0,N=2}$ in order to get the total ground state
3.2 Laser Induced Fluorescence

OH density. Starting condition is \( n(X, \nu''=0, f_1(2)) = 1, n^{\nu''=1}_A = 0, n^{\nu''=0}_A = 0 \) and \( n^{\nu''=1}_X = 0 \). The 4 level Dilecce model is governed by the following set of equations:

\[
\begin{align*}
\frac{dn_{1,f_1(2)}}{dt} &= I_s f_1(t) \left( -B_{12} n_{1,f_1(2)} + B_{21} f_{\nu''=1,N=1} n_2 \right) + \\
& \quad f_{\nu''=0,N=2} \left( A_{10} n_2 + L_0 n_3 + V_X n_4 \right), \\
\frac{dn_2}{dt} &= f_1(t) I_s (B_{12} n_{1,f_1(2)} - B_{21} f_{\nu''=1,N=1} n_2) - L_1 n_2, \\
\frac{dn_3}{dt} &= V_0 n_2 - L_0 n_3, \\
\frac{dn_4}{dt} &= (A_{11} + Q_{11}) n_2 - V_X n_4, \quad (3.25)
\end{align*}
\]

3.2.3.5 LIF calibration

In addition to the Rayleigh calibration, the LIF signal itself has to be calibrated as well. First, a correction is made for the optical emission of the plasma by taking a picture with the laser switched off and the plasma on, to capture only the optical emission. Second, it needs to be verified whether the experimental LIF signal is proportional to the simulated LIF signal for the different laser energies. In figure 3.16, the calibration for the experimental LIF signal versus the simulated LIF signal can be appreciated. The LIF signal is linear over the entire energy range. Deviation is with respect to the slope is 10%. In Appendix A.2, the LIF calibration for the other concentrations can be found.
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(a) The experimental LIF signal against the simulated LIF signal. A linear fit is made to see what range is linear, its slope is $2.7 \cdot 10^7$.

(b) Both the modeled LIF signal (blue line) and the measured LIF signal (red dots) versus the laser energy. The model is in line with the experimental data for the entire energy range.

**Figure 3.16** Comparison of the experimental and simulated LIF. The model is in line with the experimental data for the entire energy range. For the eventual OH density calculations a laser energy of 1.24 µJ per pulse is chosen. $\Delta s = 256\mu m$. 

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Table 3.4 Key rates (in s\(^{-1}\)) for different water concentrations.

<table>
<thead>
<tr>
<th></th>
<th>400 ppm</th>
<th>800 ppm</th>
<th>0.16%</th>
<th>0.65%</th>
<th>1.3%</th>
<th>2.6%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(f_1(t)I_sB_{12}f_B^{\nu=0,N=2}) ([40])</td>
<td>1.38(\times)10(^7)</td>
<td>1.38(\times)10(^7)</td>
<td>1.38(\times)10(^7)</td>
<td>1.38(\times)10(^7)</td>
<td>2.13(\times)10(^6)</td>
<td>1.38(\times)10(^7)</td>
</tr>
<tr>
<td>(f_1(t)I_sB_{21}f_B^{\nu=1,N=1}) ([40])</td>
<td>8.23(\times)10(^6)</td>
<td>8.23(\times)10(^6)</td>
<td>8.23(\times)10(^6)</td>
<td>8.23(\times)10(^6)</td>
<td>1.26(\times)10(^6)</td>
<td>8.23(\times)10(^6)</td>
</tr>
</tbody>
</table>

| RET             | 2.3\(\times\)10\(^9\) | 2.4\(\times\)10\(^9\) | 2.4\(\times\)10\(^9\) | 2.5\(\times\)10\(^9\) | 2.6\(\times\)10\(^9\) | 2.9\(\times\)10\(^9\) |

\(L_1\) \([67]\) | 9.7\(\times\)10\(^7\) | 1.0\(\times\)10\(^8\) | 1.1\(\times\)10\(^8\) | 1.8\(\times\)10\(^8\) | 2.6\(\times\)10\(^8\) | 4.3\(\times\)10\(^8\) |

\(VET\) \([67]\) | 8.0\(\times\)10\(^7\) | 8.1\(\times\)10\(^7\) | 8.2\(\times\)10\(^7\) | 8.9\(\times\)10\(^7\) | 9.8\(\times\)10\(^7\) | 1.2\(\times\)10\(^8\) |

\(Q_{11}\) | 1.5\(\times\)10\(^7\) | 2.0\(\times\)10\(^7\) | 2.9\(\times\)10\(^7\) | 8.6\(\times\)10\(^7\) | 1.6\(\times\)10\(^8\) | 3.1\(\times\)10\(^8\) |

\(A_{11}\) \([40]\) | 8.7\(\times\)10\(^5\) |

\(A_{10}\) \([40]\) | 4.6\(\times\)10\(^5\) |

\(L_0\) | 1.8\(\times\)10\(^7\) | 2.4\(\times\)10\(^7\) | 3.5\(\times\)10\(^7\) | 1.0\(\times\)10\(^8\) | 1.9\(\times\)10\(^8\) | 3.6\(\times\)10\(^8\) |

\(Q_{00}\) \([67]\) | 1.7\(\times\)10\(^7\) | 2.2\(\times\)10\(^7\) | 3.3\(\times\)10\(^7\) | 9.9\(\times\)10\(^7\) | 1.9\(\times\)10\(^8\) | 3.6\(\times\)10\(^8\) |

\(A_{00}\) \([40]\) | 1.5\(\times\)10\(^6\) |

\(^1\) \(B_{ij}\) stands for the Einstein B coefficient in mJ\(^{-1}\) from level \(i\) to level \(j\). The ratio between \(B_{12}\) and \(B_{21}\) is given by the equation in LIFBASE \([40]\). \(B_{12} = 1.8\text{mJ}^{-1}\) \([49]\), \(B_{21} = 3.1\text{mJ}^{-1}\). The value displayed here is the value at the maximum of \(f_i(t)\). \(I_s\) is 7 times smaller for 1.3% of water compared to other concentrations.
Chapter 3 Diagnostics and experimental setup

Table 3.5 RET rates (in \(10^{-16} \text{m}^{-3} \text{s}^{-1}\)) for different rotational OH(A) levels for \(\nu = 1\). \(T=300\) K\(^1\). It is assumed that the values are the same for \(\nu = 0\).

<table>
<thead>
<tr>
<th></th>
<th>Ar</th>
<th>H(_2)O</th>
<th>N(_2)</th>
<th>O(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F_2(5))</td>
<td>2.1 [69]</td>
<td>11.7 [69]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(F_1(5))</td>
<td>2.04 [69]</td>
<td>11.4 [71]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(F_1(1))</td>
<td>1.17 [69]</td>
<td>11.4 [72]</td>
<td>4.6 [72]</td>
<td>1.6 [73]</td>
</tr>
</tbody>
</table>

\(^1\) \(T_e = 371\), so an extrapolation should be done for this 24\% higher temperature. According to Jörg et al. [71], the total RET for water (which has the highest RET rate for the considered species) increase a factor 3-4 between 300 K and 1400 K due to the increase in velocity with temperature. So for a 71 K difference this would result into an increase of the RET of H\(_2\)O with 30\%. So the assumption of infinitely fast RET still holds.

Table 3.6 Rates in \(\text{m}^{-3} \text{s}^{-1}\) for the species \(\text{Ar}, \text{H}_2\text{O}, \text{O}_2\) and \(\text{N}_2\).

<table>
<thead>
<tr>
<th></th>
<th>Ar</th>
<th>H(_2)O</th>
<th>N(_2)</th>
<th>O(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RET(^1)</td>
<td>1.17 (\cdot 10^{-16}) [72]</td>
<td>11.4 (\cdot 10^{-16}) [49]</td>
<td>2.9 (\cdot 10^{-16}) [72]</td>
<td>1.5 (\cdot 10^{-16}) [73]</td>
</tr>
<tr>
<td>VET</td>
<td>2.7 (\cdot 10^{-18}) [67]</td>
<td>7.3 (\cdot 10^{-17}) [67]</td>
<td>2.3 (\cdot 10^{-16}) [67]</td>
<td>2.8 (\cdot 10^{-17}) [74]</td>
</tr>
<tr>
<td>(Q_{11})</td>
<td>0.3 (\cdot 10^{-17}) [67]</td>
<td>66 (\cdot 10^{-17}) [67]</td>
<td>0.3 (\cdot 10^{-17}) [67]</td>
<td>18.5 (\cdot 10^{-17}) [74]</td>
</tr>
<tr>
<td>(Q_{00})</td>
<td>0.03 (\cdot 10^{-17}) [67]</td>
<td>68 (\cdot 10^{-17}) [67]</td>
<td>2.8 (\cdot 10^{-17}) [67]</td>
<td>9.6 (\cdot 10^{-17}) [74]</td>
</tr>
</tbody>
</table>

\(^1\) RET of OH(A), \(\nu = 1\), which are assumed to be equal for \(\nu = 0\).
3.3 Tooth whitening

The effect of the OH density on the tooth whitening is going to be measured. First, it is discussed what the plasma settings will be. Second, it is explained how the teeth are prepared. Third, it is explained how the colours are measured.

3.3.1 Plasma settings

The plasma is fixed at a distance of 5 mm from the tooth surface in order to touch the tooth with the visible part of the jet for all concentrations. There are 4 different situations which are tested: pure Ar plasma, 1600 ppm water plasma, 2.6% of water plasma and the pure Ar flow with 2.6% of water (so plasma off).

3.3.2 Tooth preparation

Adult bovine incisor fragments are used. The pulp and nerve tissue are removed and subsequently, surfaces are treated to reduce biohazard. 10mm x 10mm fragments have been cut and embedded in clear resin for true colour measurement.

The tooth staining procedure is as follows:

1. 2 g of fine ground tea is taken.
2. 2 g of fine ground coffee is taken.
3. 200 mL of demineralised H$_2$O is boiled.
4. The above is infused for 10 min.
5. The bovine fragments in the coffee-tea mixture are stored for 96 hours in an incubator at 37°C.
6. After the incubation period has expired, the teeth are rinsed with demineralised H$_2$O.
7. As a final step, the teeth are blotted dry.
8. Take a picture of the teeth for a colour measurement, see 3.3.3.

Seven teeth are used and they are distributed in four groups:

1. two teeth pure Ar
2. two teeth Ar - 1600 ppm H$_2$O
3. two teeth Ar - 2.6 % H$_2$O
4. one tooth Ar flow - 2.6 % H2O, plasma off

The teeth are grouped in such a way that every couple of teeth, has both an initial darker, and an initial lighter one. This way, the effect of the initial tooth colour on the outcomes is minimized.

### 3.3.3 Colour measurement

The Commission Internationale de l’Eclairage (CIE) has set up a colour scale to quantify colour changes in white colours [6, 76], which can be seen both in equation 3.26 as well as in figure 3.17:

\[
\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}.
\]  

(3.26)

This colour change is measured with the Minolta CR-300 CHROMA METER which produces a 3x1 vector of the Lab value for every picture it takes. The Lab value is calibrated with the help of a white plate.
Chapter 4

Results and discussion

In this chapter, the results are presented of the optical emission spectroscopy (OES), laser induced fluorescence (LIF) and tooth whitening measurements. By OES only information about the relative excited state OH(A) is obtained, which can at most relate to relative trends of the excited state of OH concentration. LIF allows to measure the absolute ground state density of OH and with a calibration procedure and a 4 level model, absolute OH densities can be obtained. Ultimately, these experiments are used to discuss the effects observed in the tooth whitening measurements.

4.1 OES

The optical emission results for the excited state OH(A) at the wavelength range of 305.15 until 314.85 nm is measured, of which the band spectrum is plotted in figure 4.1. In order to investigate the relative OH(A) density, not only the relative OH(A) emission should be investigated, but also the quenching of this OH(A). Different water concentration results into different quenching, so the OH(A) emission needs to be corrected for the different water concentrations. The Stern-Volmer relationship provides this link between the pure OES and the OES corrected for quenching [78]:

\[
\frac{OES^0}{OES} = 1 + \tau_0 n \left( Q_{H_2O} f_{H_2O} + Q_{Ar} f_{Ar} + Q_{O_2} f_{O_2} + Q_{N_2} f_{N_2} \right), \quad (4.1)
\]

where OES is the pure OES signal and OES$^0$ is the corrected signal, $\tau_0 = 700$ ns is the lifetime of the excited state OH radical [67], $n$ is the heavy particle density, $Q_x$ is the collisional quenching rate (in s$^{-1}$) and $f_x$ is the relative concentration of the respective species. In figure 4.2, the Stern-Volmer correction factor is displayed. A drawback of the Stern-Volmer method is that a small change for higher water concentrations is exaggerated by a high quenching correction factor.
Chapter 4 Results and discussion

![Figure 4.1 OH spectrum centered at 310 nm for 4 slm Ar - 400 ppm H₂O.](image)

**Figure 4.1** OH spectrum centered at 310 nm for 4 slm Ar - 400 ppm H₂O.

Next, OES and OES⁰ are compared¹ as function of water concentration for three different situations in figure 4.3:

1. Compare the quenching effect for the entire spectrum, so 305.15 nm until 314.85 nm, over the entire length of the jet.

2. The 308.50 nm line is investigated².

3. The average is taken over the distance between 1.15 and 1.25 mm to the nozzle. This relates to the distance closest to the nozzle in case of LIF, where it is 1.2 mm. This is indicated by the rectangle in black in figure 4.1.

There is a steady decrease seen in the uncorrected OES for the spectra for 1.2 mm, the entire 308.50 line, and the full spectrum. Correction for quenching gives a steady OH(A) density until 0.6% of water, whereafter it decreases. Because of the Stern-Volmer correction, a small difference in the

¹ A background measurement for the light intensity with the plasma jet switched off is subtracted from the signal as well as a CCD noise correction is done.

² convolution of Q₁(4) and R₂(1) transition. Q₁(4) is stronger since positive spin (subscript '1') is stronger than negative spin (subscript '2') [40]. LIFBASE also indicates R₂₁(19) and Q₂₁(4), but these will be weak because it considers a spin change.
Figure 4.2 Stern-Volmer correction factor as a function of the water concentration.

OES signal for higher water concentrations is exaggerated. There is hardly any difference between the spectra for 1.2 mm, the entire 308.50 line, or the full spectrum.

The results of a decay in the OES intensity for higher water concentration are also found by Sarani et al. [79], where an Ar-H₂O mixture is used with a flow between 0.695 to 4.82 slm.
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(a) Compare the quenching effect for the entire spectrum, so 305.15 nm until 314.85 nm, over the entire length of the jet. Red line is the OES corrected for background only, blue line is also corrected for quenching.

(b) Compare the quenching effect for the integral over the entire 308.50 band. Red line is the OES corrected for background only, blue line is also corrected for quenching. Averaged over the entire plasma jet length, see green line in figure 4.1.

(c) Comparing the effect of quenching on OES for the 308.50 nm line. Red line is the OES corrected for background only, blue line is also corrected for quenching. The average OES is calculated at a distance between 1.15 and 1.25 mm to the nozzle.

(d) Comparing the OES intensity for distance closest to the nozzle, the entire length of the jet and the entire spectrum, corrected for quenching.

Figure 4.3 Comparing the effect of quenching correction for 1.2 mm to the nozzle, the average over the entire jet length and the average over the entire spectrum. Correction for quenching gives a steady OH(A) density within 15% error until 1% of water, whereafter it decreases. Because of the Stern-Volmer correction, a small difference in the OES signal for higher water concentrations is exaggerated. There is hardly any difference between the spectra for 1.2 mm, the entire 308.50 line, or the full spectrum.
In figure 4.4, image profiles of Ar and N\textsubscript{2} are displayed. Atomic oxygen is observed as well at 777.0 nm, but no parameters were determined from it. H\textsubscript{\alpha} and H\textsubscript{\beta} were not observed, most probably because of a too low S/N.

In figure 4.5, the Ar, N\textsubscript{2} and OH lines are plotted in the same figure as function of water concentration. The exposure time for N\textsubscript{2} is 60s, for Ar and OH the exposure is 10s. Since the N\textsubscript{2} and Ar measurements are from a different series, their flow is 2.5 slm, contrary to the OH flow of 4 slm.

An attempt is made to fit the measured N\textsubscript{2} spectrum with the theoretical spectrum under the assumption of a rotational distribution. It has been tried to fit the rotational temperature of N\textsubscript{2} spectrum with the help of the Specair software [39]. The results are visualized in figure 4.6. None of these provides a good fit: this indicates that the N\textsubscript{2} spectrum has a two-temperature distribution, where the lower wavelengths are fitted with the 500 K distribution and the higher wavelengths with the 700 K distribution. Moreover, it seems that the higher rotational states are overpopulated. This is due to the almost resonant energy transfer between metastables of argon to N\textsubscript{2}(C) which strongly populate high rotational states and leads to overestimations of the gas temperature [80]. The same situation occurred for OH(A), also here the inaccuracy is larger than 50 K. This has been found as well by Bruggeman et al. [81]. Bruggeman et al. have shown that electronic quenching of OH(A) by water prevents thermalization of the rotational population distribution of OH(A). This means that the observed OH(A-X) emission band is partly an image of the formation process and is determined not only by the gas temperature.
(a) Image profile of Ar at 696.5 nm for 2.5 slm Ar and 400 ppm water.

(b) Image profile of N\textsubscript{2} at 337.0 nm for 2.5 slm Ar and 400 ppm water.

Figure 4.4 Image profiles of Ar and N\textsubscript{2}. N\textsubscript{2}(C-B) emission remains high for larger distances to the nozzle. Flow rate is 2.5 slm, since these measurement have been performed in a different measurement series than the 4 slm Ar. Atomic oxygen has been measured as well at 777.0 nm, but no parameters were determined from it. H\textsubscript{α} and H\textsubscript{β} has a too low S/N.
Figure 4.5 Average normalized emission for the three most important species in the jet. OH (308.5 nm, 10s exposure, 4 slm), N\textsubscript{2} (337.0 nm, 60s exposure, 2.5 slm) and Ar (696.5 nm, 10s exposure, 2.5 slm). The flows were different since the measurements have been performed in different series. Intensity is averaged over the entire emission until 6 mm from the nozzle. N\textsubscript{2}(C-B) emission remains high even for high water concentrations. Collisional quenching is not incorporated.
(a) Fitted N$_2$ spectrum for 500 K. The fit is in red, the measured spectrum is in black. For lower wavelengths, the fit does not converge, but for higher wavelengths it does.

(b) Fitted N$_2$ spectrum for 600 K. The fit is in blue, the measured spectrum is in black. The fit converges for neither the lower wavelengths, nor the higher wavelengths.

(c) Fitted N$_2$ spectrum for 700 K. The fit is in red, the measured spectrum is in black. For lower wavelengths, the fit converges, but not for higher wavelengths.

**Figure 4.6** Fitted N$_2$ spectrum for three different temperatures, 500 K, 600 K and 700 K for 4 slm - 400 ppm H$_2$O. None of these provides with a good fit: it seems to be a two-temperature distribution, where the lower wavelengths are fitted with the 700 K distribution and the higher wavelengths with the 500 K distribution.
4.2 LIF

Several parameters have been varied to test the effect on the OH density. Before embarking to present all OH densities with varying parameters, a detailed description of how to obtain the absolute OH density in the case of 1.3% is presented. The case of 1.3% is chosen, for two reasons. First, the absolute OH density is highest for 1.3% of water and from an application point of view, the highest OH density is most interesting. In addition, Bruggeman et al. [13] have performed an absorption measurement to verify the OH density and this is only possible for the highest concentrations of OH, so in this case 1.3% and 2.6%. This experiment is discussed in 4.2.5. In order to know the reproducibility of the kINPen 09, this section will start with explaining the dependance of the plasma jet on the power.

4.2.1 Power dependence

The power dissipated in the plasma has its effect on the electron density, gas temperature and hence the OH density [1]. Therefore, it is crucial to know what power is dissipated within the plasma. However, it is not possible to investigate the effect of the power on the plasma properties of the kINPen. There is only one parameter to be adjusted, which is called ‘adjust’, see figure 4.7. This button regulates the electrical power between the electronic circuit and the plasma, however, this matching can only be read in arbitrary units, and since the kINPen is a commercial product, no information is known about the actual effect of the ‘adjust’ button. In a conversation with Weltmann [82], who manufactures the kINPen, it is explained that the ‘adjust’ button changes the $RC$ time of the internal circuit. Apart from this, no information is disclosed about the working of this knob. Therefore, it is decided to investigate the effect of the ‘adjust’ knob on the LIF intensity. For the case of 0.65% water concentration, the influence on changing the ‘adjust’ button is investigated, see figure 4.7.

For the 0.65% case, the jet is at its maximum length between 3.8 a.u. and 4.6 a.u., observed with the naked eye. In figure 4.8, the LIF intensity corrected for background is plotted as function of the ‘adjust’ setting. At the range where the jet is at its maximum length, there is a variation of 25%. The measurement of adjust 4 has been performed twice and it turns out to be differing already 25%. The adjust setting as a function of the water concentration is plotted in figure 4.9. No relation can be found between these parameters.

4.2.2 The 1.3% water case

Before reaching the point of calculating the absolute OH density from the experimental data, two aspects are discussed. First, the difference in fluo-
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Figure 4.7 The ‘adjust’ button on the kINPen, indicated with the red rectangle.

rescence from the $\nu = 1$ and $\nu = 0$ states is compared to see the effect of the VET. Second, the time dependent change in emission, coming from the $\nu = 1$ and $\nu = 0$ states is discussed. This time dependence will provide insight in the time scales of the filling and emptying of these vibrational states. With the help of these insights the absolute OH density is be determined together with an accuracy analysis.

4.2.2.1 Wavelength resolved LIF emission spectrum

By investigating the wavelength dependence, the size of the VET can be estimated. The wavelength resolved LIF emission spectrum is investigated for the OH(A-X)(1-1) and OH(A-X)(0-0) transitions. It is not possible to measure the OH(A-X)(1-0) transition, since its intensity is at noise level. This could be due to the fact that $A_{10}$ is a factor 1.9 smaller than $A_{11}$.

The following procedure is carried out for calculating the ratio between emission intensity of OH(A-X)(1-1) and OH(A-X)(0-0):

1. The sensitivity is verified by measuring the LIF spectrum in the range 304.0 nm - 312.0 nm (OH(A-X)(0-0)) and 312.0 nm and 320.0 nm (OH(A-X)(1-1)). The measured spectrum is fitted with LIFBASE [40]. This fit is made by varying the vibrational populations of both excited states $\nu = 0$ and $\nu = 1$ until the bands overlap best. It is assumed that
the rotational temperature is equal to the gas temperature here, which is 371 K for 1.3% as could be seen from figure 3.7, for 1.2 mm to the nozzle.

2. A correction for the baseline is made.

3. The Acton spectrometer provides the intensity as a function of pixel number. A calibration is made to convert the pixel number into the wavelength in nm. A linear conversion from pixel to nm does not give the correct spectrum, the wavelength step per pixel varies as a function of the pixel number. In order to correct for this, the converted wavelengths from the pixel numbers are matched with the help of LIFBASE. This is done with the help of a third order polynomial. The polynomial is of the third order since this order proved to be right for the optimum between stability and convergence.

4. The ratio between the $\nu = 1$ and $\nu = 0$ band is calculated dividing the integral from 312.0 nm until 320.0 nm by the integral from 304.0
until 312.0 nm.

In figure 4.10, the wavelength dependence of the LIF signal is displayed. The wavelength-calibrated measured spectrum is compared with the LIFBASE spectrum, created by varying the vibrational populations \( \nu = 0 \) and \( \nu = 1 \) until the experimental and theoretical spectra overlap best.

Five conclusions can be drawn:

1. The fluorescence\(^3\) is equally distributed between \( \nu = 1 \) and \( \nu = 0 \) for 1.3% of water. The measured wavelength ratio, obtained by taking the ratio of the integrated OH(A-X)(1-1) band over the OH(A-X)(0-0) band is 0.91 for \( d = 1.2 \) mm. This indicates that \( Q_{11} \) and VET timescales are competing.

2. For 1.2 mm, the ratio between the OH(A-X)(1-1) and OH(A-X)(0-0) band is 0.96 for the fitted spectrum from LIFBASE, so the accuracy with respect for the measured band ratio is 5%.

3. For 2.7 mm, the ratio between the OH(A-X)(1-1) and OH(A-X)(0-0) band for the LIFBASE spectrum is 0.96, while the measured ratio is 0.77. This difference is 25%. The reason for this disparity will be the bad S/N ratio. Moreover, it seems that the rotational distribution is not fully thermalised.

\[^3\]Equally distributed fluorescence does not necessarily mean equally distributed density, since the emission coefficients are different for OH(A-X)(1-1) and OH(A-X)(0-0), see table 3.4.
4. The wavelength resolution is only measured at two positions, since the low S/N does not allow for larger distances to the nozzle. In 4.2.4, the wavelength dependence for larger distances of the nozzle in case of 400 ppm are discussed.

5. There is a big difference between the 0.3 nm resolution of the time resolved measurement and the 8 nm range over where the model is run. This indicates the importance of making this wavelength resolved measurement to calibrate for the total emission originating from both vibrational levels.
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(a) 1.2 mm distance from nozzle. The wavelength ratio is 0.91, whereas the LIFBASE ratio is 0.96.

(b) 2.7 mm distance from nozzle. The wavelength ratio is 0.77, whereas the LIFBASE ratio is 0.96.

Figure 4.10 LIFBASE signal is compared to fitted measured signal for 1.3% of water. The fit is made at 371 K. The blue vertical line separates the integration areas for OH(A-X)(1-1) and OH(A-X)(0-0). The black lines indicate the wavelength range over which time resolved measurement is done. The LIFBASE spectrum is in red and the measured spectrum is in green.
4.2 LIF

Table 4.1 VET time constant $\tau_{VET}$ and collisional quenching for 1.2 mm to the nozzle and 1.3% water. Reaction rates can be found in table 3.6.

<table>
<thead>
<tr>
<th>species</th>
<th>%mix</th>
<th>$\tau_{VET}$ (s$^{-1}$)</th>
<th>% of total $\tau_{VET}$</th>
<th>$\tau_{Q_{11}}$ (s$^{-1}$)</th>
<th>% of total $\tau_{Q_{11}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>98%</td>
<td>5.2·10$^7$</td>
<td>53%</td>
<td>5.8·10$^6$</td>
<td>3.6%</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.3%</td>
<td>1.9·10$^7$</td>
<td>19%</td>
<td>1.5·10$^8$</td>
<td>93%</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.56%</td>
<td>2.6·10$^7$</td>
<td>27%</td>
<td>3.3·10$^5$</td>
<td>0.2%</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.14%</td>
<td>7.7·10$^5$</td>
<td>1%</td>
<td>4.9·10$^6$</td>
<td>3%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100%</td>
<td>100%</td>
<td>1.6·10$^8$</td>
<td>100%</td>
</tr>
</tbody>
</table>

4.2.2.2 Time resolution

By investigating the time-resolved fluorescence signals corresponding to $A_{11}$ and $A_{00}$, the parameters VET, $L_1$ and $L_0$ can be estimated. This section is subdivided in two subsections: OH(A-X)(1-1) emission and OH(A-X)(0-0) emission.

**OH(A-X)(1-1) fluorescence**

The $\nu = 1$ state is filled by the laser pumping and emptied by four different processes: $L_1 = Q_{11} + V_A + A_{11} + A_{10}$ (see figure 3.13 and equation 3.20). In figure 4.11a, the time evolution of the $\nu = 1$ state can be seen.

The laser profile displayed considers the measured laser profile, obtained from Rayleigh scattering. This Rayleigh signal is slightly asymmetric with a shorter rise time than decay time. Moreover, it is smoothed with a Savitsky-Golay filter. This filter is effective at preserving pertinent high frequency components of the signal and it often used for treating spectra [83].

The $\nu = 1$ fluorescence signal is measured on a relative time scale, so the following calibration is made in order to absolutely compare the time scales. It has been assumed that the $\nu = 1$ peak starts at the same time as the laser signal starts. The laser signal is measured by observing the Rayleigh scattering of the laser light. This rising flank is fitted by varying the amount of intermixed air so as to adapt to the height of the VET. This comes down to an admixture of 0.7%±0.2% of air. In table 4.1, the VET values for the main species can be seen, calculated for 0.7% of air. It can be seen that nitrogen amounts to 27% of all VET.

In order to see if the 0.7% of air admixture is reasonable, the present result is compared with the work of Yonemori *et al.* [84], Reuter *et al.* [24] and Van Gessel *et al.* [85]. It considers different jets, so this discussion should be seen as an order of magnitude indication. The admixture is expected to depend on the used gas, gas flow, tube diameter, temperature etc.
Figure 4.11 Time evolution of emission due to the OH(A-X)(1-1) and OH(A-X)(0-0) transitions for 1.3% of water at 1.2 mm to the nozzle. The decay is twice as high for the OH(A-X)(1-1) transition with respect to the OH(A-X)(0-0) transition, since for the OH(A-X)(1-1) transition VET is an additional loss channel.
4.2 LIF

(a) Visualization of the assumed inter-mixture of air with OH.

(b) Visualization of the actual intermixture of air with OH.

Figure 4.12 Modeled and real intermixture of air. At the edges of the plasma jet, the air concentration percentage will be higher than the average admixture used in the model.

Yonemori et al. investigated the admixture of a 3 slm He plasma jet. At 1 mm the admixture of air is 0.3%, averaged over the outer 1 mm of this jet. Yonemori used fluorescence decay rate for the determination of the air concentration. For the kINPen, the admixture of air is averaged over the entire cross section of the jet. It needs to be mentioned that at the locations where the plasma is in interaction with air, the OH density is lowest while the admixture of air is the highest. So this would mean that locally the admixture can be orders of magnitude higher than the average percentage mentioned here. This is visualized in figure 4.12.

Reuter et al. [24] investigated the admixture of air in a 5 slm Ar and 50 sccm O₂ admixture jet. The air concentration is measured with the help of the photo-absorption of VUV radiation by the ambient air species [24]. Their result is an admixture of air ranging from 0% to 3% of air until 6.7 mm of the nozzle. This gives an accuracy of a factor 4.3.

Van Gessel et al. [85] found that there is a 7 ± 2% admixture of air at 4.3 mm distance from the tube. It considers a microwave surfatron operating at a frequency of 2.45 GHz to create a plasma in a ceramic tube (Al₂O₃) with an inner diameter of 0.8 mm, ending in air. Through the tube Ar is flushed with a flow rate of 1.0 slm.

It can be concluded from these studies, that the admixture of air varies highly on the specific plasma and flow used. The obtained admixture is of the order of magnitude which is observed in different setups.

The decay of OH(A-X)(1-1) is analysed in the following. The fitted decay starts when the Rayleigh signal goes below 1% of its peak value. This assures that no pumping of the laser is involved anymore and the pure decay is considered. This measured decay \( L_{1n}^m \) has a time constant of \( 2.2 \cdot 10^8 \) s⁻¹ and the accuracy of the fit is 3%. The \( L_{1n}^m \) differs 15% from the theoretical value \( L_1 \) for 1.3% of water. From table 3.4, it can be deduced that for 1.3% of water, 72% of the theoretical decay \( L_1 \) is due to electronic quenching, 27% of this decay is accounted to \( V_A \), 0.2% to \( A_{11} \), 0.1% to \( A_{10} \). The electronic quenching is mainly caused by H₂O, as can be concluded from table 4.1.
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Figure 4.13 Ratio between the literature $L_\nu$ and fitted decay rates $L_\nu^m$ for $\nu=1$ and $\nu=0$ as a function of the water concentration. The data points within the ellipses are out of range due to a bad fits. Apart from these points the ratio ranges between 1.0 and 2.0.

**OH(A-X)(0-0) fluorescence**

$\nu = 0$ is pumped by $V_A$ and is emptied by $Q_{00}$ and $A_{00}$, see figure 3.13. The decay is dominated by $Q_{00}$, since $A_{00}$ is two orders of magnitude smaller than $Q_{00}$ (see table 3.4).

In figure 4.11b, the time evolution of the state $\nu = 0$ can be seen. In order to properly fit the $\nu = 0$ decay, the fitted decay starts when the $\nu = 1$ signal goes below 1% of its maximum value. This way, no feeding from the $\nu = 1$ state is involved and the pure decay is measured. This decay $L_0^m$ has a time constant of $1.2 \times 10^8 s^{-1}$, which differs 28% from $L_0$ for 1.3% of water. The accuracy of the fit is 7%, which explains partly the poorer match with the theoretical value than for the OH(A-X)(1-1) transition. For $\frac{L_1}{L_{\nu=1}}$ at 2.6%, the range over which the fit can be made is small, hence the deviation of 2.3.

In figure 4.13, the literature and fitted decay rates $L_1$ and $L_0$ can be found. It can be concluded that the measured decay and the modeled decay have a maximum variation of a factor 2.

### 4.2.2.3 Absolute $\bar{n}_{\text{OH}}$

This section discusses first the OH density itself and will then follow up with an estimate of the uncertainties in this calculations.

With the help of both the time and wavelength resolution, the 4 level
VET model can be run to calculate the absolute OH density. In figure 4.14, the spatially resolved $n_{OH}(x, y)$ density per pixel is shown. The goal of this research is not to have the $n_{OH}(x, y)$ density per pixel, but to have an average $\bar{n}_{OH}$ over the area where the laser is irradiating the plasma, since for applications the average density is more important than the density per pixel. The criterium for the average $\bar{n}_{OH}$ calculation is that the in the $y$ direction, the width is equal to the specified laser FWHM of 255.7 µm, so this equals 10 pixels (see 3.2.3.2). In the $x$ direction, the OH density is averaged over the area within the FWHM of the OH density distribution.

\[
\bar{n}_{OH}(x, y) \cdot 10^{20} \text{ m}^{-3}
\]

![Figure 4.14 Spatially resolved $\bar{n}_{OH}(x, y)$ density per pixel, densities calculated with the help of the 4 level VET model for 1.3% of water at 1.2 mm. The black solid rectangle indicates the area over which the OH density is averaged. The blue dashed rectangle indicates the area where there is scattering of laser light on the kINPen.](image)

In order to provide an error estimate for $\bar{n}_{OH}$, four aspects need to be investigated in order to estimate the maximum error, the deviations are discussed which result in an overestimation of the OH density:

1. Reproducibility of the plasma. The deviation is 25%, see 4.2.1.
2. The accuracy of the model itself. In figure 4.15, the time resolved model and experiment can be seen. The modeled time profile is in line with that of the experiment. The integration time for this calculation is 90 ns to ensure both $\nu = 1$ and $\nu = 0$ have reached 0 such that there is no emission anymore. There is a 7% difference between the integral under the measured curve and the integral under the modeled curve for
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the OH(A-X)(1-1) transition. There is a 18% difference between the integral under the measured curve and the integral under the modeled curve for the OH(A-X)(0-0) transition. Testing for the 4 level Dilecce model which neglects RET in the ground state, only gives an increase of the $\bar{n}_{\text{OH}}$ of a factor 1.2. In the time-dependant result, hardly any difference can be seen between the Dilecce and 4 level VET model.

3. Accuracy of the Rayleigh calibration. According to equation 3.24, the OH density is inversely proportional to $\eta$. An error of 5% in the linear fit results into a 5% error in the OH density.

4. Inaccuracy in determining the physical parameters which are inserted into the equations of the 4 level VET model. The effect of a change in these parameters is presented in detail in table 4.2.

(a) The laser pumping $I_s$ could be changed by a change in all of its five parameters it depends on (see equation 3.19). More pumping leads to more modeled emission, so a lower $\bar{n}_{\text{OH}}$. Considering the laser energy per pulse $E$, the energy fluctuation around its value of 1.24 $\mu$J is 3%. Joosten [49] found a fluctuation of 15%. The reason for this disparity is not clear. $g = \frac{1}{\Delta \sigma_\phi}$ has a deviation of 22% (see 3.2.3.3). The deviation in $\tau_L$ and $A_L$ are small with respect to the others and are therefore neglected. The combined effect of a higher $g$ and higher $E$ give a 20% smaller $n_{\text{OH}}$. A lower $g$ and lower $E$ result into a 25% increase of $n_{\text{OH}}$.

(b) An increase of collisional quenching $Q_{11}$ or $Q_{00}$ leads to a lower OH(A-X)(1-1) and OH(A-X)(0-0), respectively. The error is for 1.3% of water is 1.4 for $\nu = 0$ and 1.2 for $\nu = 1$, see figure 4.13. Consequently, simulated OH density drops, so the measured LIF signal is divided by a lower number, hence resulting in a higher $\bar{n}_{\text{OH}}$. The accuracies can be found in 4.2.2.2.

(c) A change in temperature has three effects. First, it is inversely proportional to $n$, which is proportional to VET and quenching. Lower temperature means a higher VET, resulting into more OH(A-X)(0-0) emission, which has a higher rate than OH(A-X)(1-1). So there is higher emission for the same $S_{\text{LIF}}$, so a lower OH density. On the other hand, higher quenching results into less emission for the same $S_{\text{LIF}}$, so a higher OH density. Second, it affects the Boltzmann factor $f_B$. A lower temperature leads to a higher $f_B$ so a lower OH density. Higher modeled pumping for the same $S_{\text{LIF}}$, results in a lower OH density. The error of the Boltzmann plot with respect to the literature values of Daeschlein [28] and Weltmann [22] is 15%. The effect on quenching is strongest, since when the simulation is run, a 15% decrease in temperature leads to an 9% increase in OH density.
4.2 LIF

(d) The admixture of air, \( f_{\text{air}} \), is unknown. This 25% range is chosen since this is the range where the fitting of the rising flank of the \( \nu = 0 \) state is still correct. The air concentration increases VET and increases quenching. The net effect is that for a 25% increase of air, \( \frac{V_{\text{ET}}}{Q} \) increases with 4%, resulting in a lower OH density.

(e) \( V_A \) is increased with 8% since this is the effect when air concentration is increased with 25%. More VET leads to more emission with \( A_{00} \), so a higher emission for the same \( S_{\text{LIF}} \), so a lower \( \bar{n}_{\text{OH}} \).

(f) An increase in water concentration leads to a higher \( V_A \), so a higher \( \nu = 0 \) so a higher simulated emission, so a lower \( \bar{n}_{\text{OH}} \). Typical variances in water content are caused by the fluctuation of the room temperature. This could be in the range of 294 K-296 K. This results into a change in \( f_{\text{H}_2\text{O}} \) between 1.25% and 1.38% of water. \( f_{\text{H}_2\text{O}} \) has an effect on both the VET and the quenching.

Figure 4.15 Measured and modeled time resolved fluorescence of OH(A-X)(1-1) and OH(A-X)(0-0), as a basis for calculating \( \bar{n}_{\text{OH}} \) for 1.3% of water at 1.2%. Difference between integral under the modeled and measured curve is 7% for OH(A-X)(1-1) and 18% for OH(A-X)(0-0). Here, a room temperature of 21°C is assumed, instead of 22°C in order to get a better fit. This comes down to 1.22% instead of 1.3%.
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Table 4.2 Key parameters and the effect of a variation on $n_{OH}$. Calculated for the case of 1.3% of water at 1.2 mm from the nozzle.

<table>
<thead>
<tr>
<th>parameter</th>
<th>effect on $n_{OH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_s$</td>
<td>20%</td>
</tr>
<tr>
<td>$L_1$</td>
<td>20%</td>
</tr>
<tr>
<td>$L_0$</td>
<td>40%</td>
</tr>
<tr>
<td>$f_{air}$</td>
<td>0.3%</td>
</tr>
<tr>
<td>$f_{H_2O}$</td>
<td>5.7%</td>
</tr>
<tr>
<td>$T_g$</td>
<td>9%</td>
</tr>
</tbody>
</table>

In table 4.2, all sizes of the errors in the OH density calculation can be seen. All errors in the parameters involved, run in the simulation, give an 99% error (so a factor 2). Delicce model gives an upper limit of 20% and there is a 25% reproducibility error due to changes in the plasma.

4.2.3 Water concentration dependence

Before discussing the absolute OH density as a function of water concentration, it is explained how the water concentration heavily influences the properties of the plasma in three ways:

1. More H$_2$O leads to an increased feedstock for OH creation, mainly caused by the following two reactions:

   \[ \text{H}_2\text{O} + e^- \rightarrow \text{OH} + \text{H} + e^- \quad (4.2) \]
   \[ \text{H}_2\text{O} + e^- \rightarrow \text{OH} + \text{H}^- \quad (4.3) \]

   Additionally, by adding water the Ar$_m$ will be depopulated and the following reaction can take place:

   \[ \text{Ar}_m + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H} + \text{Ar} \quad (4.4) \]

   which will become less important when more water is added since all Ar$_m$ is depopulated. From these three reactions, an optimum of OH production is expected.

4 It has been assumed that the intermixed air is dry, i.e. no water vapour is present in the air. In reality, the relative humidity usually has a maximum of 70% [86]. This comes down to a water percentage of 1.8% in the air. Since there is a 0.7% admixture of air assumed, this comes down to 130 ppm of water coming from humid air, mixed into the jet. For the case of 400 ppm, this gives an error of 32%. This error gets proportionally smaller for increasing the water concentration in the Ar flow. The effect of neglecting water coming from the ambient air in the determination of the OH(X) density can be estimated as follows. Water instead of nitrogen and oxygen would result in more quenching and a lower VET. So not incorporating humid air, gives a slight underestimate of the quenching and a slight overestimate of the VET. Both effects lead to an underestimation of the OH density.
2. More H$_2$O results into a more electronegative plasma, so there is a higher electron loss [87], which means that there are less electrons which can dissociate H$_2$O to produce OH [88].

3. The collisional quenching is higher for higher water concentration ($Q_{11}$ is a factor 20 higher for 2.6% than for 400 ppm and $Q_{00}$ is a factor 21 higher for 2.6% than for 400 ppm, see table 3.4). This results into a lower absolute emission from both the OH(A-X)(1-1) and OH(A-X)(0-0) state.

4. The VET gets higher for higher water concentration. This difference is 44% between 2.6% of water and 400 ppm.

5. More H$_2$O leads to a lower $\frac{VET}{Q_{11}}$, which is visualized in figure 4.16a, where $\frac{VET}{Q_{11}}$ is plotted as function of water concentration. The result is that the OH(A-X)(1-1) emission gets stronger with respect to the OH(A-X)(0-0) emission.

![Graphs](a) VET versus quenching for different water content. (b) RET versus decay for different water content.

**Figure 4.16** VET compared to quenching and RET compared to decay rates at 1.2 mm from the nozzle. VET is compared to quenching in order to compare their share in the total loss rate. RET is compared to the total loss rate, so as to indicate whether thermalization from RET is fast with respect to the sum of the other processes taking place.

Considering the last point, in figure 4.17 and table 4.3, for the different water concentrations, the ratio between the $\nu = 1$ and $\nu = 0$ band can be seen, in comparison with its LIFBASE value. The distance is closest to the nozzle, for 1.3% of water this is 1.2 mm and for the other concentrations this has been measured at 0.7 mm from the nozzle. It can be seen clearly that for higher water concentrations, the $\nu = 1$ band is increasing so this means the VET is decreasing substantially for adding more H$_2$O with respect to quenching. The time resolved fits for other water concentrations can be found in Appendix C. There is a proper fit for 0.7% ± 0.2% for 400 ppm - 1.3% of water. Only for 2.6% of water, a higher admixture is needed. This might be explained by the fact that the visible plasma is smaller for this concentration, which could indicate that the admixture of air is higher.
Chapter 4 Results and discussion

(a) 400 ppm Ratio is 0.08 measured and 0.07 LIFBASE.

(b) 800 ppm Ratio is 0.14 measured and 0.09 LIFBASE.

(c) 1600 ppm Ratio is 0.20 measured and 0.19 LIFBASE.

(d) 0.65%. Ratio is 0.55 measured and 0.68 LIFBASE.

(e) 1.3%. Ratio is 0.90 measured and 0.96 LIFBASE.

(f) 2.6%. Ratio is 1.4 measured and 1.5 LIFBASE.

Figure 4.17 Comparison between the calibrated measured signal and the theoretical LIFBASE value. In green is the measured spectrum, the LIFBASE spectrum is in red. The values can be compared in table 4.3.
4.2 LIF

Table 4.3 Comparison between the integral over the calibrated measured signal and the integral over the theoretical LIFBASE spectrum, corresponding to figure 4.17. Also the fitted air concentrations are provided. For higher water concentrations, a better fit is made with more air admixed. The sensitivity on the air concentration is low, see table 4.2.

<table>
<thead>
<tr>
<th>water concentration</th>
<th>fitted measured signal</th>
<th>LIFBASE</th>
<th>$f_{\text{H}_2\text{O}}$</th>
<th>$f_{\text{air}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6%</td>
<td>1.4</td>
<td>1.5</td>
<td>2.6</td>
<td>1.7%</td>
</tr>
<tr>
<td>1.3%</td>
<td>0.91</td>
<td>0.96</td>
<td>1.1%</td>
<td>0.9%</td>
</tr>
<tr>
<td>0.65%</td>
<td>0.55</td>
<td>0.68</td>
<td>0.65%</td>
<td>0.7%</td>
</tr>
<tr>
<td>1600 ppm</td>
<td>0.20</td>
<td>0.19</td>
<td>1600 ppm</td>
<td>0.7%</td>
</tr>
<tr>
<td>800 ppm</td>
<td>0.14</td>
<td>0.09</td>
<td>800 ppm</td>
<td>0.7%</td>
</tr>
<tr>
<td>400 ppm</td>
<td>0.08</td>
<td>0.07</td>
<td>400 ppm</td>
<td>0.7%</td>
</tr>
</tbody>
</table>

Now the effect of VET is known, the absolute density can be calculated. In figure 4.26a, the absolute $\bar{n}_{\text{OH}}$ is plotted versus the water concentration, together with the raw LIF signal. Three conclusions can be drawn:

1. $\bar{n}_{\text{OH}}$ increases linearly for increasing water concentration until 1.3%, whereafter it decreases at the maximum value of 2.6%. This optimum can be explained by the aforementioned reactions 4.2, 4.3 and 4.4. The reason that $\bar{n}_{\text{OH}}$ gets smaller for 2.6% of water is that the plasma is less stable, since the plasma has 2.6% of water, which is absorbing energy in the molecular rotations and vibrations.

2. The OH density is maximum for 1.3% of water.

3. The value of setting up a model becomes evident for two reasons. First, an absolute density can be determined. Second, it can be seen that also the relative density is different than in case of the raw LIF signal corrected for quenching.

4.2.4 Spatially resolved $\bar{n}_{\text{OH}}$

For applications in for instance tooth whitening, it is important to know how the OH density varies along the jet. Two parameters are important to investigate $\bar{n}_{\text{OH}}$ spatially resolved: the average $\bar{n}_{\text{OH}}$ and its FWHM. In order to provide $\bar{n}_{\text{OH}}$ as a function of the distance along the plasma jet, the temperature, the decay rates and air admixture have been varied as a function of the distance to the nozzle. First their effects will be discussed, before elaborating on the effect of the OH density itself and its FWHM in 4.2.4.1. The decay of both OH(A-X)(1-1) and OH(A-X)(0-0) are investigated as function of the distance to the nozzle. The measured decay time constants are visualized in table 4.5. For high water concentrations, like in
Chapter 4 Results and discussion

(a) $\bar{n}_{\text{OH}}$ and raw LIF signal versus water concentration.

(b) $\bar{n}_{\text{OH}}$ and raw LIF signal divided by $L_1$.

Figure 4.18 $\bar{n}_{\text{OH}}$ versus water concentration. From the fact that the behaviour of both the raw LIF and the raw LIF corrected for quenching is different than the modeled LIF, the value of the model becomes clear in addition to calculating the absolute density.

...omitted...

...omitted...

In order to determine the effect of the admixture of air, the measurement of 400 ppm is used. When using 1.3% measurements, the high quenching by water would overrule the effect of the nitrogen. More air results into a higher VET and a higher quenching, and the ratio of VET over quenching increases with a factor 1.25 when double the amount of intermixed air. This would result into more emission from OH(A-X)(0-0) with respect to OH(A-X)(1-1). This higher modeled emission would result in a lower OH density. In figure 4.19, the spectra are seen as function of the distance to the nozzle.

Four conclusions can be drawn.
1. It can be seen that for 400 ppm the OH(A-X)(0-0) transition is relatively stronger than in case of 1.3% of water, comparing figures 4.19 and 4.10. This is since VET/Q_{11} is 5.3 for 400 ppm and 0.61 for 1.3%. The VET is so strong in the case of 400 ppm water that most of the OH is transferred to the \( \nu = 0 \) state.

2. The S/N is worse for 6.7 mm from the nozzle. This is since the fluorescence intensity is 4.6 times lower in the case of 6.7 mm versus 0.7 mm.

3. It can be concluded that the VET does not change significantly for a higher distance to the nozzle. Therefore, the fitted air concentration of 0.7\%\pm0.2\% at 1.2 mm from the nozzle can be used for the entire range of 0.7 mm until 6.7 mm of the nozzle. This value is valid for all concentrations, except for 2.6\% of water. This is probably due to the fact that the plasma gets less stable due to its high molecular content.

4. It can be seen that the LIFBASE spectrum in red does not change significantly between 78\% and 92\% of the population in \( \nu = 1 \) in the range of 0.7-6.7 mm from the nozzle. So there is an inaccuracy of 7\% for the determination of the population in level \( \nu = 1 \).
Table 4.4 $\bar{n}_{\text{OH}}$ at 1.2 mm from the nozzle, signal-to-noise ratio (S/N) and the percentage of water which is converted to OH, given for different water vapour pressures. $T_g$ and $f_B$ for different water concentrations at 0.76 mm, except for 1.3% where it is at 1.2 mm. The S/N for 1.3% of water is smaller than for the other concentrations, since it is measured in different conditions.

<table>
<thead>
<tr>
<th>water concentration</th>
<th>$\bar{n}_{\text{OH}}$ ($10^{20}\text{m}^{-3}$)</th>
<th>$\bar{n}_{\text{OH}}$ (Dilecce) ($10^{20}\text{m}^{-3}$)</th>
<th>S/N</th>
<th>$\bar{n}_{\text{OH}}$ (ppm)</th>
<th>%H$_2$O</th>
<th>$T_g$(K)$^1$</th>
<th>$f_B$[40]</th>
<th>length jet (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6%</td>
<td>1.9</td>
<td>2.5</td>
<td>3.7·10$^2$</td>
<td>9.7</td>
<td>0.04</td>
<td>371±16</td>
<td>0.168</td>
<td>S/N too low</td>
</tr>
<tr>
<td>1.3 %</td>
<td>3.3</td>
<td>3.5</td>
<td>24</td>
<td>16.7</td>
<td>0.16</td>
<td>371±16</td>
<td>0.168</td>
<td>7.8</td>
</tr>
<tr>
<td>0.65 %</td>
<td>1.0</td>
<td>1.3</td>
<td>$1.1\cdot10^3$</td>
<td>5.1</td>
<td>0.08</td>
<td>368±8</td>
<td>0.169</td>
<td>9.6</td>
</tr>
<tr>
<td>1600 ppm</td>
<td>0.2</td>
<td>0.2</td>
<td>$6.1\cdot10^2$</td>
<td>1.0</td>
<td>0.06</td>
<td>378±8</td>
<td>0.166</td>
<td>11.0</td>
</tr>
<tr>
<td>800 ppm</td>
<td>0.1</td>
<td>0.1</td>
<td>$2.5\cdot10^2$</td>
<td>0.4</td>
<td>0.05</td>
<td>371±10</td>
<td>0.168</td>
<td>9.7</td>
</tr>
<tr>
<td>400 ppm</td>
<td>0.1</td>
<td>0.1</td>
<td>$4.6\cdot10^2$</td>
<td>0.5</td>
<td>0.12</td>
<td>366±8</td>
<td>0.170</td>
<td></td>
</tr>
</tbody>
</table>

$^1$ The deviation given considers the maximum deviation, i.e. there is upper and lower bound. Here the maximum of these two is given.
4.2 LIF

Figure 4.19 Wavelength dependence for various distances to the nozzle in case of 400 ppm. The 400 ppm case is displayed, since its S/N is better than in case of 1.3% of water. In green is the measured spectrum, the LIFBASE spectrum is in red. It can be seen that the LIFBASE spectrum in red does not change significantly between 78% and 92% of the population in \( \nu = 1 \) in the range of 0.7-6.7 mm from the nozzle. So there is an inaccuracy of 7% for the determination of the population in level \( \nu = 1 \).
Chapter 4 Results and discussion

4.2.4.1 $n_{OH}$ cross section

The $n_{OH}$ cross section is can be plotted along the laser beam for 4 different distances from the nozzle, see figure 4.20. A gradual decrease in $\bar{n}_{OH}$ can be seen and a decrease in FWHM. Note that only an average air concentration is incorporated, see figure 4.13.

![Graphs showing $n_{OH}$ and FWHM at different distances](image)

(a) 1.2 mm from the nozzle. $\bar{n}_{OH} = 2.8 \times 10^{21}$ m$^{-3}$, FWHM=1.9 mm.
(b) 2.7 mm from the nozzle. $\bar{n}_{OH} = 2.6 \times 10^{21}$ m$^{-3}$, FWHM=1.4 mm.
(c) 4.2 mm from the nozzle. $\bar{n}_{OH} = 1.2 \times 10^{21}$ m$^{-3}$, FWHM=1.3 mm.
(d) 5.7 mm from the nozzle. $\bar{n}_{OH} = 0.73 \times 10^{21}$ m$^{-3}$, FWHM=1.0 mm.

Figure 4.20 $\bar{n}_{OH}$ and FWHM at 4 different distances to the nozzle for 1.3% of water. A gradual decrease can be seen for both $\bar{n}_{OH}$ and FWHM for longer distance to the nozzle. Length of UV emission is 10.3 mm.

In figure 4.21, the spatial resolved $\bar{n}_{OH}$ and its FWHM is displayed. A gradual decrease can be seen for both $\bar{n}_{OH}$ and FWHM for longer distance to the nozzle

To conclude this part, the difference in height of 0.5 mm between the OH density measurement and the time resolved, wavelength resolved and gas temperature measurements on the 400 ppm, 800 ppm, 1600 ppm, 0.65%, 1.3% and 2.6% need to be discussed:

1. The wavelength dependent spectrum does not significantly change over

---

\(^5\)From this figure, an indication can be given about the error made in $\bar{n}_{OH}$ because of the difference of 5 mm in distance to the nozzle. When interpolating between the 1.2 mm and 2.7 mm measurement, it can be seen there is a 18% lower density for a 0.5 mm larger distance to the nozzle. So this means that for comparing the 1.2 mm of 1.3% of water with the 0.7 mm case of the other concentrations, the $\bar{n}_{OH}$ is even 18% higher.
4.2 LIF

Figure 4.21 Spatially resolved \( \bar{n}_{\text{OH}} \) and FWHM for 1.3\% of water. A gradual decrease can be seen for both \( \bar{n}_{\text{OH}} \) and FWHM for longer distance to the nozzle.

1. The temperature change over 0.5 mm equals 4.5 K (see 3.2.3.1). This is within the error of the Boltzmann plot (see table 4.4), so this does not need to be corrected for.

2. The temperature change over 0.5 mm equals 4.5 K (see 3.2.3.1). This is within the error of the Boltzmann plot (see table 4.4), so this does not need to be corrected for.

3. The OH density changes \( 7 \times 10^{20} \) over 0.5 mm; an error of 18\%.

4. The time resolved measurements are used for determining \( L_1 \) and \( L_0 \) do not vary for the distance to the nozzle.

In order to extrapolate the results beyond the measurement at 5.7 mm from the nozzle, the raw LIF signal can be used. The only factor which is changed in the model over a distance of 5.7 mm is the raw LIF signal and a 2\% temperature decrease, since the temperature is assumed to start decaying after 5 mm. The error which will be made in extrapolating with the help of the raw LIF signal, is that a possible change of admixture of air is not incorporated and that no temperature correction is done. Both effects results into a decrease of the OH density, so the result is an overestimation of the OH density. The result can be seen in figure 4.22.
Chapter 4 Results and discussion

Figure 4.22 Comparison of the measured and extrapolated $n_{\text{OH}}$ as function of the distance to the nozzle. The biggest deviation is a factor 1.6. The extrapolation gives an overestimate since the temperature decrease is not incorporated.
4.2 LIF

4.2.5 Comparison of LIF with absorption and OES experiment

In figure 4.23, the absolute OH density can be seen as a function of the distance to the nozzle for the absorption experiment for 1.3% and 2.6%. Details can be found in Bruggeman et al. [21]. The absorption length is obtained from the position dependent FWHM. A correction has been made for the spatial dependant $f_B$ from figure 3.7.

The error bars are higher for a smaller distance to the nozzle. This can be explained by the fact that the optical emission is higher for a closer distance to the nozzle, disturbing the absorption measurement (see section 4.1). Detection limit is at around 6 mm distance to the nozzle, because of low S/N due to decreasing OH density. Accuracy in absorption is a factor two, because of the inaccuracy of making a baseline fit. The accuracy in LIF is a factor two as well. The difference in absolute density between LIF and absorption is a factor 2 for both 1.3% of water and 2.6% of water, see figure 4.24. LIF is a factor 2 lower than absorption. The accuracy of LIF is a factor two, so this is within the experimental error.

In figure 4.25, LIF and OES are plotted as function of the water concentration. OH(A) remains flat until 1% and then decreases. For higher concentrations, there is a high Stern-Volmer correction factor, so the results are less reliable. OH(X) rises until 1.3% and then decreases. This difference could be explained that for more water, more OH(X) is created and at the same time OH(A) production gets less efficient because of the electronegativity of the plasma.

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This is under the assumption that the presented model would be correct. The accuracy factor would be even higher when incorporating errors due to the basic assumptions made.
Chapter 4 Results and discussion

(a) LIF versus absorption as function of distance to the nozzle for 1.3%.

(b) LIF versus absorption as function of distance to the nozzle for 2.6%.

Figure 4.24 LIF versus absorption as function of distance to the nozzle for 1.3% and 2.6%.

Figure 4.25 LIF and OES as function of water concentration. OH(A) remains flat until 1% and then decreases. For higher concentrations, there is a high Stern-Volmer correction factor, so the results are less accurate. OH(X) rises until 1.3% and then decreases. This difference could be explained that for more water, more OH(X) is created and at the same time OH(A) production gets less efficient because of the electronegativity of the plasma.
4.3 Tooth whitening

In figure 4.26, the effect of plasma treatment over time can be seen. The error bars are calculated by the standard deviation on the three pictures which were taken for every measurement.

Three conclusions can be drawn:

1. There is a significant effect of the plasma with respect to the zero measurement of the mere gas flow, the difference is a factor 6.

2. The varying water concentration has no significant influence:
   - The final value of $\Delta E$ is 5-7 regardless of water concentration for darker teeth. This colour change is not visible with the naked eye.
   - For lighter teeth, there seems to be a slight difference between the three measured concentrations. In figure 4.27, $\bar{n}_{OH}$ is plotted as function of their distance to the nozzle for three concentrations: 1.3% of water, 1600 ppm and 800 ppm. This in order to investigate why in figure 4.26b the concentration of 0% water is higher than 1600 ppm. The reason why 800 ppm is used instead of 400 ppm is that the time resolved fit is better for 800 ppm than for 400 ppm (see Appendix C). A difference in OH density does not explain why the 0% treatment results into a higher whitening effect than the 1600 ppm measurements.
   - The time constant for an increase of $\Delta E$ is 5-7 is 20 minutes regardless of water concentration.

3. $\Delta E$ is caused by a higher $L$ value (whiter teeth), a smaller $a$ value (decrease in redness) and constant $b$ (yellowness).

4. The effect is three times smaller than in the work of Lee et al. [6], where a He jet is combined with $\text{H}_2\text{O}_2$ treatment. The tooth whitening in
Chapter 4 Results and discussion

Figure 4.27 $\bar{n}_{\text{OH}}$ as function of distance for varying water concentrations.

the case of Lee et al. is higher, because of the dissociation of H$_2$O$_2$. This whitening effect is visible with the naked eye.

There are 3 limitations to the study performed.

1. Only around 5% of the area being photographed is treated with the plasma jet because of the 2 mm diameter of the kINPen needle. So the area of interaction should be increased.

2. Moreover, only 7 teeth were measured, with a high variation in initial tooth colour.

3. For different water concentration, there is a different jet size while the measurement has been performed on the same height while the tip of the plasma jet is always touching the tooth surface.
Chapter 5

Conclusion and outlook

5.1 Conclusion

The plasma reproducibility is 25%. Apart from this, in this chapter the other main findings will be presented, together with an outlook on future research opportunities.

5.1.1 OES

A decrease is found in the OH(A) emission for increasing water content despite the increase in OH density. This holds both for pure emission as well as the emission corrected for quenching. As a function of the distance to the nozzle, the OH(A) is increasing. When correcting for quenching, OH(A) density remains stable within 15% until 1%. For higher water concentrations the OH(A) density decreases. However, because of the high quenching correction, the results get less accurate.

It is not possible to use the OH emission as a relative utilization of the ground state OH density. When fitting the nitrogen temperature, a temperature fit with the lowest fit at 500 K and the highest fit at 700 K. This means that the excited state distribution is not thermalised and cannot be used for gas temperature measurements.

5.1.2 LIF

LIF measurements have been combined with a 4 level VET model to find absolute densities, with an accuracy of a factor 2.0. For both 1.3% and 2.6% of water, the density measured with LIF is 2 times lower than measured with absorption. Since accuracy in LIF is a factor two, this means that the difference in absolute density are just within error range. The density measured by LIF has been investigated as function of the distance to the nozzle, where $\bar{n}_{\text{OH}}$ decreases with an order of magnitude from $10^{20}$ m$^{-3}$ to $10^{19}$ m$^{-3}$ over the 10 mm visible range of the jet. It has been possible to confirm until 6.7
mm that both the quenching and the admixture of air remain constant as a function of the distance to the nozzle. The modeled and measured time resolved results overlap with the highest error of 18%. Also the present model has been compared with the model of Dilecce and this provides a deviation of 25%. Setting up the present model is valuable, since simply using the raw LIF signal, even when corrected by the quenching constant, OH density dependance for varying water concentrations. Additionally, the gas temperature has been determined with the help of a Boltzmann, resulting in an accuracy of 15%. The water concentration results in a linear increase of the OH density until it reaches it maximum at 1.3%, whereafter it decreases. It is interesting to compare LIF and OES, since LIF provides the absolute ground state density OH(X) and OES provides the relative density OH(A), when corrected for quenching. The result of OES is that OH(A) density remains flat until 1% and then decreases. For higher concentrations, there is a high Stern-Volmer correction factor, so the results are less reliable. OH(X) rises until 1.3% and then decreases. This difference could be explained that for more water, more OH(X) is created and at the same time OH(A) production gets less efficient because of the electronegativity of the plasma.

5.1.3 Tooth whitening

There is a significant effect of the plasma with respect to the zero measurement of using the mere gas flow, while the variation of the water concentration has no significant effect. However, the whitening effect can only be detected by a camera and not by the naked eye. The tooth whitening is three times smaller with respect to the method using H$_2$O$_2$.

5.2 Outlook

5.2.1 Tooth whitening

Three aspects could be investigated to test if plasma tooth whitening could become successful. First, it should be tested whether a higher OH density results into a stronger whitening effect. Tooth whitening experiments could be performed with a plasma with a larger plasma diameter. This way, a bigger area could be treated at once. The drawback is that a bigger plasma jet requires a higher power to create and sustain the discharge, resulting in heating of the gas. This gas heating could be circumvented by using a coaxial gas flow specifically dedicated to cooling. The Ar gas could also be bubbled through hydrogen peroxide. The plasma will dissociate the hydrogen peroxide into 2 OH radicals. This way, the OH density can be significantly increased. Second, the effect of UV should be investigated. There is 3.6 eV needed to break a single carbon-carbon bond. This energy can be reached
by photons with a wavelength lower than 340 nm. A third method is to compare the plasma whitening by liquid hydrogen peroxide whitening. A liquid can reach also the dentine of the tooth, so it could have a whitening effect there. The OH radicals only reach the tooth enamel.

5.2.2 Improvements LIF setup

For the LIF setup, the S/N could be improved so as to measure wavelength dependencies for a longer distance to the nozzle when a different ICCD would be used. The 4QuikE has no sufficient cooling and hence a limited S/N.

5.2.3 Electron temperature and electron density

In order to give an in-depth view on the plasma chemistry, the electron temperature and electron density should be measured. Thomson scattering is a common tool for determining the electron temperature.

Zhu et al. [31] describe a method where the line-ratio of different Ar lines are used for determining the electron density.

5.2.4 OH in water

Since there is a water layer on the tooth, interaction of the plasma with water is an important effect to investigate. When determining how much OH is formed in the water, terephthalic acid should be used as reagent, since it is most specific and exclusively reacts with OH [89]. TA works as follows. TA reacts with OH into HTA, which emits light at 425 nm, while TA molecules themselves do not. This is displayed in figure 5.1. Then the fluorescence is directly proportional to the HTA density, which has a 30% conversion [90]. With the help of a known amount of HTA which can be bought in pure form, an absolute calibration can be made, so an absolute OH concentration can be measured. OH has a life time in the order of microseconds (Van Gils et al. [91]), in water so it needs to be investigated if the reaction with TA can compete with the reactions in water.
Chapter 5 Conclusion and outlook

Figure 5.1 Formation of HTA via the reaction of TA and OH radical\cite{89}. 

\begin{align*}
&\text{TA} & \text{HTA} \\
&\text{O} & \text{O} \\
&\text{OH} & \text{OH} \\
&\text{O} & \text{O} \\
&\text{O} & \text{OH} \\
&\text{Non-fluorescent} & \text{Fluorescent} \\
&\text{310 nm} & \text{425 nm}
\end{align*}
Acknowledgements

First, I would like to thank my direct TU/e supervisor Peter Bruggeman. From Peter I have learned much in critical thinking. My thanks go also out to Daiyu Hayashi, supervisor from Philips and from whom I have learned how research is done in companies. Sven Hofmann I would like to thank for spending the days in the lab constructing a new setup. From Tiny Verreycken I have received great assistance during the performance of the LIF experiments and in the analysis thereafter. Ruud van der Horst has been helping out in a great way with the modelling of the LIF experiments. Eddie van Veldhuizen, Ab Schrader en Lock Baede were always there for me if there were practical arrangements to be made. The atmosphere in the groups in general and in the student rooms in particular at both TU/e and Philips has always been great. Especially the days with Koen van Gils, Thomas Lemmens, Peter Verhoeven, Rogier van den Bos and Kim Alards were great. Feedback has always been helpful and we have had great laughs! Last, I would like to express my respect and gratefulness for Robbert Mahler, who has supported me throughout the entire thesis.
Chapter 5 Conclusion and outlook
Appendix A

Other water concentrations

In this chapter, the measurements for other concentrations than 1.3% of water are discussed. The difference in laser energy and camera has affected the Rayleigh measurement, the LIF calibration and the linebroadening. All of these three measurements are discussed next.

A.1 Rayleigh calibration

For water concentrations other than 1.3%, the Andor camera rather than the 4QuikE has been used. Therefore, the Rayleigh calibration is different. Also, the laser energy is different.

In figure A.1, the Rayleigh intensity versus laser energy is plotted. The linear range is 5 times higher than in the case of the 1.3% of water. In case of 1.3% water, the dye of the laser got older, so its energy decreases [59].
Appendix A Other water concentrations

Figure A.1 Rayleigh signal versus the energy of the laser pulse times the pressure. Plasma and gas flow are switched off. The calibration constant $\alpha$ can be determined: $\alpha = 2.712 \cdot 10^6 \pm 0.066 \cdot 10^6 (J \cdot Pa)^{-1}$. For the fit, only the values up until 1.05 J Pa are incorporated (see vertical red line). Moreover, the fit is forced through the origin since for no Rayleigh signal, there must be 0 signal, because a background correction has been performed.
A.2 LIF simulation calibration

Figure A.2 Comparison of the experimental and simulated LIF. For energies in excess of 10 µJ, the Rayleigh signal is not linear anymore. The LIF measurements have been performed at an energy of 8.1 µJ.

A.2 LIF simulation calibration

For the LIF experiments with a different water concentration than 1.3%, a different laser energy has been used and hence there is a different calibration of the experimental LIF signal versus the simulated LIF signal and a different relation to the laser energy.

In figure A.2, the experimental versus simulated LIF as well as its function of energy is displayed.
Appendix A Other water concentrations

Figure A.3 Experimental broadening in 4 slm Ar jet in wavelength (nm). \( \Delta \lambda_G = 2.3 \text{ pm}, \Delta \lambda_L = 2.1 \text{ pm}, \text{FWHM} = 4.0 \text{ pm} \).

A.3 Line broadening

The line broadening for other water concentrations than 1.3% is displayed in figure A.3. \( \Delta \lambda_G = 2.3 \text{ pm}, \Delta \lambda_L = 2.1 \text{ pm}, \text{FWHM} = 4.0 \text{ pm} \). FWHM is 33% wider than in case of 1.3% of water, due to a 5 times higher laser energy.
Appendix B

RET rotational levels

The RET value depends on the rotational level. In this section, the calculation of this RET for $F_1(1)$ and $f_1(2)$ is explained for Ar, N$_2$ and O$_2$.

For Ar, the work of Kienle et al. [72] is used. In figure 10 of this work can be seen that there is a ratio of 1.8 between $F_1(5)$ and $F_1(1)$. For calculating $F_1(1)$, multiply the $F_1(5)$ rate by 1.8. From Joosten [49], it can be determined that the ratio between the OH($A, \nu = 0, F_2(5)$) and OH($A, \nu = 0, F_1(5)$) =1.03 in general. There is a 10% difference between $F_1(1)$ and $F_1(2)$, hence a 10% of difference between $F_1(1)$ and $f_1(2)$. For H$_2$O, no information is given about $F_1(2)$, so it is assumed that $f_1(2)=F_1(1)$.

For N$_2$, the total RET is compared with the total RET of H$_2$O and it is 2.5 times smaller [72]. So also for N$_2$ it is assumed that $f_1(2)=F_1(1)$.

For O$_2$, no total RET rates for the level $F_1(1)$ can be found, only ensemble-average RET rate constants over the range $N'' = 1 - 14$ [73] is given. In order to estimate the rate for $F_1(1)$ in O$_2$, the ensemble averaged rate of O$_2$ is compared with that of H$_2$O. The ensemble averaged rate for O$_2$ is 7.3 times smaller than that of H$_2$O, so the rate is $1.5 \cdot 10^{-16}$ m$^{-3}$ s$^{-1}$. 

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Appendix B RET rotational levels
Appendix C

Time resolved results

In figure C.1, the time resolved results for 2.6%, 1.3% and 0.65% can be found. In figure C.2 the time resolved results for 1600 ppm, 800 ppm and 400 ppm can be found. Both 4 level model and 4 level Dilecce model give a good fit for 2.6%-800 ppm of water. For 400 ppm, the fit is off. This could be explained by the fact that the inaccuracy for such a low flow is high. Note the difference in time scale between figure C.1 and figure C.2. This is since for low water concentrations, the decay of level $n_3$ is low.
Appendix C Time resolved results

Figure C.1 Time resolved states for concentrations 2.6%, 1.3% and 0.65%. The left columns describes the 4 level VET model, the right column describes the 4 level Dilecce model.
Figure C.2 Time resolved states for concentrations 1600 ppm, 800 ppm and 400 ppm. The left columns describes the 4 level VET model, the right column describes the 4 level Dilecce model. Time scale is larger than in case of figure C.1, because the quenching is smaller for these lower water concentrations.
Appendix C Time resolved results
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