Time-resolved absolute OH density of a nanosecond pulsed discharge in atmospheric pressure He–H₂O: absolute calibration, collisional quenching and the importance of charged species in OH production

This content has been downloaded from IOPscience. Please scroll down to see the full text.
2014 Plasma Sources Sci. Technol. 23 045005

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 131.155.151.148
This content was downloaded on 19/12/2014 at 11:16

Please note that terms and conditions apply.
Time-resolved absolute OH density of a nanosecond pulsed discharge in atmospheric pressure He–H₂O: absolute calibration, collisional quenching and the importance of charged species in OH production

T Verreycken¹, N Sadeghi² and P J Bruggeman¹,³

¹ Department of Applied Physics, Technische Universiteit Eindhoven, PO Box 513, 5600 MB Eindhoven, The Netherlands
² LIPhy (UMR 5588) & LTM (UMR 5129), Université de Grenoble / CNRS, Grenoble F-38041, France
³ Department of Mechanical Engineering, University of Minnesota, 111 Church Street SE, Minneapolis, MN 55455, USA

E-mail: pbruggem@umn.edu

Received 17 March 2014, revised 14 May 2014
Accepted for publication 23 May 2014
Published 17 June 2014

Abstract
The time-resolved OH density in a nanosecond pulsed filamentary discharge in an atmospheric pressure He–H₂O(0.05%) mixture is measured using laser induced fluorescence. The lifetime of the excited OH(A) state is found to be strongly time dependent during the plasma pulse, with the shortest decay time occurring at the moment the plasma is switched off. The measured LIF intensity is corrected for this time-resolved quenching and calibrated using Rayleigh scattering. Time-resolved electron density ($n_e^{\max} = (7.6 \pm 0.8) \times 10^{21} \text{m}^{-3}$), He ($^3S_1$) metastable density (He_m^{\max} = (1.6 \pm 0.3) \times 10^{20} \text{m}^{-3}), gas temperature ($T_g^{\max} = (350 \pm 60) \text{K}$) and optical emission are presented and used in the interpretation of the observed time dependence of the OH density. Based on these experimental data, it is shown that for the present discharge conditions, OH is mainly produced by charge transfer reactions to water followed by dissociative recombination of the water ion. In addition, two often encountered issues with the calibration of OH LIF are highlighted with an example.

Keywords: OH dynamics, nanosecond pulsed discharge, OH density calibration

(Some figures may appear in colour only in the online journal)

1. Introduction

OH is a radical that plays an important role in many plasma applications. In environmental remediation OH is an important oxidizer for e.g. volatile organic compounds (VOC’s), NOx and SOx [1, 2]; in biomedical treatment OH is part of the active ‘plasma cocktail’ besides NO and ozone [3]; in plasma-enhanced combustion OH radicals produced by the plasma increase the combustion efficiency [4–6]; and in chemical synthesis OH is one of the building blocks of H₂O₂, which is considered as an important agent in the chemical reactivity of plasmas in and in contact with liquids [7]. To investigate the OH production mechanisms it is necessary to obtain absolute OH densities. In most cases, particularly for filamentary discharges as in this case, laser induced fluorescence (LIF) of OH is used, which allows one to obtain a high resolution...
in both space and time. However, to obtain absolute densities, apart from a calibration by e.g. Rayleigh scattering a model of the collisional transfer processes is required which can be very complex, especially at atmospheric pressure.

At atmospheric pressure, plasmas are mostly filamentary in nature. The existence of these filaments, with diameters of the order of 100 μm and lifetimes as small as 10 ns, is correlated with strong gradients in plasma properties in both space and time, which can significantly affect the plasma chemistry. The electron temperature in transient filamentary discharges is often high, while the gas temperature is usually relatively low [8]. This leads to an efficient production of radicals, as the energy applied is effectively used for dissociation and ionization rather than for gas heating.

In this work the filamentary discharge is stabilized in space between two needle electrodes at a sufficiently short distance, which allows the application of diagnostics with a high resolution [9]. The discharge is investigated in a mixture of water with an atomic gas, helium. This facilitates modeling the observed OH dynamics because of the lower amount of reaction channels. As described in [9] two discharge modes occur, a low- (applied dc voltage <3 kV) and a high-density (applied dc voltage >3 kV) plasma mode. The names low- and high-density mode are related to the strong difference in the electron density or current density. In the high-density mode, a strong depletion of the LIF signal is observed and the maximum LIF signal and OH density are located outside the plasma filament. In [9] the OH production and electron density in a high-density discharge are proposed to be due to charge transfer and subsequent dissociative recombination. Since the OH density is at the plasma boundary and the maximum electron density, obtained from emission lines, is presumably related to the plasma core, it is hard to link both processes without a complex 2D model which includes transport processes. A qualitative proof of the proposed mechanism was thus not made in [9]. In the current work, the low-density mode in He + 0.05% H2O, without the depletion of the OH density in the core of the discharge, is studied, in which case the electron density decay could be measured at the same location where the maximum LIF signal is measured, i.e. inside the plasma filament. In addition, we also investigate the effect of the metastable atoms on the OH density. Also, some additional improvements for accurate LIF measurements are proposed.

The experimental setup and methods are shown in section 2. Then first some important calibration issues are addressed. Subsequently the discharge kinetics of the low-density discharge in He + 0.05% H2O are described. The time-resolved optical emission, OH density and collisional quenching are shown in sections 4.1, 4.2 and 4.3, respectively. Finally, conclusions are drawn in section 5.

2. Experimental setup and methods

The discharge is created in a pin-to-pin electrode configuration with an inter-electrode distance of approximately 2 mm. The same setup is used in [9, 10]. High voltage pulses are provided by a DEI PVX-4110 HV pulser, whose dc high voltage is delivered by a Spellman power supply (10 kV, 15 mA) and the repetition frequency and pulse width are set with a function generator (Agilent 33220A). In the current work, positive high voltage pulses (Vapplied = 1.5 kV) are applied to the upper electrode with a repetition frequency of 1 kHz and a pulse duration of 170 ns. This corresponds to the low-density mode, as defined in [9]. A delay generator (BNC, model 575) is synchronized with the function generator that controls the high voltage pulses, to adjust the delay of the laser and the diagnostics (intensified Charge-Coupled Device (iCCD) cameras, time digitizer) relative to the voltage pulse. Voltage and current are obtained with a high voltage probe (Tektronix P6015) and a current monitor (Pearson 2877) just before the high voltage enters the vacuum vessel. The time origin is the start of the rising edge of the HV pulse. For more details the reader is referred to [9].

The discharge is generated in helium with an admixture of 0.05% H2O. A total flow of 3 l min−1, obtained using a Bronkhorst EL-FLOW Select mass flow meter (0.08 to 4 l min−1) is constantly refreshing the gas in the vacuum vessel which has a volume of approximately 8 l. The water admixture is added to the helium flow using a Bronkhorst High-Tech B. V. ’CEM’-system (Controlled Evaporation Mixing). In this system, distilled water is drawn from a container and measured by a liquid flow meter (μ-FLOW series L01, 250 mg h−1 H2O). A determined amount of water is mixed with helium and led into the evaporator to achieve total evaporation at a certain temperature.

2.1. Diagnostics

Time dependent spatially averaged optical emission spectra of the discharge are obtained with an iCCD camera (4 Quik E SR) coupled to a 27.5 cm focal length monochromator (ACTON). To collect as much light as possible, an optical fiber was introduced into the vessel through a vacuum coupling, and placed close to the filament. In time-resolved intensity measurements, a 150 grooves mm−1 grating is used and 1000 accumulations are taken. When recording high resolution spectra of Hα (which are used for electron density determination), the intensity is accumulated over 15 000 pulses using a grating with 1200 grooves mm−1. The time resolution is 10 ns for the emission spectra recorded with the 150 grooves mm−1 grating, and 30 ns for the emission spectra of OH and Hβ (recorded with the 1200 grooves mm−1 grating).

Fluorescence of OH is induced with a frequency doubled dye laser (Sirah CBR-LG-24-HRR), with Rhodamine 6G as the dye, pumped by a Nd : YAG laser (Edgewave Innoslab IS611-E) at 532 nm. The P1(2) transition of the OH(ν′ = 1) ←(X, ν′′ = 0) system at 282.6 nm is used to study time and spatially resolved LIF. This transition is nicely separated from neighbouring lines and no overlap occurs during excitation. Additionally, the ground level J1(2) has the largest relative population of all rotational levels in the temperature range under investigation [11].

The laser pulse has a repetition frequency of 1 kHz and a pulse width of about 6 ns FWHM, as measured with a photomultiplier (Hamamatsu R636-10) operating in photon
counting mode. The photomultiplier is coupled to a Jobin Yvon THR 1000 monochromator, which operates as a 0.3 nm bandwidth filter. The individual photon signal from the photomultiplier is processed by a discriminator and is read out by an Ortec 9353 time digitizer card, which counts the pulses with a time resolution of up to 2 ns, limited by the response time of the photomultiplier. This same setup is also used to measure the time-resolved fluorescence intensities originating from different vibrational bands. LIF measurements are performed in the linear regime, the energy of the laser is 0.5 µJ per pulse as measured with a power meter (Quan tum 3A-P-CAL, S/N 107785). The diameter of the laser beam at the position of the plasma is about 250 µm, as measured from the FWHM of the Rayleigh intensity of the beam in N₂ at atmospheric pressure. More details about the LIF setup can be found in [9].

The fluorescence signal from the centre of the discharge is detected through a quartz window of the vacuum vessel under an angle of 90° with the laser beam. Time and spatially resolved images of the plasma emission and fluorescence are taken with an iCCD camera (Andor DHS34) equipped with a Nikkor 105 mm f/4.5 UV lens. The exposure time of the images is 10 ns. To obtain the LIF images, a bandpass filter with a central wavelength of 313 nm and FWHM of 10 nm is used to filter out most of the optical emission. Any plasma light that is still present during the LIF measurement is corrected for by subtracting a background plasma emission image obtained at the same conditions. Each measurement is an accumulation of 1000 pulses.

2.1.1. Gas temperature. To determine the gas temperature two methods are used. First, the gas temperature is obtained by excitation LIF. With this method, the rotational temperature of the ground state of OH is measured. Different rotational levels of the ground state are excited and from the obtained (broadband) LIF intensities a Boltzmann plot is made (see also [12]). The intensities Iᵢ that are obtained after exciting different levels i are related to the rotational temperature according to

\[ Iᵢ \propto (2Jᵢ + 1)Bᵢ \exp \left( -\frac{Eᵢ}{k_BT_{rot}} \right), \]

where Jᵢ is the total angular momentum of level i, Bᵢ is the Einstein B coefficient of the transition taken from [13], Eᵢ is the energy of rotational level i taken from [14], k_B is the Boltzmann constant and T_{rot} is the rotational temperature. The transitions that are excited in this work are P₁(1) to P₁(6). As this method can suffer from transition dependent Einstein emission coefficients and rotational level dependent collisional transfer and quenching rates, as is explained in [15] and [16], we have verified this method with the gas temperature obtained from the rotational temperature of the OH(A; ν' = 1) state in [9]. The latter temperature is determined from the spectrally resolved fluorescence signal of the OH(A-X) (1–1) and (0–0) transitions, when the ground state is excited using the P₁(2) transition.

Second, the gas temperature is obtained from the plasma induced emission spectra of OH(A-X). These measurements are performed in Grenoble with the same 2 m monochromator (SOPRA) as used in [10, 17] for UV absorption measurements, equipped with a 1200 grooves mm⁻¹ grating working in the 4th diffraction order, and backed by a 12.8 µm pitch PIMAX3 (Roper Scientific) iCCD. The optical emission spectra were recorded between 308 and 309 nm. The gas temperature is calculated from the Boltzmann plot of the Q₁(5–6) and P₁(2) lines. For each of the lines the intensity is spectrally integrated.

2.1.2. Electron density. As in [9, 18], the electron density is determined from the Stark broadening of the H₉ Balmer line. Apart from Stark broadening, the instrumental width and van der Waals broadening are taken into account. As the gas temperatures are low (<400 K, see further) Doppler broadening is negligible [5]. The instrumental width is determined with a low pressure Hg/Ar lamp and has a FWHM of 0.13 ± 0.03 nm. The van der Waals broadening (in nm) is determined from

\[ \Delta \lambda_{vdW} = \frac{2.4}{T_{e}^{3/2}}, \]

where the constant 2.4 is calculated for helium in the same way as the constant is calculated for air in [5]. A gas temperature of 350 K is assumed during the entire pulse.

To calculate the Stark width, the Stark broadening profiles of H₉ in [19] are used for an effective emitter-perturber reduced mass µ∗ of 10 and an electron temperature of 1 eV. Gigosos uses this reduced mass, µ∗, which simulates a plasma which is not in thermal equilibrium (T_e ≠ T_g):

\[ \mu^{∗} = \mu \cdot \frac{T_{e}}{T_{g}}, \]

where µ = 0.8 is the reduced mass for H–He. For several electron densities between 5 × 10¹⁰ m⁻³ and 1 × 10²³ m⁻³, a convolution is performed of the Stark, van der Waals and instrumental profiles. The FWHM of these convoluted lines is then plotted as a function of the electron density, from which we obtain a FWHM correlation for our specific conditions. With a Voigt fit the FWHM of the measured line profiles are obtained and the FWHM of the correlation is used to determine the electron density.

2.1.3. Helium metastable density. The density of helium (³S₁) metastables is measured using tunable diode laser absorption spectroscopy. A DL DFB system (diode laser distributed feedback, Toptica) with a wavelength tunable around 1083 nm is used to record the time-resolved absorption at different frequencies around 1083 nm. A scheme of the setup used is given in figure 1. To avoid any saturation effects, a filter with 5% transmittance is placed in front of the laser to reduce the laser power to a few µW. The laser beam is then separated into three beams by a thick beam splitter which provides two weak beams by partial reflections. The main beam is directed into the plasma, while one of the secondary beams crosses a low pressure helium discharge cell and the other one crosses a 25 cm long Fabry–Pérot interferometer. The photodiodes detecting these secondary beams have an area of 3 × 3 mm² and a sensitivity of 0.5 V/(µW).
absorption signal from the helium discharge cell serves for the diode laser frequency calibration in an absolute scale and the Fabry-Pérot interferometer is used for the precise calibration of the laser frequency shift when tuned. The main laser beam is focused on the plasma filament with a lens (f = 20 cm), to provide a beam diameter of about 170 µm. After passing the discharge vessel through Brewster windows, the laser beam is detected by an InGaAs photodiode (1811 New Focus) with a diameter of 0.3 mm, a 125 MHz band-pass and a sensitivity of 0.03 V/µW. Frequency-resolved absorption profiles were obtained from time-resolved absorption signals recorded when scanning the narrow bandwidth laser around the line centre frequency, by taking steps of about 1 GHz.

The recorded 1083 nm line is composed of three transitions, which are summarized in table 1. The He (2^3S1) metastable density is estimated from the surface S(t) of the absorption profile (GHz), given by [20]

\[ S(t) = \int_0^{\infty} \ln \left( \frac{I_0(v)}{I(v, t)} \right) dv = h\nu_0 B_{kl} \langle N_i(t) \rangle , \]

(4)

where \( I_0(v) \) and \( I(v, t) \) are the transmitted signals at laser frequency \( v \) before the plasma pulse and at time \( t \), respectively. \( h \) is Planck’s constant (Js), \( \nu_0 \) the centre frequency of the line (GHz), \( B_{kl} \) the absorption coefficient of the transition (m^2 s^-1 J^-1), \( l \) the absorption length (m), and \( \langle N_i(t) \rangle \) the mean absolute density of absorbing atoms at time \( t \) (m^-3). This can be calculated from

\[ \langle N_i(t) \rangle = \frac{1}{h\nu_0 B_{kl}} S(t) = \frac{4\epsilon_0 m_e c^2}{e^2 f_{ik}} S(t) \]

\[ = \frac{1}{f_{ik}} \times 3.8 \times 10^{14} S(t), \]

(5)

where \( \epsilon_0 \) is the vacuum permittivity (F m^-1), \( m_e \) the mass of an electron (kg), \( c \) the speed of light (m s^-1), \( e \) the elementary charge (C) and \( f_{ik} \) the oscillator strength of the lines. When the surface of the entire profile is used, the oscillator strength to be used in equation (5) is 0.54, the sum of individual oscillator strengths. The absorption length is estimated from the absorption signal measured at different off axis positions with an increment of 100 µm. As there are strong temporal and spatial gas temperature gradients in the plasma filament, a detailed analysis of the line profile is not performed.

### 2.1.4. OH absolute density calibration

Absolute calibration of the OH LIF signal using Rayleigh scattering. This method is explained in detail in [10].

### 3. OH density calibration pitfalls

Absolut calibration of the OH LIF signal using Rayleigh scattering involves a complex model of the occurring collisional processes between the investigated levels. It requires the knowledge of rates for quenching, vibrational energy transfer and rotational energy transfer; and the knowledge of the experimental conditions such as gas temperature, laser pulse duration, area of the laser beam and the spectral overlap of the laser with the excited absorption transition. A sensitivity analysis of the above parameters is performed in [10]. An additional issue is a correct representation of the level structure of OH(X 2Π) [14, 22]. Usually spin-doubling, which is splitting the rotational level in \( f_1 \) and \( f_2 \), is taken into account. Spin-doubling also occurs in the OH(A 2Σ) state which is often investigated in optical emission spectroscopy. But in contrast with the OH(A 2Σ) state, where the orbital angular momentum \( \Lambda = 0 \), in the OH(X 2Π) state also \( \Lambda \)-doubling occurs, splitting the rotational level further in \( f_1, f_1', f_2 \) and \( f_2' \). The latter is often not taken into account in OH LIF calibrations, which results in an underestimated OH density by a factor 2. The calculation of the population fraction \( f_{J'} \) of the \( J'' \) rotational level in the ground state OH(X) should thus be done by the following formula

\[ f_{J'} = \frac{(2J'' + 1)}{2Q_{tot}(T)} \exp \left( -\frac{E_{J'}}{kT} \right), \]

(6)

where \( E_{J'} \) is the energy of the rotational level, \( Q_{tot}(T) \) the rotational partition function, \( k \) the Boltzmann constant and \( T \) the rotational temperature. Unfortunately \( \Lambda \)-doubling was also overlooked in previous work of the authors of this work. In equation (3) of [17], the factor 2 was by misprint in the denominator and the OH densities determined from broadband UV absorption and by LIF calibrated with Rayleigh scattering in [10, 17, 23, 24] are a factor 2 too low. However this does not alter the conclusions made in the above references.

Another important issue exists when the LIF signal of OH is measured in a transient plasma. In this case it is known.

### Table 1. Characteristics of the helium lines at 1083 nm used for He (2^1S1) metastable absorption measurements.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength (nm)</th>
<th>Oscillator strength [21]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^2)S_1 \rightarrow (^2)P_0</td>
<td>1082.909</td>
<td>0.06</td>
</tr>
<tr>
<td>(^2)S_1 \rightarrow (^2)P_1</td>
<td>1083.025</td>
<td>0.18</td>
</tr>
<tr>
<td>(^2)S_1 \rightarrow (^2)P_2</td>
<td>1083.034</td>
<td>0.30</td>
</tr>
</tbody>
</table>
that the gas temperature is often changing, which results in a change in population of the investigated OH level. What is not immediately clear when a transient plasma is investigated, is that also other plasma conditions (e.g. pressure, composition) might change, resulting in a time dependent quenching decay time of the LIF signal. The decay time of the LIF signal then needs to be measured at each time together with the total LIF signal, to be able to correct the time dependent LIF signal (and thus OH density) for this. An example is shown in figure 2, for a high-density discharge in He + 0.84% H₂O, with similar conditions as the discharge treated in [9]. In this case, the correction for time-resolved quenching changes the time-resolved OH density significantly. In section 4.3 the time-resolved quenching for the conditions treated in this work is discussed in detail, but we note that for high electron densities also electron induced quenching can occur.

4. Discharge kinetics

As described in [9], in the low-density mode the voltage shows a drop towards the end of the pulse, when the plasma fills the inter electrode volume. At the same time the current rises. The current and voltage waveforms are shown in figure 4, the capacitive current is subtracted from the measured current signal. In this section, first the plasma properties deduced from time-resolved optical emission spectroscopy and He metastable density are discussed, followed by the time-resolved OH density and collisional quenching. The OH production mechanisms are also identified.

4.1. Time-resolved optical emission

Overview emission spectra between 300 and 850 nm, measured during and immediately after the current pulse, are shown in figure 3. The spectra are corrected for the wavelength dependent sensitivity of the detection system. Helium lines dominate the overview spectra, while optical emission of OH(A–X) could not be observed with the ACTON spectrometer for a water concentration as low as 500 ppm. Significant emission of He⁺ is detected, in particular just after the discharge is switched off.

The gas temperatures, as obtained by excitation LIF and optical emission of OH(A–X), are shown in figure 4 as a function of time. Values obtained by both methods are in agreement within the experimental accuracy, and they do not exceed 400 K. At the end of the current pulse the gas temperature is around 350 K, it then slowly decreases to about room temperature.

The electron density obtained from the line broadening of Hβ is shown in figure 5. The maximum electron density \((7.6 ± 0.8) \times 10^{21} \text{ m}^{-3}\) is obtained during the current peak.

The time-resolved optical emission intensities of He, O, He and OH are shown in figure 6. To obtain the time-resolved intensities of He (667 nm) and Hα (656 nm), the emission lines measured with a resolution of about 0.2 nm are integrated over the entire line profile to avoid an influence of the change in broadening of the lines on the obtained intensities. The emission of OH is obtained from the area of the \(P_1(2)\) line of the OH[(A; \(v' = 0\) ) \(->\) (X; \(v'' = 0\)]) system, recorded with the
in the OH(A–X) emission in a helium Dielectric Barrier Discharge (DBD) [26]. The maximum in He2 emission after the plasma is switched off confirms that excimers are formed in 3-body electron ion recombination processes like [27]

$$2e + \text{He}_2^+ \rightarrow \text{He}_2^+ + e,$$  \hspace{1cm} (7)

$$e + \text{He}_2^+ + \text{He} \rightarrow \text{He}_2^+ + \text{He}.$$  \hspace{1cm} (8)

To determine the primary ion, the ionization rates of He ($E_i = 24.6$ eV) and H2O ($E_i = 12.6$ eV [28]) are obtained using Bolsig [29] and the cross sections for H2O from [30], in a similar way as in [31]. For a voltage of about 1.5 kV (see figure 4) and an interelectrode distance of 2 mm, the reduced electric field is estimated to be about 30 Td at room temperature. At this $E/N$ value and considering the more than three orders of magnitude larger He density compared to H2O, the production rate of He$^+$ is much larger than that of H2O+. So for the present conditions, the dominant primary ion will then be He$^+$. These helium ions will be lost, apart from electron–ion recombination reactions, in the following charge transfer reactions [32]:

$$\text{He}^+ + 2\text{He} \rightarrow \text{He}_2^+ + \text{He} \quad 1.4 \times 10^{-43} \text{ m}^6 \text{s}^{-1},$$  \hspace{1cm} (9)

$$\text{He}^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH} + \text{He} \quad 2.04 \times 10^{-16} \text{ m}^3 \text{s}^{-1},$$  \hspace{1cm} (10)

$$\text{He}^+ + \text{H}_2\text{O} \rightarrow \text{OH}^+ + \text{H} + \text{He} \quad 2.86 \times 10^{-16} \text{ m}^3 \text{s}^{-1},$$  \hspace{1cm} (11)

$$\text{He}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{He} \quad 6.05 \times 10^{-17} \text{ m}^3 \text{s}^{-1},$$  \hspace{1cm} (12)

$$\text{He}^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}(A) + \text{He} \quad 5 \times 10^{-19} \text{ m}^3 \text{s}^{-1}.$$  \hspace{1cm} (13)

The rates for these reactions (compiled from [32]) indicate that, under the present conditions, reaction (9) is an order of magnitude faster than all other reactions. They also suggest that the production of H$^+$ and OH$^+$ is about 10 times more likely than the production of H2O$^+$.

The measured time-resolved He ($^1S_\text{A}$) metastable density is shown in figure 5. A maximum is observed before the current peak, which might be related to the streamer ignition during which $E/N$ is very high and a low electron density is present, although with high energy electrons. With increasing electron density, the temperature of bulk electrons is in the range of a few eV and the ionization rate of He$_\text{m}$ overpasses their excitation rate from the ground state. After the voltage is switched off, the electrons cool down, ionization is stopped and the He$_\text{m}$ state is populated by electron–ion recombination and radiative cascade from the $3p^3P_J$ state, whose radiative lifetime is about 100 ns.

The He metastable density is almost two orders of magnitude lower than the electron density. He metastables can create OH in Penning ionization reactions such as [32]

$$\text{He}_\text{m} + \text{H}_2\text{O} \rightarrow \text{He} + \text{OH} + \text{H}^+ + e$$  \hspace{1cm} (14)

$$\text{He}_\text{m} + \text{H}_2\text{O} \rightarrow \text{HeH}^+ + \text{OH} + e$$  \hspace{1cm} (15)

with a rate of $2.6 \times 10^{-17} \text{ m}^3 \text{s}^{-1}$ and $8.5 \times 10^{-18} \text{ m}^3 \text{s}^{-1}$ respectively. These reactions are too slow compared to the rate of $5 \times 10^{-16} \text{ m}^3 \text{s}^{-1}$ obtained in the model of the time-resolved OH density (see further). OH can also be produced

Figure 5. Time-resolved electron density and He metastable density. The current waveform is shown as a reference.

Figure 6. Time-resolved optical emission of He (667 nm), O (777 nm), He2 (656 nm), He3 (465 nm) and OH(A–X) (309 nm). The current waveform is shown as a reference. The intensity of He2 is multiplied by 10 for clarity. The OH(A–X) ($P_1(2)$) intensity is measured independently and is not scaled to the other intensities.
through the dissociative recombination of H$_2$O$^+$ (see table 2) ions produced by the Penning ionization of H$_2$O

\[
\text{He}_m + \text{H}_2\text{O} \rightarrow \text{He} + \text{H}_2\text{O}^+ + e
\]

with a rate of $6.6 \times 10^{-16}$ m$^3$ s$^{-1}$. However, as the He$_m$ density is two orders of magnitude lower than the He$^+$ density, H$_2$O$^+$ is not the dominant ion and ionic processes will dominate over He (1$^3S$) metastable reactions in the production of OH radicals.

The question remains if molecular metastable species can have a higher density than atomic metastables. Molecular helium metastates are created for instance by the reaction

\[
\text{He}_m + 2\text{He} \rightarrow \text{He}_{2,m} + \text{He}
\]

with a rate of $2.5 \times 10^{-46}$ m$^6$ s$^{-1}$ [33]. As the decay time of He$_m$, dominated by reaction (16), is more than an order of magnitude faster than the decay time of He$_{2,m}$ by reaction (17), the density of He$_{2,m}$ produced by reaction (17), cannot exceed a tenth of the He$_m$ density. This estimated He$_{2,m}$ density is consistent with other published work. Stevelfelt et al [34] studied a 6 ns pulsed discharge in atmospheric helium, and found that the density of the lowest molecular metastable state ($a^3\Sigma_u^+$) is one order of magnitude lower compared to the density of He (1$^3S$), which is, in their experiment, of the same order as the electron density ($10^{15}$ m$^{-3}$). It is suggested in the work of Stevelfelt et al that this low density is potentially due to a collisional coupling to the radiating A$^3\Sigma_u^+$ state. In addition, Liu et al studied He–H$_2$O mixtures by a global model for different H$_2$O concentrations, for discharges with an electron density of $10^{17}$–$10^{18}$ m$^{-3}$, and found a molecular metastable density which is consistently smaller compared to the atomic metastable density [32]. Finally, in microwave discharges at elevated temperatures (2500 K) it is also assumed that the dissociation of the dimer in collisions with a ground state helium atom is very fast, leading to a small molecular metastable density [35]. The above examples motivate why the total metastable density can be well estimated from the measured density of He (1$^3S$) metastables, and no significant contribution of He metastables is expected on the OH kinetics in the afterglow.

### 4.2. Time-resolved OH density

In figure 7 the time dependent OH density, calibrated using Rayleigh scattering, is shown. Since it is found that the decay time of the LIF signal after excitation by the laser (and thus the collisional quenching) is not constant throughout the entire discharge, the measured LIF intensity needs to be corrected for this. The origin of the different decay time of the LIF signal is discussed in the next section. Both uncorrected and corrected time-resolved OH densities are shown in figure 7. The obtained LIF intensities are also corrected using the temperature dependent Boltzmann factor of the level that is excited, to obtain the total OH(X) density. The gas temperatures used for this correction are obtained from figure 4.

An extensive chemical model to explain the observed OH density is impossible due to the lack of accurate branching ratios of several electron–ion recombination reactions which are involved in the OH production. However, we summarize the key conclusions that can be made to determine the mechanism:

- The electrons in atmospheric pressure helium have an energy transfer collision frequency of $4 \times 10^8$ s$^{-1}$ [36]. This means that the electron temperature will drastically decrease within 10 ns after the voltage pulse, which is much shorter than the delay of 1 µs in the maximum of the OH density. Electron dissociation is thus not involved in the OH production in the afterglow.
- Helium metastable reactions with water produce mainly water and water fragment ions. Electron–ion recombination reactions have a higher rate than metastable induced water dissociation reactions. As the metastable density is almost two orders of magnitude lower than the ion density, ionic reactions will dominate the OH production in the afterglow.
- The maximum OH density in the afterglow equals the maximum electron (and ion) density during the discharge pulse. This indicates that an effective conversion mechanism from ions to OH radicals is present.

These conclusions lead to the scheme shown in figure 8. Note that in line with the discussion above, the scheme does not include He dimer metastables. In addition, one ion can lead

---

**Table 2.** Most important ionic reactions involved in the production of OH in recombining plasmas. The rates are obtained from [32].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient $k$ (m$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$ + H$_2$O → H$_2$O$^+$ + H</td>
<td>$6.9 \times 10^{-15}$</td>
</tr>
<tr>
<td>O$^+$ + H$_2$O → H$_2$O$^+$ + O</td>
<td>$2.6 \times 10^{-15}$</td>
</tr>
<tr>
<td>OH$^+$ + H$_2$O → H$_2$O$^+$ + OH</td>
<td>$1.5 \times 10^{-15}$</td>
</tr>
<tr>
<td>OH$^+$ + H$_2$O → H$_2$O$^+$ + O</td>
<td>$1.3 \times 10^{-15}$</td>
</tr>
<tr>
<td>H$_2$O$^+$ + OH → H$_2$O$^+$ + O</td>
<td>$6.9 \times 10^{-15}$</td>
</tr>
<tr>
<td>H$_2$O$^+$ + OH → H$_2$O$^+$ + OH</td>
<td>$1.9 \times 10^{-15}$</td>
</tr>
<tr>
<td>HeH$^+$ + H$_2$O → H$_2$O$^+$ + He</td>
<td>$4.3 \times 10^{-16}$</td>
</tr>
<tr>
<td>He$^+$ + H$_2$O → H$_2$O$^+$ + He</td>
<td>$6.05 \times 10^{-17}$</td>
</tr>
<tr>
<td>H$_2$O$^+$ + e → OH + H</td>
<td>$5.1 \times 10^{-14}T_e^{-0.5}$</td>
</tr>
<tr>
<td>H$_2$O$^+$ + e → OH + 2H</td>
<td>$1.1 \times 10^{-13}T_e^{-0.5}$</td>
</tr>
</tbody>
</table>

---

**Figure 7.** Time-resolved measured OH and electron density for the low-density mode in He + 0.05% H$_2$O. The current waveform is shown as a reference.
to the production of up to three OH radicals without even considering higher water cluster ions.

Assuming that H2O+ and/or H2O* are the dominant ions and their density equals the electron density, the electron density decay should be caused by electron–ion dissociative recombination. However, the measured electron density decays with a rate of $2.5 \times 10^{-15}$ m$^3$ s$^{-1}$, which is too slow to be explained by the dissociative recombination with water ions ($k_{dr} \sim 10^{-15}$ m$^3$ s$^{-1}$ at 350 K [37]). The slow electron density decay can be explained by dissociative recombination of OH+ ($6 \times 10^{-15}$ m$^3$ s$^{-1}$ at $T_e = T_g = 350$ K [38]), or by charge transfer processes of atomic ions (H+, O+, He+) with water ($k_{ct} \sim 10^{-15}$ m$^3$ s$^{-1}$) followed by dissociative recombination of water ions (see table 2).

Given that the decay in electron density relates to ions which not directly lead to OH production, the time constant of OH production in the afterglow will be determined by self-destruction processes of OH, which not directly lead to OH production, the time constant of dissociative recombination of atomic ions (H+, O+, He+) with water.

![Suggested scheme for the production of OH](image)

Figure 8. Suggested scheme for the production of OH in the investigated low-density discharge in He + 0.05% H$_2$O.

![Measured time-resolved fluorescence decay times](image)

Figure 9. Measured time-resolved fluorescence decay times of OH(A–X) (1–1) and calculated time-resolved fluorescence decay times taking into account the change in gas temperature.

where $k_Q(T)$ is the temperature dependent quenching rate [41] and $\tau_{rad}$ the radiative lifetime of OH(A–X). The calculated decay times shown in figure 9 are calculated for the temperature measured using LIF (see figure 4). For 500 ppm H$_2$O at 300 K, for a quenching rate of $6.6 \times 10^{-16}$ m$^3$ s$^{-1}$, the decay time is 105 ns. The calculated decay times are in agreement with the measured decay times. Before $\tau = 400$ ns a significantly shorter decay time is measured. Since the decay time at room temperature is 105 ns and a higher gas temperature would result in a longer decay time, the shorter decay time can not be explained by an increase in temperature.

A possible explanation is a change in gas composition. OH(A) is quenched less by OH, H and O than by H$_2$O (see table 3), and less quenching would result in a longer decay time, but when H$_2$O is highly dissociated, the density of quenchers increases. For a density of the order $10^{12}$ m$^{-3}$ (see figure 7) the dissociation is only about 10% of the water density, which is not enough to explain the measured decay time. In addition, the high ion/electron density could increase the quenching by charge transfer reactions or by electron quenching. Teulet et al have reported rate coefficients for

$$\text{OH(A) + e} \rightarrow \text{OH(B) + e},$$

which has the largest rate for the possible electron quenching processes of OH(A). The rate $k_e$ (calculated for $T_e = T_g$) is $9 \times 10^{-26} T^{2.76} \exp(-54911.4/T)$ [42]. For an electron density...
of $7.6 \times 10^{21}$ m$^{-3}$ (as measured at 200 ns), the time scale for electron quenching would be reduced to 42 ns for $T_e \approx 1.3$ eV, as obtained using the rate for reaction (23). Electron quenching can thus be considered to be the main reason for the measured short decay times for the investigated case. Note that the decay of the OH fluorescence shows signs of deviation of an exponential decay. However, because of the noisy signal due to the strong OH emission of the plasma a quantitative analysis is not possible.

5. Conclusion

Time-resolved electron density, He ($^3S_1$) metastable density, gas temperature and OH density were obtained in a low-density mode of a nanosecond pulsed plasma filament in atmospheric He–H$_2$O (0.05%). A time dependent quenching of the LIF signal was observed. The decay time of the LIF signal is significantly shorter during the plasma current pulse, which might be due to electron induced quenching. It is shown that the He metastable density is about two orders of magnitude smaller than the electron density and that the increase in OH density after the pulse is caused by ionic reactions which include a 2-step process of charge transfers from OH$^+$, He$^+$, H$^+$, O$^+$ to H$_2$O and electron–water ion recombination.

Acknowledgments

The authors acknowledge funding by STW (Stichting Technologische Wetenschappen). The Réseau Plasma Froids of CNRS/MRCT (France) is acknowledged for providing the DFB diode laser.

References


<table>
<thead>
<tr>
<th>Table 3. Quenching rate coefficients for OH(A) quenching at $T = 300$ K in units of $10^{-16}$ m$^3$ s$^{-1}$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collider</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>H$_2$O</td>
</tr>
<tr>
<td>OH</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>O</td>
</tr>
</tbody>
</table>