Laser Induced Plasmas in Liquid Water: From Single Pulse Breakdown to Repetitive Breakdown

by

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Abstract

Optical breakdown in water created by 10ns pulsed Nd:YAG laser operating at \(\lambda=1064\) nm was studied. Spatial and temporal information was obtained with two intensified CCD cameras while spectral data were recorded using a time-integrating spectrometer. We have studied three water samples with different impurity content (ultrapure, distilled, and tap water) and followed the plasma evolution over a timespan of a few hundred nanoseconds. Images taken by the two synchronized cameras, systematically delayed relative to each other, show that the center of emission intensity in single plasma events moves toward the incoming laser beam. For repetitive breakdown, the center of intensity of the pulse moves beyond the focal point away from the laser beam. The emission of both single pulse plasmas as well as repetitive breakdown plasmas are dominated by a broad, blackbody-like spectral feature with corresponding temperatures generally exceeding 20,000 K. Superimposed is a weak hydrogen Balmer-alpha line with a full width at half maximum exceeding 50 nm. Interpreted as purely Stark broadened, this width corresponds to electron densities well above \(10^{18} \text{ cm}^{-3}\).
Acknowledgements

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Chapter 1

Introduction

A plasma is a collection of positively and negatively charged particles whose overall charge is approximately zero. It is different from the other three states of matter, namely solid, liquid, and gas because it has strong electromagnetic fields due to the ions and also because it is influenced much more easily by an applied electromagnetic field than the other states. Plasmas are quite common in nature, from lightning to auroras to the solar atmosphere. They can also be created by applying strong electric fields through an avalanche effect or electromagnetic fields such as lasers by direct ionization. Plasmas created by lasers are often referred to as laser induced plasmas (LIPs) and the phenomenon of creating plasma using a laser is known as laser induced breakdown (LIB).

LIB can occur in any media: solid, liquid, or gas. When intense laser light is focused onto the medium, the high irradiance causes the material to breakdown. The plasma can then be studied using experimental apparatuses to determine some of its characteristics such as size, temperature, density, and lifetime among many others. Since plasmas are representative of the medium in which they are created, these characteristics vary greatly from one substance to another.

LIB has been studied in all three states of matter, but the focus of this paper is specifically on water. Research on water is of great interest to the medical community, especially in the field of ophthalmology. Water is a very good simulant of vitreous humor, the liquid inside the eye, and so it is much easier to carry out
experiments with water, which is more accessible, than vitreous humor. In laser eye surgery, the plasmas created by LIB in the eye are used to cut intraocular tissue. However, these plasmas also pose a threat for ocular damage in situations of accidental exposures of the eye to high power pulsed lasers [1]. Plasmas in water can also be used to obtain information about metals dissolved in the water using a process known as laser induced breakdown spectroscopy [2]. LIB in water can be used to study shock waves and cavitation bubbles as well. Cavitation bubbles are important for ships because these occur around the propellers, and can cause damage to the propellers. There are many methods of creating cavitation bubbles, such as placing electrodes in the water and applying a high voltage sufficient to cause breakdown. Other methods include boiling water and electrolysis. However, these methods do not produce the bubbles in a fixed location and often times change the dynamics of the bubbles. In contrast, bubbles created by LIB are created in fixed locations and there is also no influence on their dynamics since the laser pulse is gone before the bubbles start to move around. Shock waves and cavitation bubbles are also present in LIB in the eye, and they can cause damage to the ocular tissue there as well [1].

Previous studies of laser induced plasmas in water have been able to determine the sequence of events that are associated with this phenomenon [3]. These include the breakdown followed by light emission and then formation of shockwaves and cavitation bubbles. The light emission of the plasma has helped to calculate its lifetime, temperature, and electron densities [4], [5]. A lot of work has been done on the breakdown threshold and its mechanisms, which include cascade ionization through inverse Bremsstahlung absorption [6], [7]. Information such as the
distribution of the laser pulse energy into the various components of the plasma have also been calculated to better understand the energy balance of the system [6].

In our experiment, a Q-switched Nd:YAG pulse laser with its fundamental wavelength of 1064 nm is focused using a lens into a container filled with water. Once the laser power is high enough that the irradiance is greater than the breakdown threshold of water, a plasma is formed. The plasma is visible to the naked eye and is accompanied by an acoustic shockwave and bubble formation. The plasma is then studied by either intensified charge-coupled device (iCCD) cameras or a spectrometer depending on whether we are interested in the spatiotemporal or the spectral characteristics of the plasma.

As for the topics covered in this paper, Chapter 2 will discuss the experimental setup and procedures. This includes details on the equipment and the methods of calibrations and analysis. In Chapter 3, the focus will be results on the single pulse plasma and its formation in three different waters. Information such as the lifetime, intensity, and spectra will be provided. This will be accompanied by some introduction to the single pulse breakdown as well. In Chapter 4, the discussion will be concentrated on plasmas produced by firing the laser at multiple repetition rates, such as 1 Hz, 2 Hz, and 5 Hz. Similar information as the single pulse plasmas will be presented about these repetitive breakdowns. Finally, Chapter 5 will provide a conclusion of the findings and the future work of this research project.
REFERENCES


Chapter 2

Experimental Setup & Procedures

2.1 Overview

In this chapter, the setup of the experiments and the procedures involved in the data taking process will be discussed. The entire process can be separated into three main parts: (1) characteristics and operation of the laser, (2) preparation and characteristics of the water target, and (3) the detection of the plasma. An explanation of the analysis of the captured images and the calibration of the spectrometer will also be provided in this chapter.

A schematic view of one of the experimental setups is shown in Figure 2.1. A Q-switched Nd:YAG laser beam of wavelength 1064 nm is focused using a lens of focal length 10 cm that is anti-reflection coated for high power at 1064 nm wavelength. The shape of the lens is optimized to reduce spherical aberration for 1064 nm (ESCO Optics, Best Form Lens). After the focusing of the laser beam into the water cell, emission from the subsequent breakdown and plasma is then imaged onto two intensified Charge-Coupled-Device (iCCD) cameras with the help of two converging lenses of focal length 10 cm and a beam splitter. The beam splitter is an uncoated quartz microslide that transmits 92% of the light and reflects the other 8%. The two cameras are appropriately synchronized and then take pictures of the same plasma event. Images are stored for subsequent inspection and analysis on computers using the proprietary camera software. Figure 2.1 shows one setup used in these
experiments for the two camera arrangement described above. The two camera system allows a single plasma to be observed twice, whereas with a single camera, a plasma can only be imaged once due to the slow readout time of the camera. Figure 2.2 shows the setup for a single camera; here we typically employ a multi-element adjustable camera lens (Olympus OM-System Zuiko f=80mm) for imaging. Finally, Figure 2.3 shows the setup of the spectrometer, which uses a fiber optic cable to collect light from the plasma. Unlike the camera, the spectrometer is not synchronized with the laser because it cannot be triggered as with a high temporal resolution. For Figure 2.3, the raw spectrum of the plasma is directly viewed on the computer using the software that controls the spectrometer.

Figure 2.1: Schematic view of the two cameras experimental setup.
Figure 2.2: Schematic view of a single camera setup.

Figure 2.3: Schematic view of the spectrometer setup.
2.2. Laser System

The laser used in these experiments was a Q-switched Nd:YAG Continuum NY-6120 laser. The fundamental wavelength is 1064 nm, which was used in all experiments, but higher harmonics can be generated as well, including the second harmonic at 532 nm and third harmonic at 355 nm. The pulse duration is 8 ns (FWHM) and the beam diameter is approximately 10 mm just before entering the focusing lens. The laser is capable of running in single pulse mode, where a pulse is fired upon command from the remote box (RB601). It can also be operated at fixed repetition frequencies, such as 1 Hz, 5 Hz, 10 Hz, and 20 Hz. These fixed frequencies are created by choosing the repetition rate of the flashlamp, and then selecting the number that will divide the flashlamp repetition rate to obtain the Q-switch frequency. For example, if the flashlamp repetition rate was 20 Hz and the number chosen to divide it was 2, then for every 2 flashes of the flashlamp, one Q-switch pulse would be fired at 10 Hz [1]. Because the repetition rate of the flashlamp is limited to 20 Hz, the maximum frequency that the laser can fire at is also 20 Hz.

The energy per pulse of the laser can be selected in one of two ways: either by changing the voltage applied to the flashlamp on the control unit (CU601) or by changing the delay between flashlamp firing and Q-switch trigger using the remote box. However, these two methods are not entirely equivalent, because changing the applied voltage on the flashlamp and thus the power delivered to them can alter the spatial beam profile of the laser. Such an alteration can lead to different focusing behavior and thus to a change of the conditions for breakdown. Therefore, the energy
per pulse of the laser is now changed using the second method. The energy per pulse is determined from the average power which is measured using a calibrated volume absorbing power meter (Ophir 30A-P). Using the equation $E = \frac{P}{f}$, where $E$ is the desired pulse energy, $P$ the measured average power, and $f$ the laser repetition frequency. For example, for a power measurement of 5 W with the laser running at 20 Hz, the energy per pulse would be $E = \frac{(5 \text{ W})}{(20 \text{ Hz})} = 250 \text{ mJ}$. The laser is capable of reaching energies of 300 mJ per pulse. One note that should be made is that when the power of the laser is changed with either methods, the delay of the Q-switch trigger is changed as well. This was discovered empirically and found that a change of power from 5 W to 2 W using the dial for controlling the applied voltage level to the flashlamps resulted in a change of approximately 50 ns. However, this can be easily fixed by changing the delay on the external delay generator (Stanford Research Systems DG535 or DG645). It is important to fix the timing issue so that the camera can be triggered properly, otherwise, data acquisition would not be very accurate.

2.2 Target

The water in which the plasma is created sits in a container that is made of stainless steel with three uncoated quartz windows (see Figure 2.4). The outside dimensions of the rectangular body of the container are 15.2 cm x 3.8 cm x 3.8 cm with a filling capacity of about 110 cm$^3$. The quartz windows are 0.3 cm thick, 10.16 cm long, and 2.54 cm wide. Two small pipes attached to the top are used to fill and drain the container. Removable windows are situated along the long axis on both ends of the container. On the laser entrance side, the glass window is anti-reflection coated
for 1064 nm light thus preventing breakdown in air caused by the reflected portion of the high power laser pulse. A beam dump is situated immediately behind the uncoated exit window to safely stop the remaining laser beam.

![Image](image.png)

**Figure 2.4:** The water holding container.

Three “types” of water have been used in this experiment: tap, distilled, and ultrapure. The tap water is obtained from the faucet in the lab, without any further treatment. The distilled water is commercial distilled (Acadia Pure Steamed Distilled Water). The ultrapure water is obtained from a water purification filtration machine (Milli-Q Plus Water Purification System) located in the lab of Prof. Mukerji of the MB&B department at Wesleyan. Because distilled and ultrapure water are obtained in large quantities, they are stored in sealed containers and only the amount needed for the experiments is taken at a time. The distilled water is kept in its original plastic gallon bottle, while the ultrapure water is stored in a thoroughly cleaned 2 L glass container with a cork stopper. The tap water is taken directly from the faucet as needed.
Only certain properties are known for the three water types, in some cases only from the supplier. For the tap water, according to the 2012 Middletown Water Quality Report, the turbidity of the water in the Wesleyan University area had an average value of 0.07 NTU [2]. Turbidity measures the cloudiness of a fluid that is caused by individual particles. The unit of measurement for turbidity is the Nephelometric Turbidity Unit (NTU), which is obtained from a calibrated nephelometer. As a light beam is sent through a sample fluid the nephelometer, which sits perpendicular to the beam axis measures the amount of light scattered from the sample. The more light is scattered, the higher the amount of suspended particles in the sample fluid. The amount of suspended particles is an important factor in the experiments because they are impurities and contribute to the breakdown threshold. The assumption is that these impurities have a lower threshold for ionization, and so their presence can decrease the breakdown threshold. As a comparison, the maximum turbidity level allowed for drinking water in the U.S. by the Environmental Protection Agency is 5 NTU. The 2013 Water Quality Report has not yet been published, but according to the report from 2012, the range for the turbidity was 0.04-0.18 NTU [2]. The distilled water has a turbidity of 0.073 NTU according to its supplier [3], and no turbidity value is reported for the ultrapure water. Since the turbidity values of distilled and tap water are so close to each other, this measurement cannot provide details about their relative suspended particle concentrations, besides the fact they are very similar. However, this is not experimentally observed to be true as the thresholds for distilled and tap are quite different. The resistivity of the ultrapure water is reported to be 18.2 MΩ·cm and its total organic carbon (TOC) level should be less
than 10 ppb [4]. The resistivity gives a measure of how strongly the water opposes the flow of electrons. If the resistivity is very low, then the water is conductive, which would make diffusion of electrons much easier. This quantity helps to identify how quickly a plasma formed in the water will be quenched. The ultrapure water is purified using reverse osmosis and is also treated with ultraviolet radiation. In general, the refractive index for water is 1.33 and the absorption coefficient of water at 1064 nm is 0.15 cm$^{-1}$ [5].

A simple laser light absorption experiment has been performed to see if the amount of light absorbed differed between the three waters. Differences in the absorption of the laser light would tell how readily each water absorbs the laser radiation and thus which would reach the breakdown threshold most easily. To that end, the laser beam power was measured before and after the water filled container. The focusing lens was removed to prevent breakdown since plasmas also absorb laser radiation. The laser was run at 20 Hz during this experiment. Before entering the container, the average laser power measured was 4.8 ± 0.1W in all cases considered. After passing through the container the average laser power for the tap water was 0.210±0.005 W, for the distilled water it was 0.217±0.005 W, and for the ultrapure water it was 0.214±0.005 W. Clearly these three values agree within their error bars. Thus, based on light absorption alone, we cannot draw conclusions about any differences in the properties of the waters used in our experiments. We speculate that, apart from possible systematic errors, e.g. due to faulty calibration of the power meter, the “missing” intensity may be due to spontaneous Rayleigh and Brillouin scattering.
For all experiments, fresh batches of water were used. This kept the experiments cross-contamination free and as pure as possible.

2.4 Plasma Detection

2.4.1 Time-Resolved Imaging

Two different detection methods were used to study the plasmas: two-dimensional image capture by intensified Charge-Coupled-Device (iCCD) cameras and wavelength resolved emission detection by a compact, 0.101 m spectrometer (Ocean Optics, HR2000+). The iCCD cameras used were the Andor iStar DH734 Gen II and the Andor iStar DH334T-18U-03. For future reference, Andor DH734 will be referred to as “camera 1” and DH334 as “camera 2”. Table 2.1 provides a summary of the features of the two cameras. Both cameras also are equipped with internal digital delay generators which control the operation of the image intensifier and thus camera gating and which are capable of 1 ns precision.

<table>
<thead>
<tr>
<th></th>
<th>DH734</th>
<th>DH334T</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCD array (pixel):</td>
<td>1024 x 1024</td>
<td>1024 x 1024</td>
</tr>
<tr>
<td>Pixel size:</td>
<td>13 μm x 13 μm</td>
<td>13 μm x 13 μm</td>
</tr>
<tr>
<td>Optical gating:</td>
<td>2 ns</td>
<td>&lt;2 ns</td>
</tr>
<tr>
<td>Spectral range:</td>
<td>180-850 nm</td>
<td>180-850 nm</td>
</tr>
<tr>
<td>Operation temperature:</td>
<td>-15°C</td>
<td>-20°C</td>
</tr>
</tbody>
</table>

Table 2.1: Overview of the features of the two ICCD cameras.

Both cameras were operated with the same proprietary Andor Solis software but with a version number depending on the camera age. The cameras were synchronized with each other by two suitably delayed trigger pulses from a single, external digital delay generator (Stanford Research DG535) which in turn was
synchronized with the breakdown event by a trigger from the laser. Once the plasma was observed, the internal delay of each camera is kept at zero delay and the timing of its individual trigger from the external delay generator was adjusted until “first light” emission was detected. The nominal start of the plasma breakdown was defined by the disappearance of any detectable emission when the delay was decreased by 1ns; this delay was termed “0 ns”. Again, at 0 ns, no sign of the plasma would be visible, but at 1 ns, the very first emission from the plasma could be detected. After the start of the plasma is thus established for both cameras and their synchronization achieved, any desired relative delay is simply obtained by choosing appropriate values of their internal delay generators. With a single camera setup, obviously no need for synchronization exists but synchronization with the breakdown event proceeds in the same way.

The advantages of these iCCD cameras versus non-gated digital cameras are essentially twofold: the amplification of low light signals and the capability of triggering and gating the camera with nanosecond precision. These controls are accomplished via the image intensifier component of the camera. The operation of the image intensifier is elaborated on in Appendix A.

A sample raw image from an Andor iStar camera is shown in Figure 2.6. The x and y dimensions are both spatial, and the intensity value of the pixel selected by the cursor location is given by the number next to “Data” on the bottom of the window. The image shown in Figure 2.6 is that of a plasma event in distilled water.
The second detection apparatus is a 0.1 m fiber optic coupled spectrometer (Ocean Optics, HR2000+). This all-in-one spectrometer features a built-in linear 2048 pixel CCD array, each pixel of size 14 μm x 200 μm. The nominal spectral range is 200-1100 nm and the integration time can be chosen anywhere from 1 ms to 65 s. The focal length is 101 mm and the aperture size is f/4. Although the spectrometer is portable with its fairly small size (148.6 mm x 104.8 mm x 45.1 mm), it is not suitable for placing directly in the optical path [6]. Thus, a fiberoptic cable (Ocean Optics QP 600-2-SR) is used to direct the light from the plasma to the spectrometer. The

**Figure 2.6**: An image of a water plasma taken by one of the Andor cameras.
diameter of the fiberoptic cable is 600 μm. The resolution of the spectrometer is not constant, and it is shown in Figure 2.7 for the relevant subset of 300-1100 nm.

The spectrometer is computer controlled via proprietary software (SpectraSuite, version 2.0.162). For our experiments two parameters are adjusted via the software: integration time and number of scans to average. The integration time is equivalent to the exposure time of a camera and determines, together with the repetition frequency of the laser, how many breakdown events are being summed into one spectrum. “Scans to average” is a menu option which averages the specified number of spectra into a single output file. When emission is weak and very large numbers of spectra must be taken, the “scans to average” function is usually used to improve the quality of the spectra and to reduce the number of files.

2.5 Image Analysis and Calibrations

In order to analyze relative intensities of different images, such as the one shown in Figure 2.6, the corresponding data must be adjusted so that two images with

![Figure 2.7: Spectral resolution of the Ocean Optics spectrometer.](image)
different gate and gain values are comparable. Variations in the gate are corrected by simply dividing the total intensity by the gate value, since the intensity is linearly proportional to the gate duration. For the gain correction we use a polynomial expression for the intensity enhancement factor versus software gain setting that was empirically derived in the following way. A Halogen-Tungsten white light source (Oriel Instruments 68931) of constant irradiance is shone on the camera and images are taken with a variety of gain values. The intensity of the images as a function of the gain is then plotted and the polynomial fit for the data is then used to interpolate correction factors for gain values that were not specifically measured. This gain correction factor is then used to divide the background corrected total intensity. Measured white light data and the polynomial fits for the gain correction factors for the two cameras are shown in Figures 2.8 and 2.9, respectively. The overall image correction can thus be summarized by equation 2-1. $I_c$ is the corrected intensity, $I_r$ the raw intensity, $I_{bg}$ the background intensity taken by closing the shutter of the laser so that no laser pulse comes out, $g$ is the gate value and $g_n$ is the gain correction factor.

$$I_c = \frac{I_r - I_{bg}}{g \cdot g_n}$$ \hspace{1cm} (2 - 1)

In Figure 2.8 the equation of the fitted line is

$$I = 10^{(-2.66144 + 0.01132 \cdot \text{gain} + 1.84961 \times 10^{-6} \cdot \text{gain}^2 - 2.08448 \times 10^{-8} \cdot \text{gain}^3)}$$

with a $R^2$ value of 0.99995.
A Python program was created to analyze the images and produce the total intensity of the plasmas. The program essentially uses equation 2-1 to obtain the

![Figure 2.7: Normalized gain correction factor for Andor iStar DH734. The red dots are the experimental data points, and the blue line is the polynomial fit to the log(intensity)-linear(gain) plot.](image1)

![Figure 2.8: Gain correction factor for Andor iStar DH334T. The blue dots are the experimental data points, and the black line is the polynomial fit. The equation of the polynomial fit and the associated R² value is shown on the plot.](image2)
correct total intensity from an Andor camera image. The Python program is also capable of outputting the 1-D center of intensity (COI) of images. We have introduced the COI concept in complete analogy to the 1-D center of mass. The dimension along which the center of intensity is calculated is the x-axis of the images, the direction parallel to the laser beam axis. Since the COI is a 1D quantity, the images first need to be fully vertically binned. It is also necessary to provide the magnification of the images if the COI is to be in absolute length units and not just in pixel number. The magnification is also important for calculating the size of the plasmas that are imaged onto the cameras. The equation for the center of intensity is shown in equation 2-2, where $x_n$ and $I_n$ are horizontal position and associated vertically binned intensity respectively.

$$x_{COI} = \frac{\sum I_n x_n}{\sum I_n} \quad (2-2)$$

Because the magnification of the images is required for this part of the analysis, that value is obtained by imaging an object of known size on the camera. Since the size of a pixel is known for the camera, the magnification will be given by equation 2-3, where $m$ is the magnification, $l$ (pixel) the size of the image in pixels, $p$ (m/pixel) is the size of a pixel in meter, and $O$ (m) is the size of the object in meters.

$$m = \frac{l \text{ (pixel)} \times p \text{ (m/pixel)}}{O \text{ (m)}} \quad (2-3)$$

For the Ocean Optics spectrometer a second type of calibration needs to be done, namely for its wavelength dependent detection efficiency. Together with all of the other objects in the optical path, such as the lenses, fiberoptic, and quartz windows the spectrometer is calibrated using a Halogen-Tungsten white light source
with known and certified spectral brightness. When it is run at the factory settings, its output is a spectrum with known intensity values. The detection efficiency \( e(\lambda) \) of the system is thus nothing but the ratio of measured and certified intensity and can then be used to obtain the final, detection efficiency using the following formula,

\[
I(\lambda) = \frac{I_{\text{meas.}}(\lambda) - I_{\text{bg}}(\lambda)}{I_{\text{WL meas.}}(\lambda) / I_{\text{WL manf.}}(\lambda)} * \left( \frac{1}{IT} \right) \tag{2 - 4}
\]

In equation 2-4, \( I(\lambda) \) is the corrected spectrum, \( I_{\text{meas.}}(\lambda) \) is the raw spectrum, \( I_{\text{bg}}(\lambda) \) is the background spectrum, \( I_{\text{WL meas.}}(\lambda) \) is the measured white light spectrum, and \( I_{\text{WL manf.}}(\lambda) \) is the white light spectrum provided by the manufacturer when the light was calibrated and IT is the integration time. These white light calibrations were done for all three of the waters since the different waters can have different transmission properties due to the particles in the water. The setup for these calibrations was the exact same setup as for the raw spectra, with the addition of the white light source behind the water cell aligned with the fiberoptic cable. Ideally, the white light source should be in the water at the same location as the plasma, however this is not possible for two reasons: the water cell is not large enough to fit the white light and it also cannot be submerged in water since that will damage the light source. The angle of the fiberoptic cable axis relative to the emission axis of the light source or the plasma does not heavily affect the spectrum. Only angles larger than 25 degrees start to distort the spectra, but that is a very large angle and easily noticeable during the setup.
References


Chapter 3

Single Pulse Breakdown

3.1 Introduction and theory

The phenomenon of laser induced plasmas in water can be described by a sequence of separate yet also linked events: breakdown, light emission, shockwave, and cavitation bubble formation and collapse [1]. Breakdown can occur in one of two ways, multiphoton ionization or cascade ionization. In multiphoton ionization, two or more photons are absorbed simultaneously by the particle so that there is enough energy to ionize it. Because multiple photons are needed for ionization to occur, high irradiances are usually required. This process is known to create “seed” electrons in pure media. For cascade ionization, one or more free electrons is needed to be present in the focal volume before the laser pulse. These “seed” electrons are usually present in impure media due to the ionization of impurities through thermal excitation. In pure media however, the seed electrons are created by multiphoton ionization first. The cascade effect occurs when the seed electrons absorb laser radiation during collisions with neutral particles via the inverse Bremsstahlung absorption mechanism. The absorption of a photon by a free electron requires the collision with another particle to satisfy energy and momentum conservation [2], [3]. Since the free electron has obtained energy that is greater than the ionization potential it can now ionize a bound electron through collision and thus produce a second free electron, a process known as impact ionization. Repetitions of this process during the laser pulse multiplies the number of free electrons and creates a “cascade” or “avalanche” effect,
and leads to breakdown. Figure 3.1 shows a visualization of this process and treats the water as a semiconductor.

Figure 3.1: The sequence of photoionization, inverse Bremsstrahlung absorption, and impact ionization that occurs during the cascade buildup of electrons. Adapted from [3].

The absorption of the laser beam rapidly heats up the plasma to high temperatures and creates a visible plasma emission. The high plasma temperature is accompanied by high plasma pressure which causes a shockwave to expand at supersonic speed. At the center of the shockwave and at the location of the decaying plasma a cavitation bubble forms that also expands albeit at a much lower velocity [2]. Eventually, at our experimental conditions at around 200 μs, this bubble collapses again and fragments into small, irregular regions. Experiments in other groups performed with lower input energy reveal a sequence of re-expansions and collapses [10].
3.1.1 Free electron rate equation

Just as there are different ways to increase the number of free electrons in the plasma, there are also multiple ways to diminish their number. Specifically, the density of the free electrons as a function of time can be approximately modelled by a rate equation that has the form [2], [4]

\[
\frac{d\rho}{dt} = \left(\frac{d\rho}{dt}\right)_{MP} + \eta_C \rho - g \rho - \eta_A \rho - \eta_R \rho^2
\]  

(3 - 1).

The first two terms on the right side of the equation describe gain mechanisms of the free electron density \(\rho\), through multiphoton ionization \(\left(\frac{d\rho}{dt}\right)_{MP}\) and cascade ionization \((\eta_C \rho)\). The cascade ionization rate, \(\eta_C\), is the probability per unit time that a free electron will collide with a bound electron and ionize it. The last three terms are loss mechanisms: (i) the first is the diffusion of electrons out of the focal volume, with \(g\) as the diffusion rate, (ii) the next one is due to attachment to neutral molecules, where \(\eta_A\) is the attachment rate, (iii) and the last term is the loss due to electron-ion recombination, where \(\eta_R\) is the recombination rate. The reason for the \(\rho^2\) factor in the last term is of the fact that recombination is proportional to both electron and positive ion density and that, as long as only single ionization needs to be considered, the latter is equal to the former. This rate equation can be used to predict breakdown thresholds as well as tracking the free electron density over the lifetime of the plasma. Depending on the conditions of the plasma formation, certain terms may not be necessary, such as the diffusion term for ultrashort laser pulses [2].
3.1.2 Breakdown thresholds

The breakdown thresholds can be calculated using equation 3-1, but what about experimental determination of these thresholds? According to Kennedy et al. there are two methods that are used to experimentally determine the breakdown threshold [2]. One is known as the “flash” endpoint, where a plasma hot and dense enough to produce an emission visible to the naked eye is considered the threshold. However, this method is not reliable for pulse durations shorter than 5 to 10 picoseconds. The reason for no visible flash in the ultrashort laser pulse plasmas is because they are associated with having low density and low blackbody temperatures. The emission peak of the blackbody shifts to the infrared, and so causes the visible flash to disappear [2], [5]. Thus, there is a need for determining the breakdown threshold via a different method, which is known as the “bubble” endpoint. As discussed in section 3.1.1, formation of cavitation bubbles is associated with LIP in water, and such bubbles can be used to determine if breakdown has occurred or not. Plasmas identified by “bubble” endpoints are smaller, cooler and less dense than those identified by the flash endpoint [2].

The threshold of any medium is dependent on both the medium characteristics such as ionization energy and impurity content, as well as the beam characteristics, such as wavelength, pulse width and beam diameter at focus, otherwise known as the spot size. For cascade breakdown, the irradiance threshold is directly proportional to the ionization energy of the medium. When the loss terms are small, the threshold is inversely proportional to the pulsewidth, \( \tau_p \), as well. For multiphoton breakdown, the threshold is weakly dependent on the pulsewidth through \( \tau_p^{-1/K} \), where \( K \) is the
number of photons equivalent to the ionization energy [2]. In the nanosecond pulsewidth regime, the breakdown threshold is lower for impure water, that is water with high number of impurities, than pure water and is inversely proportional to the spot size. As for the wavelength dependence on the breakdown threshold, it is proportional for the wavelength, with 532 nm having a lower threshold than 1064 nm. This is because the multiphoton-initiated cascade breakdown process is much easier with a lower wavelength since each photon carries a larger energy and thus a fewer number of photons is required to initiate the breakdown process. However, impure water at 1064 nm still has a lower threshold than the 532 nm, which is independent of impurity content.

3.1.3 Moving breakdown model

Once breakdown has occurred, the visible plasma plume can be observed for its spatiotemporal dynamics. At the start of the laser pulse, the plasma is nominally at the focal point, but with the photons still coming in, the plasma expands toward the laser beam. This expansion is explained by the moving breakdown model. This model assumes that breakdown occurs independently at each location along the beam axis, as long as at that location the laser irradiance exceeds the breakdown threshold of the medium [6]. The expansion of the plasma will thus depend on the temporal and spatial profile of the laser beam [2]. The temporal part is significant because a certain location along the beam axis away from the focal point will only achieve breakdown at the time that the laser irradiance is at the threshold irradiance. Similarly, the spatial
profile matters because it determines the focusing conditions of the laser beam.

Figure 3.2 shows an illustration of the moving breakdown model.

In addition to the moving breakdown model explained above, it is well known that a plasma is able to partially absorb and partially scatter laser radiation, a phenomenon known as plasma shielding [2], [7]. The distributed shielding can be described as the extent to which a layer of the plasma prevents the transmission of laser radiation further downstream. This shielding reduces the amount of radiation available at and beyond the focal point as the plasma evolves. Thus plasma formation beyond the focal point is not observed and the plasma forms asymmetrically, with a longer tail on the incoming laser beam side. Figure 3.3 from [2] shows a schematic diagram of this asymmetry that is predicted by the moving breakdown model. It also shows that since the plasma only extends up to a certain length by the time of the peak of the pulse, the length of a plasma is partially determined by the pulse width. The other parameter that affects the length of the plasma is the irradiance [6].
Figure 3.2: Illustration of the moving breakdown model. (a) Geometrical structure of a (half) Gaussian beam with the focus at $z=0$. Shaded areas show the spatial distribution of the power at two different locations along the beam axis. (b) The temporal shape of a laser pulse whose peak power is assumed to exceed at $z=0$, the threshold power required for breakdown in the medium by a factor of 2. The left edge of each shaded area in (b) is the instant of breakdown $t_i$ corresponding to the axial location $z_i$. At $z=z_{max}$, breakdown occurs only in correspondence with the peak of the pulse ($t=0$). Adapted from [6].

Figure 3.3: A contour plot of the spatiotemporal evolution of the aqueous plasma predicted by the moving breakdown model for a 10 ns, 532 nm pulse with the beam waist $r_0=7\mu$m. The irradiance used here is 10 times the threshold irradiance. The thin lines represent the $I_0/e^2$ width of the unperturbed laser beam. Note that $t=0$ ns is the peak of the laser pulse, not the start. Adapted from [2].
3.2 Breakdown Threshold Observation

As discussed in chapter 2, all experiments for this research project were performed with the laser operating at 1064 nm. For the three different waters that were used as the medium in which the plasmas were created, it was found that in tap water consistent plasma production could be seen with pulse energy of 100 mJ or higher. By consistent visible breakdown would be observed for 90% of the laser pulses. In comparison, the pulse energy required to consistently produce plasmas in either distilled or ultrapure water was 150 mJ or above. At pulse energies below these levels, plasma would be produced for some pulses, but not all of them. It was somewhat arbitrarily decided to use a standard pulse energy of 250 mJ so as to be safely above breakdown threshold insuring that for each pulse fired, a plasma would be created.

As the rest of this chapter will be devoted to delving into the nature of the single pulse plasma, Figure 3.4 gives a sample of some of the plasmas that were observed in distilled water with a pulse energy of 250 mJ. The images in the figure are for constant gain and gate settings of the camera and use the same intensity display scale. It can be easily seen that at 0 ns delay, no plasma is visible (this was the case for every laser pulse), which is the condition for setting the zero for the camera as described in section 2.4. The pictures also reveal that most of the intense emission of the plasma occurs within the first 50 ns. The homogeneity of the intensity that is seen in this figure in contrast to Figure 2.6 could be due to not properly focusing the image on the camera.
Figure 3.4: Sample pictures of the distilled water plasmas taken with camera 2. The pulse energy of the 1064 nm laser beam was 250 mJ. The red arrow shows the direction in which the laser beam propagates.

3.3 Spatially integrated intensity of the three water plasmas

A lot can be learned by studying the light emission of the water plasmas. As a first round of characterization, the intensity of the plasma over its lifetime was observed. Figure 3.5 shows the spatially integrated emission intensity of the plasmas in the three different waters as function of time. The intensities have been corrected for both gate and gain of the camera, and the values obtained by the Python program discussed in section 2.4. As the figure shows, all three of the water plasmas, tap,
distilled, and ultrapure essentially evolve over time in the same fashion. The appropriately scaled temporal profile of the Nd:YAG laser intensity is included in the plot to show that the initial plasma growth directly follows the laser beam. Because the camera is not sensitive in the infrared, a photomultiplier with higher quantum efficiency in the infrared was used to capture the temporal beam profile. An interesting feature of the laser pulse is the second “bump” that occurs around 30 ns. Initially, this was puzzling feature was thought to be an artifact (e.g. electrical noise or ringing of the photomultiplier signal). However, the bump would not go away even after changing over to another photomultiplier. What is even more interesting is the fact that there is a slight increase in the integrated plasma intensity curves around 30 ns as well. This led us to speculate that the laser pulse has a weak (ca. 1%) secondary peak which influences the plasma intensity curve in much larger proportion (emission increase is much larger than 1%). A more precise characterization of the laser pulse and any possible correlated plasma intensity change would be more conclusive.

Although the initial decay of the plasma intensity is fast, the sensitive camera still detects emission signal from the plasma as late as 1μs. With high camera gain setting, camera gate duration of only 10 ns is sufficient. According to Kennedy et al. the plasma luminescence lifetime for nanosecond pulses should be close to that of the pulse width, and the decay time shorter than the pulse width [2]. This is not in agreement with the data in the plot. The FWHM of the laser pulse is roughly 8 ns, but the decay of the plasma intensity is much longer. The first decay time according to Kennedy is the fast electron-ion recombination lifetime. The secondary decay time, which goes on for much longer is the slow electron-neutral attachment lifetime [2].
One of the motivations for trying out these different waters was to investigate if the plasma formation process is different among them. As discussed in section 3.1.2, the breakdown for impurity filled water is lower than that of pure water. Thus, the hypothesis was that for the same pulse energy, the intensity of the impure water should be higher than the intensity of the pure water. However, Figure 3.5 does not seem to show this trend. All three of the water plasma intensities seem to be more or less at the same level.

![Figure 3.5](image-url): The integrated intensity of the three different water plasmas. The pulse energy of the laser was 250 mJ.
3.4 Center of intensity of the three water plasmas

In addition to the integrated intensity analysis, the center of intensity (CoI) of the three water plasmas was investigated. The Python program which gives the spatially integrated intensity also calculates the center of intensity for the same data sets in Figure 3.5. Figure 3.6 shows the center of intensity curves for the three water plasmas. The error bars are the standard deviations calculated from the multiple images taken of the same delay. The approximate location of the “focal point” is also included in the plot as a reference. An arrow superimposed on the plot shows the direction of the laser beam propagation. All three curves show a trend of the COI moving away from the focal point in the direction towards the laser, i.e. opposite to the laser propagation. This is the moving breakdown mechanism at work for the first 40 ns, while the laser pulse is present. It seems that the COI continues to move in the same direction until about 80 ns, the explanation for which is not yet clear. The location of the focal point was estimated as the average midpoint of the plasma along the beam axis at the 2 ns delay calculated from the data of all three water types. Although the initial center of intensity at the 2 ns delay seems to be beyond the focal point, the error bars of these COIs and the error bar of the calculated focal point (not shown) overlap. It’s also understandable for the early plasma to go slightly beyond the focal point, at which time, the plasma is still fairly symmetric about the focal point, since not enough time has passed for shielding to have taken effect. There is a noticeable difference in the COI curves of the three waters, the largest movement shown by tap, then distilled, and the least by ultrapure. This is speculated to be due to the different sizes of these plasmas. At least for the ultrapure, which is much
shorter in comparison to the other two. Since the ultrapure plasma does not expand as much, its COI also does not change as much.

![Graph](image)

**Figure 3.6:** The center of intensity of the three different water plasmas. The pulse energy of the laser was 250 mJ. The vertical line indicates the end of the laser pulse.

### 3.5 Spatially integrated intensity for different laser powers

The integrated intensity of the distilled water plasma as laser power changed was also investigated. Figure 3.7 shows the integrated intensity curves for the different powers. Surprisingly, these curves do not show a direct relationship between the laser power and the integrated intensity as would be predicted [6], [8]. These different powers represent different pulse energies, that is 250 mJ, 200 mJ, 150 mJ, and 100 mJ for the 5W, 4W, 3W, and 2W respectively. Since the length of the plasma is known to be directly proportional to the pulse energy, the larger the plasma, the higher the intensity of the plasma that would be expected assuming a similar intensity.
distribution for all plasma sizes. However, this does not seem to be the case. The total plasma emission intensities from various laser powers seem to be relatively close to each other and they all follow the same trend. It should be noted that these different powers were obtained by changing the voltage applied to the flashlamps before the Q-switch method was “discovered”. As mentioned in section 2.2, changing the power this way can change the conditions for breakdown. However, the observed good consistency of the integrated intensity curves shown in Figure 3.7 indicates that the different experimental method is unlikely to lead to a drastically different result.

![Figure 3.7: The integrated intensity of the distilled water plasmas for varying powers of the laser.](image)

### 3.6 Spectra of the three different water plasmas

Using the Ocean Optics spectrometer, time and space integrated spectra of the three different water plasmas were recorded. Figure 3.8 shows the three different spectra. They all behave the same way, a broad continuum with a weak sign of the
Hydrogen Balmer-alpha line at the 656.3 nm. Once again, the relative intensities of the three different water plasmas are not as expected. However, it should be noted that the Ocean Optics spectra are not fully spatially integrated since accepting angle of the fiberoptic cable is not large enough to capture the entire plasma. The measured spectra can be fitted with blackbody curves to obtain an approximation for the temperature of the plasmas. Figure 3.9 shows one example of the fitted blackbody curves for the tap water. Work from other groups indicates blackbody temperatures of 15,000 K [9] and 16,000 K [10], respectively whereas we find temperatures on the order of 49,000 K for the tap water in Figure 3.9. For the other two spectra shown in Figure 3.8, the fitted blackbody temperatures were even higher than the tap, much higher than any previously reported temperatures. The difference in the temperatures obtained could be due to the higher energy input of our experiments compared to the ones in the literature, 200 mJ vs 100 mJ respectively.
Figure 3.8: Ocean Optics spectra of the three different waters with laser pulse energy at 200 mJ.

Figure 3.9: Ocean Optics spectra of tap water plasma with laser pulse energy at 200 mJ. The blue curve is fitted onto the spectra, and the temperature is extracted from this curve.
References


Chapter 4

Repetitive Breakdown

4.1 Introduction

While a large number of studies of plasma formation in liquids has been done, most of them deal with the single pulse breakdown mechanism. The few cases in which repetitive breakdown has been investigated are for spectral analysis of the double-pulse laser-induced breakdown spectroscopy (DP-LIBS). The DP-LIBS method is used for chemical analysis in bulk water, as the second pulse is used to make the plasma from the first pulse last much longer and to cause it to emit more light for spectral analysis [1], [2]. In these DP-LIBS experiments, because the second pulse is meant to extend the lifetime of the original plasma, the interpulse delay is short, on the order of ns to μs. The characterization of repetitive pulse experiments with interpulse delay on the order of milliseconds has not been reported in the literature thus far. To the best of my knowledge, with this thesis information on repetitive breakdown plasma is being presented for the first time.

As was discussed in section 2.2 about the operation of the laser, it is possible to run the laser at multiple frequencies, from 1 Hz to a maximum of 20 Hz. The interpulse for these would then be 1s and 50 ms respectively. We have looked at the plasma formation for laser repetition frequencies of 1 Hz, 2 Hz, 5 Hz, and 10 Hz. Figure 4.1 shows the evolution of the 20 Hz plasma in term of the plasma length as a function of the number of the laser pulse. This plot gives a good overview of the
generic evolution of the repetitive breakdown process. A transition phase with changing plasma appearance for the first few pulses, whose typical number depends on the repetition frequency, is followed by an equilibrium or quasi steady-state phase. In Figure 4.1, the transition phase is represented by the red and blue data points (which somewhat arbitrarily indicate two regions with different rate of change), and the equilibrium phase is represented by the green data points.

**Figure 4.1:** Temporal evolution of the distilled water plasma. The repetition frequency is 20 Hz with a pulse energy of 250 mJ.

### 4.2 Integrated intensity

Just as was done for the single pulse case (see Figures 3.5 and 3.6), the effect of the three different waters on plasma formation was investigated for repetitive breakdown. Figures 4.2, 4.3 and 4.4 show the total intensities of repetitive breakdown
in the different waters. In time dependence of the single pulse experiments (Figures 3.5 and 3.7), the spatially integrated intensity was typically obtained with a camera gate width of 2 ns, which is only a small fraction of the plasma lifetime. Now, the gate width for the repetitive pulse case was set to 1 ms. Thus, these total intensity values represent both space and time integrated intensities of the plasmas. There are several trends that appear in the three different waters. For all three waters and for all the repetition frequencies above 1 Hz, the intensity seems to decrease with the pulse number. For ultrapure water, even at 1 Hz a slight drop might be present (although the fluctuation in the data is high and the conclusion is not certain). Also for all three different waters, as the repetition frequency increases the rate of change with pulse number seems to increase. This is illustrated in the figures with the exponential fit trendlines. The decay rates for the different waters and repetition rates are presented in Table 4.1. These trends are quite clear for distilled and tap water, but for the ultrapure water, the data points are more scattered and the trend with repetition rate is not very clear if it is present at all. Presumably, the absence of a clear trend is connected to the smaller number of impurities in the ultrapure water. With fewer impurities in ultrapure water, which means that at the focal volume, the number of impurities would not always be consistent for a given amount of time. This could lead to the scattered behavior of the data points observed for ultrapure water.
Figure 4.2: The integrated intensity of the 1 Hz, 2 Hz, 5 Hz, and 10 Hz plasmas created in tap water. The pulse energy for each of these repetition rates was 250 mJ.

Table 4.1: The decay rates from the exponential fits on the integrated intensities of the different waters and repetition rates. Note:
Figure 4.3: The integrated intensity of the 1 Hz, 2 Hz, 5 Hz, and 10 Hz plasmas created in distilled water. The pulse energy for each of these repetition rates was 250 mJ.

Figure 4.4: The integrated intensity of the 1 Hz, 2 Hz, 5 Hz, and 10 Hz plasmas created in ultrapure water. The pulse energy for each of these repetition rates was 250 mJ.
4.3 Center of intensity

The center of intensity was also calculated for repetitive breakdown plasmas in the different waters. Contrary to single pulse plasma in which the COI parameter was tracked over the plasma lifetime, COI values for repetitive breakdown plasmas are evaluated for the time integrated image and now track the change in plasma location from pulse to pulse. Figures 4.5, 4.6, and 4.7 show the COI trends for the different waters and varying laser repetition frequencies. The “focal point” in these plots was calculated via the same method used in the single pulse COI plots, i.e. by taking the midpoint of the first pulse plasmas (labelled one) in the three different waters. The biggest difference between the single pulse COI trends and the repetitive breakdown COI trends is that the latter moves downstream in the direction of laser propagation rather than opposite to it. To our knowledge, this behavior has not been reported in the literature. One possible mechanism that is yet to be tested can be described by the idea that after each pulse, the shockwave accompanying the plasma clears the impurities in the focal volume, and for the pulse thereafter, the laser beam must travel farther down the beam path to find impurities for breakdown. The clearing away of the impurities would also cause the total intensity of the plasma to decrease with increasing pulse number, which is consistent with the results in section 4.2. Once again, the same trend of decreasing COI with pulse number holds And, like in the single pulse experiments, the trend is least developed in the case of ultrapure water where the data once again show the largest amount of scattering. For this type of water, the data also seems to indicate that for 2 Hz the COI oscillates around the focal point. One might even see some evidence for oscillations of the COI around a
linear trendline for the other repetition frequencies in ultrapure water and even for distilled water. However, only more data and a closer analysis will reveal whether this behavior is real or only a statistical fluke. There is no convincing sign of this oscillation in the tap water, which shows a constant movement away from the focal point for all the repetition frequencies except for 1 Hz, which more or less stays at the same position for all the pulses.

Figure 4.5: The center of intensity of the 1 Hz, 2 Hz, 5 Hz, and 10 Hz plasmas created in distilled water. The pulse energy for each of these repetition rates was 250 mJ.
Figure 4.6: The center of intensity of the 1 Hz, 2 Hz, 5 Hz, and 10 Hz plasmas created in tap water. The pulse energy for each of these repetition rates was 250 mJ.

Figure 4.7: The integrated intensity of the 1 Hz, 2 Hz, 5 Hz, and 10 Hz plasmas created in ultrapure water. The pulse energy for each of these repetition rates was 250 mJ.
4.4 Spectral observations

Integrated emission spectra of the repetitive breakdown plasmas were taken for 2 Hz, 5 Hz, and 10 Hz in the three different waters. Figures 4.8, 4.9, and 4.10 show these spectra, which have been corrected for detection efficiency as well as integration time and number of pulses. The result of applying these corrections to a single spectrum produces what a repetitive breakdown plasma would emit. During data collection, the transient phase was avoided, thus the spectra shown represent the emission of the plasmas in their quasi-equilibrium states. The wiggles in the ultraviolet region of the spectra near about 330 nm are unknown features, which only arise after applying the detection efficiency correction. None of these features have been observed according to the literature, and due to the fact that the calibration lamp used for the detection efficiency is quite old, these features in the UV, as well as the large fluctuations at wavelengths larger than about 750 nm are not considered to be real aspects of the spectra. However, the blackbody continuum and the Hydrogen-Balmer alpha line at around 660 nm have been observed by other groups, and so we take the spectral range from 400 nm to 700 nm to be valid. Any narrow spikes that may appear in the spectra are potentially due to single pixels misreading the signal. This can happen if the pixel has been damaged. Therefore a clear indication for such blemishes is the unchanging location of such peaks independent of changes in the experimental conditions.
Figure 4.8: The Ocean Optics spectra of the 2 Hz, 5 Hz, and 10 Hz plasmas created in distilled water. The pulse energy for each of these repetition rates was 250 mJ.

Figure 4.9: The Ocean Optics spectra of the 2 Hz, 5 Hz, and 10 Hz plasmas created in tap water. The pulse energy for each of these repetition rates was 250 mJ.
These spectra were fitted with blackbody curves to extract their temperature. This is done by using the least $\chi^2$ sum fit of the blackbody curve to the spectra from 425 nm to 700 nm for the distilled and ultrapure water plasma spectra and 400 nm to 700 nm for the tap water plasma spectra. Table 4.1 summarizes the temperatures that were obtained through the blackbody fits as well as the full width at half maximum (FWHM) of the Lorentzian Hydrogen-Balmer alpha line fits. The equation used to fit the spectra is shown below:

$$I(\lambda) = \frac{A}{\lambda^5} \cdot \frac{1}{e^{\frac{B}{\lambda T}} - 1} + \frac{C \cdot D}{(\lambda - E)^2 + D^2} + \frac{F \cdot G}{(\lambda - H)^2 + G^2} + J$$  \hspace{1cm} (4 - 1)$$

In equation 4-1, A, B, C, D, E, F, G, H, J, and T are adjustable parameters that can be used to optimize the fit. T is the temperature of the blackbody curve, and $\lambda$ is the wavelength. The first term is Planck’s law of blackbody radiation, and the second and third terms are used for the H-$\alpha$ and H-$\beta$ lines with Lorentzian functional form. Seed values for the adjustable parameters are initially picked to get equation 4-1 to be near
the optimum fit, and then the “Solver” function in Excel takes over and calculates the best fit by minimizing the $\chi^2$ sum.

<table>
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<th>BB Temperature (K)</th>
<th>FWHM of H-(\alpha) (nm)</th>
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</thead>
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<td></td>
</tr>
<tr>
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<td>16,000</td>
<td>82</td>
</tr>
<tr>
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</tr>
<tr>
<td>10 Hz</td>
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<td>72</td>
</tr>
<tr>
<td>Distilled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Hz</td>
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<td>174</td>
</tr>
<tr>
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</tr>
<tr>
<td>10 Hz</td>
<td>30,000</td>
<td>160</td>
</tr>
<tr>
<td>Ultrapure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Hz</td>
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<td>160</td>
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</tr>
<tr>
<td>10 Hz</td>
<td>30,000</td>
<td>140</td>
</tr>
</tbody>
</table>

Table 4.2: The Blackbody temperatures and H-\(\alpha\) FWHM obtained from the blackbody and Lorentzian curves fitted on the spectra of the repetitive breakdown plasmas in the three waters.

Of the values that are shown in Table 4.1, only two of them are in the vicinity of temperatures found in the literature [3], [4], namely the 14,000 K and 16,000 K values for tap water plasmas of repetition frequency 2 Hz and 10 Hz, respectively. All other values are significantly larger than those reported in the literature. However, the fit of the Planck curve to our data is not very robust in part because of the limited spectral range. Therefore, the temperature values in table 4.1 should be considered as preliminary. Improvement in the UV calibration of the detection system should help to consolidate the temperature values. Compared to the values presented by Griem [5] and Escarguel [6], the plasma temperatures and FWHM of the H-\(\alpha\) lines in Table 4.1 are much larger. If the width of the Balmer-\(\alpha\) line is interpreted as coming only from Stark broadening, the corresponding electron densities would have to be much larger than $10^{18}$ cm$^{-3}$. Line broadening for such high electron densities have not yet been reported in the literature. However, a significant part of the observed broadening of
atomic lines in the water plasma could be due to pressure broadening and, to a lesser degree, to Doppler broadening. The Stark effect can be explained by the collisions of the emitting atoms with electrons and ions, which broadens the emission line and shifts the peak wavelength [7].

References


Conclusion & Future Directions

The work on the laser induced plasmas in bulk liquid water has yielded information about the intensity, center of intensity, and spectra of the plasmas. The plasmas generated in tap, distilled, and ultrapure water all show similar patterns of behavior, such as their intensity over the course of their lifetimes and the expansion up the beam path in support of the moving breakdown model. All of them also have a broad continuum in their spectra and show signs of the Hydrogen Balmer-α line. The repetitive breakdown data has produced some interesting results, with their transition and equilibrium phases of existence and the movement down the beam path from the focal point. Their spectra also have broad continuums and show signs of the Hydrogen Balmer-α line, although the temperatures and FWHM that have been obtained are much larger than those found in the literature.

There are many directions in which the continuation of this work can go towards, from the understanding of the movement of the center of intensity in repetitive breakdown to better modeling the spectra and understanding the large temperatures and electron densities that are in disagreement with the literature. With the help of time resolved spectroscopy, perhaps the issues can be handles better. In a completely different direction, there has been observation of forward light emission from the breakdown events, and it is unclear whether the light is being emitted by the
luminous plasma or if it is scattering of the laser light. Studying of the shockwaves and cavitation bubbles is another direction in which the research could go in. There are many avenues to take for further exploring the laser induced plasma in water, as questions arise every time something new is discovered about this phenomenon.
Appendix A

The major elements of the image intensifier include the photocathode, the microchannel plate, and the phosphor screen. Figure 2.5 shows schematic representations of these components of the image intensifier, taken from the camera manual [1]. The photocathode is responsible for converting photons of the image into photoelectrons based on the quantum efficiency of the photocathode. The photoelectron is then accelerated toward the microchannel plate by an electric field (part (b) of Figure 2.5). If the voltage on the photocathode is positive, then the photoelectrons will not have sufficient energy to leave the photocathode and enter the microchannel plate, rendering the intensifier OFF. However, by changing the voltage to be negative, the intensifier can effectively be turned ON. This process of changing the voltage on the photocathode is called gating, and the gate values entered in Solis will be how long the voltage stays negative before returning to the positive voltage and thus turning the intensifier OFF. The high potential across the microchannel plate (600 to 1000 V) causes an avalanche effect and increases the number of electrons, thus amplifying the signal. Changing the gain value on the Solis software changes the voltage applied on the microchannel plate. At the end of the microchannel plate, one photoelectron has been converted into many electrons in the form of a cloud (Figure 2.5, part (d)). The cloud of electrons is then lastly accelerated by a potential of a few thousand volts to the phosphor screen on the inside of the fiber-optic output window, which is coupled to the CCD. The high potential not only adds energy to the cloud of
the electrons, but also makes sure that the cloud does not spread to maintain the spatial location representative of the initial photon entering the intensifier.

Figure 2.5: The Andor iStar image intensifier (a), and its componentsts (b)-(d).