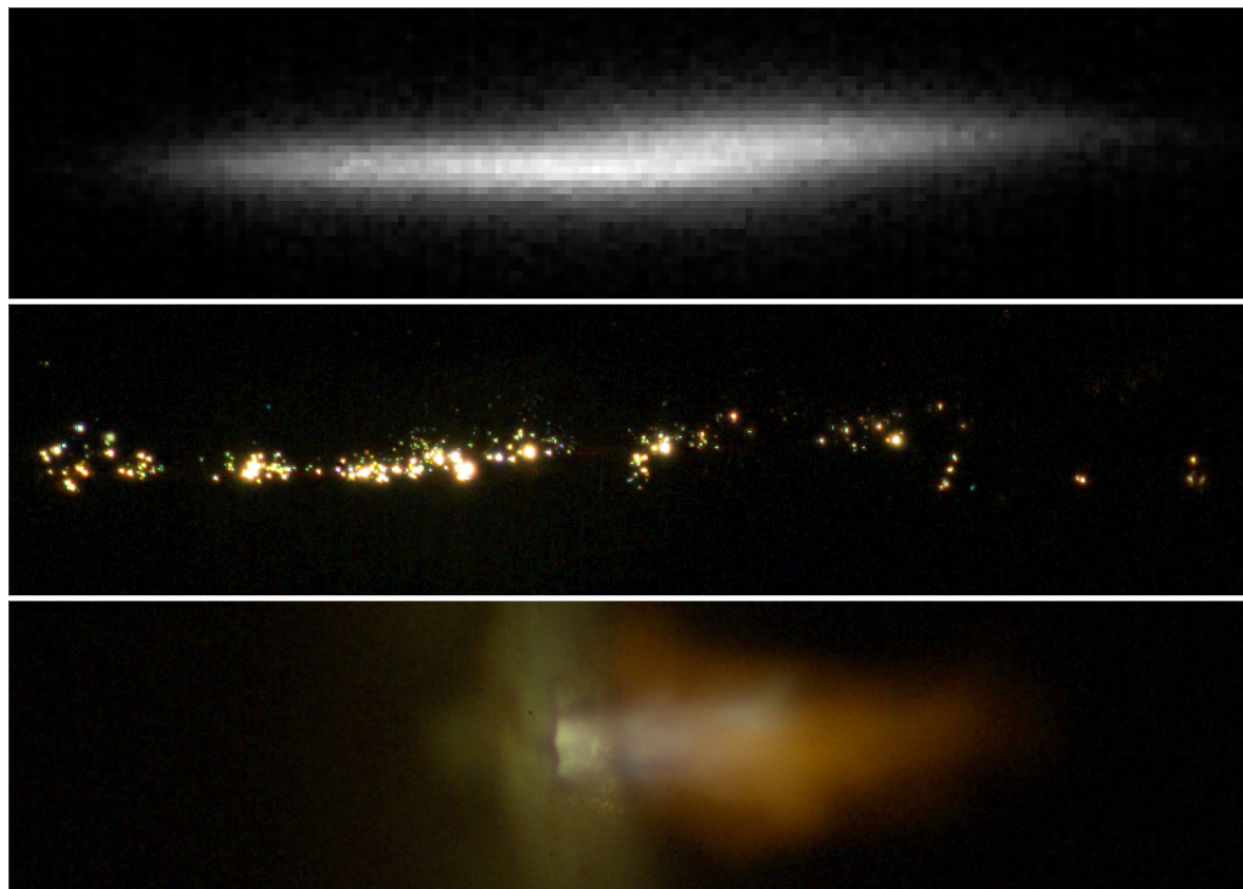




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Diagnosis of Ultrafast Laser-Induced Optical Breakdown

Towards applications in live-tissue bone microtomy

Master's thesis in Physics

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CHALMERS UNIVERSITY OF TECHNOLOGY

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Department of Physics and Astronomy
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UNIVERSITY OF GOTHENBURG

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Cover: Femtosecond laser-induced optical breakdown leading to the creation of a plasma in ambient air (top), driving laser filamentation and gas bubble formation in liquid water (middle), and the ablation of porcine bone tissue (bottom).

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Abstract

The process of cutting tissue samples into ultrathin slices to study the cross-sectional area is known as microtomy, and is widely used in medical and biological research. Traditional mechanical cutting introduces challenges for tissues like bone, as the hard outer layer and soft marrow core require freezing or fixation that damage cellular structures. These challenges can be overcome by utilizing ultrafast lasers in the femtosecond regime, which leverage precise optical breakdown and negligible thermal transfer to cut micrometer-thin slices of fresh bone with intact marrow cells. The purpose of this thesis is to characterize the underlying physics of this process and suggest methods to improve the overall ablation efficiency. This was achieved by investigating the spatial, spectral, and temporal dynamics of optical breakdown induced by a 775 nm, 1 kHz femtosecond laser across three distinct target media: ambient air, liquid water, and porcine bone. The interactions were characterized using high-speed spatial imaging, VIS–NIR spectrometry, and ultrafast temporal photodetection coupled with an in-house developed statistical deconvolution model.

The empirical results demonstrated that ambient air acts as the optimal bulk propagation medium for the laser, exhibiting high pulse-to-pulse stability and rapid nanosecond-scale plasma decay. Conversely, bulk liquid water was dominated by severe nonlinear optical distortions, including filamentation, severe spectral broadening, and macroscopic bubble structures that reflected laser light, rendering it inadequate for precise material ablation. During the ablation of porcine bone, the continuously ejecting plasma plume exhibited distinct calcium transition lines and decayed over hundreds of nanoseconds to microseconds; orders of magnitude slower than the air plasma. This slow dissipation provides direct experimental evidence that restricted geometries cause significantly slower plasma decay than free geometries, and that high-repetition-rate (MHz) laser systems may encounter plasma shielding effects. To maximize cutting efficiency and mitigate damage to the tissue, this thesis proposes utilizing ambient air as the primary propagation medium and employing a gentle ablation strategy with low pulse energy and high repetition rate. Finally, a number of topics for future research are proposed, including an effort to produce a comprehensive review paper of the field; using humidified air streams to reduce tissue dehydration and alleviate debris removal; dynamically tuning pulse energy to account for material heterogeneity and trench geometry; and developing a predictive model for optimal parameter windows for a given laser system.

Keywords: Ultrafast Laser, Laser-Induced Optical Breakdown, Bone Microtomy.

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Christian Russberg & Adrian Sandberg, Gothenburg, July 2026

On the Use of Artificial Intelligence

Throughout this thesis work (January–June 2026), the large language model Google Gemini 3.1 Pro has been used. Many of the figures in this thesis were created using Python, for which Gemini was used to assist in writing and editing code. Similarly, it assisted in writing and editing Python code for much of the numerical data analysis, including in particular the spatial dimension analysis and statistical modeling presented in section 4. In the writing of this thesis, it was sometimes used to restructure or suggest reformulations of our draft text to improve the overall structure, vocabulary and flow, as well as reconcile our different writing styles. In all cases, the output of Gemini was thoroughly vetted and edited to align with our standards and avoid any possible errors.

Christian Russberg & Adrian Sandberg, Gothenburg, July 2026

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1. Introduction

1.1 Background

Major advances have been made in ultrafast laser technologies over the last 50 years, and today laser pulses as short as on the order of femtoseconds can be produced even in commercially available laser systems in many different applications [1–3]. These ultrashort laser pulses differ from traditional continuous wave (CW) laser beams in a few crucial ways. Rather than passing a pump beam through a gain medium and optical resonator to produce a continuous output, ultrafast pulsed lasers work by mode-locking, where the relative phase of resonant optical modes inside an optical cavity are manipulated such that they interfere to produce a single ultrashort pulse [4]. This allows the intensity of these pulses to be several orders of magnitude greater than traditional laser beams, enough to immediately ionize almost any material into a plasma through tunnel- and multiphoton ionization when focused [5, 6]. Simultaneously, the pulses are so temporally short that very little heat transfer to the material has time to occur, making it possible in principle to drill or cut in materials with great precision without damaging the surrounding structures [1, 7, 8]. This unique property has opened the door for groundbreaking new possibilities within many research fields, not least among them medicine [6, 9–11]: one such breakthrough came in the early 1990’s with Laser-Assisted in Situ Keratomileusis (LASIK), where femtosecond lasers started being used for corneal surgeries [12–14].

Lately, a new and potentially groundbreaking medical application has emerged: ultrafast laser bone microtomy [15–18]. Microtomy is the process of cutting a sample into multiple thin slices to allow for study of the tissue cross section. This is usually achieved mechanically with sharp blades [19]. However, mechanical cutting is challenging for certain types of tissue such as bone, which has a soft marrow core inside a hard outer layer (cortex). Cutting this type of tissue mechanically typically requires some kind of fixation, embedding or freezing before cutting to prevent crushing the marrow, and this can greatly alter the structure of the tissue [15, 17, 18, 20]. Furthermore, the risks for potential shear stresses and tearing of samples also increase drastically during mechanical cutting [21]. Medical CW lasers, on the other hand, work primarily through linear heat absorption that melts or burns the target area, which naturally also is undesirable in this context [21]. These problems can be circumvented by using ultrafast lasers instead, due to their high precision and low heat transfer compared to traditional CW lasers. Using femtosecond lasers, micrometer-thin slices of bone tissue with intact marrow and cell structure at the cross section can be achieved, paving the way for new research in bone marrow-mediated diseases like leukemia [22].

A significant challenge for newcomers to ultrafast laser ablation in medical applications, however, is the absence of a comprehensive, up-to-date review compiling fundamental physics, different implementation strategies, and the current research landscape. While Vogel et al. (2005) [6] provides a robust theoretical foundation, it naturally predates any advancements made in the field in the last 20 years. Other reviews [7, 9, 23, 24] offer lots of valuable insights into the theory and different implementation strategies, but are either narrower in scope or focus on topics that are only tangential to biological tissue ablation. Consequently, establishing a solid understanding of the field currently requires studying numerous independent sources, which is time-consuming and introduces the risk of misinterpreting the many theoretical models and results, or overlooking critical, hard-to-find literature.

1.2 Purpose and Scope

While providing a fully comprehensive review of the current research landscape is outside the scope of this thesis, the overarching purpose of this work is to explore ways to improve ultrafast laser microtomy. To effectively reach this goal, it is crucial to first provide a comprehensive theoretical backbone regarding the ultrafast (femtosecond) laser, optical breakdown of materials, and the subsequent dynamics of the induced plasma. Following this theoretical foundation, we perform a series of experiments to make a baseline diagnosis of the optical breakdown in three different target media: ambient air, distilled water, and porcine bone. The scope of our experimental work is limited to three non-invasive measurement methods: pulse-to-pulse spatial imaging using a high-speed camera, VIS-NIR emission spectrometry, and ultrafast temporal imaging using an ultrafast photodiode.

These specific methods and target media were chosen due to constraints in lab equipment and time. Measurements that would have otherwise been of interest, such as frame-by-frame analysis of the plasma formation, the effect of different laser repetition rates, temperature evolution, or the effects of different atmospheric conditions (different pressures, noble gas medium, etc.), were impossible to capture with the equipment at hand. Furthermore, due to limited access to fresh tissue, all bone-cutting experiments were performed by drilling into dry porcine rib bone rather than cutting thin slices of living tissue. While this does not simulate the hydrated medium required to keep cells alive, the dry bone still provides an excellent medium for the fundamental diagnostic purposes of this thesis. Ultimately, the results from these diagnostic experiments will be interpreted based on the provided theoretical foundation. This will allow us to establish physically motivated rules-of-thumb for optimal operating parameters, aiming to maximize ablation precision and speed while minimizing damage to the surrounding tissue. Finally, we will use these findings to propose avenues for future research.

2. Theory

2.1 Properties of the Femtosecond Laser Pulse

The laser system used in this work is a CPA2001 femtosecond laser system. As briefly mentioned in the introduction (section 1.1), it operates using mode-locking techniques, where resonant optical modes inside an optical cavity are phase-matched to produced single, ultrashort laser pulses [4]. These pulses are then amplified using chirped pulse amplification (CPA), where the pulse is stretched, passed through a gain medium, and subsequently contracted again to produce pulses with field intensities above the optical damage regime of the gain medium [25].

The exact properties of the produced laser pulses are not known exactly. This is primarily due to the sensitive nature of the system. It is virtually impossible to get a perfectly stable output even over short periods, let alone accounting for various drift effects over longer time spans. That said, it is within reason to use heuristic estimates to give a picture of the nature of the laser pulses in question. For this purpose, we will use Gaussian optics to describe the properties of the laser pulse, the theory for which we refer to the seminal book by A. E. Siegman [26].

The only parameter we know a priori is the laser wavelength, at 775 nm (NIR). Beyond that, we can assume that the laser pulses are near-Gaussian, with a beam quality of $M^2 \approx 1.2$ and an output $1/e^2$ beam width of approximately 2.5 mm. This is expanded to 7 mm and subsequently focused using a $f = 70$ mm lens. The smallest beam width a Gaussian beam can achieve at the focus due to wave diffraction is called the beam waist w_0 , described by

$$w_0 = \frac{\lambda f M^2}{\pi w_L}, \quad (2.1)$$

where w_L is the expanded beam width at the input of the lens. In our case, the beam width is approximately 3 μm . The length of the focus is commonly described by the Rayleigh length, which is the distance along the propagation where the beam cross sectional area becomes twice that of the focus, i.e. where the beam width is $\sqrt{2}w_0$, and can be calculated using

$$z_R = \frac{\pi w_0^2}{\lambda M^2}. \quad (2.2)$$

In our case, it is approximately 30 μm . By doubling the Rayleigh length we get the confocal parameter $b = 2z_R$, which is more relevant when for example characterizing the length of a generated laser or plasma filament. The beam waist, Rayleigh length, and confocal parameter are illustrated in figure 2.1.

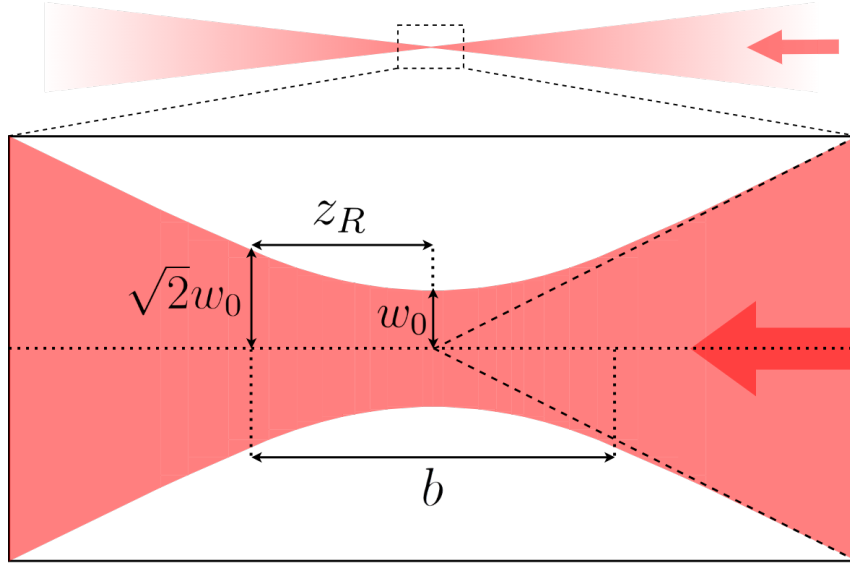


Figure 2.1: Illustration of the $1/e^2$ beam width of Gaussian beam around the focus, including the beam waist w_0 , Rayleigh length z_R , and confocal parameter b .

With the spatial dimensions of the beam sorted, we can construct a model of the overall pulse shape, assuming the pulse full width at half maximum (FWHM) is 150 fs. Adding a propagating temporal envelope to the standard Gaussian beam envelope [27], we get a propagating intensity profile of the form

$$I(r, z, t) = I_0 \frac{z_R^2}{z^2 + z_R^2} \exp\left(-2 \frac{r^2}{w_0^2} \frac{z_R^2}{z^2 + z_R^2}\right) \exp\left(-4 \ln(2) \frac{(t - z/c)^2}{\tau_l^2}\right), \quad (2.3)$$

where z is the distance along the propagation and r the cylindrical radial distance from the pulse center. The pulse length at FWHM is given by τ_l and the peak intensity at the focus ($r = t = z = 0$) by I_0 . From this, we can also get the cycle-averaged electric field amplitude using

$$\mathcal{E}(r, z, t) = \sqrt{\frac{2}{\epsilon_0 c}} I(r, z, t),$$

where ϵ_0 is the free-space permittivity. In order to compute I_0 and the corresponding $\mathcal{E}_0$, we have to know the total pulse energy. The pulse energy at the output can reach $>800 \mu\text{J}$, although this will be attenuated using various optical components such as crystal polarizers. By denoting the pulse energy E_{pulse} , we can relate it to peak intensity by integrating a transverse plane, which describes instantaneous power, over time like

$$E_{pulse} = \int_{-\infty}^{\infty} \int_0^{\infty} I(r, z, t) 2\pi r dr dt.$$

The integral is independent of z and yields the relation

$$E_{pulse} = \frac{I_0 \pi w_0^2 \tau_l}{4} \sqrt{\frac{\pi}{\ln(2)}}. \quad (2.4)$$

The relation between pulse energy and peak intensity is linear, and a pulse energy of $500 \mu\text{J}$ would for example equal a peak intensity of $I_0 \approx 2 \times 10^{20} \text{ W/m}^2$.

2.2 Nonlinear Optics

Microscopically, the likelihood of interactions between particles and photons, such as non-ionizing photoabsorption or elastic scattering, are governed by properties like particle charge, polarizability, and quantized energy levels. In linear optics, the macroscopic average of these effects is described by the complex refractive index

$$\tilde{n}(\omega) = n(\omega) + i\kappa(\omega).$$

The real part, n , dictates the overall phase velocity of light in the medium, while the imaginary part, κ , also called the extinction coefficient, dictates the rate at which the electromagnetic field is attenuated by the medium. This is related to the linear absorption coefficient α_{abs} through

$$\alpha_{\text{abs}}(\omega) = \frac{2\omega\kappa(\omega)}{c}. \quad (2.5)$$

In a standard linear regime, an electromagnetic field propagating along z will attenuate by a factor of $e^{-\alpha_{\text{abs}}z}$. This absorbed energy is primarily taken up as excitations in vibrational and electronic states, which subsequently thermalizes into bulk heat. However, if the optical electromagnetic field is intense enough, it modifies the optical properties of the material it interacts with. In this regime the standard, linear optical parameters are replaced with their nonlinear, intensity-dependent counterparts. The most common approach to modeling these is by means of Taylor expansion in I or $\mathcal{E}$ [5]. For example, the absorption coefficient expands to $\alpha_{\text{NL}} = \sum_{m=0} \alpha_m I^m$, where α_0 is the linear α_{abs} from before. The higher-order terms account for the effective energy lost to nonlinear processes, which begin to dominate over linear bulk heating as intensity increases.

Alongside nonlinear absorption, the intense field also modifies the real part of the refractive index, leading to spatial propagation effects that drastically alter the pulse profile. The most critical of these is the balance between Kerr self-focusing and plasma self-defocusing.

2.2.1 The Kerr Effect and Self-Focusing

The optical Kerr effect is the direct change in the refractive index as a result of the intense optical field. It is defined by the first-order expansion of the non-linear refractive index like

$$n = n_0 + n_2 I + \mathcal{O}(I^2), \quad (2.6)$$

where n_0 is the linear and n_2 the nonlinear refractive index component [5]. Since our laser pulse has a Gaussian spatial profile, the intensity is highest at the center of the beam. This creates a positive gradient in the refractive index that acts as a converging lens, causing the beam to self-focus, further driving up the peak intensity.

In atmospheric air, n_2 has been estimated to be roughly $(1 - 6) \times 10^{-23} \text{ m}^2/\text{W}$ [28], whereas for water it has recently been measured at $(8 \pm 1.4) \times 10^{-20} \text{ m}^2/\text{W}$ [29] for

$\lambda = 800$ nm. For laser pulses with peak intensities around 10^{20} W/m², such as in our case with 500 μ J pulse energy, higher-order terms (such as n_4) can be neglected [29]. At these intensities, strong self-focusing effects take place in dense media like water, while remaining less pronounced in atmospheric air.

2.2.2 Plasma Self-Defocusing and Laser Filamentation

If the instantaneous intensity is strong enough, optical breakdown may occur, ionizing the neutral material into a plasma through photo-ionization. This releases free electrons that can interact directly with the electromagnetic field, which reduces the local refractive index and scales linearly with the plasma density [30]. The plasma density is highest at the center of the beam where the intensity is greatest, creating a negative refractive index gradient that acts as a diverging lens. This plasma self-defocusing directly counteracts Kerr self-focusing, and the balance between these two effects can lead to intensity clamping or the formation of long propagation channels known as laser filaments [31].

2.2.3 Spectral Broadening and Supercontinuum Generation

As the intense laser pulse propagates and undergoes the focusing effects described above, its temporal and spectral profiles are also altered. In a nonlinear medium, the time-dependent intensity of the femtosecond pulse, $I(t)$, leads to a corresponding time-varying refractive index from the optical Kerr effect (see equation 2.6). This temporal variation induces a time-dependent phase shift across the pulse, generating new frequency components in a process known as self-phase modulation (SPM). Since the leading edge of the pulse experiences an increasing refractive index while the trailing edge experiences a decreasing one, SPM typically broadens the spectrum symmetrically around the central laser wavelength [30]. However, when the intensity is sufficient to induce optical breakdown, the generation of a free-electron plasma introduces a second, asymmetric spectral broadening. The surge in plasma density as the pulse propagates causes a drop in the local refractive index during the trailing edge of the pulse. This asymmetry in refractive index leads to spectral broadening with stronger shift towards shorter wavelengths, an effect known as plasma blueshift [30].

In the extreme case, the combined effects of SPM and plasma blueshift can result in such pronounced spectral broadening that the narrow bandwidth of the incident laser turns into a broad white-light spectrum. This phenomenon is known as supercontinuum generation (SCG) and was discovered by Alfano and Shapiro in 1970 [32–34]. The extent of both the Kerr effect and plasma generation scales with the density and band-gap of the material [35], so the degree of spectral broadening varies significantly between different targets. In the context of this project, it can be expected that dense, condensed media like water and bone tissue will exhibit stronger spectral broadening, perhaps even enough to create a supercontinuum, whereas the effects in air will likely be minimal.

If the laser light exhibits significant spectral broadening, any scattered or reflected laser light onto spectroscopic equipment will obscure other light sources such as plasma emissions. It is therefore important to be aware of this effect so that it can be identified and accounted for in the recorded spectroscopic data.

2.3 Optical Breakdown and Photoionization

As alluded to previously, nonlinear changes in the optical properties of a medium are not limited to direct changes in its response to the field, but can be manifested due to optical damage or other fundamental changes in the material. A term used colloquially in nonlinear optics is optical breakdown, referring to the process where the electromagnetic field is able to ionize the molecules, releasing free electrons and changing the fundamental optical properties of the medium. If the electromagnetic field is strong enough to directly rip the electrons from their parent nuclei, the process is called direct ionization or barrier-suppression ionization (BSI) [5]. The necessary field strength to achieve this is

$$\mathcal{E}_{\text{thresh}} > \mathcal{E}_{\text{at}} = \frac{e}{4\pi\epsilon_0 a_0^2} \approx 5 \times 10^{11} \text{ V/m},$$

corresponding to a field intensity of

$$I_{\text{thresh}} > \frac{1}{2}\epsilon_0 c \mathcal{E}_{\text{at}}^2 \approx 4 \times 10^{20} \text{ W/m}^2.$$

However, this is not the intensity threshold for the onset of photo-ionization in general. Through quantum mechanical effects, the electrons can tunnel through a slightly suppressed atomic potential by tunnel ionization, or acquire enough energy to directly escape the potential barrier by means of near-instantaneous consecutive photoabsorption, also called multiphoton ionization. From these effects, a material can even reach full ionization at field intensities far below BSI. The peak field intensity of the laser pulses employed in this project, as calculated in chapter 2.1, are all less than the BSI limit, reaching at most half in the case of 500 μJ pulse energy, and tunnel and multiphoton ionization will thus be the dominant ionization processes in our experiments.

2.3.1 Tunnel Ionization

Consider the spherically symmetric atomic potential of an atom or molecule as the Coulomb potential created by a positive nucleus at the origin. Now consider an incident optical electric field that interacts linearly with the nuclear Coulomb field, such that an equivalent energy state to that of a ground-state electron is created outside the potential well at some distance R from the origin. If the incident field is strong enough, there is a chance that the electron can overcome the net potential barrier by way of quantum tunneling, as shown in figure 2.2 below.

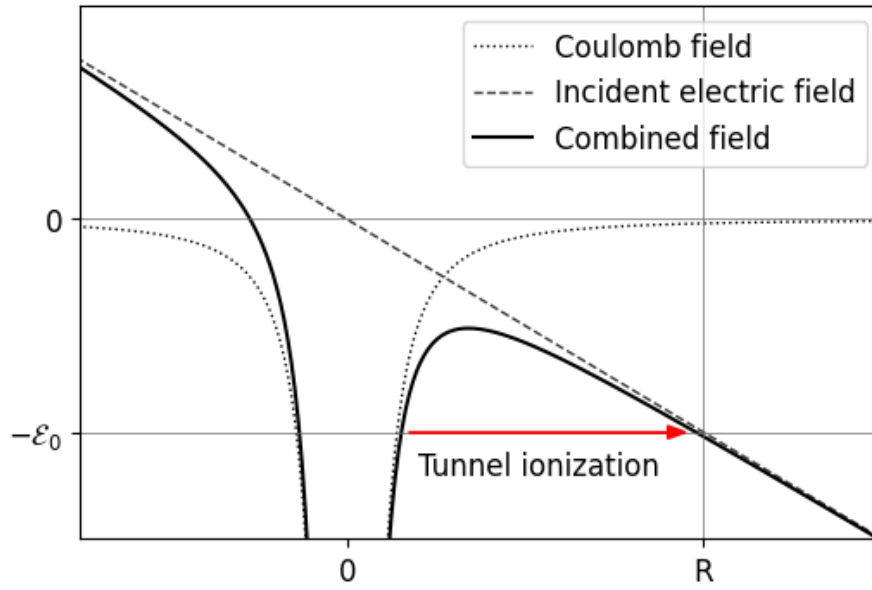


Figure 2.2: Qualitative diagram of tunnel ionization. The field strength at the ground state of the electron is given by $-\mathcal{E}_0$.

The probability of tunneling is not only dependent on the field strength, but also the field frequency. Slower fields will result in a larger time window during which the electron can tunnel. Hence, tunnel ionization favors electric (or optical) fields with lower frequency [36].

2.3.2 Multiphoton Ionization

Photo-ionization occurs when the bound electron in an atom absorbs a photon with energy higher than the atom's ionization potential I_P . The surplus energy is converted into kinetic energy for the ion and electron such that total momentum and energy is conserved. The probability of this interaction is described by the photo-ionization cross section σ , and stronger fields (higher photon flux) therefore have a faster total ionization rate. However, if the photon energy is lower than the ionization potential, the electron cannot escape the atomic potential barrier, and the absorbed photon energy may only be enough to briefly change the electric or vibrational state of the electron. The electron will then relax to its ground state, releasing the absorbed energy in the form of a photon.

In very strong fields, however, there is a non-negligible chance of more than one photon being absorbed by the electron before it has time to relax: so-called multiphoton absorption. If enough photons are absorbed to overcome the atomic potential barrier, the electron has been ionized by way of multiphoton ionization, as demonstrated in figure 2.3.

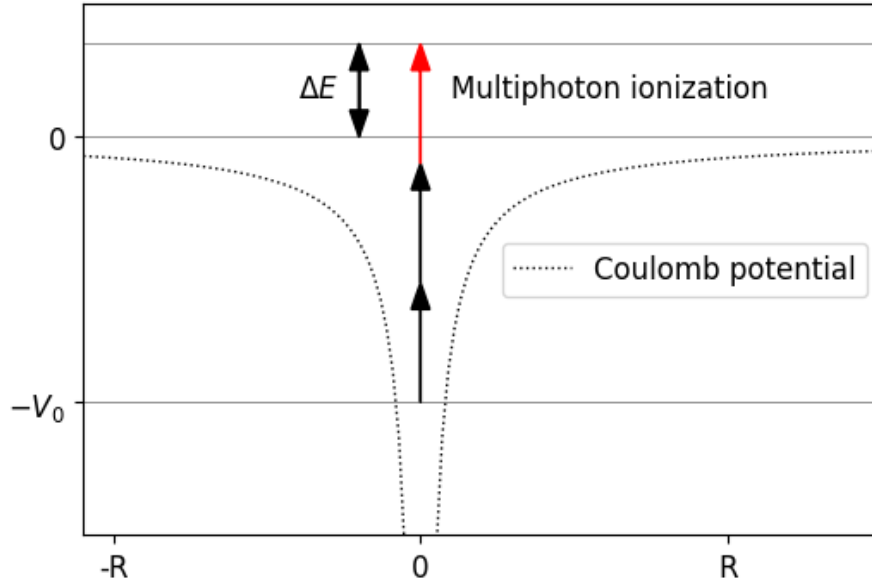


Figure 2.3: Qualitative diagram of multiphoton ionization. The ground state energy is given by $-V_0$ and the surplus electron energy by ΔE .

Photon energy is proportional to its frequency, so multiphoton ionization naturally favors optical fields with higher frequency, down to the discrete nature of the ionization process. Consider, for example, n identical photons whose sum of energies is higher than the ionization potential:

$$nE_\gamma(\omega) \geq I_P > (n-1)E_\gamma(\omega).$$

For simplicity, we will assume the photo-absorption cross section σ stays constant with ω . In this simplified case, the frequency of the photons by δ will not actually increase the ionization cross section until the sum of energies of $n-1$ photons overcomes the quantized ionization potential, i.e.

$$\begin{aligned} (n-1)E_\gamma(\omega + \delta_1) \geq I_P > (n-1)E_\gamma(\omega + \delta_2) &\implies \\ \implies \sigma(\omega + \delta_1) > \sigma(\omega + \delta_2) = \sigma(\omega). \end{aligned}$$

The cross-section of multiphoton ionization intuitively decreases very rapidly as the number of required photons increases, and the corresponding n -photon cross-sections are related to the non-linear expansion terms in the non-linear optical susceptibility of the material. The mathematics that describe the cross-section for n -photon ionization are very involved and require solving the time-dependent Schrödinger equation (TDSE) of the system, for which we will refer to the derivations in R. W. Boyd's seminal book on nonlinear optics [5].

Taking air as an example, simplifying it to two separate gas populations of molecular oxygen (O_2 , $I_P \approx 12.1$ eV) and molecular nitrogen (N_2 , $I_P \approx 15.6$ eV), we can calculate the number of photons required for multiphoton ionization. Assuming photon wavelengths of 775 nm, corresponding to 1.6 eV photon energy, we see that

oxygen requires 8, and nitrogen 10, photons. These calculations do not, however, take into account the interplay of barrier suppression and tunnel ionization of the potential, which will affect the actual number of photons required to ionize the material at any point in time.

2.3.3 The Keldysh Parameter and Ionization Models

The total ionization rate for an intense laser will be some combination of these two effects, and the relative importance is described by the Keldysh parameter, which was formulated by Keldysh in his 1965 paper on ionization by strong electromagnetic waves [36]. It is defined as

$$\gamma \equiv \frac{\omega \sqrt{2m_e I_P}}{\mathcal{E}_e},$$

where ω is the angular frequency of the field, and m_e and e are the electron mass and charge, respectively. When $\gamma \gg 1$ multiphoton ionization dominates, whereas when $\gamma \ll 1$ tunnel ionization dominates. For the laser system described in section 2.1, the Keldysh parameter for a number of common molecules, for different pulse energies and intensities, can be found below in table 2.1. The ionization potentials used were the standard 12.1 eV and 15.6 eV for O_2 and N_2 , respectively, and the optical Charge Transfer ionization potential of 6.5 eV for liquid water [37]. For the purposes of our project, pulse energies no lower than 50 μJ will be used, for which the peak intensities correspond to Keldysh parameter values of at most 0.25. It is therefore assumed that tunnel ionization is the primary ionization mechanism, although multiphoton ionization can become important on the tails of the pulses near that lower bound of 50 μJ .

Table 2.1: Peak intensity and Keldysh parameter value for a selection of different pulse energies and molecules. The peak intensity is calculated from the pulse energy using equation 2.4 and beam parameters listed in section 2.1.

E_{pulse} (μJ)	I_0 (10^{18} W/m ²)	γ (O_2)	γ (N_2)	γ (H_2O)
500	220	0.070	0.079	0.051
50	22	0.22	0.25	0.16
5	2.2	0.70	0.79	0.51
0.5	0.22	2.2	2.5	1.6

There are several methods for calculating the ionization rates for a specific medium. The most accurate, albeit very computationally demanding, is solving the corresponding TDSE directly [38, 39]. There also exist simpler, more computationally efficient models, such as the Ammosov-Delone-Krainov (ADK) model for tunnel ionization (most useful in the $\gamma \ll 1$ regime) [40], or the more commonly employed Perelomov-Popov-Terent'ev (PPT) model, which is accurate in both the tunneling and multiphoton regime [41–44]. For diatomic molecules, useful for modeling ionization rates in air, extensions to ADK and PPT, called MO-ADK and MO-PPT, respectively, have been developed [45–47]. Open-source numerical tools for nonlinear optics like Luna employ these methods, and can be used to simulate the ionization process in different media [48].

2.4 Plasma Dynamics

The process of ionization is very fast, on the order of as-fs, so a plasma is created almost instantaneously with respect to the pulse length (≈ 150 fs) [5]. The free electrons will interact directly with the laser pulse as long as it exists, absorbing energy primarily via inverse bremsstrahlung (IB) [6]. As a rule of thumb, it is usually assumed that the electron temperature induced by ultrafast laser pulses is on the order of 1 eV. The heavy atoms and ions do not interact meaningfully with the field directly, and any energy they gain is primarily from non-radiative decay of excited electron states or from kinetic energy transfer. The exact initial electron and ion temperatures, as well as the ionization degree, depend on the specific medium and characteristics of the laser pulse and can vary massively.

2.4.1 Electron Avalanche and Impact Ionization

As the electron freed by tunnel and multiphoton ionization gain additional energy from the electromagnetic field, they will start colliding with ions and neutral atoms. If the electrons gain enough energy, these collisions may result in so-called impact ionization, where the transferred kinetic energy from an electron is enough to ionize a neutral particle (and, more rarely, even ions), described by



The corresponding impact ionization cross section typically increases with higher electron energies. Since this process increases the number of free electrons, it can cascade in a chain reaction called an electron avalanche, leading to exponential ionization of the medium [49, 50]. This process is limited only by the energy distribution of the total electron population.

2.4.2 Shockwave Generation

The combination of inverse bremsstrahlung and avalanche ionization leads to a surge in both electron population and temperature, while neutrals and ions remain relatively cold. This leaves the plasma in a thermodynamic non-equilibrium, and the resulting pressure exerted on the surroundings is described by the plasma pressure, defined as

$$P = n_i k_B T_i + n_e k_B T_e. \quad (2.8)$$

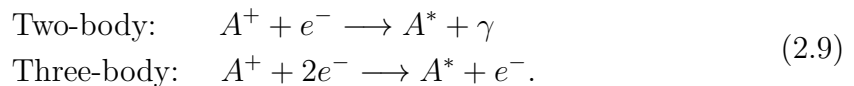
This pressure scales linearly with both ionization degree and the individual population temperatures. In atmospheric air, if the electron temperature is 1 eV and ionization rate is 1%, the pressure contribution from the electrons is already 40 kPa. The pressure contribution from neutral atoms and ions, assuming the ions are room-temperature, will equal atmospheric pressure at ≈ 100 kPa, meaning the electrons create a massive overpressure, enough to create a shockwave followed by a rapid expansion of the plasma. Much research has been conducted on the formation, expansion and matter-interaction of these generated shockwaves [51–55], so this project will not focus on investigating these further.

With respect to bone microtomy applications, it is crucial to note that in bone tissue, with particle densities typically ≈ 1000 times greater than air, a 1% ionization degree would yield an overpressure of 40 MPa, increasing to the GPa regime for a fully ionized plasma with ≥ 1 eV electron temperatures. This is on the same order, or even greater than, the compressive strength of the different types of human bone tissue [56], which poses a serious risk of shockwave-induced damage. This constitutes a soft bottleneck to the precision and ablation efficiency of bone tissue, and is a topic that will require attention in future research.

2.4.3 Plasma Expansion and Decay

Depending on the geometry of the system and the spatial distribution of the plasma, the expansion dynamics will vary. A spherically symmetric plasma in a free geometry, such as a homogeneous gaseous surrounding, will expand isotropically. A plasma created at a gas-solid interface will not be able to expand in all directions, instead colliding with the solid interface and subsequently directing its expansion as a jet plume outwards into the less obstructive gaseous medium. This ejection of ionized material in a plasma plume is the primary mechanism behind ablation of matter in condensed target materials, and whatever energy is contained within the ejected plasma is therefore transported away from the surface, instead diffusing into the surrounding gas.

Regardless of geometry, the expanding plasma, being in non-equilibrium with itself and the surroundings, will undergo thermalization by means of kinetic collisions between the hot electrons and the colder ions and neutral particles. These collisions can both be elastic and inelastic, over time transferring kinetic energy from the electrons to the neutrals and ions and equilibrating their temperatures. Collisions with surrounding neutrals at the propagation front of the expanding plasma, specifically, leads to a rapid cooling of the plasma. This can be understood from a thermodynamic perspective: rapid adiabatic expansion of a particle ensemble requires work, which comes at the cost of internal kinetic energy in the plasma, leading to a loss in temperature. Collisions with neutrals can also lead to impact ionization or excitations in atomic states, and collisions between electrons and ions can result in recombination, where an electron is captured and the surplus energy is carried away either by radiative emission of a photon (two-body recombination) or another electron (three-body recombination) [57] described by



The corresponding recombination cross sections are dependent on the kinetic energy of the electrons relative to the ions, with higher energy typically corresponding to a smaller cross section, and three-body recombination dominating over two-body recombination in denser plasmas.

At thermal equilibrium there will be a corresponding equilibrium in plasma density where impact ionization (equation 2.7) and electron recombination (equation 2.9) rates are equal. Since the laser-induced plasma is surrounded by a medium (typically air) at ambient conditions, kinetic and radiative thermal diffusion will eventually relax the plasma into a neutral, room-temperature gas. The rate at which this happens will depend on the particle and energy distribution of the plasma, as well as particle-specific properties like how optically thick it is with respect to its own and external radiation. As a rule of thumb, one can assume that non-equilibrium plasmas too cold to sustain themselves in thermal equilibrium will decay very rapidly due to rapid recombination events, whereas thermal plasmas survive much longer, decaying instead at the rate of thermal diffusion to their surroundings.

2.4.4 Plasma Shielding and Ejection Plumes

In high-repetition rate laser systems there is a possibility that the time between pulses is faster than the decay of the plasma. The free electrons from the previous pulse will then linger and again interact with the electromagnetic field of the next pulse, absorbing energy and further prolonging the decay process. The second plasma population created around the focus will then rapidly expand and mix with the original population, compounding the total plasma density. This process is then repeated until an equilibrium plasma life cycle is achieved. If this equilibrium population is dense enough, it may absorb a significant amount of the laser pulse energy before it even reaches the focus, thereby effectively shielding the target material from the laser and reducing ablation efficiency. Several independent research papers [7, 58–60] hypothesize that plasma shielding causes a decrease in cutting efficiency for repetition rates starting at around $\gtrsim 100$ kHz. Independent research, specifically on visualizing the evolution of the plasma plume from femtosecond laser ablation on gas-solid interfaces, suggests life times on the order of microseconds, which supports this hypothesis [61, 62].

However, observations of plasma shielding do seem to be limited to condensed matter interfacing with a gas, as research on ultrafast laser-induced plasma decay in pure air and water all suggest much faster decays than the repetition rates of even the fastest laser systems. Research on air plasmas, [63–66], conclude decay rates on the order of single or at most tens of nanoseconds, and a study on distilled water, [67], found that it decays even faster than air, on the order of tens of picoseconds. Plasmas in water decaying faster than in air is likely attributable to electron solvation due to the unique and highly polar characteristics of water molecules [68].

The reason these ejected plasma plumes survive longer than free-geometry plasmas is attributed to continuous evaporation and ejection of the target surface as a result of the geometric restriction on plasma expansion. As explained in the previous section, when the initial plasma is formed it will try to expand isotropically. Outwards, it is free to expand into the ambient air surroundings, driving a propagating shockwave in the front, whereas inwards it is met with a solid surface preventing expansion. This causes the plasma to be partially trapped, unable to expand freely, and therefore

remains hot for longer. This allows for thermal diffusion of energy into the solid surface, evaporating and ejecting it over time scales much longer than the decay of free-geometry plasmas, and can be described using hydrodynamic models [62]. The overall structure of the ablation zone and plasma plume has been characterized in prior research, and includes named regions such as the Knudsen layer immediately above the thermal core [69]. In figure 2.4 the overall structure can be observed.

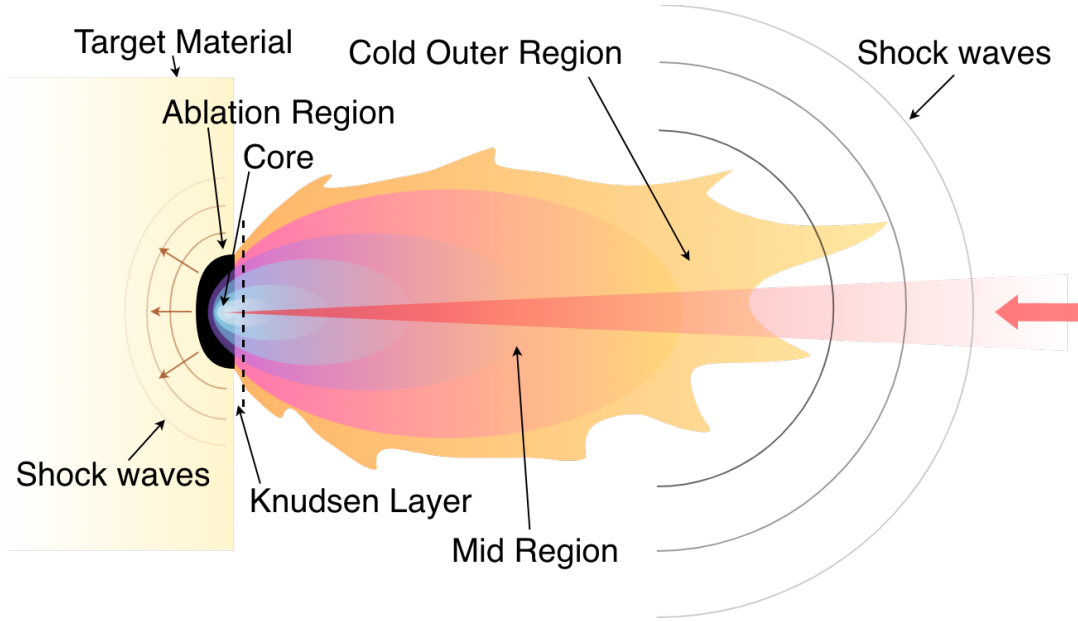


Figure 2.4: The full structure of the ablation zone and plasma plume created at a gas-solid interface by an incoming laser, including named layers.

2.5 Plasma Emission Spectrum

Following the onset of optical breakdown and the subsequent expansion of the plasma, the system begins to decay as discussed in Section 2.4. During this life cycle, the plasma primarily dissipates its internal energy radiatively through the emission of photons. The specific mechanisms driving these emissions, such as the radiative recombination and inelastic collisions introduced previously, vary temporally and spatially, governed by the evolving electron density and temperature [70]. Consequently, capturing the emission spectrum provides useful qualitative and quantitative insights into the plasma, including the elemental composition of the target medium. The plasma is highly transient and spatially inhomogeneous, so an integrated emission spectrum captures a time- and space-averaged combination of several distinct radiation mechanisms rather than what the plasma might look like at any given instant in time. Generally, these mechanisms can be categorized into two main spectral components: broad continuum emissions and discrete bound-bound transitions.

2.5.1 Continuum Emission

In the immediate aftermath of ionization, the plasma is characterized by a high density of energetic free electrons and cold ions. During this early stage, continuum emissions dominate the spectral profile, arising primarily from two different mechanisms. The first is two-body recombination radiation, or free-bound emission, as previously described in section 2.4.3:



The energy of the resulting photon γ equals the sum of the electron's initial kinetic energy and the binding energy of the final state. Because the electron energy distribution within the plasma is continuous, so is the resulting emission spectrum. Notice that this recombination inherently leaves the newly formed atom in an excited state (A^*), which can result in additional radiative emissions when it decays to the ground state.

The second mechanism is bremsstrahlung, or free-free emission [71, 72]. As free electrons accelerate or decelerate in the local electric fields of the heavier ions, they emit photons across a continuous range of wavelengths. Using the theory and equations in primary literature [73], one can estimate the bremsstrahlung emission spectrum for non-relativistic plasmas. For electron temperatures on the order of 1 eV, the emission spectrum manifests as a mostly flat white background in the visible wavelength range, as demonstrated in figure 2.5. As the electron temperature falls below 1 eV, the emission intensity drops very rapidly, meaning bremsstrahlung effects will be limited mostly to the early stages of the plasma life cycle.

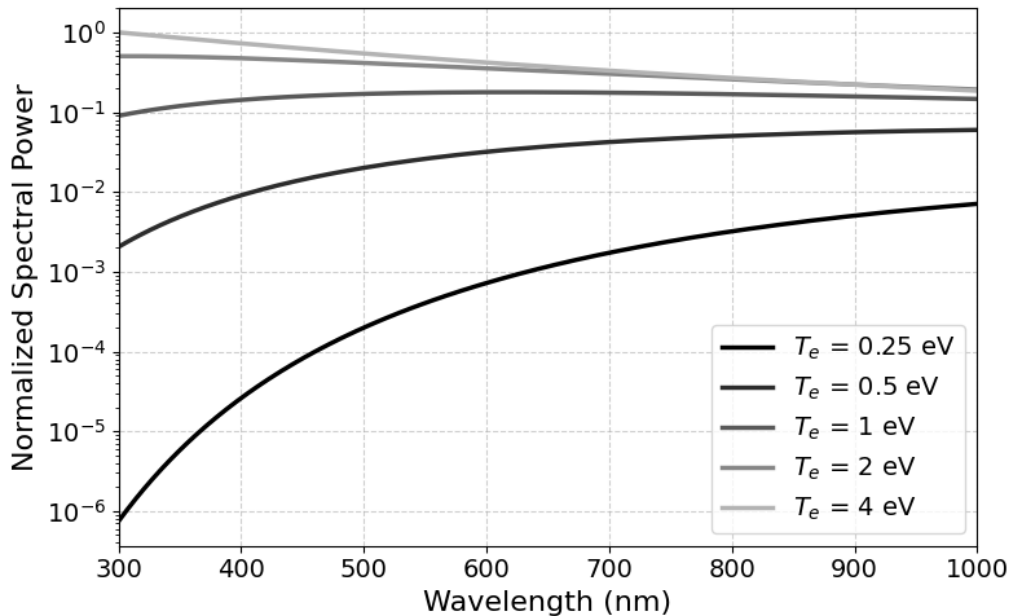


Figure 2.5: Bremsstrahlung emission spectrum in the 300–1000 nm wavelength regime from a fully ionized air plasma with arbitrary volume for different electron temperatures. Notice the sharp drop in intensity as the plasma cools down below 1 eV.

2.5.2 Discrete Transitions

As the plasma continues to expand and cool, the kinetic energy of the free electrons decreases, and the overall recombination rate begins to outpace the impact ionization rate [70]. In this cooler regime, inelastic collisions between electrons and ions and neutral atoms result in ionic or atomic excitations. These excitations have quantized energy levels, resulting in a set of discrete emission wavelengths during radiative decay. In the earlier stages of the plasma life cycle, the ion population will be at its highest, producing bound-bound transition emissions as

$$e^- + A^+ \longrightarrow e^- + A^{+*} \text{ then } A^{+*} \longrightarrow A^+ + \gamma.$$

Similarly, as the recombination process described in Equation 2.10 accelerates, the resulting excited atoms will eventually decay [57]. As the plasma cools further, the ion population falls while the neutral atom population surges. Similarly to ionic emissions, the neutral atoms will undergo excitation followed by bound-bound decay like

$$e^- + A \longrightarrow e^- + A^* \text{ then } A^* \longrightarrow A + \gamma.$$

As mentioned, due to the quantized nature of these excitations, the wavelength λ_γ of the emitted photon is strictly determined by the discrete energy difference between the higher and lower bound energy states (ΔE) via the relation [74]

$$\lambda_\gamma = \frac{hc}{\Delta E},$$

where h is the Planck constant and c is the speed of light. Since these quantized energy gaps are unique to the electron shell structure of each specific element and ionization state, the resulting spectral lines are distinct for each atomic species [74]. Identifying these peaks in the emission spectrum, using standard databases like the National Institute of Standards and Technology (NIST) allows for identification of the radiating particles [75].

Finally, it should be noted that the precise shape of the captured spectrum can be influenced by secondary effects such as Stark broadening of the characteristic peaks, molecular band emissions, or spectral broadening effects. While these effects may alter the general shape of the spectrum, they fall outside the primary scope of the elemental analysis performed here, though they remain an underlying factor in the physical measurements.

2.6 Thermal Effects

The thermodynamic outcome of the light-matter interaction depends primarily on the relation between linear thermal absorption and nonlinear ionization rates. As discussed in the previous sections, linear absorption α_{abs} (equation 2.5) relates to the absorption of the electromagnetic field as internal energy, which subsequently converts to thermal energy, whereas higher-order terms describe nonlinear effects such as photo-ionization. If thermal absorption dominates, the laser pulse energy

is primarily converted into bulk heat. This thermal energy diffuses outward into the surrounding material, causing widespread melting and thermal damage, which is highly detrimental in bone tissue microtomy applications, where precision and survival of cells on the cross-sectional surface are both crucial.

Since femtosecond laser pulses deliver a significant amount of energy much faster than the thermal relaxation time for most materials (which is typically on the order of picoseconds to nanoseconds), nonlinear ionization rates dominate the interaction. Before the absorbed energy has time to diffuse into the surrounding solid bulk as heat, the exposed material is near-instantaneously converted into a dense plasma. This plasma, as explained in sections 2.4.3 and 2.4.4, will expand very rapidly due to the localized overpressure (equation 2.8). In solid-gas interfaces, the geometry prevents isotropic expansion, trapping parts of the plasma in a hot, pressurized core. Over time, this core ejects material outwards in a plasma plume jet, and in the ideal scenario almost all of the absorbed energy is ejected from the ablation zone in this way. However, the plasma plume has been observed to survive on timescales up to microseconds due to continuous evaporation of the target surface, so thermal diffusion clearly still occurs. Therefore, achieving clean ablation requires balancing the laser pulse energy and repetition rate to optimize the ratio of ionization degree and material ejection to residual thermal diffusion. For any given pulse shape, there likely exists an optimal pulse energy window that maximizes this efficiency. Below this window, the field fails to drive strong nonlinear ionization. Linear absorption dictates the interaction, and the energy merely heats the target without generating enough localized pressure for effective ejection. Above this optimum, the resulting plasma becomes excessively dense and hot, creating a larger thermal core that diffuses more thermal energy to the surroundings and thus takes longer to relax.

3. Experimental Setup

3.1 Laser System, Beam Path and Mounting of Target Material

In principle, focusing a laser pulse onto a given point in space and collecting data using different spectroscopic equipment is straightforward. In practice, femtosecond laser systems used in scientific research require precise knowledge and control over many parameters to ensure stable output and repeatable results. Below are outlined the most important equipment used along with the optical beam path.

The light source in the system is a CPA2001 femtosecond laser system that has a nominal output wavelength of 775 nm, pulse length of ≈ 150 fs, and beam quality $M^2 \approx 1.2$. The system is powered by a pump laser system driven by a 1 W power supply, and is mode-locked using a Clark-MXR DT-505 Pockels cell driver. Mode-locking the system requires manual adjustment of the delay settings on the DT-505, and temperature fluctuations and other alignment drifts occasionally necessitate manual tuning. The output repetition rate of the CPA2001 is dictated by the RF divider on the DT-505, which is set to its maximum of 1001.7 Hz.

The output of the CPA2001 system is then manipulated using an optical beam path whose main features include a crystal polarizer for manual attenuation of the laser pulse energy, a beam expander with magnification factor 3, a set of scanning mirrors, and a 70 mm F-Theta lens to focus the beam down to $w_0 \approx 3 \mu\text{m}$. The scanning mirrors were used only in the initial calibration of the beam path, and were not utilized during any of the experiments. A schematic of the beam path is presented below in figure 3.1. Before each measurement, the laser pulse energy was measured using a power meter and adjusted manually using the crystal polarizer. Therefore, all reported pulse energies in this thesis are only estimates based on time-averaged measurements from the power meter, and do not account for losses by for example the beam expander, scanning mirrors, or the focusing lens.

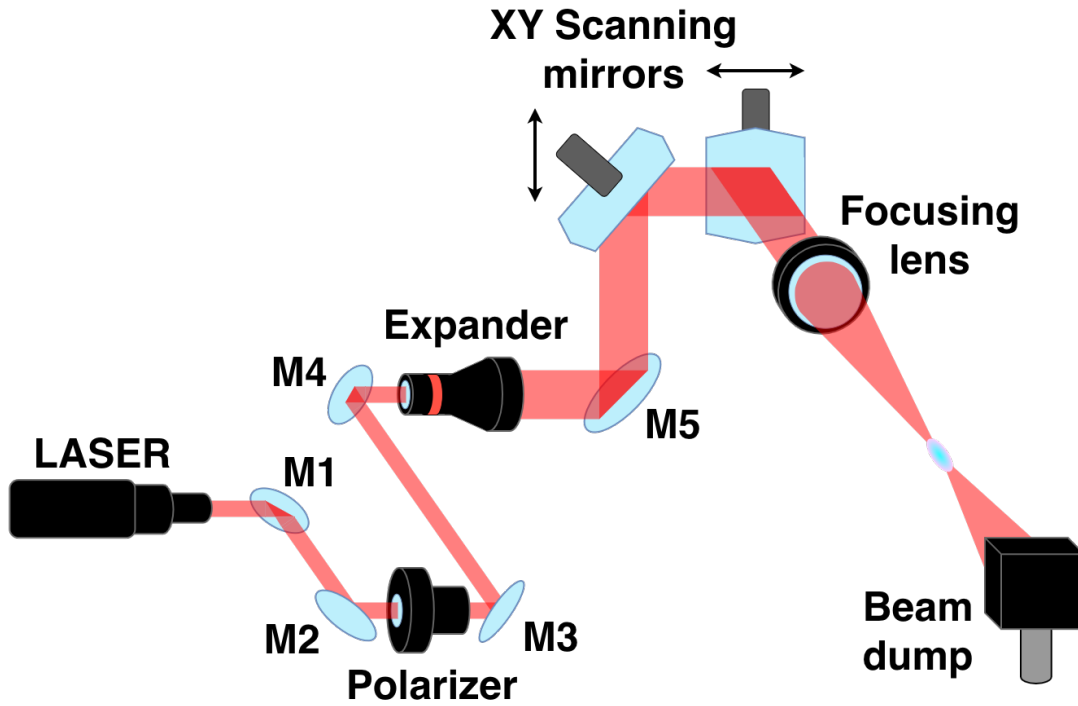


Figure 3.1: The optical beam path used to manipulate the raw output of the CPA2001 femtosecond laser. The focusing lens has a focal length of 70 mm. M1–M5 denote rigid alignment mirrors.

For ambient air (lab conditions: 1 atm, 25 ± 5 °C, $\approx 50\%$ humidity), no sample preparation is required, and the laser pulse is simply focused on a spot in free space. When investigating liquid water as target material, a high-purity quartz cuvette, with inner dimensions of 20 x 20 x 37 mm and >1 cm beam path, was filled with distilled water and placed on top of a platform such that the focus was approximately centered on its inside as shown in figure 3.2. For bone tissue, a porcine rib bone from a wild boar (*Sus scrofa*) was attached to a motorized mount that could be controlled along all three spatial axes, also shown in figure 3.2.

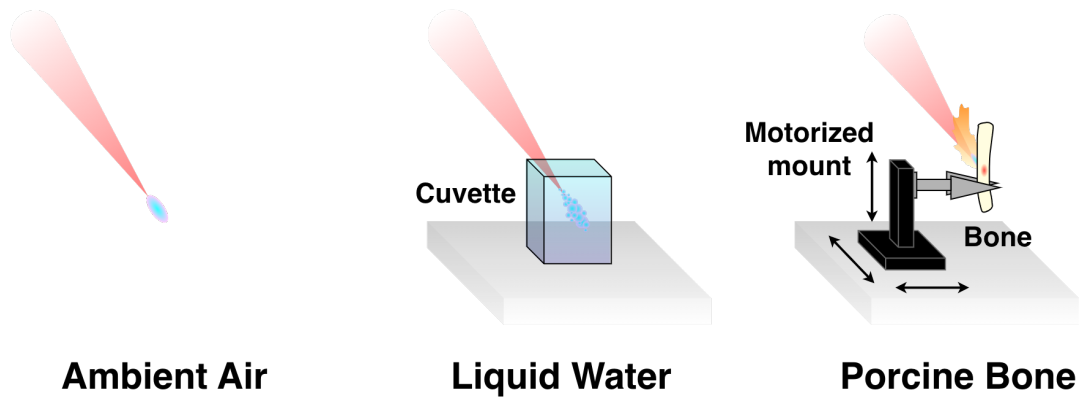


Figure 3.2: The different methods of mounting the target material around the laser focus.

3.2 Spectroscopic Equipment and Data Acquisition

The characterization of the laser-induced plasma was achieved using three types of spectroscopic equipment: a high-speed CMOS camera, a diffraction-grated spectrometer, and an ultrafast photodiode. These were all mounted and used separately such that the field-of-view to the recorded event was identical. With the spectrometer, reference measurements of the laser pulse spectrum and impulse response of the photodiode were taken.

3.2.1 High-Speed Camera

For spatial imaging of the beam focus, a Phantom Miro LAB310 high-speed CMOS camera with a telescope objective was used. The camera was mounted on a multi-axis rail mount, allowing for adjustment along all three spatial axes. To synchronize the internal clock of the camera to the output of the CPA2001 laser system, the non-delayed Audio output of the DT505 driver was re-routed to the trigger input of a pulse generator, with one output channel routed back to the delay input of the DT505, and the other to the I/O-1 external source input of the camera. The relative delay between the two output channels of the pulse generator could then be adjusted to synchronize the camera shutter to the laser pulse arriving at the focus. Camera settings and data acquisition were both done using the Phantom PCC software, where the frame sample rate was locked to equal the repetition rate of the laser, and the resolution, ISO and exposure time were adjusted as appropriate. The data handling is described in the respective sections for the different target materials.

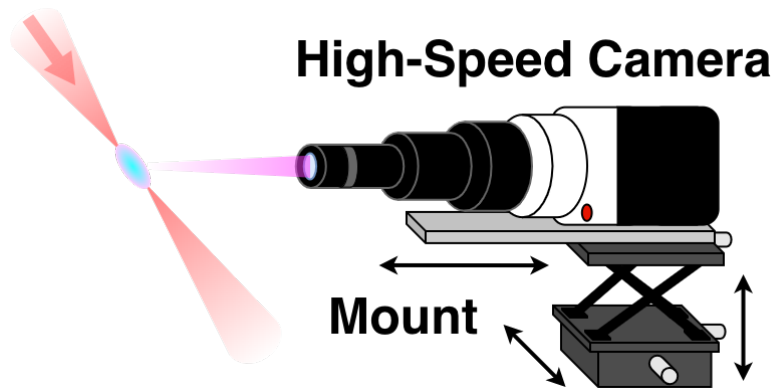


Figure 3.3: The High-Speed Camera mounted on a 3-axis adjustable mount.

3.2.2 Spectrometer

To capture the spectral profile of the laser-induced plasma, a diffraction-grated Ocean Optics Red Tide 650USB Fiber Optic Spectrometer with a 400–2100 nm VIS-NIR Low OH content fiber optic cable was used. The spectrometer has a resolution of 1 nm, wavelength range of 200–1100 nm, and is factory-calibrated for wavelength

and amplitude correction. This calibration was corroborated using an EKSPLA NT342 laser system with adjustable wavelength, which found only a -1 nm error in the wavelength correction. To detect a signal from the plasma, the plasma emission was focused using a 35 mm plano-convex lens and aligned onto the fiber optic cable using a mirror on a 3-axis mount, as presented below in figure 3.4. To limit light pollution, this setup was enclosed in a cardboard shielding. Data acquisition was done using the SpectraSuite software application.

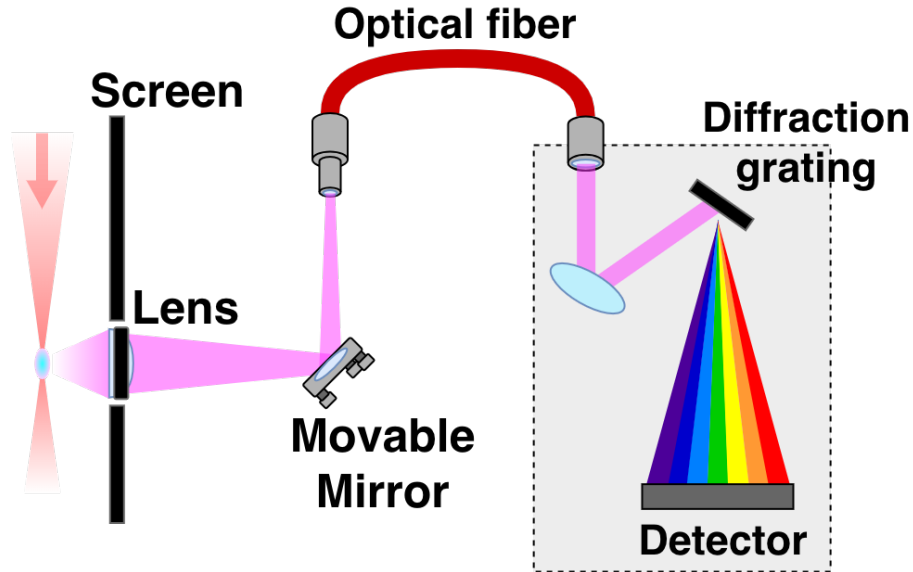


Figure 3.4: Experimental setup for capturing the plasma emission spectrum with minimal light pollution.

3.2.3 Photodiode

While the high-speed camera has a minimum exposure time of 1 μs , it is in principle possible to use either stroboscopy or exposure delays to record and stitch together the temporal evolution of events that happen much faster than this. However, equipment limitations precluded the use of stroboscopy, and exposure delay was insufficient either because the recorded event was much faster than the impulse response of the shutter, or due to poor pulse-to-pulse reproducibility. Instead, to capture the temporal evolution of the plasma signals, a Thorlabs DET10A/M Si based, free-space ultrafast photodiode with a nominal rise time of 1 ns and wavelength bandwidth of 200–1100 nm was used.

For measuring the plasma signals, the same setup as for the spectrometer was used, as described in the previous subsection (section 3.2.2), and is presented below in figure 3.5. The photodiode signal was captured using a Tektronix TDS 3054 Oscilloscope with a bit depth of 8 and sample rate of 5 GHz, and subsequently exported using the Tektronix Openchoice software application.

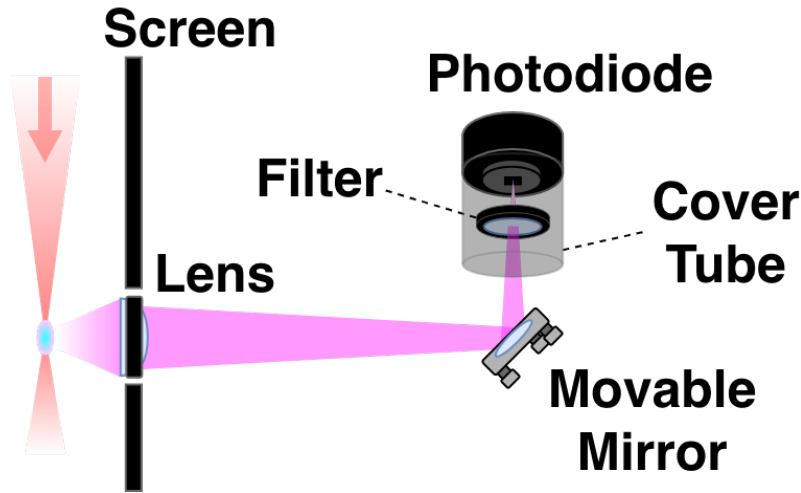


Figure 3.5: Experimental setup used to capture the temporal evolution of the plasma signal with minimal light pollution.

3.3 Reference Measurements

Before analyzing the laser-induced plasmas, reference measurements of the system were necessary. The first was capturing the fundamental laser emission spectrum to ensure any scattered incident light could be accurately identified and isolated from the plasma spectra. The second was measuring the impulse response of the photodiode. Since plasma decay rates can approach or exceed sub-nanosecond timescales, knowing the inherent resolution of the photodiode is necessary to extract the plasma emission signals from the raw data.

3.3.1 Laser Wavelength Spectrum

To capture the pure laser spectrum, the standard beam path was temporarily reconfigured. As illustrated in figure 3.6, the spectrometer and a second crystal polarizer were mounted into the beamline. The polarizer provided the necessary additional attenuation to prevent saturating the spectrometer, while still allowing the fundamental CPA2001 pulse to be aimed directly into the optical fiber. The captured laser spectrum is presented in figure 3.7 and shows that rather than a single peak at the nominal wavelength of 775 nm, we observe three distinct peaks with a combined center-of-mass of exactly 775 nm. The reason it has more than one wavelength peak is likely due to imperfections in the internal mode-locking cavity that give rise to three fundamental resonant wavelengths rather than just one. While the spectral density is lower than for a single peak of the same spectral power, there are no known resonance effects in any of the target materials that will be significantly affected by this. Altogether, the nominal wavelength was corroborated and the exact shape will not significantly affect performance.

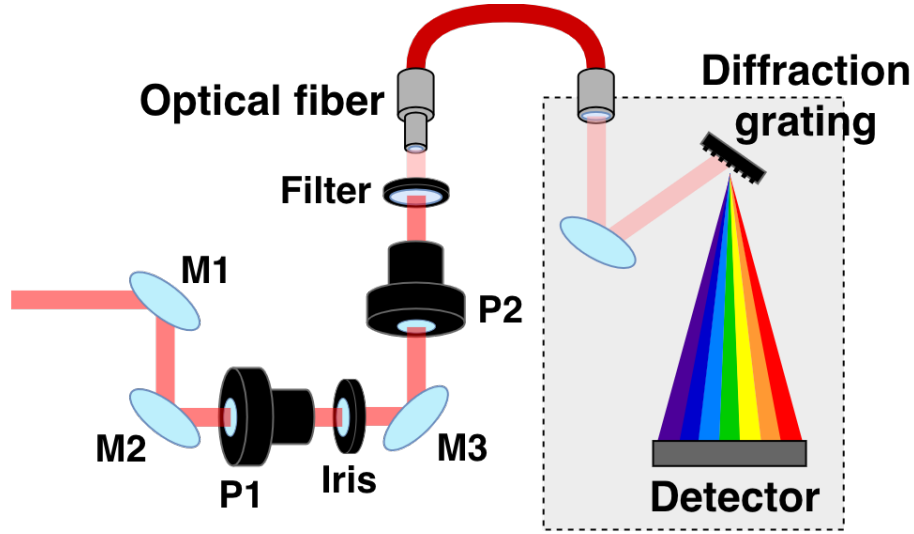


Figure 3.6: Experimental setup for capturing the femtosecond laser spectrum.

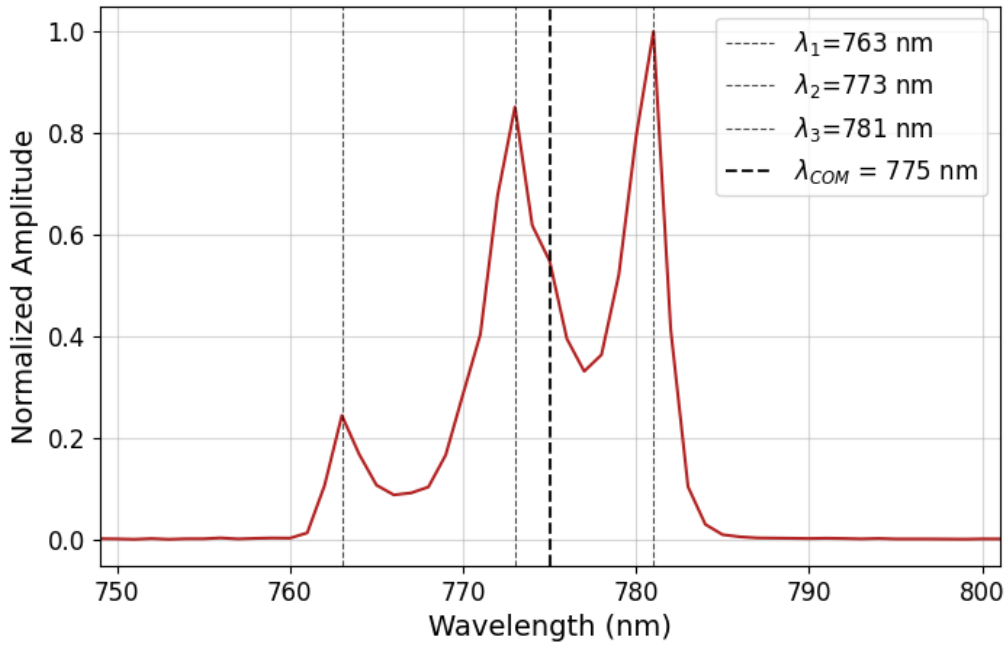


Figure 3.7: Captured laser reference spectrum, including identified peaks and the overall center-of-mass wavelength.

3.3.2 Photodiode Impulse Response

To verify the nominal 1 ns rise time and establish an impulse response function, the photodiode was placed directly in the beam path. The laser pulse is only around 150 fs long, acting as a single delta impulse compared to both the nominal photodiode rise time and the temporal resolution of the oscilloscope. Down to nonlinear or saturation effects within the photodiode itself, the measured signal should therefore

be equal to its impulse response. To this end, as shown in figure 3.8, a second crystal polarizer combined with a 700 nm shortpass filter was utilized to heavily attenuate the beam. To maximize the signal-to-noise ratio, the resulting impulse signal was averaged over 512 laser pulses on the oscilloscope before being exported. The background-removed impulse response is presented in figure 3.9. The FWHM of the impulse response was computed to 1.41 ns, in line with the nominal 1 ns FWHM reported by Thorlabs. Signal reflections inside the BNC cables used to connect the photodiode to the oscilloscope were unavoidable, so the same cables used for capturing the impulse response were used in all subsequent photodiode measurements to ensure consistency and reproducibility.

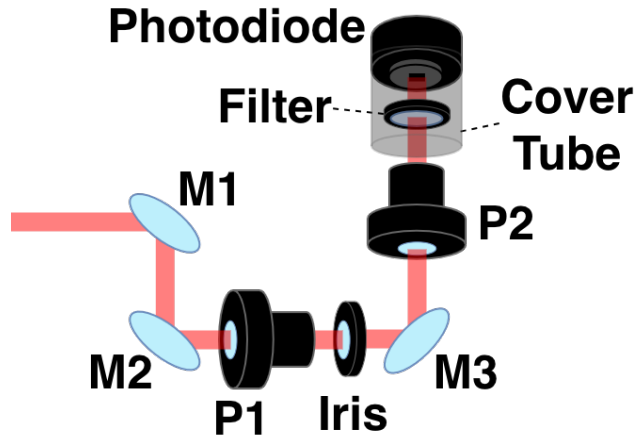


Figure 3.8: Experimental setup for capturing the impulse response of the photodiode.

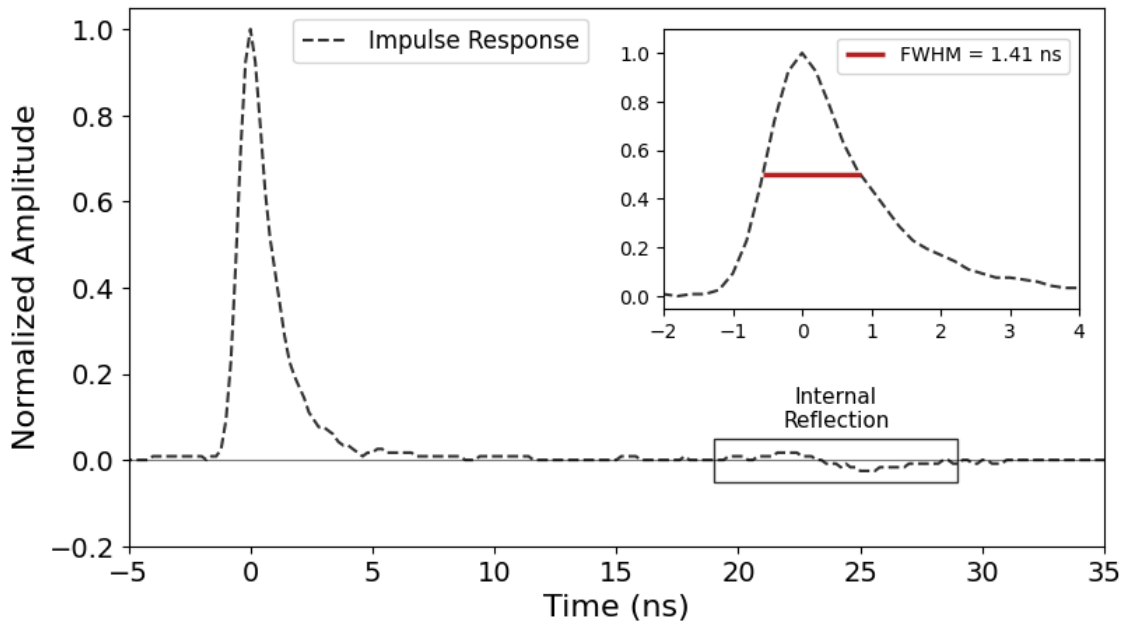


Figure 3.9: Captured impulse response for the photodiode, including the internal signal reflection and the computed FWHM of 1.41 ns.

4. Ambient Air

Ambient, room-temperature air (lab conditions: 1 atm, 25 ± 5 °C, $\approx 50\%$ humidity) was selected as the first target material for two primary reasons. First, air serves as an ideal reference medium for initial baseline measurements against which other media can be compared, as it does not require any sample preparation and naturally replenishes to an identical initial state between measurements. Both nonlinear optics and plasma physics in air have been extensively researched, so a robust theoretical foundation exists for benchmarking and interpreting the experimental results, and informing the data analysis methodologies used for other materials. Second, air represents the default environment for most practical applications of ultrafast laser ablation. Ablation of organic tissue is typically performed under standard atmospheric conditions, rather than in specialized immersion fluids (e.g. water or noble gases). It is assumed that air humidity will not have a significant impact on our results, as even fully humid air at room temperature contains only a couple percent water vapor by number density. The laser-air interactions will therefore be assumed to be dominated by molecular oxygen and nitrogen regardless of humidity, unless our baseline spectroscopic results would suggest otherwise.

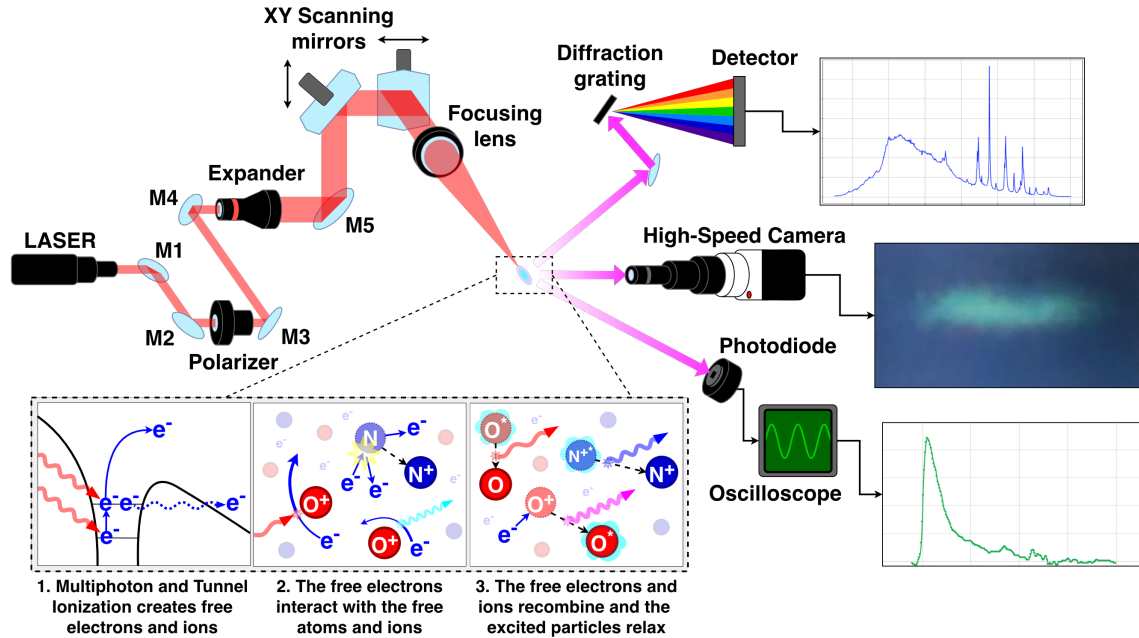


Figure 4.1: The laser beam focused into ambient air inducing a plasma. The emission spectrum is measured by a spectrometer, the temporal evolution by a photodiode, and the spatial imaging by a high-speed camera.

For these measurements, the general experimental setup described in the previous chapter was used with no other reconfigurations than when installing the respective spectroscopic instruments. Figure 4.1 illustrates the overall configuration and expected physical mechanisms of the laser-air interaction. The overall characterization of the induced air plasma starts with spatial imaging, establishing information about the shape and size of the plasma as well as indicators toward the decay rate and spectral profile before these were examined in detail.

4.1 Spatial Imaging

In the PCC software, the exposure time was set to $1\ \mu\text{s}$ to minimize ambient light pollution, and the exposure index to ISO 8000 to get a good balance between signal strength and signal-to-noise ratio. The signal delay from the pulse generator could then be adjusted manually such that the full plasma signal was captured by each frame. When this was achieved, the camera could be positioned such that the plasma was in focus at maximum optical magnification. For each laser pulse energy, as well as the background, 10 000 consecutive frames were recorded. The raw frames were then averaged and converted to grayscale in the image processing program ImageJ, and converted to a dark-field image by subtracting the averaged background. In order to determine the spatial scale of the processed images, a reference object with known width of $260\ \mu\text{m}$ was captured in focus using the same optical settings on the camera. The processed images with brightness normalized to the respective peak pixel value can be observed for different pulse energies in figure 4.2. All images are positioned identically in physical space to demonstrate how the plasma profile backward-propagates against the propagation direction as the pulse energy is increased. This is because the leading edge absorbs much of the laser pulse before it reaches the focus, leading to plasma self-defocusing and overall less energy to ionize the air behind the focus. This is consistent with the findings in reference literature [70]. The camera is unable to resolve the plasma for pulse energies below $\approx 79\ \mu\text{J}$, above which the observed size consistently grows with no sign of saturation.

While the profiles for lower pulse energies appear more cigar-shaped, the higher-energy profiles, particularly for $500\ \mu\text{J}$, instead exhibit noticeable distortion. In order to better visualize this, the image was imported into a Python script, where the center of mass of the plasma profile was first computed using `scipy.ndimage` and defined as $R = Z = 0$, where Z is the propagation direction and R is the radial distance. Using a Gaussian smoothing filter with $\sigma = 1$ on the image to smooth out any noise that may affect the peak observed pixel value, a contour plot could then be produced and presented in figure 4.3. The distortion is attributed primarily to the beam quality (see section 2.1), compounded with the nonlinear behavior of self-focusing and ionization. Due to this asymmetry, estimates for the spatial dimensions of the plasma were produced by doing a 1-D projection along the horizontal and vertical axes. These projections are robust against local distortion since they integrate the total pixel value along each respective axis. The FWHM length and width could then be computed using linear interpolation along the projected axes. The projection, including FWHM dimensions, are visualized in figure 4.4.

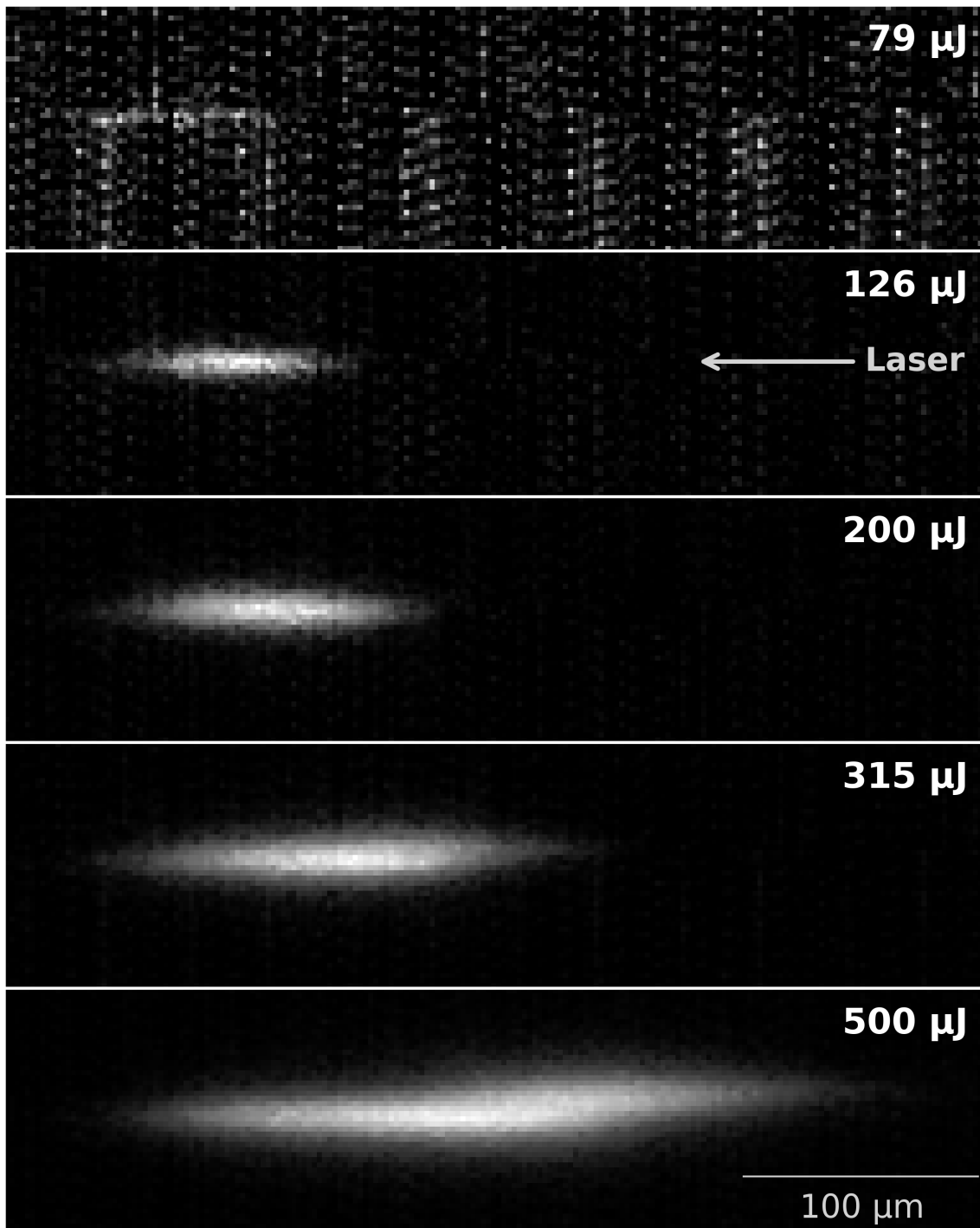


Figure 4.2: Laser-induced plasma captured by the high-speed camera for different pulse energies evenly spaced in $\log_{10}$ -space. Images are in grayscale and normalized to their respective peak pixel value.

This process was repeated for the different pulse energies, and the resulting pulse-energy-dependent FWHM dimensions are compiled in figure 4.5. Due to the poor signal-to-noise ratio, signals below $126 \mu\text{J}$ could not be resolved using this method and are as such excluded. Overall, the size grows consistently with pulse energy, starting at around $66 \mu\text{m}$ in length and $9 \mu\text{m}$ in width for $126 \mu\text{J}$. This is very

close to the confocal length $b \approx 60 \mu\text{m}$ and beam waist diameter $2w_0 \approx 6 \mu\text{m}$, and goes even lower with decreasing pulse energy (observe e.g. $79 \mu\text{J}$ in figure 4.2). Since the actual evolution of the plasma was not possible to capture, this does not necessarily mean that the plasma does not expand significantly, only that this was the most radiative region during the integration time. The extent to which the plasma expands could be much larger than observed here, but would not be resolved because it would correspond with lower electron density and temperature, hence fewer photon emissions.

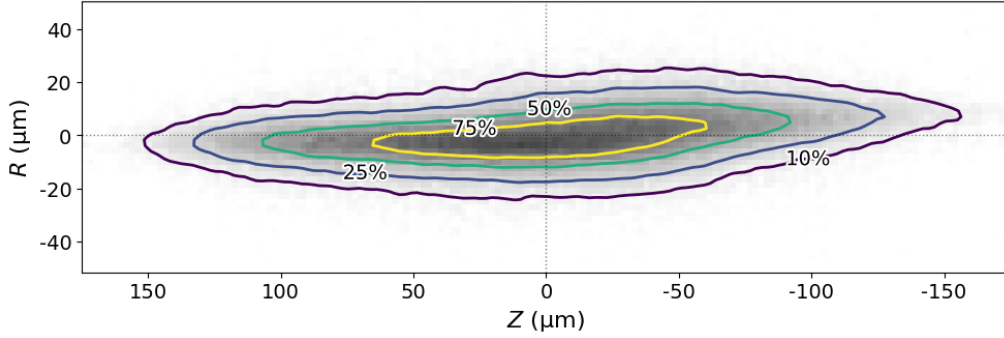


Figure 4.3: Contour plot of the relative pixel values of the plasma profile image for $500 \mu\text{J}$ pulse energy.

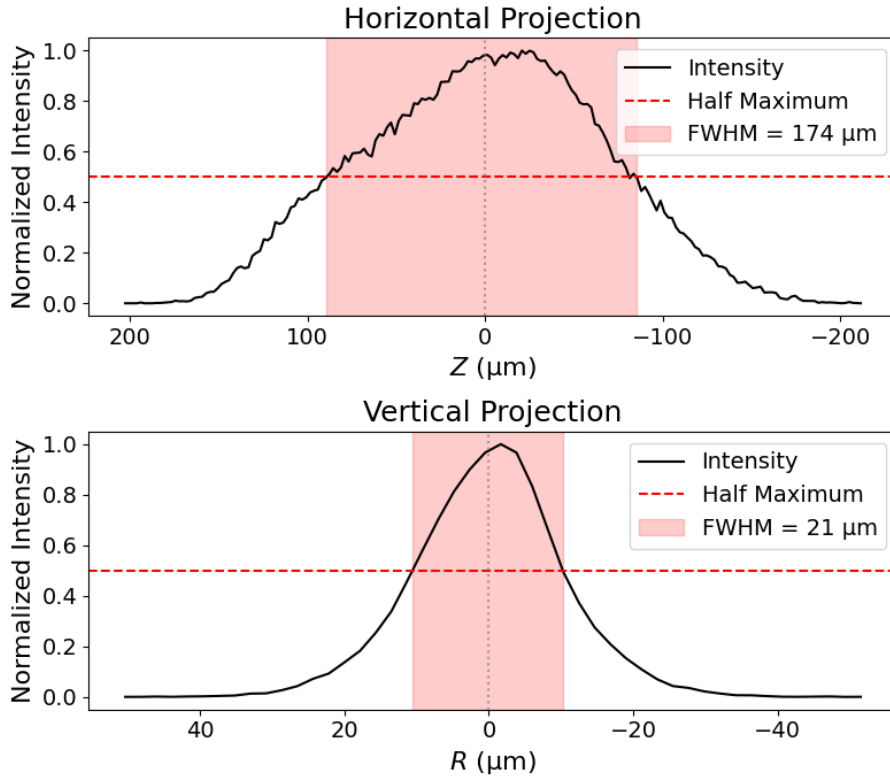


Figure 4.4: Projected intensity profile for $500 \mu\text{J}$ pulse energy along the Z and R axes, respectively, including the corresponding computed average FWHM dimensions.

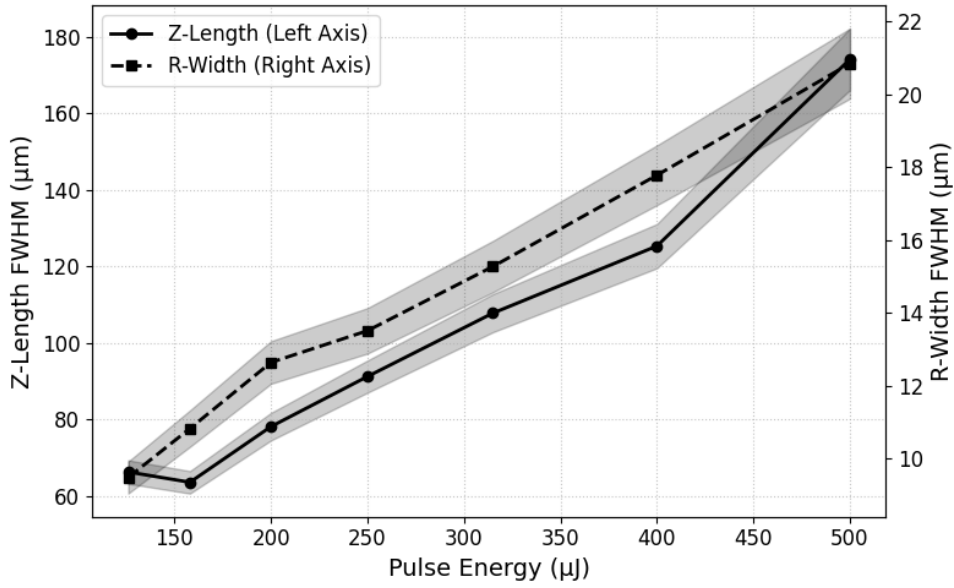


Figure 4.5: FWHM dimension estimates along Z and R for different pulse energies. Error bounds are due to initial error estimate of pixel dimensions.

4.2 Spectrometry

To characterize the plasma emission spectrum for different pulse energies, 11 measurements were taken for the same pulse energies as before, spanning 50–500 μJ with even steps in $\log_{10}$ -space. The signal for each pulse energy was integrated for 3 seconds and averaged over 5 consecutive measurements, spanning a total integration time of 15 seconds. The emission spectrum for all measured energies, as well as all identified characteristic atom and ion emission lines and the region dominated by continuum emission, are shown in figure 4.6. The characteristic shape of the spectrum is remarkably consistent across the full range of pulse energies, and all identified peaks correspond to either atomic oxygen or nitrogen and their respective +1 and +2 ions. This is entirely expected from air, which consists to 99% of just oxygen and nitrogen gas. The reference data for the characteristic peaks were taken from the NIST database [75].

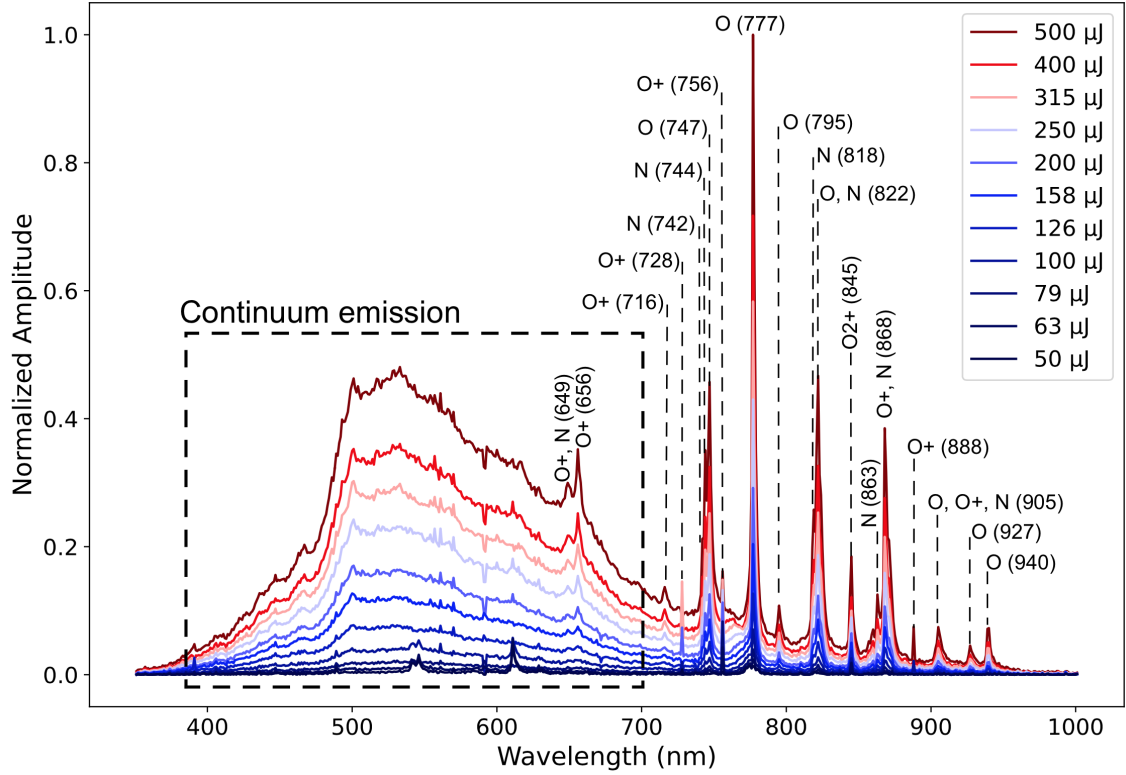


Figure 4.6: The normalized and noise subtracted measured emission spectra for all pulse energies, with characteristic spectral lines and continuum emission region marked.

The limited wavelength resolution of 1 nm is evident in the spectrum. For example, there should exist a triplet of characteristic lines with similar amplitudes for O_I between 777.2–777.5 nm [75], however in our results they are combined into the single peak at 777 nm. Another limitation is the transmission bandwidth of the fiber optic cable used, exemplified by the drop off in the continuum spectrum at around 500 nm. While the fiber optic cable is rated for 400 nm, it is possible this is just a threshold value and that the actual transmission rate starts dropping off much earlier. Because the spectrometer itself is compatible with multiple different fiber optic cables, this is likely unaccounted for in the factory amplitude correction.

Beyond characteristic transition lines, the spectrum is dominated by continuum emissions, particularly in the 400–700 nm region. This is likely a combination of both radiative two-body recombination and Bremsstrahlung (see section 2.5), although the shape is hard to characterize. Since the electron energy distribution over time and the corresponding recombination cross sections are unknown, combined with the unknown transmission spectrum of the fiber optic cable, it is impossible to determine to what extent the observed continuum spectrum corresponds to which physical mechanism.

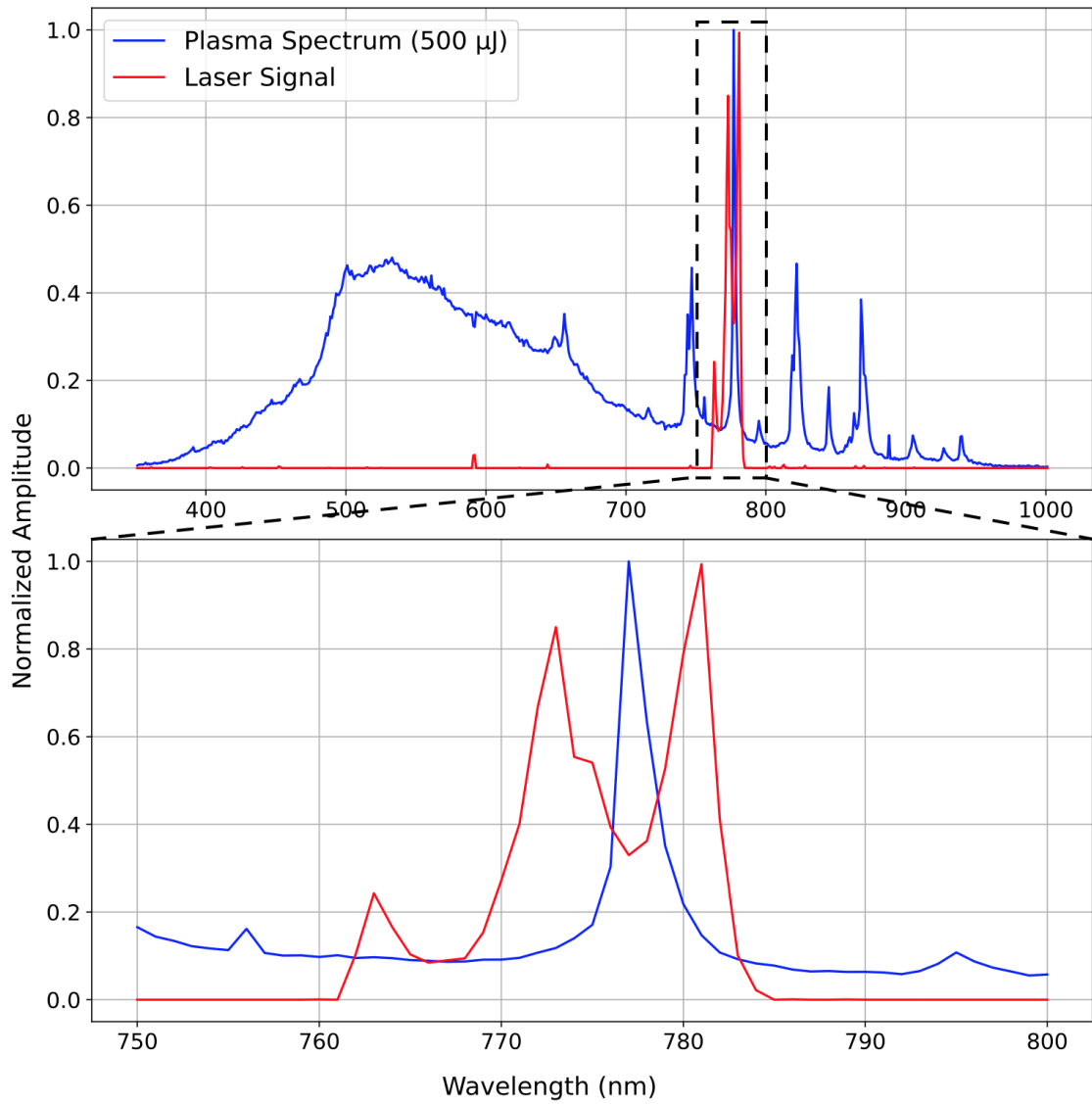


Figure 4.7: The normalized laser spectrum overlaid on the measured emission spectrum for 500 μJ .

Comparing the captured plasma spectrum to the laser reference spectrum, as shown in figure 4.7 for 500 μJ pulse energy, we can see that it contains little to no scattered laser light. Similar results were observed for the full range of pulse energies. This is an important observation, as it means no unnecessary amount of energy is scattered or reflected beyond what is absorbed in the ionization and plasma formation process.

4.3 Temporal Evolution

The results from the spectrometry (see figure 4.6) showed both continuum emissions, primarily in the 400–700 nm wavelength domain, as well as atomic emissions, primarily in the 700–1000 nm domain, so it was of interest to investigate whether these

exhibited different temporal evolutions. A photodiode signal contains no spectral information, so to separate these domains a shortpass and longpass filter were used. The shortpass filter was a Thorlabs FESH0700 filter with 400–690 nm bandwidth, and the longpass filter a Thorlabs FGL715 filter with cut-on wavelength of 715 nm. Identical measurements were taken with the two respective filters, as well as a reference measurement without filter. The results for 500 μJ pulse energy, compared to the measured impulse response of the photodiode, are presented in figure 4.8.

The measured amplitudes were of the same order of magnitude in all three measurements. Clearly, there are differences between the longpass-filtered and shortpass-filtered signals that are also consistent with the fact that the unfiltered signal lies somewhere in-between. Secondly, these are all also clearly different from the impulse response, although the signal widths are of the same order of magnitude. To extract the corresponding decay rates of each signal, therefore, numerical and statistical methods are required.

To this end, a Markov chain Monte Carlo (MCMC) based Bayesian algorithm named Iterative Bayesian Deconvolution (IBD) was developed whose mathematical framework, intermediate results, and statistical benchmarking are detailed in appendix A.1. The model is designed to operate bottom-up on four a priori datasets: the three measured plasma signals and the instrument impulse response. The core physical assumption, informed by the spectral analysis in section 4.2, is that the measured signals are a linear combination of two distinct physical processes. First, continuum emissions that completely dominate the 400–700 nm (shortpass) domain, and second, atomic emissions that are almost exclusively detected in the 700–1000 nm (longpass) domain. The underlying mechanisms behind these distinct types were described in section 2.5. The three datasets can therefore be modeled as different linear combinations of these two types of processes, with the unfiltered data being the direct sum of the shortpass and longpass data.

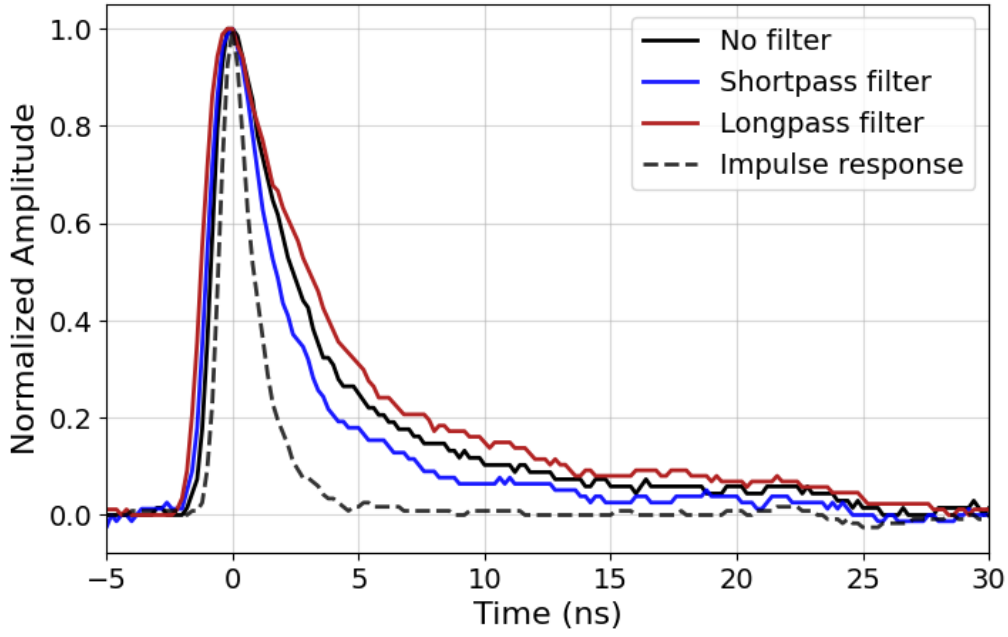


Figure 4.8: Measured emission signal data from the air plasma induced by $500 \mu\text{J}$ pulse energy, including using a long-pass and short-pass filter, respectively, compared to the measured impulse response.

To parameterize the system, IBD utilizes a simple power-law equation that captures the general, time-averaged behavior of a non-linear, monotonically decaying system with time-dependent decay rates:

$$f(\theta, t) = \begin{cases} \frac{A}{(1+\frac{t}{\tau})^b}, & t \geq 0 \\ 0, & t < 0 \end{cases}, \quad \theta = \{A, \tau, b\} \quad (4.1)$$

where A , τ , and b are the governing inference parameters. This power-law simplification of decay processes is commonly employed in chemistry, and is appropriate here because there is no closed-form expression that accurately captures the time evolution of radiative emission decay in this type of non-equilibrium plasma. The deconvolution is subsequently executed in three iterative steps. First, the power-law parameters for the continuum emission are inferred using the 400–700 nm dataset. Second, these results are utilized as informed priors to analyze the 700–1000 nm dataset, which is modeled as a sum of two separate power-law equations. Finally, the combined parameters from the first two steps are evaluated against the unfiltered dataset to verify that the parameter convergence is stable and consistent across the entire system. The resulting inferred parameters for the case $500 \mu\text{J}$ pulse energy are presented in table 4.1 and the resulting model fit and inferred source signal in figure 4.9.

Table 4.1: IBD parameter posteriors (median $\pm$ standard deviation) in the case of 500 μ J pulse energy for the different datasets.

Parameter	Shortpass	Longpass	No filter
τ_{cont} (ns)	0.96 ± 0.04	0.95 ± 0.04	0.87 ± 0.07
b_{cont}	1.41 ± 0.02	1.41 ± 0.02	1.41 ± 0.01
A_{cont}	15.3 ± 0.2	7.7 ± 2.0	23.0 ± 1.1
τ_{disc} (ns)	N/A	2.61 ± 0.31	2.12 ± 0.14
b_{disc}	N/A	1.36 ± 0.03	1.34 ± 0.02
A_{disc}	N/A	11.3 ± 1.6	10.9 ± 1.2

What is immediately striking about these results is the consistency between all 6 parameters across three different datasets, suggesting the underlying physics has been captured in accordance with the prior assumptions. While the priors are informed, the model will converge to statistically superior values if such exist. This is evident in the broadening of the posterior for the continuum decay rate τ_{cont} for the unfiltered data, whose mean lies far outside the error bound of the previous steps that informed its prior, as well similarly for the bound-state decay rate τ_{disc} . It was also separately proven during the statistical benchmarking described in appendix A.1. The scale parameters are consistent with the initial assumption that the emission signals can be combined linearly, since the scale parameter A_{cont} for the unfiltered data is within the error bound for the sum of the two prior A_{cont} values, and similarly for A_{disc} .

The only parameter whose error bounds across datasets do not overlap is the bound-state decay rate τ_{disc} , although the corresponding p -value of 0.15 is not statistically significant. Additionally, the corresponding forward-convolved fit to the unfiltered data has an R^2 value of 0.999, which suggests a very strong statistical fit. Altogether, the results are very promising from both a physical and statistical perspective, and it is concluded that the continuum and atomic emissions have been successfully separated and modeled, respectively, from the raw data.

Having established confidence in these results, their meaning can be interpreted. The most compelling result is the characteristic decay rate τ , which is ≈ 1 ns for continuum emissions and $\gtrsim 2$ ns for discrete atomic emissions. Continuum emissions decaying faster is consistent with prior expectations, as they are dominant for high-energy electrons and thus primarily occur in the early stages of the plasma life cycle. Atomic transitions, on the other hand, rely on electrons cooling down enough to only induce atomic excitations rather than re-ionizing them. This reliance on the plasma cooling down over time for the emission profile is inherently slower, explaining why the overall characteristic decay time is longer.

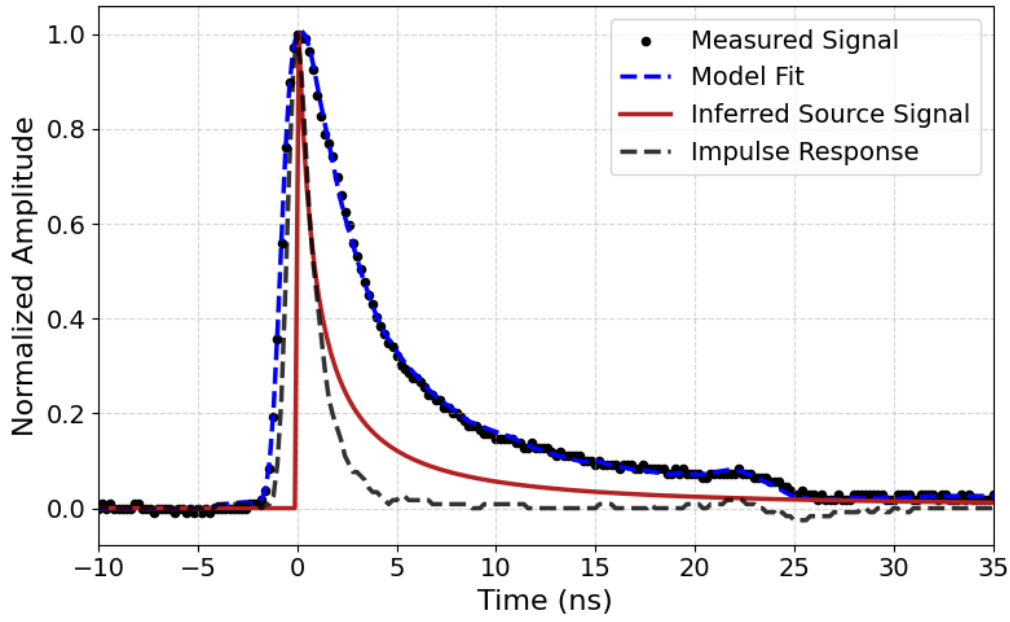


Figure 4.9: The forward-convolved IBD model fit compared to measured unfiltered signal data for 500 μJ pulse energy, including impulse response and the non-convolved model for reference.

While the decay rates are distinctly different, the power parameters b are relatively much closer, at $b_{\text{cont}} \approx 1.41$ and $b_{\text{disc}} \approx 1.35$, although there is no overlap between the respective error bounds. The power parameter b determines the shape of the decay curve and is a result from weighting all the different underlying physical mechanisms behind the respective emissions. Because the source of continuum emissions (radiative n -body recombination, Bremsstrahlung, two-photon emissions) are very different from atomic emissions (atomic excitations), it is entirely expected that the resulting power parameters would be different. However, the fact they are relatively close, considering there is no imposed upper bound on their priors, suggests they could still be coupled to the overall macroscopic evolution of the plasma.

The 500 μJ dataset provided a robust signal-to-noise ratio (SNR) sufficient to resolve all seven (6 physical and 1 nuisance) model parameters, but extending this high-dimensional inference across the full range of lower pulse energies introduced statistical limitations. As pulse energy decreases, the emission intensity naturally weakens, leading to a diminished SNR. The available data becomes insufficient to constrain all parameters, resulting in parameter spaces with multiple local likelihood maxima or inadequate statistical convergence. Therefore, it was not possible to construct a full mapping of the inferred parameters for all datasets. However, for the subset of measurements where the model converged reliably, the results consistently supported the benchmark findings: the continuum decay time τ_{cont} remained within the 0.5–1.5 ns range, while the atomic transition decay time τ_{disc} was consistently slower at around 1.5–2.5 ns. This confirms that the two processes have consistent relative behavior, and that the overall decay time is on the order of nanoseconds and does not significantly deviate into the picosecond or tens-of-nanosecond regimes.

5. Liquid Water

Having characterized the plasma generated in air, the next target material of interest is pure water. In many applications of femtosecond laser ablation, the target material either contains or is submerged in water. This is also true in the case of bone tissue ablation, where the surface of the bone is often coated in a liquid solution (containing mostly water) to prevent the sample drying out, as well as the tissue itself containing some amount of water. How focused ultrafast lasers interact in a pure water environment is the first step towards understanding more complex systems. Water is approximately 1000 times denser than air and typically follow incompressible hydrodynamic behavior, so one cannot just extrapolate the results from the previous chapter. Additionally, it is simple enough to construct a controlled environment of pure, distilled water, and perform the same methodological and analytical steps as with air.

Using a high-purity quartz cuvette with inner dimensions of 20 x 20 x 37 mm and >1 cm beam path, distilled, room temperature water could be placed around the focal region. Using the same spectroscopic equipment as with air, see figure 5.1, spatial, spectral and temporal data could be captured.

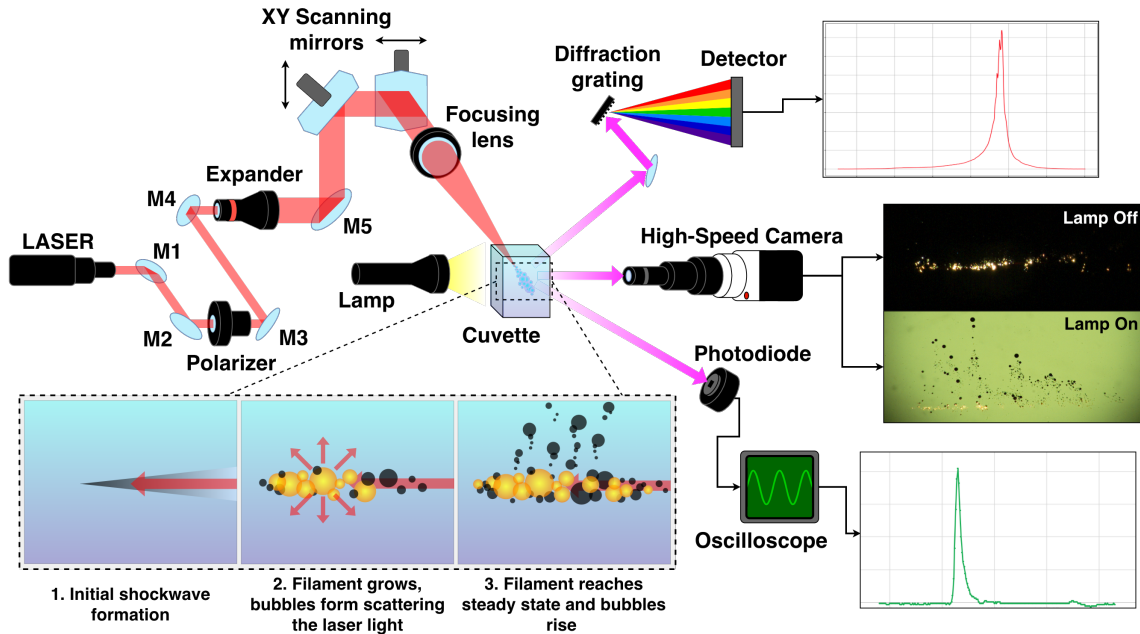


Figure 5.1: The laser beam focused into a cuvette of distilled water at room temperature inducing a plasma and bubble formation. The emission spectrum is measured by a spectrometer, the temporal evolution by an ultrafast photodiode, and the spatial imaging by a high-speed camera.

5.1 Spatial Imaging

Unlike in air, successive laser pulses at 1 kHz do not yield identical results; rather, they give rise to cumulative bubble formation over hundreds of milliseconds. This transience prevents the use of simple frame averaging to produce high-resolution dark-field images of the focal region, but it opens the door for a spatio-temporal analysis. To investigate these dynamics, the focal region was captured using two distinct methods: first without external lighting to isolate the emission profile, and then with LED backlighting to observe bubble formation via shadowgraphy. To be able to capture enough of the LED backlight, the exposure time was increased to 90 μs in both cases while keeping the ISO at 8000 to be consistent with the measurements on air. Although several pulse energies were tested, the temporal evolution was best resolved using 158 μJ , as presented in figure 5.3. This specific choice of pulse energy was because larger pulse energies created bubble structures that extended beyond the spatial range of the LED backlight region.

The evolution of the plasma and bubble formation can be divided into three primary phases. During the initial optical breakdown phase ($t = 0$ to 1 ms), the first pulse creates a shockwave jet near the focus without generating light strong enough for the camera to resolve. Its characteristic wedge shape, extending more than 10 Rayleigh lengths, strongly suggests filamentation of the laser pulse. The subsequent pulse ($t = 1$ ms) creates a similar shockwave alongside visible light emissions. This light originates from the interfaces of the gas bubbles generated by the preceding pulse, primarily attributed to scattered laser reflections, though contributions from plasma emissions cannot be strictly ruled out.

Following the initial breakdown is an expansion phase ($t = 10$ to 500 ms) where each successive pulse contributes to a rapidly expanding region of bubbles. Interestingly, this formation is not limited to expansion from the initial focal point, as bubbles begin to form independently further back along the propagation axis. By $t = 100$ ms, a buoyant mass of gas bubbles begins to rise, and by $t = 500$ ms, the spatial extent of the observed light and the bubble filament reaches its maximum.

Finally, the system enters a quasi-stable equilibrium state, at approximately $t = 1$ s, as the tail end of the profile recedes and stabilizes. In this state, the macroscopic bubble structure can be divided into three distinct spatial domains as shown in figure 5.2:

1. **The Focal Region:** The furthest extent of bubble generation along the propagation axis, maintaining a consistent bubble distribution.
2. **The Central Plume:** Immediately preceding the focus, exhibiting the highest total rate of bubble formation and the most pronounced laser light reflections.
3. **The Plume Tail:** Further back along the axis, occupying the largest volume but containing the lowest bubble density and size.

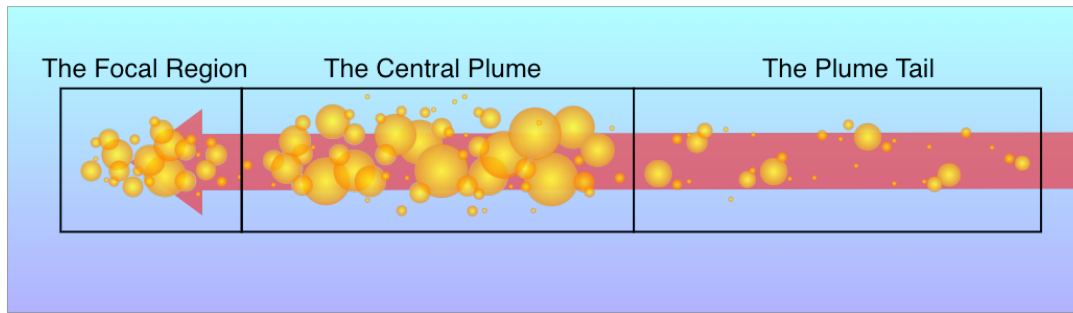


Figure 5.2: The macroscopic bubble structure divided into three distinct spatial regions.

These spatio-temporal dynamics were qualitatively similar across all tested pulse energies, though higher energies corresponded to larger plumes and longer stabilization times (up to ~ 2 seconds for $500 \mu\text{J}$). These results are consistent with those reported by [51], who utilized the same laser system as this work.

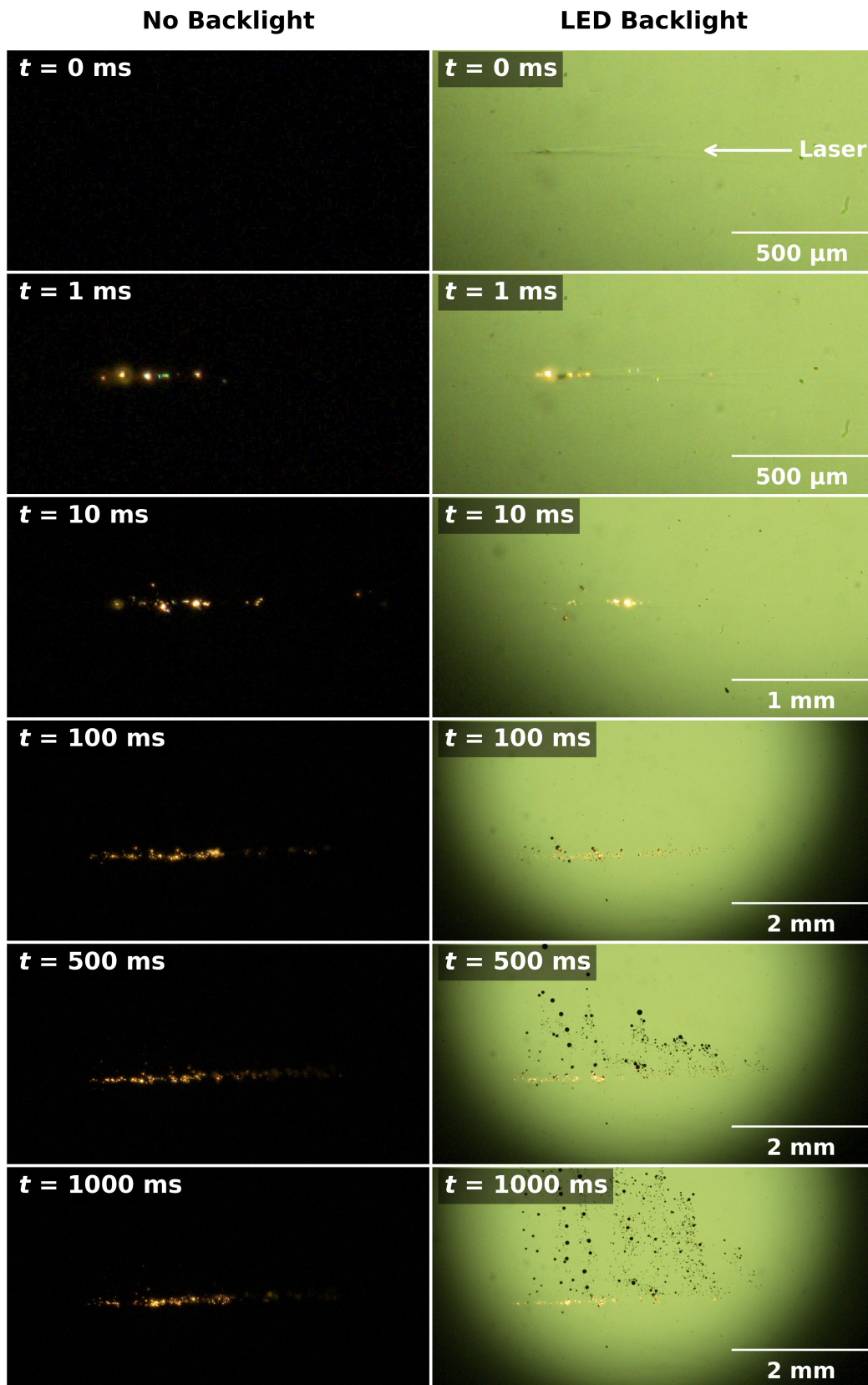


Figure 5.3: Time-resolved visualization of laser reflection and bubble formation at $158 \mu\text{J}$ pulse energy over 1000 ms. Comparison between unlit (left) and LED-backlit (right) environments.

5.2 Spectrometry

The spectral profile of the steady-state bubble filament was then examined. While the local characteristics of the filament are highly transient by virtue of continuous bubble formation, collapse, and buoyancy, it is possible to macroscopically divide the filament into three major spatial domains. First is the focal region, which represents the furthest extent of bubble generation along the propagation axis and displays a relatively consistent bubble distribution. Immediately preceding this along the propagation direction is the high-density central plume, which exhibits the highest rate of bubble formation and the strongest laser light reflection. Finally, preceding the central plume is the low-density plume tail; while this region occupies the largest volume, it contains the lowest bubble density and size.

The spectral characteristics of each region were captured using the spectrometer. The different regions were captured by moving the tip of the fiber cable, as shown in figure 5.4, to the corresponding focal spots. Additionally, due to its lower density, the tail plume required a longer integration time to achieve photon counts comparable to the other two regions. A graphical visualization of these distinct regions and their corresponding normalized spectra at three different pulse energies is presented in figure 5.5.

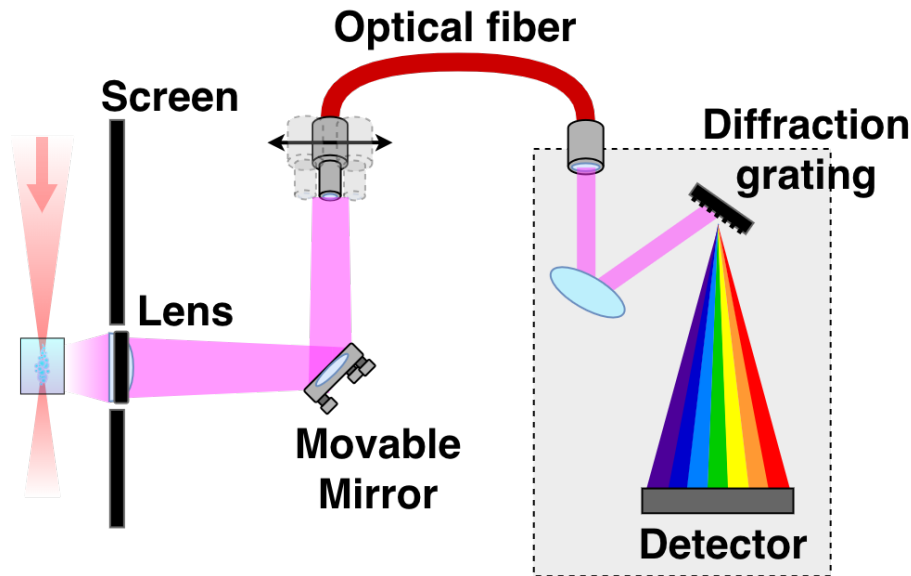


Figure 5.4: Experimental setup for capturing the emission spectrum of water with minimal light pollution.

The immediate observation is the lack of any identifiable atomic spectral lines in any of the recorded spectra. Instead, the captured light is overwhelmingly scattered and reflected, spectrally broadened laser light, whose shape is very similar to results in previous research [35]. Since the spectral broadening extends across the entire recorded spectrum, it obscures any potentially identifiable plasma emissions.

Additionally, the shape of the recorded spectra changes with pulse energy, exhibiting larger spectral broadening of the fundamental laser wavelength at higher energies, consistent with expectations from theory in nonlinear optics (see section 2.2). For pulse energies in the region of $500\text{ }\mu\text{J}$, the spectral broadening was so stark that the light appeared white, typical of supercontinuum generation.

Interestingly, this inconsistency in spectral shape is also present when comparing different spatial regions at a constant pulse energy. There is no obvious relationship or predictable trend between the relative spectra of the focal region, the central plume, and the tail plume, even though one would expect more pronounced spectral broadening with longer propagation distances within the nonlinear medium. These results suggest the laser pulse undergoes filamentation, as this would explain why spectral broadening can be observed in spatial regions separated by more than 100 Rayleigh lengths.

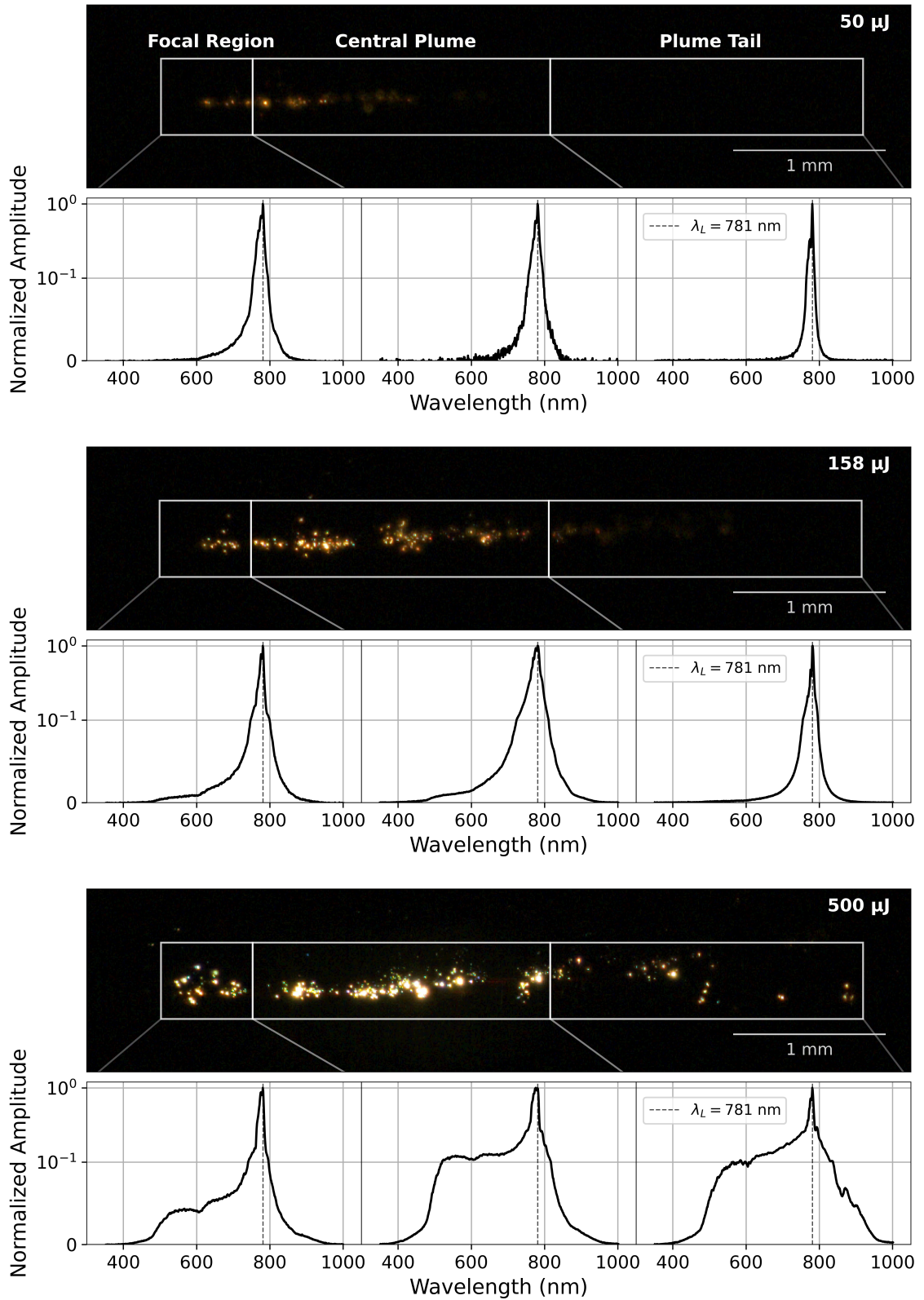


Figure 5.5: Graphic visualization of the three macroscopic filament regions for different pulse energies. White boxes from left to right: focal region, central plume region, tail plume region. The largest peak in the reference laser spectrum (781 nm) is included for reference.

5.3 Temporal Evolution

To further verify whether the observed spectrum is indeed purely from spectrally broadened laser reflections, or if some plasma emissions can still be resolved, the photodiode was again employed. All three spatial regions of the bubble filament were captured, with and without filters, and for different pulse energies in an extended range of 19–500 μJ .

In all cases, the captured signal was indistinguishable from the impulse response. Examples of captured signals compared to the impulse response are presented in figure 5.6 for reference. At 19 μJ with no filter, the signal strength is identical to that of the previously measured impulse response. At 500 μJ , a shortpass filter was used to reduce the signal strength below the saturation regime of the diode.

While the presence of nonlinear spectral broadening of the laser light is highly suggestive of field intensities approaching, or even exceeding, the ionization regime of water, there is no observed plasma decay process in the photodiode data. Although water plasmas in unbounded geometries were expected to decay much faster than air, whose decay rate was already on the order of the impulse response, due to electron solvation (see section 2.4.4), it could still have been possible to decay a weak plasma signal if the plasma was hot enough to thermally sustain itself for an extended period. Altogether, the results from the photodiode further reinforce the interpretations made from the other spectroscopic data.

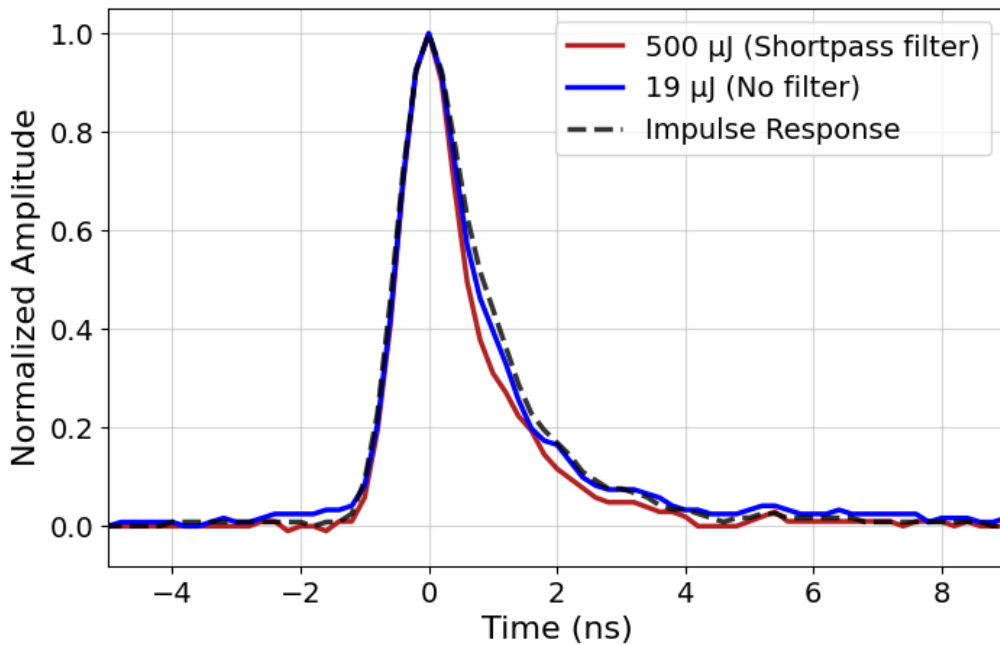


Figure 5.6: Measured emission signal at origin for 19 μJ (unfiltered) and 500 μJ (shortpass filtered) pulse energies, compared to the measured impulse response.

6. Porcine Bone

The final and perhaps most important target material evaluated in this project was porcine rib bone from a wild boar (*Sus scrofa*). Unlike air and pure water, bone tissue is a complex solid containing a large variety of compound molecules in highly heterogeneous structures. Fluids like air and water, with their simpler chemical compositions, will eventually relax to restore the initial macroscopic state of the system. This allows for a macroscopic steady-state interaction between the laser pulse and the material. Steady-state interaction is particularly useful as it allows for a higher degree of reproducibility and makes data acquisition much more convenient.

As a solid, bone tissue will not revert to its initial state. Instead, ablated material is ejected, leaving a permanent ablation zone (crater) in its place. Consequently, to ensure similar conditions for each successive laser pulse, the bone surface must be moved at a constant rate and fixed distance relative to the laser focus, thereby continuously replenishing the target surface. This technique was employed to the extent possible with the available equipment while studying the spectral characteristics and temporal evolution using the spectrometer and photodiode, respectively.

In the context of bone microtomy, steady-state phenomena are of less interest, as the specific purpose is to permanently ablate the material. During this process, the surface of the target sample moves through the laser focus, causing the physical geometry of the system to change from one pulse to the next. To investigate this phenomenon, the bone sample was moved axially toward and through the focus, effectively drilling the bone at a single location. The high-speed camera was used to visualize this process, capturing transient interactions that are impossible to resolve with the spectrometer or photodiode.

To simplify the system and isolate the ablation behavior of the bone tissue itself, the surface was not coated with a liquid solution. While such coatings are sometimes applied in conventional laser microtomy to prevent the bone from drying out, they were omitted here to avoid introducing additional variables.

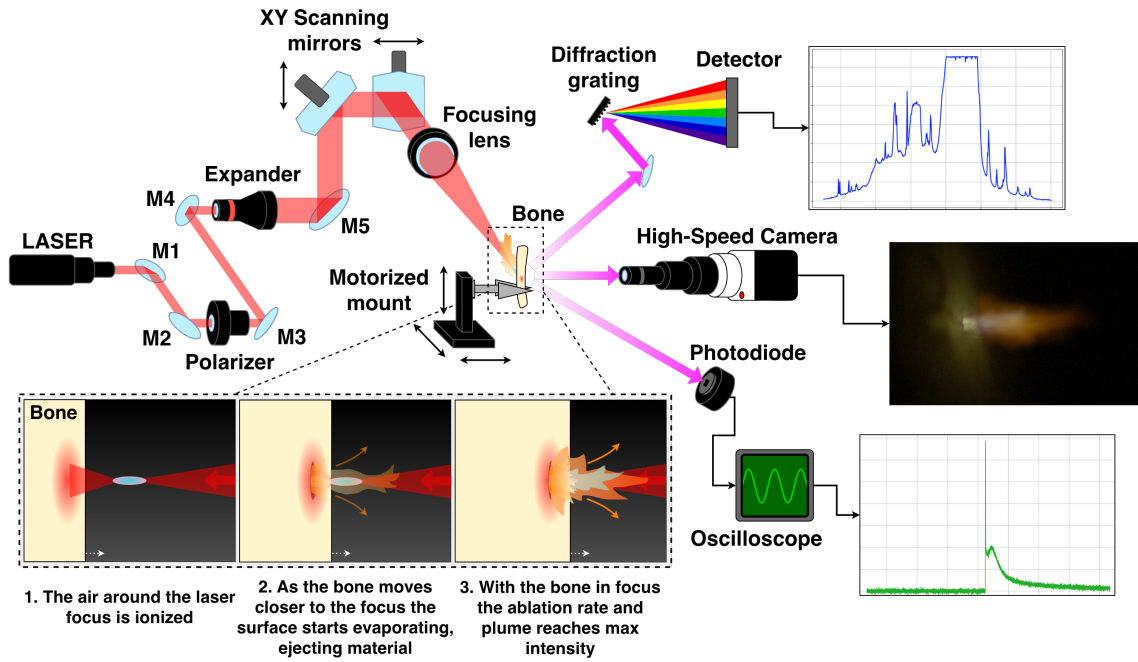


Figure 6.1: The laser beam focused onto the surface of a porcine rib bone sample attached to a motorized mount. The emission spectrum of the cutting is measured by a spectrometer, the temporal evolution by an ultrafast photodiode, and the full event imaged by a high-speed camera.

6.1 Spatial Imaging

The high-speed camera was synchronized with the laser pulses, as described earlier in section 3.2.1, establishing the laser-induced air plasma in the focal plane as a reference. The exposure time was set to $90\ \mu\text{s}$ and ISO to 8000 to be consistent with the spatio-temporal imaging in pure water. The bone sample, oriented with its surface normal to the axis of laser propagation, was then moved axially toward the laser focus at a constant velocity of $2\ \text{mm/s}$ using the motorized mount. This procedure was repeated on fresh surface locations for pulse energies ranging from $50\ \mu\text{J}$ to $500\ \mu\text{J}$. The temporally resolved visualization for the $500\ \mu\text{J}$ pulse energy is presented in figure 6.2, while the resulting ablation craters for a selection of pulse energies are shown in figure 6.3.

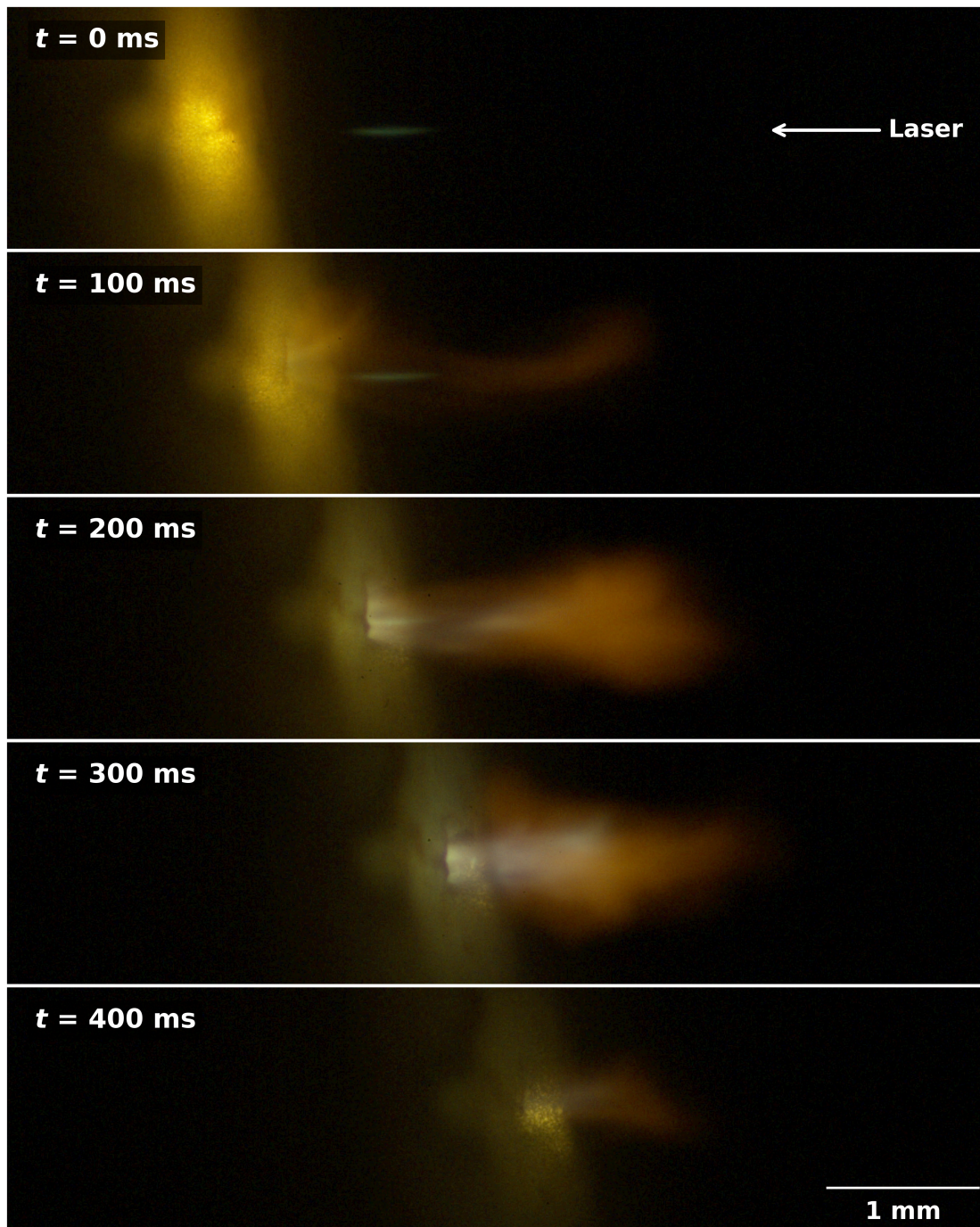


Figure 6.2: Time-resolved visualization of the ablation process of porcine bone tissue, where the bone was moved towards the laser focus against the propagation direction at a constant velocity of 2 mm/s. Here, the pulse energy was set to 500 μ J.

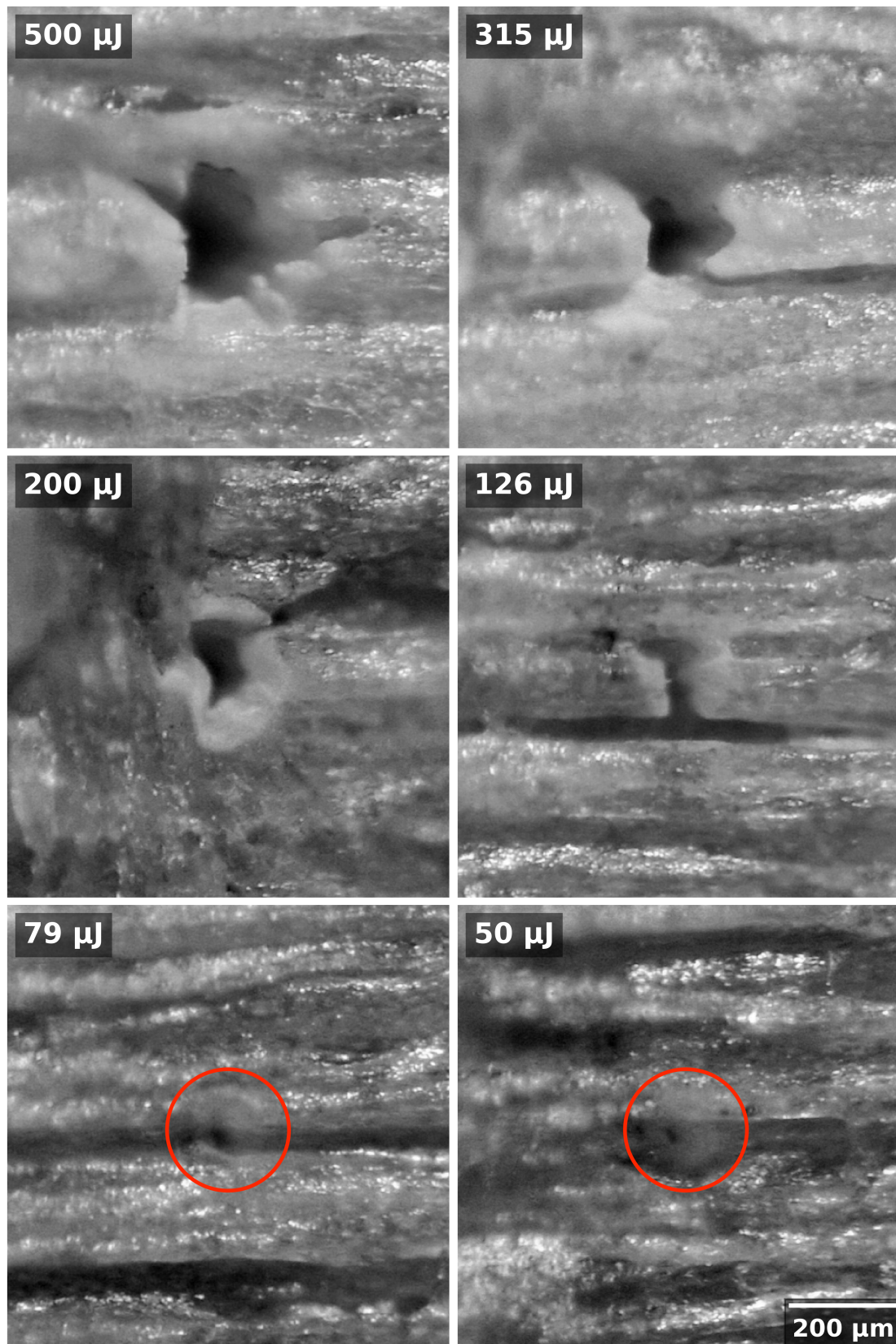


Figure 6.3: Ablation craters on the porcine rib bone surface resulting from moving the bone towards the laser focus against the propagation direction at a constant velocity of 2 mm/s, for different pulse energies.

Some interesting observations can be made from the temporally resolved imaging in figure 6.2. First, there is much visible scattering of the laser on the bone surface, and the yellow hue suggests spectral broadening. Second, even long before the focus reaches the surface, material ablation occurs and a plume begins to form. By the time the focus reaches the surface, an ablation crater has already developed, and the plume noticeably intensifies in both size and emission intensity. When the focus is entirely inside the crater, the plume reaches its maximum spatial extent and intensity. During this stage, the plume takes on a whiter hue, suggesting higher electron temperatures. Once the bone completely engulfs the focus, indicating that the ablation rate is slower than the 2 mm/s translation velocity, the laser is unable to ionize the material. Instead, the energy is absorbed and scattered, causing the ablation process to quickly cease. In this regime, since the absorbed energy is not able to escape from the material, thermal damage could be observed in some cases when the laser was engulfed for prolonged periods. These dynamics were qualitatively similar across the tested pulse energies, with the primary differences being the overall intensity of the ablation plume (decreasing with lower pulse energies) and the distance from the focus at which the initial plume formed (shortening with lower pulse energies).

Comparing the resulting ablation craters across the 50 μJ to 500 μJ range highlights the importance of pulse energy for efficient and precise ablation. While higher energies clearly ablate a larger volume of material in the same timeframe, this comes at the cost of precision. High-energy craters are amorphous and reach diameters on the order of 100 μm . This is substantially wider than both the measured FWHM of the air plasma ($\approx 20 \mu\text{m}$ at 500 μJ , see figure 4.4) and the computed theoretical beam width of 6 μm (see Section 2.1). Conversely, ablation craters generated by lower pulse energies, specifically from 79 μJ and below, are far more circularly symmetric and approximately an order of magnitude smaller in width. No burn marks were observed around any of the ablation craters.

Using the non-exponential part of the Gaussian pulse propagation formula in equation 2.3 and rough distance estimations based on the images from the high-speed camera, as well as the spatial profiling of the air plasma (see section 4.1), we can get a rough estimate of the lowest peak intensity required to ablate a visible amount of bone tissue. Taking the first frame where an ejection plume is visible, and assuming the laser focus is at the center-of-mass of the air plasma, the distance to the bone surface is estimated to be roughly $1.2 \pm 0.2 \text{ mm}$. Using equation 2.3, we get $I_{min} \approx 5 \times 10^{17} \text{ W/m}^2$, with an upper bound of $7 \times 10^{17} \text{ W/m}^2$ and a lower bound of $4 \times 10^{17} \text{ W/m}^2$. The pulse energy used was 500 μJ , and the Rayleigh length 60 μm as computed in section 2.1. For this pulse energy, we can compute the effective ablation zone, i.e. the radius inside which $I > I_{min}$, for different z, r at $t_0(z) = z/c$. The results are presented below in figure 6.4. As can be observed, while the ablation zone near the focus is relatively small ($\approx 5 \mu\text{m}$ in all cases), the sizes expand away from the focus, an effect that becomes more pronounced as pulse energy is increased.

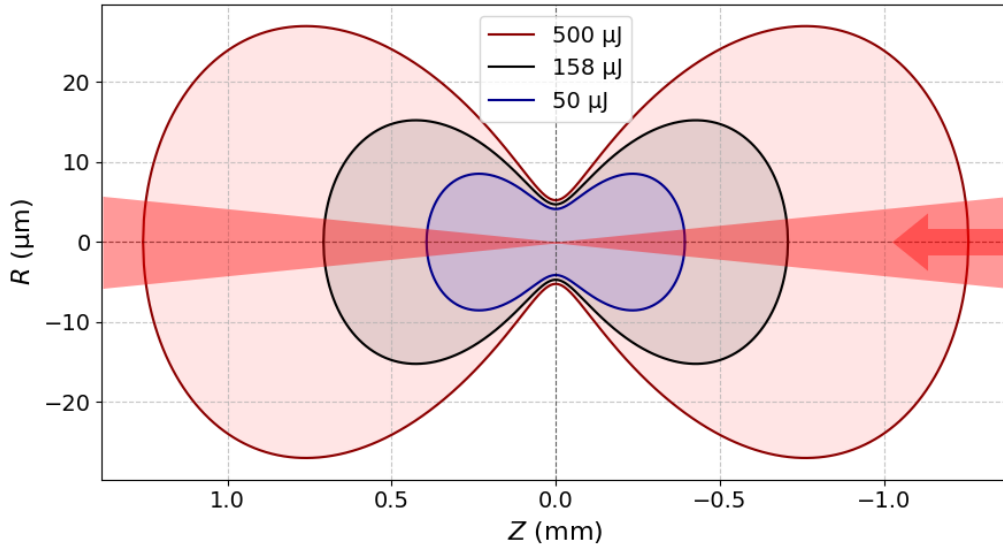


Figure 6.4: Estimated effective ablation zone based on the computed threshold ionization intensity of $I_{min} = 5 \times 10^{17} \text{ W/m}^2$ for different pulse energies.

To achieve this threshold intensity only at the focus, the pulse energy should be set to $\approx 1 \mu\text{J}$, with a lower bound of $0.8 \mu\text{J}$ and an upper bound of $1.6 \mu\text{J}$, calculated using equation 2.4 and $w_0 = 3 \mu\text{m}$. While the associated effective ablation zone, and therefore also the amount of removed material, is much smaller for each pulse, this could be circumvented by increasing the repetition rate proportionally. This more gentle ablation strategy would in principle produce highly localized ablation and likely with less excess energy absorption that diffuses as bulk heat (see e.g. the theory on plasma trapping and plume formation in section 2.4.4). If precision is less important than overall ablation rate, however, increasing the pulse energy is recommended.

6.2 Spectrometry

The spectral properties of the bone ablation process were then investigated. Similar to the case of water, the characteristics of bone tissue ablation exhibited much pulse-to-pulse variance. Because of this, the captured spectra represent time-averaged emissions over the duration of the entire cutting event. To perform the measurements, the bone surface was first fixed as close to the focus as possible without engulfing it entirely, then translated perpendicular to the laser propagation direction at a constant rate of 2 mm/s . During this translation, the spectrometer collected data.

Given the highly transient and variable nature of the process, combined with very poor signal-to-noise ratios for lower pulse energies, data of spectral measurements will only be presented here for $500 \mu\text{J}$ pulse energy. Results were, however, qualitatively similar across all tested pulse energies. In total, 8 composite spectra were captured, with each data point consisting of an average of two measurements utilizing a 1-second

integration time each. While the uneven target geometry introduced significant variance between individual measurements (see appendix figure A.5), several defining characteristic emission peaks remained consistent across all trials. Figure 6.5 presents the normalized, noise-subtracted average of these 8 measurements, highlighting both the identifiable atomic transition lines and the spectral region dominated by the scattered incident laser light.

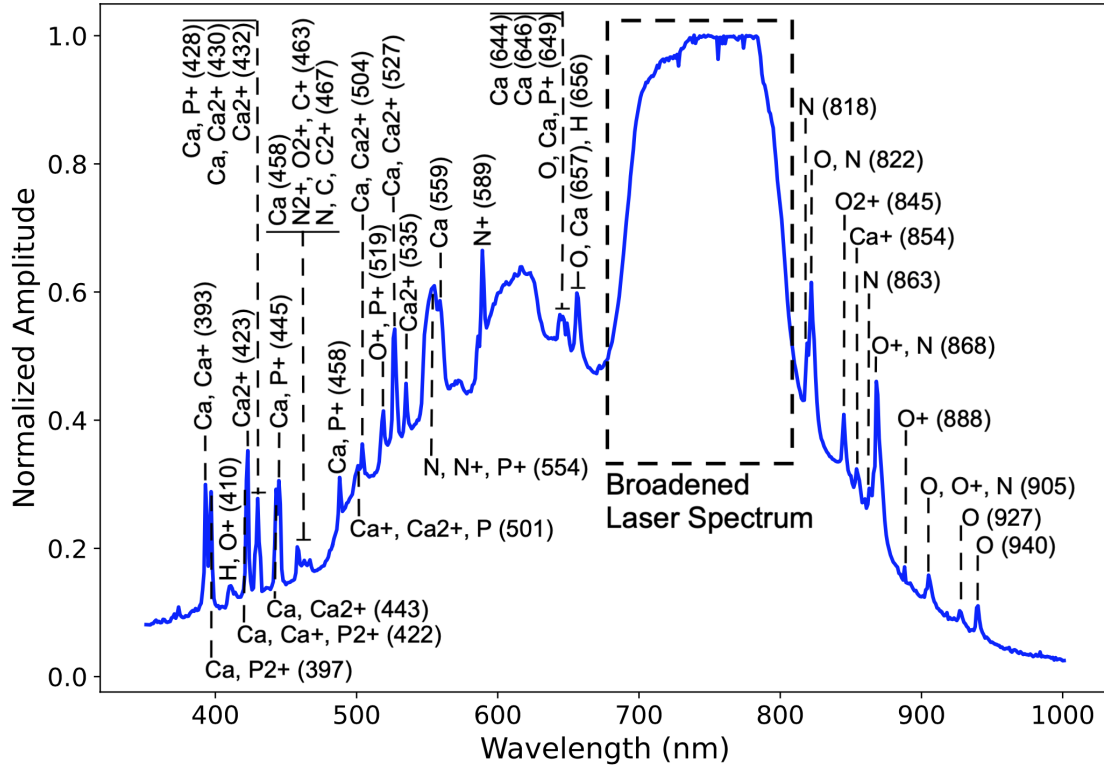


Figure 6.5: The processed emission spectrum for bone tissue ablation at 500 μJ pulse energy, with characteristic spectral lines and scattered, spectrally broadened laser light marked.

The spectrum is dominated by a broad peak corresponding to the spectrally broadened, reflected laser pulse, and the degree of spectral broadening varied between individual measurements, similar to the differences between spatial regions in water (see e.g. figure 5.5). Although this broadened peak obscures characteristic emission lines around 750–800 nm, an array of new characteristic emission lines that were absent in the preceding air (figure 4.6) and water (figure 5.5) spectra could be successfully isolated in the 400–700 nm regime. Most notably, the spectrum exhibits pronounced bound-bound transitions for atomic and ionic calcium (both the +1 and +2 ionic states), ionic phosphorus, and atomic hydrogen. Additionally, discrete oxygen and nitrogen transition lines that could not be resolved in either air or water, such as O+ at 410 nm and 519 nm, N at 467 nm, and N+ at 589 nm, were identified.

It should be noted that several of these transition lines overlap, making it difficult to identify them with confidence. Nevertheless, since bone tissue is primarily composed of calcium- and phosphorus-rich hydroxyapatite, as well as organic collagen (hydrogen, nitrogen, and oxygen), the detection of these specific elements acts as a strong indicator that the atomic emissions of the ejected bone plasma plume were successfully captured. All spectral line identifications were cross-referenced with the NIST Atomic Spectra Database [75].

6.3 Temporal Evolution

As indicated by the spatial imaging and spectrometry results, a significant portion of the optical emission surrounding the ablation zone consists of scattered laser light. To mitigate its influence on the photodiode measurements, the 400–690 nm shortpass filter utilized in previous sections was mounted directly in front of the photodiode. Consistent with the spectrometry procedure, the bone sample was translated perpendicular to the laser propagation direction at a fixed distance, though this was again subject to variations arising from bone surface roughness and curvature. This process permitted a sufficient time window to acquire a running-average signal on the oscilloscope during the ablation process. However, due to pulse-to-pulse variations, the dynamics of each ablation event were unique, and differences in signal amplitude at specific temporal points could span several orders of magnitude. Consequently, a series of individual raw measurements were also recorded to serve as a baseline reference. Because random noise dominates the systematic background for individual snapshot measurements, a Savitzky-Golay filter was applied to smooth the high-frequency variations. For the running-average measurements, averaging over 64 samples proved most effective. For consistency, the Savitzky-Golay filter was used on this data as well. The raw signal amplitudes (normalized to the global maximum across all datasets) were presented to better showcase the differences between individual measurements, since individual normalization would be sensitive to the amount of captured laser reflections and distort the relative signal amplitudes and decay rates. Representative examples of the individual snapshots and the running-average measurements are presented in figures 6.6 and 6.7, respectively.

An immediate observation from the data is the presence of a signal component that decays on a significantly longer timescale than either the laser reflections or the previously characterized air plasma. On short timescales, the laser reflection and air plasma signals are resolved as narrow peaks centered around $t = 0$, exhibiting largely consistent profiles between data sets. On longer timescales, the dynamics of the ablation plume can be observed, with substantial variance between data series in terms of amplitude, signal morphology, and decay rate. For instance, differing decay rates cause two of the individual signals in figure 6.6 to intersect at approximately $t \approx 120$ ns. Regarding signal morphology, most individual measurements display a distinct rise-decay-rise-decay profile, with the secondary local maximum occurring anywhere between $t \gtrsim 0$ to $t \gtrsim 300$ ns. Due to this variation between individual events, the 64-sample running averages generally smoothed these features into a more monotonically decaying curve, though the dual-peak structure occasionally

persisted even here. For these averaged signals, one can observe a significant decrease in the signal decay rate, likely due to the plasma plume transitioning from the initial shock front of ionized material to the slower thermal evaporation of the surface. The signal-to-noise ratio was also good enough for internal signal reflections in the BNC cables to be pronounced.

These variations are attributed to the fact that the photodiode is aligned to the air plasma volume around the focus, whereas the actual ablation zone fluctuates relative to this point from pulse to pulse. Consequently, the expanding plume must propagate from the ablation site into the photodiode's line-of-sight before detection occurs, causing the characteristic secondary rise and decay signal. Fluctuations in the initial plume morphology (as observed in figure 6.2) compound these variations. The variability and non-reproducible nature of these signals, even for running-average measurements, discourages deterministic modeling of the data. In the case of air, the signals were highly stable and reproducible, which justified a statistical modeling approach to characterize it for future reference. For bone tissue, this is not the case. While empirical models such as a modified IBD (see section 4.3) could technically be fitted to individual traces, they carry minimal predictive value if the underlying event cannot be reproduced reliably. Even if more sophisticated equipment and methods were employed to guarantee identical geometric conditions for each consecutive pulse, the corresponding results would mean little in practice where variations are unavoidable. Therefore, our analysis for bone tissue must remain fundamentally qualitative.

In this regard, it is still clear that plasma shielding may pose a problem for high-repetition rate laser systems, because the ejection plumes decay orders of magnitude slower than the air plasmas. In our observations, the photon emission rate of the ejection plume decays by less than two orders of magnitude in $1\ \mu\text{s}$, and depending on the time-averaged relation between photon emissions and plasma density during this time span, this could mean as little as one order of magnitude decrease in plasma density (e.g. in the case $S_{\text{source}} \propto \dot{n} \propto n^2$). For 1 MHz repetition-rate systems or faster, our observations support the hypothesis that the ejection plume can compound over many pulse cycles, which may saturate in a regime where the ablation rate is measurably weaker than in ambient air (see section 2.4.4).

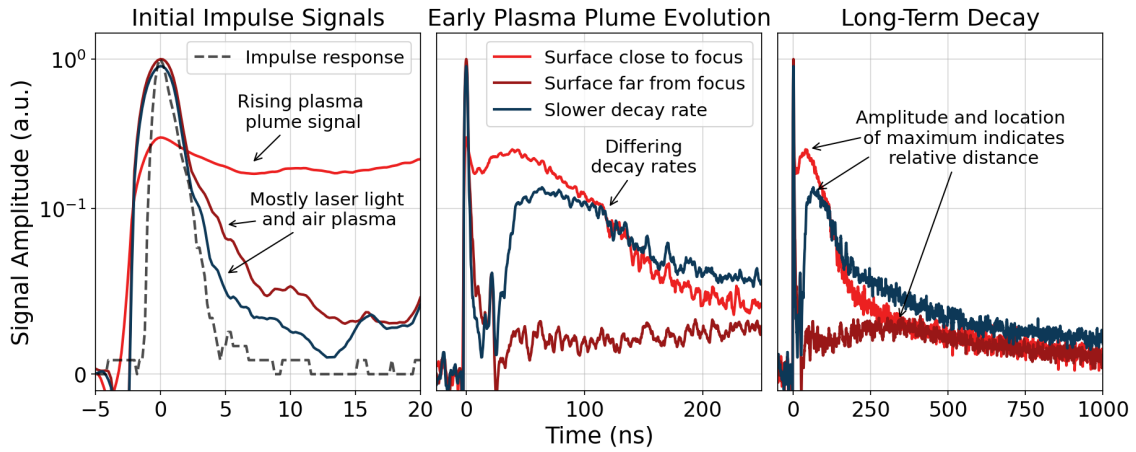


Figure 6.6: Snapshot examples of photodiode signals during the ablation process of porcine bone tissue. Left: short time scale, with impulse response for reference, highlighting the short rise and decay of laser reflections and the air plasma. Center: longer time scale, highlighting the rise, peak and decay of the plasma plume signal. Included as well is the intersection of two signals, indicating different decay rates. Right: full time scale, highlighting that all signals last into the microsecond regime.

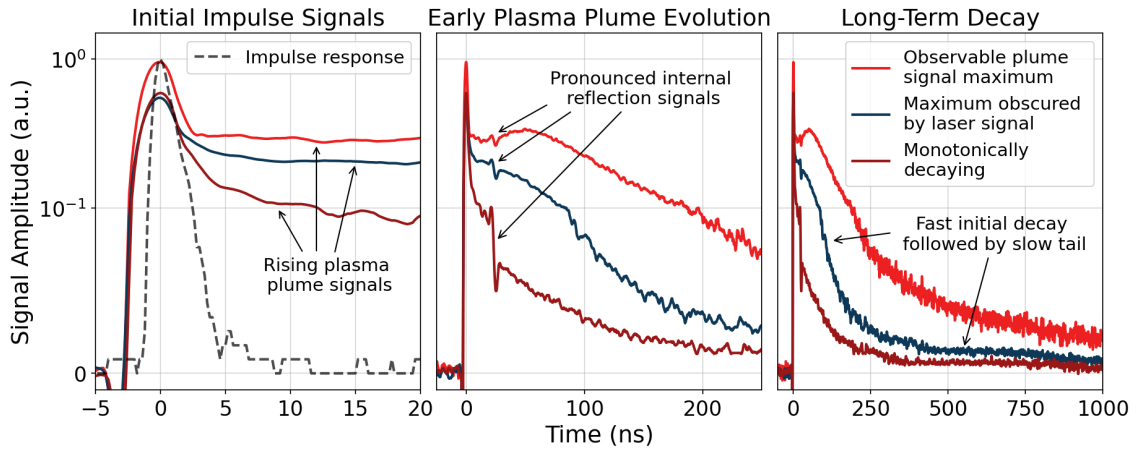


Figure 6.7: Examples of photodiode signals of the running average of 64 individual measurements during the ablation process of porcine bone tissue. Left: short time scale, with impulse response for reference, highlighting the short rise and decay of laser reflections and the air plasma, and the transition to a plasma plume signals. Center: longer time scale, highlighting the initial evolution of the plasma plume signal. Averaging many individual measurements improves signal-to-noise ratio and the internal reflections inside the BNC cables become more pronounced. Right: longer time scale, highlighting the significant reduction in decay rate and that the signals consequently last into the microsecond regime.

7. Discussion

7.1 Summary of the Results

7.1.1 Ambient Air

The results in air exhibited exceptional pulse-to-pulse stability across all pulse energies tested and for all spectroscopic equipment used, and were all qualitatively and/or quantitatively similar to established prior research. The high stability allowed for higher resolution imaging via frame averaging, and overall air was the only target material where the exact spatial profile of the plasma could be visualized and computed. This yielded useful information about distortions in the laser pulse shape and how that compounds with the nonlinear nature of photoionization.

It was also the only target material with no observed scattering or reflections of the laser light, which allowed for both spectral characterization and measurements of the temporal evolution near the laser wavelength regime. For the spectrometry, the entire 400–1000 nm wavelength regime could be mapped, showing exceptional consistency across the full range of pulse energies, and clear separation between continuum emissions that dominate in the shorter wavelength regime (400–700 nm), while bound-bound transitions were pronounced in the longer wavelength region (700–1000 nm), particularly around the 750–800 nm region which would otherwise have been obscured had the laser light been significantly spectrally broadened and reflected.

For the temporal evolution measurements, limitations in the photodiode rise time meant the observed temporal evolution could not be taken as the raw data, but instead had to be separated using signal deconvolution methods. To this end, an iterative MCMC-based Bayesian inference model dubbed Iterative Bayesian Deconvolution (IBD) was developed, which was able to infer the parameter values of a simplified decay model to separately characterize the continuum and bound-bound transition processes. As expected, the inferred model for the continuum emissions decayed faster ($\tau \approx 1$ ns) than the bound-bound transitions ($\tau \approx 2$ ns), and overall the plasma decayed much faster than the repetition rate of most ultrafast laser systems.

7.1.2 Liquid Water

In many ways, the results in water were the complete opposite from air: the pulse-to-pulse stability is replaced by a highly transient bubble plume structure whose bubble interfaces reflected a significant amount of laser light. Even when looking at just a single pulse, no plasma emissions could be resolved and it was necessary to

employ shadowgraphy to visualize the laser filamentation and shockwave creation. The spatio-temporal evolution of the bubble structure was visualized with both dark-field imaging and shadowgraphy, and subsequently characterized into three distinct temporal regimes and three distinct spatial regimes.

Using the three distinct spatial regimes as a landmark, the spectral properties of the entire bubble structure was captured, showing overwhelmingly spectrally broadened, reflected laser light, with no visible identifiable water plasma transition lines. The overall shape of the captured laser light varied both spatially and for different pulse energies.

Finally, the temporal measurements were partially inconclusive, as the captured signals were all indistinguishable from the impulse response of the photodiode. While the overwhelming majority of the signal was attributed to laser reflections, it was not possible to entirely exclude water plasma emissions based on prior research that suggested decay times on sub-nanosecond time scales due to electron solvation.

While all these results altogether were insufficient for deeper analysis, they were qualitatively consistent with prior research, and yielded useful insights into the complexities of nonlinear optics and ultrafast physics in the context of practical applications of the technology.

7.1.3 Porcine Bone

Measurements on porcine bone tissue introduced a new set of challenges compared to the fluid targets. Bone is mostly solid, with a rough surface that does not replenish between pulses, so achieving pulse-to-pulse stability would require precise repositioning for every consecutive laser pulse. Due to equipment limitations, this was not feasible, and consequently, the measurement methodology was adapted for each type of measurement. While it was impossible to perfectly recreate the conditions of prior research, our results were qualitatively similar.

For spatial imaging, the bone was translated axially toward the laser focus to observe the spatio-temporal evolution of the ablation process, the ejected plasma plume, and the resulting crater formation. Ablation in bone was found to initiate earlier than in air, limiting the use of the air plasma volume as a reliable spatial reference. Using the captured image series, an approximate intensity threshold for bone ablation was derived and spatially mapped. This visualization revealed that the radial extent of the ablation threshold can grow significantly wider than the beam waist, identifying a potential bottleneck for ablation precision. Notably, while the resulting craters showed no visible signs of thermal damage, higher pulse energies consistently produced larger and less circular craters, whereas the lowest energies yielded highly circular craters an order of magnitude smaller in diameter.

For spectrometry, the bone was instead translated transversely to maintain a relatively constant distance to the focus. Despite variances in incident angle and focal distance due to surface roughness, averaging multiple discrete measurements yielded an informative average spectrum. The spectrometer captured emissions around the focal volume, so the resulting signal was a composite of air plasma emissions, spectrally broadened laser reflections from the bone surface, and the ejected target plasma plume. Using the air and water spectra as baselines, all three optical components could be isolated. Most notably, the bone plasma plume exhibited a dense array of clearly identifiable bound-bound transition lines characteristic of calcium.

The temporal measurements utilized a similar transverse translation technique. Across all data series, three distinct components were again identifiable: laser reflections, air plasma decay, and the emission of the ejected plasma plume. The plasma plume was particularly notable, exhibiting position-dependent signal amplitudes and distinct, extended decay rates. The signal peak of the expanding plume took up to 300 ns to reach the line-of-sight of the photodiode, and subsequently decayed over hundreds of nanoseconds. Plasma plume emissions were resolvable into the microsecond regime, providing direct experimental evidence that plasma shielding may constitute a challenge for MHz-repetition rate laser systems.

7.2 Significance of Results

7.2.1 Ideal Propagation Medium

In the context of ultrafast laser ablation of biological tissue, the choice of the surrounding propagation medium is a critical parameter that dictates both cutting efficiency and precision. The two most accessible and commonly utilized media in this context are ambient air and liquid water, each presenting distinct physical advantages and limitations.

Based on the experimental observations, ambient air emerges as the optimal bulk propagation medium. Air requires no sample preparation and is inherently transparent to the NIR wavelengths typically emitted by femtosecond laser systems. More importantly, air exhibits exceptional pulse-to-pulse stability and highly predictable behavior, allowing its interaction with the laser to be accounted for with high accuracy.

Suspending the target material in a low-pressure vacuum can therefore confidently be ruled out, as it would provide little to no practical advantages compared to air, while making operations more cumbersome and expensive. The nonlinear effects and distortion of the laser pulse when interacting in air are not pronounced enough to significantly impact precision, and based on the calculations in section 2.4.2, the plasma pressure created by the laser already dwarfs atmospheric pressure, so a vacuum would not alleviate the plasma plume ejection process meaningfully. Additionally, low pressure risks structural damage, rapid water evaporation, and cell death in most biological tissue.

Water also proved to be a poor propagation medium for a different set of reasons. The interaction between the laser pulses and water is dominated by extreme nonlinear optical effects, leading to optical filamentation, severe and unpredictable spectral broadening, and the continuous generation of a macroscopic bubble plume that subsequently reflects much of the laser light. Collectively, these phenomena result in severe distortion and dispersion of the laser pulses, which is highly inadequate in the context of precise material ablation.

While bulk submersion is actively detrimental to beam propagation, water remains useful to prevent tissue dehydration. A practical compromise would be the application of a thin liquid film on the bone surface, as this approach would preserve the tissue while allowing the laser pulse to propagate primarily through the stable ambient air, interacting with the fluid only at the immediate ablation zone.

An alternative to liquid-film coating would be to use specialized gas humidifiers that eject fully moisturized air with no microscopic vapor particles, such as the MH Humidifier series by Salaera or the MHG series by ProUmid. This would significantly reduce the tissue dehydration compared to typical lab conditions ($\approx 50\%$ humidity), while also acting to transport the ejected debris away from the ablation zone and laser propagation path. Even if the stream is too weak to transport away all of the debris between individual pulses, any amount of net flow will reduce the effects of plasma plume accumulation and corresponding plasma shielding effects.

7.2.2 Ideal Pulse Characteristics for Bone Tissue Ablation

As discussed in section 2.6, optimizing ablation efficiency while preventing collateral tissue damage is a complex task governed by the interplay of many nonlinear effects. While a universal, deterministic parameter set is beyond the scope of this work, the theory and empirical results can be used to suggest a systematic optimization strategy superior to blind empirical parameter sweeps. First, we propose general rules-of-thumb for the fundamental pulse characteristics in the ideal case, although equipment limitations will naturally constrain the tunability of these:

- **Pulse length:** Should be as short as possible (< 1 ps) to prevent linear thermal diffusion. However, too short pulses (e.g. $\ll 100$ fs) may prevent sufficient electron heating, resulting in a plasma that is too cold to drive material ejection.
- **Pulse shape:** The focal volume should be minimized to maximize ablation precision. This is achieved by maximizing the expanded beam width before the lens and decreasing the focal length (see equation 2.1).
- **Repetition rate:** Should be maximized ($\gg 1$ kHz) since ablation speed is proportional to the number of pulses per unit time, barring shielding effects or limitations of the power supply that limit pulse energy.

- **Pulse energy:** Dynamically tunable, especially with an Acousto-Optic Modulator (AOM). Higher energies increase the effective ablation volume (see figure 6.4), yielding higher material removal rates at the expense of precision.

There are also physical bottlenecks when the end goal is a clean ablation zone with minimal damage to the surroundings:

- **Thermal damage:** If the ablation zone geometry physically restricts material ejection (for example a deep, narrow trench or hole), trapped energy diffuses as heat. It was observed during setup calibration that burying the laser focus within the bone prevents ejection, leading to burning the tissue. The specific cutting geometry therefore imposes a strict upper limit on pulse energy.
- **Shockwave damage:** As discussed in Section 2.4.2, plasma-induced overpressure can exceed the compressive strength of bone tissue. This can cause permanent damage to the surrounding tissue and imposes an upper limit on the pulse energy.
- **Plasma shielding:** High-repetition-rate pulses targeted at a small localized area will interact with the plasma plume from previous pulses, absorbing the incoming energy and reducing ablation efficiency. These shielding effects can be mitigated by ensuring the focus moves to a fresh surface for every consecutive pulse, or by introducing a net air flow from e.g. an air jet.
- **Tissue dehydration:** If the ablation process is slow, tissue dehydration can become a problem. By either coating the tissue in a thin liquid film, or by blowing humidified air (which can also remove ejected material), the dehydration process can be slowed down.

To establish quantitative estimates for these limits without relying solely on empirical testing, a two-step theoretical modeling approach can be employed. First, numerical tools such as Luna can simulate the non-linear pulse propagation and corresponding photoionization [48], yielding precise estimates for the initial spatial distribution and density of the free electrons. Second, by coupling these initial plasma parameters with established hydrodynamic models for laser-induced shockwaves in condensed media, which are frequently approximated using aqueous baselines in biological applications [50, 52], the localized plasma overpressure can be estimated. By constraining this theoretical peak pressure to remain below the established compressive yield strength of bone tissue [56], an upper limit for the pulse energy can be determined prior to application.

Finally, because the evolving cut geometry is the primary physical constraint on material ejection, dynamic tuning of the laser pulse energy during the microtome process is proposed. When the sample is fresh, the flat solid-gas interface provides maximal geometric freedom for the expanding plasma plume, allowing for higher incident pulse energies. As the cut progresses and a narrow trench forms, this outward

expansion becomes increasingly restricted. To prevent trapped energy from diffusing as bulk heat, the pulse energy should be dynamically lowered as the trench deepens. The heterogeneous structure of bone tissue, especially considering the softer and more delicate marrow compared to the surrounding harder cortex, compounds this issue. Implementing an appropriate dynamic energy tuning, for example with the use of an AOM, would maximize overall cutting efficiency compared to employing a static pulse energy bounded by the upper limits for the deepest trench geometries and most delicate parts of the tissue.

7.3 Limitations

The scope, methodology, and results of this project were constrained by available equipment and time. The main hardware limitations are detailed below, followed by an explanation of how time constraints defined the final scope of the project:

- **Laser system:** The CPA2001 laser system utilized produces ≈ 150 fs pulses at a repetition rate of 1 kHz. While adequate for the majority of experiments conducted in this work, these specifications are below contemporary research levels, where sub-100 fs pulses and repetition rates extending into the MHz regime are possible. This specifically prevented the empirical observation of plasma shielding, as even the slowest plasma plume decay rates in our targets were orders of magnitude faster than the 1 kHz repetition rate of the system.
- **Spatial imaging:** While the camera allowed for imaging down to the sub-microsecond regime using synchronized delay generators, the temporal resolution was restricted by the ≈ 100 ns rise time of the sensor. This prevented imaging the evolution of the air plasma. A pump-probe imaging system was unavailable, which would have otherwise enabled this via ultrafast stroboscopy.
- **Spectrometry:** The VIS–NIR spectral range of the available spectrometer provided critical insights, but the vast majority of atomic recombination lines (particularly for the primary constituents of air and water) occur in the deep UV regime (e.g., $I_p(\text{O}_2) = 12.07 \text{ eV} \leftrightarrow \lambda = 103 \text{ nm}$). Furthermore, the 1 nm spectral resolution prevented deep analysis of individual bound-bound peak profiles, which would have enabled advanced diagnostics such as Boltzmann thermometry to estimate effective plasma temperatures.
- **Temporal evolution:** The impulse response FWHM of the photodiode setup was ≈ 1.4 ns. This obscured the emission signal of the air plasma, and required the development of statistical and numerical deconvolution methods. However, this hardware limit made resolving any water plasma definitively impossible, as these are expected to decay orders of magnitude faster. Additionally, the oscilloscope used to capture the averaged photodiode signal was limited to a bit depth of 8, and its legacy data transfer architecture prevented exporting consecutive signals individually, which would have otherwise allowed for higher effective bit rates in post-processing.

Since the interaction dynamics of these materials are complex, the overall thesis for this project was inherently open-ended and exploratory. Much time was spent on continuously formulating and testing different hypotheses, over time converging towards the overarching narrative presented in this report. Due to time constraints this iterative process inevitably left a number of loose ends on the experimental side, where additional follow-up experiments would have been useful to provide deeper insights into phenomena discovered during the data analysis. A full list of follow-up experiments will not be provided here; rather, a list of avenues we consider particularly interesting for future research will be discussed in the following section.

7.4 Proposals for Future Investigations

The physical system explored in this project comprises many interacting, nonlinear phenomena that individually have received attention in fundamental physics research, such as the different nonlinear optical effects, laser-induced shockwave generation, and plasma expansion and decay dynamic. The challenge in this project was to bring these individual branches of research together to form a more cohesive picture in the context of bone tissue microtomy. Based on the theory and empirical results presented in this report, we propose avenues for future investigation that address the main concerns raised previously in this work.

7.4.1 Review Paper or Compendium of the Research Field

As mentioned in the introduction, there already exist a number of very insightful papers, especially by Vogel et al. [6], that are highly recommended as a first reading when entering the field. Complementing this paper are most of the other cited works in this thesis. It is not the case that there isn't much useful information on the subject, but rather that all this useful information is spread thin across many papers and other literature spanning more than 20 years. Even just covering all the bases necessary to confidently interpret the baseline investigations done in this work required reading dozens of papers published over the last 30 years.

Therefore, although it would undeniably be an enormous undertaking, we strongly recommend an effort to compile as much as possible of all of the theory, implementation strategies, results, and what the current state of the research field is into a single seminal review paper or compendium. This would be invaluable for anyone entering the field, but not less so for those already part of it. It would anchor all of the necessary theory to prevent misconceptions from being perpetrated (which is unavoidable in the current state of the field due to the vast breadth of physical processes involved; we make no illusions about this work being free from such misconceptions), be a great source to read up on all of the different research areas currently being investigated, and could identify topics that seem particularly promising or require more attention.

7.4.2 Humidified Air Streams

Our results concluded that ambient air was the optimal bulk propagation medium because of the severe nonlinear effects and bubble formation observed in water. This raises the question of how best to mitigate biological tissue dehydration. Thin-film liquid coating is the current standard and avoid most of the identified problems of bulk water, but another promising possibility is active humidified air streams. Research should investigate whether fully saturated, droplet-free air streams can simultaneously fulfill two functions: preserving the hydration of the tissue surface, and removing ejected material. Studies should focus on quantifying the dehydration rates in ambient air, with liquid coating, and with humidified air, respectively, as well as the required gas flow rates necessary to effectively remove material depending on parameters like pulse energy and repetition rate.

7.4.3 Trench Geometry and Dynamic Pulse Energy Tuning

As established by both theoretical arguments and experimental results in this work, the geometry of the ablation zone acts as the primary physical constraint on the expansion of the plasma, leading to a plume formation in the case of a solid-gas interface. Within this context, while a flat interface offers maximum geometric freedom, continuous ablation of a material inherently carves an increasingly deep trench. This further restricts plume expansion and increases the risk of trapping ablated material that subsequently diffuses its energy thermally to the surroundings. Future investigations should systematically quantify how evolving trench dimensions affect material ejection rates and the corresponding safe upper limit for incident pulse energy (given a specific pulse shape). Ultimately, this research should aim to develop a framework for the dynamic, real-time attenuation of laser pulse energy during a microtomy session in order to maximize overall ablation efficiency while avoiding tissue damage.

7.4.4 Predictive Parameter Optimization Model

The strategy proposed in this report for determining ideal pulse characteristics is only a preliminary framework. Currently, establishing the optimal balance between pulse duration, shape, energy, and repetition rate still requires empirical calibration. Ideally, a generalized, quantitative predictive model that can predict an optimal parameter window based on laser and material properties should be developed. By combining nonlinear pulse propagation solvers (such as Luna) with established hydrodynamic models for shockwave formation and propagation as well as inverse bremsstrahlung heating rates, it should in principle be possible to construct such a model. This would allow researchers and engineers to input their specific laser system parameters alongside target material properties (density, composition, ionization potentials, compressive strength, etc.) to output an optimal operating parameters window, eliminating the need for blind empirical parameter sweeping and reducing the risk of damaging the material.

8. Conclusion

In this thesis, the spatial, spectral, and temporal characterization of femtosecond laser-induced plasmas in air, water, and bone tissue has been achieved through high-speed spatial imaging, VIS–NIR spectrometry, and ultrafast photodiode detection. Together with the relevant theory, a physical framework for the fundamental interaction between ultrafast lasers and different materials has been formulated, aiming to inform future research in the context of ultrafast laser bone microtomy and similar applications.

The empirical results demonstrated that ambient air is a superior bulk propagation medium to water because of its exceptional pulse-to-pulse stability, minimal nonlinear optical effects, lack of laser scattering, and plasma decay rates on the order of nanoseconds. Conversely, bulk water exhibited laser filamentation, severe spectral broadening, and transient bubble formation that reflected much of the laser light, making it a poor choice as a bulk propagation medium for precise material ablation. Additionally, low-pressure vacuum systems were discarded as an alternative to air because the theoretical advantages, such as fewer nonlinear optical effects and faster material ejection, were heavily outweighed by practical disadvantages, such as cumbersome and expensive implementation, and significant risk of tissue damage and dehydration.

During the ablation of porcine bone, optical breakdown and material ablation were detected at far lower intensities than in air. Using estimates based on the spatial imaging, the effective ablation zone volume along the laser propagation axis was estimated, showing that it grows significantly past the focus. The effective ablation zone naturally grows in size as pulse energy is increased, corroborated by the observed growth in ablation crater size. For the temporal evolution measurements, it was observed that the plasma plume ejects and decays over much longer time spans than the air plasma, lingering all the way into the microsecond regime. This provided direct evidence that plasma shielding effects can become a problem for MHz repetition rate laser systems if no mitigation strategies are employed.

Finally, the theory and empirical observations in this work were used to formulate suggestions for future research in ultrafast laser bone microtomy. These included an effort to produce a comprehensive review paper for the research field; using humidified air streams to simultaneously slow down tissue dehydration and remove ejected material; studying the impact of trench geometries on material ejection rates and whether a dynamic pulse energy tuning strategy could be produced to maximize ablation efficiency; and finally, exploring if a generalized optimal parameter prediction model could be developed to eliminate the need for blind parameter sweeps.

References

- [1] S. Niu et al., “Recent Advances in Applications of Ultrafast Lasers,” *Photonics*, vol. 11, no. 9, p. 857, 2024. DOI: 10.3390/photonics11090857. [Online]. Available: <https://www.mdpi.com/2304-6732/11/9/857>.
- [2] K. König, “Medical femtosecond laser,” *Journal of the European Optical Society-Rapid Publications*, vol. 19, no. 2, p. 36, 2023. DOI: 10.1051/jeos/2023032. [Online]. Available: <https://jeos.edpsciences.org/articles/jeos/abs/2023/02/jeos20220044/jeos20220044.html>.
- [3] H. Lubatschowski, “Overview of Commercially Available Femtosecond Lasers in Refractive Surgery,” *Journal of Refractive Surgery*, vol. 24, S102–S107, 2008. DOI: 10.3928/1081597X-20080101-18.
- [4] D. R. Paschotta, “Mode Locking,” *RP Photonics Encyclopedia*, 2021. DOI: 10.61835/dm2. [Online]. Available: https://www.rp-photonics.com/mode_locking.html.
- [5] R. W. Boyd, *Nonlinear Optics*, 4th ed. San Diego: Elsevier Science & Technology, 2020.
- [6] A. Vogel, J. Noack, G. Hüttman, and G. Paltauf, “Mechanisms of femtosecond laser nanosurgery of cells and tissues,” *Applied Physics B*, vol. 81, no. 8, pp. 1015–1047, 2005. DOI: 10.1007/s00340-005-2036-6. [Online]. Available: <http://link.springer.com/10.1007/s00340-005-2036-6>.
- [7] L. Gemini, S. Al-Bourgol, G. Machinet, A. Bakkali, M. Faucon, and R. Kling, “Ablation of Bone Tissue by Femtosecond Laser: A Path to High-Resolution Bone Surgery,” *Materials*, vol. 14, no. 9, p. 2429, 2021. DOI: 10.3390/ma14092429. [Online]. Available: <https://www.mdpi.com/1996-1944/14/9/2429>.
- [8] L. J. Mortensen et al., “Femtosecond laser bone ablation with a high repetition rate fiber laser source,” *Biomedical Optics Express*, vol. 6, no. 1, pp. 32–42, 2015. DOI: 10.1364/BOE.6.000032. [Online]. Available: <https://opg.optica.org/boe/abstract.cfm?uri=boe-6-1-32>.
- [9] S. H. Chung and E. Mazur, “Surgical applications of femtosecond lasers,” *Journal of Biophotonics*, vol. 2, no. 10, pp. 557–572, 2009. DOI: 10.1002/jbio.200910053. [Online]. Available: <https://onlinelibrary.wiley.com/doi/abs/10.1002/jbio.200910053>.

- [10] S. Svanberg, "Some Medical and Biological Applications of Ultrafast Lasers," in *Ultrafast Optics IV: Selected Contributions to the 4th International Conference on Ultrafast Optics, Vienna, Austria*, F. Krausz, G. Korn, P. Corkum, and I. A. Walmsley, Eds., New York, NY: Springer, 2004, pp. 437–448. DOI: 10.1007/978-0-387-34756-1_55. [Online]. Available: https://doi.org/10.1007/978-0-387-34756-1_55.
- [11] H. Lubatschowski et al., "Medical and biological applications for ultrafast laser pulses," in *Third International Symposium on Laser Precision Microfabrication*, vol. 4830, SPIE, 2003, p. 537. DOI: 10.1117/12.486505. [Online]. Available: <https://www.spiedigitallibrary.org/conference-proceedings-of-spie/4830/1/Medical-and-biological-applications-for-ultrafast-laser-pulses/10.1117/12.486505>.
- [12] F. H. Loesel et al., "Ultraprecise medical applications with ultrafast lasers: Corneal surgery with femtosecond lasers," in *Medical Applications of Lasers in Dermatology, Cardiology, Ophthalmology, and Dentistry II*, vol. 3564, SPIE, 1999, p. 86. DOI: 10.1117/12.339141. [Online]. Available: <https://www.spiedigitallibrary.org/conference-proceedings-of-spie/3564/0000/Ultraprecise-medical-applications-with-ultrafast-lasers--corneal-surgery-with/10.1117/12.339141>.
- [13] T. M. P. Callou, R. Garcia, A. Mukai, S. Bechara, N. Giacomini, and R. Souza, "Advances in femtosecond laser technology," *Clinical Ophthalmology*, p. 697, 2016. DOI: 10.2147/OPTH.S99741. [Online]. Available: <https://www.dovepress.com/advances-in-femtosecond-laser-technology-peer-reviewed-article-OPTH>.
- [14] F. Morales-Wong, A. Navas, G. E. Yañez-Oviedo, and K. Mohamed-Noriega, "Femtosecond laser applications in corneal surgery," *Taiwan Journal of Ophthalmology*, vol. 13, no. 3, pp. 293–305, 2023. DOI: 10.4103/tjo.TJO-D-23-00083. [Online]. Available: <https://pmc.ncbi.nlm.nih.gov/articles/PMC10712744/>.
- [15] H. Lubatschowski, "Laser Microtomy," *Optik & Photonik*, vol. 2, no. 2, pp. 49–51, 2007. DOI: 10.1002/opph.201190252. [Online]. Available: <https://onlinelibrary.wiley.com/doi/abs/10.1002/opph.201190252>.
- [16] C. Kunert-Keil, H. Richter, I. Zeidler-Rentzsch, I. Bleeker, and T. Gredes, "Histological comparison between laser microtome sections and ground specimens of implant-containing tissues," *Annals of Anatomy - Anatomischer Anzeiger*, vol. 222, pp. 153–157, 2019. DOI: 10.1016/j.aanat.2018.12.001. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0940960218301584>.
- [17] P. M. GmbH Rowiak, *Microtomy with Femtosecond Lasers*. [Online]. Available: <https://www.photonics.com/Articles/Microtomy-with-Femtosecond-Lasers/a38890>.

-
- [18] F. G. Will, T. Block, P. Menne, and H. Lubatschowski, "Laser microtome: All optical preparation of thin tissue samples," in *Commercial and Biomedical Applications of Ultrafast Lasers VII*, vol. 6460, SPIE, 2007, p. 17. DOI: 10.1117/12.713905. [Online]. Available: <https://www.spiedigitallibrary.org/conference-proceedings-of-spie/6460/1/Laser-microtome-all-optical-preparation-of-thin-tissue-samples/10.1117/12.713905>.
 - [19] Y. M. Abd El-Aziz et al., "Mastering the art of sectioning: A comprehensive guide to slide-microtome technology and histological applications," *Frontiers in Veterinary Science*, vol. 12, p. 1635706, 2025. DOI: 10.3389/fvets.2025.1635706. [Online]. Available: <https://pmc.ncbi.nlm.nih.gov/articles/PMC12414758/>.
 - [20] H. Lubatschowski, F. Will, S. Przemeck, and H. Richter, "Laser Microtomy," in *Handbook of Biophotonics*, J. Popp, V. V. Tuchin, A. Chiou, and S. H. Heinemann, Eds., 1st ed., Wiley, 2012, pp. 151–157. DOI: 10.1002/9783527643981.bphot014. [Online]. Available: <https://onlinelibrary.wiley.com/doi/10.1002/9783527643981.bphot014>.
 - [21] S. Amini-Nik et al., "Ultrafast Mid-IR Laser Scalpel: Protein Signals of the Fundamental Limits to Minimally Invasive Surgery," *PloS one*, vol. 5, 2010. DOI: 10.1371/journal.pone.0013053.
 - [22] C. Haase, D. Richter, and C. P. Lin, "Laser Micromachining of Bone as a Tool for Studying Bone Marrow Biology," *Methods in molecular biology (Clifton, N.J.)*, vol. 2567, pp. 163–180, 2023. DOI: 10.1007/978-1-0716-2679-5_11. [Online]. Available: <https://pmc.ncbi.nlm.nih.gov/articles/PMC10287113/>.
 - [23] M. Calvarese, T. Meyer-Zedler, M. Schmitt, O. Guntinas-Lichius, and J. Popp, "Recent developments and advances of femtosecond laser ablation: Towards image-guided microsurgery probes," *TrAC Trends in Analytical Chemistry*, vol. 167, p. 117250, 2023. DOI: 10.1016/j.trac.2023.117250. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0165993623003370>.
 - [24] J. Feng et al., "A Review of an Investigation of the Ultrafast Laser Processing of Brittle and Hard Materials," *Materials*, vol. 17, no. 15, p. 3657, 2024. DOI: 10.3390/ma17153657. [Online]. Available: <https://www.mdpi.com/1996-1944/17/15/3657>.
 - [25] D. R. Paschotta, "Chirped-pulse Amplification," *RP Photonics Encyclopedia*, 2021. DOI: 10.61835/3ts. [Online]. Available: https://www.rp-photonics.com/chirped_pulse_amplification.html.
 - [26] A. E. Siegman, *Lasers*. Mill Valley, California: University Science Books, 1986.
 - [27] *Gaussian beam*, 2026. [Online]. Available: https://en.wikipedia.org/w/index.php?title=Gaussian_beam&oldid=1348604652.
 - [28] J. Schwarz, P. Rambo, M. Kimmel, and B. Atherton, "Measurement of nonlinear refractive index and ionization rates in air using a wavefront sensor," *Optics Express*, vol. 20, no. 8, p. 8791, 2012. DOI: 10.1364/OE.20.008791. [Online]. Available: <https://opg.optica.org/oe/abstract.cfm?uri=oe-20-8-8791>.

- [29] I. Betka, *Nonlinear optical refractive index measurements of pure water via Z-scan technique at 800 nm*. 2025. DOI: 10.1364/opticaopen.28357892.
- [30] A. Couairon and A. Mysyrowicz, “Femtosecond filamentation in transparent media,” *Physics Reports*, vol. 441, no. 2, pp. 47–189, 2007. DOI: 10.1016/j.physrep.2006.12.005. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S037015730700021X>.
- [31] A. Braun, G. Korn, X. Liu, D. Du, J. Squier, and G. Mourou, “Self-channeling of high-peak-power femtosecond laser pulses in air,” *Optics Letters*, vol. 20, no. 1, pp. 73–75, 1995. DOI: 10.1364/OL.20.000073. [Online]. Available: <https://opg.optica.org/ol/abstract.cfm?uri=ol-20-1-73>.
- [32] R. R. Alfano and S. L. Shapiro, “Emission in the Region 4000 to 7000 Å Via Four-Photon Coupling in Glass,” *Physical Review Letters*, vol. 24, no. 11, pp. 584–587, 1970. DOI: 10.1103/PhysRevLett.24.584. [Online]. Available: <https://link.aps.org/doi/10.1103/PhysRevLett.24.584>.
- [33] R. R. Alfano and S. L. Shapiro, “Observation of Self-Phase Modulation and Small-Scale Filaments in Crystals and Glasses,” *Physical Review Letters*, vol. 24, no. 11, pp. 592–594, 1970. DOI: 10.1103/PhysRevLett.24.592. [Online]. Available: <https://link.aps.org/doi/10.1103/PhysRevLett.24.592>.
- [34] R. R. Alfano and S. L. Shapiro, “Direct Distortion of Electronic Clouds of Rare-Gas Atoms in Intense Electric Fields,” *Physical Review Letters*, vol. 24, no. 22, pp. 1217–1220, 1970. DOI: 10.1103/PhysRevLett.24.1217. [Online]. Available: <https://link.aps.org/doi/10.1103/PhysRevLett.24.1217>.
- [35] A. Brodeur and S. L. Chin, “Band-Gap Dependence of the Ultrafast White-Light Continuum,” *Physical Review Letters*, vol. 80, no. 20, pp. 4406–4409, 1998. DOI: 10.1103/PhysRevLett.80.4406. [Online]. Available: <https://link.aps.org/doi/10.1103/PhysRevLett.80.4406>.
- [36] L. V. Keldysh, “Ionization in the field of a strong electromagnetic wave,” in *Selected Papers of Leonid V Keldysh*, WORLD SCIENTIFIC, 2023, pp. 56–63. DOI: 10.1142/9789811279461_0008. [Online]. Available: https://www.worldscientific.com/doi/10.1142/9789811279461_0008.
- [37] M. U. Sander, K. Luther, and J. Troe, “On the Photoionization Mechanism of Liquid Water,” *Berichte der Bunsengesellschaft für physikalische Chemie*, vol. 97, no. 8, pp. 953–960, 1993. DOI: 10.1002/bbpc.19930970802. [Online]. Available: <https://onlinelibrary.wiley.com/doi/abs/10.1002/bbpc.19930970802>.
- [38] K. C. Kulander, “Time Dependent Hartree Fock Theory of Multiphoton Ionization,” in *Topical Meeting on Multiple Excitations of Atoms*, Seattle, Washington: Optica Publishing Group, 1986, TuB3. DOI: 10.1364/MEA.1986.TuB3. [Online]. Available: <https://opg.optica.org/abstract.cfm?URI=MEA-1986-TuB3>.
- [39] J. L. Krause, K. J. Schafer, and K. C. Kulander, “Calculation of photoemission from atoms subject to intense laser fields,” *Physical Review A*, vol. 45, no. 7, pp. 4998–5010, 1992. DOI: 10.1103/PhysRevA.45.4998. [Online]. Available: <https://link.aps.org/doi/10.1103/PhysRevA.45.4998>.

-
- [40] M. V. Ammosov, N. B. Delone, and V. P. Krainov, “Tunnel ionization of complex atoms and of atomic ions in an alternating electromagnetic field,” *Soviet Journal of Experimental and Theoretical Physics*, vol. 64, p. 1191, 1986. [Online]. Available: <https://ui.adsabs.harvard.edu/abs/1986JETP...64.1191A>.
 - [41] A. M. Perelomov, V. S. Popov, and M. V. Terent’ev, “Ionization of Atoms in an Alternating Electric Field,” *Soviet Journal of Experimental and Theoretical Physics*, vol. 23, p. 924, 1966. [Online]. Available: <https://ui.adsabs.harvard.edu/abs/1966JETP...23..924P>.
 - [42] A. M. Perelomov and V. S. Popov, “Ionization of Atoms in an Alternating Electrical Field. III.,” *Soviet Journal of Experimental and Theoretical Physics*, vol. 25, p. 336, 1967. [Online]. Available: <https://ui.adsabs.harvard.edu/abs/1967JETP...25..336P>.
 - [43] A. M. Perelomov, V. S. Popov, and M. V. Terent’ev, “Ionization of Atoms in an Alternating Electric Field: II.,” *Soviet Journal of Experimental and Theoretical Physics*, vol. 24, p. 207, 1967. [Online]. Available: <https://ui.adsabs.harvard.edu/abs/1967JETP...24..207P>.
 - [44] N. Shlomo and E. Frumker, “In situ characterization of laser-induced strong field ionization phenomena,” *Light: Science & Applications*, vol. 14, no. 1, p. 166, 2025. DOI: 10.1038/s41377-025-01808-y. [Online]. Available: <https://www.nature.com/articles/s41377-025-01808-y>.
 - [45] X. M. Tong, Z. X. Zhao, and C. D. Lin, “Theory of molecular tunneling ionization,” *Physical Review A*, vol. 66, no. 3, p. 033402, 2002. DOI: 10.1103/PhysRevA.66.033402. [Online]. Available: <https://link.aps.org/doi/10.1103/PhysRevA.66.033402>.
 - [46] T. K. Kjeldsen and L. B. Madsen, “Strong-field ionization of diatomic molecules and companion atoms: Strong-field approximation and tunneling theory including nuclear motion,” *Physical Review A*, vol. 71, no. 2, p. 023411, 2005. DOI: 10.1103/PhysRevA.71.023411. [Online]. Available: <https://link.aps.org/doi/10.1103/PhysRevA.71.023411>.
 - [47] Z. Nie et al., “Cross-polarized common-path temporal interferometry for high-sensitivity strong-field ionization measurements,” *Optics Express*, vol. 30, no. 14, p. 25696, 2022. DOI: 10.1364/OE.463424. [Online]. Available: <https://opg.optica.org/abstract.cfm?URI=oe-30-14-25696>.
 - [48] C. Brahms and J. C. Travers, *Luna.jl*, 2026. DOI: 10.5281/ZENODO.5513570. [Online]. Available: <https://zenodo.org/doi/10.5281/zenodo.5513570>.
 - [49] B. C. Stuart, M. D. Feit, A. M. Rubenchik, B. W. Shore, and M. D. Perry, “Laser-Induced Damage in Dielectrics with Nanosecond to Subpicosecond Pulses,” *Physical Review Letters*, vol. 74, no. 12, pp. 2248–2251, 1995. DOI: 10.1103/PhysRevLett.74.2248. [Online]. Available: <https://link.aps.org/doi/10.1103/PhysRevLett.74.2248>.

- [50] J. Noack and A. Vogel, "Laser-induced plasma formation in water at nanosecond to femtosecond time scales: Calculation of thresholds, absorption coefficients, and energy density," *IEEE Journal of Quantum Electronics*, vol. 35, no. 8, pp. 1156–1167, 1999. DOI: 10.1109/3.777215. [Online]. Available: <https://ieeexplore.ieee.org/document/777215/>.
- [51] E. N. Glezer, C. B. Schaffer, N. Nishimura, and E. Mazur, "Minimally disruptive laser-induced breakdown in water," *Optics Letters*, vol. 22, no. 23, p. 1817, 1997. DOI: 10.1364/OL.22.001817. [Online]. Available: <https://opg.optica.org/abstract.cfm?URI=ol-22-23-1817>.
- [52] T. Juhasz, G. A. Kastis, C. Suárez, Z. Bor, and W. E. Bron, "Time-resolved observations of shock waves and cavitation bubbles generated by femtosecond laser pulses in corneal tissue and water," *Lasers in Surgery and Medicine*, vol. 19, no. 1, pp. 23–31, 1996. DOI: 10.1002/(SICI)1096-9101(1996)19:1<23::AID-LSM4>3.0.CO;2-S. [Online]. Available: <https://onlinelibrary.wiley.com/doi/abs/10.1002/%28SICI%291096-9101%281996%2919%3A1%3C23%3A%3AAID-LSM4%3E3.0.CO%3B2-S>.
- [53] O. Koritsoglou, D. Loison, O. Uteza, and A. Mouskeftaras, "Characteristics of femtosecond laser-induced shockwaves in air," *Optics Express*, vol. 30, no. 21, p. 37 407, 2022. DOI: 10.1364/OE.468224. [Online]. Available: <https://opg.optica.org/abstract.cfm?URI=oe-30-21-37407>.
- [54] B. Strycker, M. Springer, A. Traverso, A. Kolomenskii, G. Kattawar, and A. Sokolov, "Femtosecond-laser-induced shockwaves in water generated at an air-water interface," *Optics Express*, vol. 21, no. 20, p. 23 772, 2013. DOI: 10.1364/OE.21.023772. [Online]. Available: <https://opg.optica.org/oe/abstract.cfm?uri=oe-21-20-23772>.
- [55] M. Vreugdenhil, D. Van Oosten, and J. Hernandez-Rueda, "Dynamics of femtosecond laser-induced shockwaves at a water/air interface using multiple excitation beams," *Optics Letters*, vol. 43, no. 20, p. 4899, 2018. DOI: 10.1364/OL.43.004899. [Online]. Available: <https://opg.optica.org/abstract.cfm?URI=ol-43-20-4899>.
- [56] E. F. Morgan, G. U. Unnikrisnan, and A. I. Hussein, "Bone Mechanical Properties in Healthy and Diseased States," *Annual review of biomedical engineering*, vol. 20, pp. 119–143, 2018. DOI: 10.1146/annurev-bioeng-062117-121139. [Online]. Available: <https://pmc.ncbi.nlm.nih.gov/articles/PMC6053074/>.
- [57] J. M. Alvarino and E. Martinez, "Two-body and three-body atomic recombination reactions," *Journal of Chemical Education*, vol. 60, no. 1, p. 53, 1983. DOI: 10.1021/ed060p53. [Online]. Available: <https://pubs.acs.org/doi/abs/10.1021/ed060p53>.
- [58] J. Zhan et al., "Ablation enhancement and plasma shielding effects during multiple pulses irradiation with different femtosecond laser repetition rates," *Journal of Manufacturing Processes*, vol. 155, pp. 1–11, 2025. DOI: 10.1016/j.jmapro.2025.10.019. [Online]. Available: <https://linkinghub.elsevier.com/retrieve/pii/S1526612525010989>.

-
- [59] Y. Song and Y. Guan, "Magnetic-field-assisted femtosecond laser drilling of bone in ambient environment," in *AOPC 2019: Advanced Laser Materials and Laser Technology*, P. Zhou, J. Zhang, T. Taira, W. Li, and S. Jiang, Eds., Beijing, China: SPIE, 2019, p. 52. DOI: 10.1117/12.2547963. [Online]. Available: <https://www.spiedigitallibrary.org/conference-proceedings-of-spie/11333/2547963/Magnetic-field-assisted-femtosecond-laser-drilling-of-bone-in-ambient/10.1117/12.2547963.full>.
- [60] N. Ren, K. Xia, H. Yang, F. Gao, and S. Song, "Water-assisted femtosecond laser drilling of alumina ceramics," *Ceramics International*, vol. 47, no. 8, pp. 11 465–11 473, 2021. DOI: 10.1016/j.ceramint.2020.12.274. [Online]. Available: <https://linkinghub.elsevier.com/retrieve/pii/S0272884220338906>.
- [61] H. Hou, B. Yang, X. Mao, V. Zorba, P. Ran, and R. E. Russo, "Characteristics of plasma plume in ultrafast laser ablation with a weakly ionized air channel," *Optics Express*, vol. 26, no. 10, p. 13 425, 2018. DOI: 10.1364/OE.26.013425. [Online]. Available: <https://opg.optica.org/abstract.cfm?URI=oe-26-10-13425>.
- [62] S. Zhang and Y. C. Shin, "Hydrodynamic expansion and plume splitting of the ultrafast laser-induced plasma during ablation of multi-element metallic materials under atmospheric condition," *Journal of Applied Physics*, vol. 135, no. 8, p. 083 101, 2024. DOI: 10.1063/5.0180514. [Online]. Available: <https://pubs.aip.org/jap/article/135/8/083101/3266878/Hydrodynamic-expansion-and-plume-splitting-of-the>.
- [63] S. Pokharel and A. A. Tropina, "Characteristics of femtosecond laser induced filament and energy coupling by nanosecond laser pulse in air," *Journal of Applied Physics*, vol. 137, no. 21, 2025. DOI: 10.1063/5.0263315. [Online]. Available: <https://pubs.aip.org/aip/jap/article/137/21/213303/3348548/Characteristics-of-femtosecond-laser-induced>.
- [64] J. Bak, S. Pokharel, R. Miles, and A. Tropina, "Plasma decay and energy coupling of femtosecond laser-induced plasma filaments in N₂–O₂ mixtures," *Journal of Applied Physics*, vol. 138, no. 4, p. 043 302, 2025. DOI: 10.1063/5.0278618. [Online]. Available: <https://doi.org/10.1063/5.0278618>.
- [65] N. L. Aleksandrov et al., "Decay of femtosecond laser-induced plasma filaments in air, nitrogen, and argon for atmospheric and subatmospheric pressures," *Physical Review E*, vol. 94, no. 1, p. 013 204, 2016. DOI: 10.1103/PhysRevE.94.013204. [Online]. Available: <https://link.aps.org/doi/10.1103/PhysRevE.94.013204>.
- [66] A. Patel et al., "Ionization rate and plasma dynamics at 3.9 micron femtosecond photoionization of air," *Physical Review E*, vol. 106, no. 5, p. 055 210, 2022. DOI: 10.1103/PhysRevE.106.055210. [Online]. Available: <https://link.aps.org/doi/10.1103/PhysRevE.106.055210>.

- [67] I. Saxena, K. Ehmann, and J. Cao, “Laser-induced plasma in aqueous media: Numerical simulation and experimental validation of spatial and temporal profiles,” *Applied Optics*, vol. 53, no. 35, p. 8283, 2014. DOI: 10.1364/AO.53.008283. [Online]. Available: <https://opg.optica.org/abstract.cfm?URI=ao-53-35-8283>.
- [68] N. Sakakibara, T. Ito, K. Terashima, Y. Hakuta, and E. Miura, “Dynamics of solvated electrons during femtosecond laser-induced plasma generation in water,” *Physical Review E*, vol. 102, no. 5, p. 053207, 2020. DOI: 10.1103/PhysRevE.102.053207. [Online]. Available: <https://link.aps.org/doi/10.1103/PhysRevE.102.053207>.
- [69] K. Chaudhary, S. Z. H. Rizvi, and J. Ali, “Laser-Induced Plasma and its Applications,” in *Plasma Science and Technology - Progress in Physical States and Chemical Reactions*, IntechOpen, 2016. DOI: 10.5772/61784. [Online]. Available: <https://www.intechopen.com/chapters/49562>.
- [70] N. Kawahara, J. Beduneau, T. Nakayama, E. Tomita, and Y. Ikeda, “Spatially, temporally, and spectrally resolved measurement of laser-induced plasma in air,” *Applied Physics B*, vol. 86, no. 4, pp. 605–614, 2007. DOI: 10.1007/s00340-006-2531-4. [Online]. Available: <https://doi.org/10.1007/s00340-006-2531-4>.
- [71] M. Lamoureux, C. Möller, and P. Jaeglé, “Bremsstrahlung and radiative-recombination emissivity coefficients in non-Maxwellian plasmas,” *Physical Review A*, vol. 30, no. 1, pp. 429–434, 1984. DOI: 10.1103/PhysRevA.30.429. [Online]. Available: <https://link.aps.org/doi/10.1103/PhysRevA.30.429>.
- [72] J.-B. Sirven, B. Bousquet, L. Canioni, and L. Sarger, “Time-resolved and time-integrated single-shot laser-induced plasma experiments using nanosecond and femtosecond laser pulses,” *Spectrochimica Acta Part B: Atomic Spectroscopy*, vol. 59, no. 7, pp. 1033–1039, 2004. DOI: 10.1016/j.sab.2004.05.009. [Online]. Available: <https://linkinghub.elsevier.com/retrieve/pii/S0584854704001375>.
- [73] S. Ichimaru, *Statistical plasma physics* (Frontiers in physics v. 87, 88). Boulder, Colo: Westview, 2004.
- [74] U. Fantz, “Basics of plasma spectroscopy,” *Plasma Sources Science and Technology*, vol. 15, no. 4, S137–S147, 2006. DOI: 10.1088/0963-0252/15/4/S01. [Online]. Available: <https://iopscience.iop.org/article/10.1088/0963-0252/15/4/S01>.
- [75] A. Kramida and Y. Ralchenko, *NIST Atomic Spectra Database, NIST Standard Reference Database 78*, 1999. DOI: 10.18434/T4W30F. [Online]. Available: <http://www.nist.gov/pml/data/asd.cfm>.

A. Appendix

A.1 Iterative Bayesian Deconvolution

Herein is described the motivations behind, and mathematical structure of, the Iterative Bayesian Deconvolution (IBD) algorithm developed for this project. Results on the data for 500 μJ pulse energy, as well as statistical benchmarking, is also included.

A.1.1 Physical Motivation From A Priori Data

When a photodiode absorbs a photon, a characteristic electric current is generated in the active layer, called the *impulse response*. When many different photons are absorbed at different times, the many individual impulse responses will add linearly together to form the total output signal, with reservation for saturation effects in the case of very intense light. Mathematically, this means that any observed non-saturated signal is the integral of the time-distribution of photons (source signal) multiplied by the corresponding impulse response function, given by

$$S_{out}(t) = \int_{-\infty}^{\infty} f_{source}(\tau) S_{impulse}(t - \tau) d\tau. \quad (\text{A.1})$$

For source signals on characteristic time scales much longer than the time scale of the impulse response, the impulse response acts approximately as a delta function, and the output signal will be approximately equal to the source signal. For source signals much shorter than the impulse response, the opposite is true. This is the case when the impulse response was empirically determined using the femtosecond laser as source signal. Plotting the output signal from the plasma using different filters next to the measured impulse response, we can compare the relative time scales.

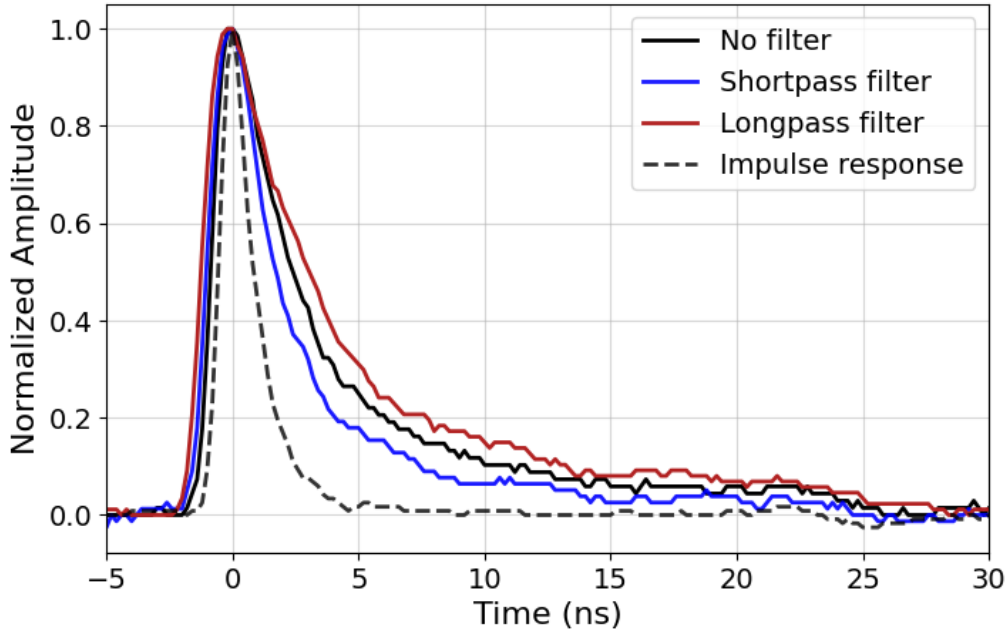


Figure A.1: Measured signal data from the plasma, including using a long-pass and short-pass filter, respectively, compared to the measured impulse response. Pulse energy was $500 \mu\text{J}$.

While the signals plotted in figure A.1 above are normalized to better compare the temporal characteristics, the short-pass signal and long-pass signal are of the same order of magnitude for all pulse energies tested. Two hypotheses can be formulated from the figure:

- 1) The source signal and impulse response function act on comparable time scales.
- 2) The photon emission processes dominant in the short-pass domain (400–700 nm) decay faster than those dominant in the long-pass domain (715–1100 nm), with the unfiltered signal being somewhere in-between.

Point 1) means that in order to model the source signal one must account for the convolution with the impulse response. Point 2) implies that different physical processes are behind the emissions measured in the two wavelength domains. Based on the findings from the spectrometry analysis (section 4.2), we can assume that the short-pass domain will be entirely dominated by continuum emissions, whereas the long-pass domain will be a combination of continuum and atomic transition processes. Because the photodiode is more sensitive to longer wavelengths, the relative contributions from these will be disproportionally large compared to the raw emission spectrum.

In order to do a statistically robust inference of the source signal, an iterative three-step Bayesian inference (BI) strategy was formulated:

- 1) Model the short-pass domain to infer the decay profile of the continuum emission processes.
- 2) Using the parameter posteriors from the previous step to inform the continuum emission profile in the long-pass domain, one can infer the decay profile of the bound-state transition decay profile.
- 3) Finally, using the posteriors from both previous steps, infer the total decay profile for the unfiltered signal.

This three-step model is motivated by statistical funnel analysis: the short-pass domain, being the simplest system with a single dominant physical process, will require fewer statistical parameters and prior information to model. Using the results from this step, one can constrain the priors for the following steps, effectively reducing the number of free parameters. The final step involving the unfiltered data acts as a validation step, since it is assumed this signal should approximately be equal to the sum of the filtered signals. This step has no explicit parameter hierarchy since all of their priors are informed. If the model converges in a stable manner and produces results that correspond to the previous steps, we can assume the model is working as intended and is able to extract the different emission processes.

A.1.2 Model Selection

In order to execute a BI scheme, one first needs a model. Unfortunately, we are faced with trying to model a signal that depends nonlinearly upon very complex phenomena. The plasma emits photons when its electrons and ions interact, for example when they recombine. The intuitive assumption would therefore be that the emission of photons must have some dependence on the rate of decay of the plasma density. Assuming the optical properties of the plasma does not change significantly during the decay process, we can simplify the dependence simply as

$$S_{source}(t) \propto \dot{n}^a(t), \quad (\text{A.2})$$

where a is some unknown power. Furthermore, the rate of decay $\dot{n}$ will itself depend on which continuum emission processes are dominant. In a stable thermal plasma, the emission processes within it would not change in significance over time. However, in our case we are dealing with a highly unstable non-equilibrium plasma that very rapidly expands, cools down, and recombines into a neutral gas.

To take the specific example of radiative electron recombination, which is just one of the processes behind the continuum emissions: it can not be assumed that the rate at which a certain n -body recombination process is taking place is constant over time. The ODE that dictates the recombination process can thus be generalized as

$$\dot{n}(t) = - \sum_{k=1}^{\infty} r_k(t) n^k(t), \quad (\text{A.3})$$

where $k = n - 1$ relates to a specific n -body recombination process, and $r_k(t)$ is its corresponding time-dependent reaction rate. This ODE, even if $r_k(t)$ were known,

very likely does not have a closed-form solution, and is therefore unsuitable to use as a model for a BI scheme. However, knowing that the solution to this ODE, and therefore also to $\dot{n}(t)$, must be monotonically decreasing in time since there is no external energy input into the plasma, we can follow the standard practice in reaction chemistry and simplify the system into a single *effective* decay process

$$\dot{n}(t) \approx \dot{n}_{eff}(t) = \frac{A}{(1 + \frac{t}{\tau})^b}. \quad (\text{A.4})$$

This expression uses only three parameters: A scales it linearly, τ is the characteristic decay rate, and b weighs the (time-averaged) relative importance of different n -body recombination processes. Taking this to the p :th power to get f_{source} does not change its form, allowing us to define our effective source signal model as

$$f(\theta, t) = \begin{cases} \frac{A}{(1 + \frac{t}{\tau})^b}, & t \geq 0 \\ 0, & t < 0 \end{cases}, \quad \theta = \{A, \tau, b\} \quad (\text{A.5})$$

While this form loses much of its diagnostic power in terms of identifying and characterizing specific recombination mechanisms, it is physically well-motivated and not very sensitive to changes within its parameter space. It can also be used to model the combined effects of recombination, Bremsstrahlung and any other continuum (or atomic) emissions as long as they can be considered monotonically decaying processes. This makes it a suitable candidate for a model that allows for stable, statistically robust convergence within a BI scheme.

A.1.3 The Three-Step Algorithm

Using the `emcee` package in Python, a Markov Chain Monte Carlo (MCMC) routine was created in order to implement the 3-step BI scheme. Starting with the shortpass domain, equation A.5 was used as source signal model. This model was then convolved with the impulse response data using `scipy.signal.fftconvolve`, after which an additional nuisance parameter t_{shift} was necessary to shift the convolution output in time to synchronize it with the measured signal. The model was then fitted to the data using positive uniform log-priors and the log-likelihood function

$$L(\theta|\mathcal{D}) = -\frac{1}{2} \frac{SSE(\theta, \mathcal{D})}{\sigma_{noise}(\mathcal{D})}, \quad (\text{A.6})$$

where SSE is the sum of squared errors between the data and model (using θ as parameters), and σ_{noise} the standard deviation of the signal floor noise. This choice of log-likelihood function is used for all steps of the three-step inference process, and is motivated under the assumption that the noise in the data was additive and Gaussian. The resulting median values and standard deviations for the parameters were stored and used to inform the priors in the next step.

For the longpass domain, as stated before, it is assumed that the same continuum decay processes as in the shortpass domain will be present, as well as atomic transitions. Therefore, equation A.5 is modified to include an additional signal term:

$$f_{2-process}(\theta, t) = f(\theta_{cont}, t) + f(\theta_{disc}, t). \quad (\text{A.7})$$

The priors for τ_{cont} and b_{cont} in the first term are Gaussian and informed using the median and standard deviations from the previous step. Its amplitude A_{cont} is a free parameter since it is independent from the previous step. Overall, this first term will have less freedom in parameter space, allowing the new, second term to converge properly. In total, this model has 7 parameters including the additional time shift hyperparameter, of which two are informed and the rest uninformed using uniform log-priors. The fitted median values and standard deviations for the parameters were stored for the next and final step.

The final step is inferring the decay profile of the full, unfiltered signal using the same model as in step 2 (equation A.7). The priors were Gaussian and based on the posteriors from previous steps. The prior for A_{cont} was the sum of the two previous posterior means and variances, while the priors for τ_{cont} and b_{cont} were taken as the average of the two previous posteriors. Finally, the priors for A_{disc} , τ_{disc} , and b_{disc} were taken directly from the posterior in the previous step.

A.1.4 Results

The posteriors for all three steps for the case of 500 μJ pulse energy are presented below in table A.1 and a plot comparing the inferred model to the output signal and the impulse response in figure A.2.

Table A.1: Parameter posteriors (median $\pm$ standard deviation) in the case of 500 μJ pulse energy for the unfiltered data, using equation A.7 as model and informed priors from the filtered data.

Parameter	Short-pass	Long-pass	No filter
τ_{cont} (ns)	0.96 ± 0.04	0.95 ± 0.04	0.87 ± 0.07
b_{cont}	1.41 ± 0.02	1.41 ± 0.02	1.41 ± 0.01
A_{cont}	15.3 ± 0.2	7.7 ± 2.0	23.0 ± 1.1
τ_{disc} (ns)	N/A	2.61 ± 0.31	2.12 ± 0.14
b_{disc}	N/A	1.36 ± 0.03	1.34 ± 0.02
A_{disc}	N/A	11.3 ± 1.6	10.9 ± 1.2

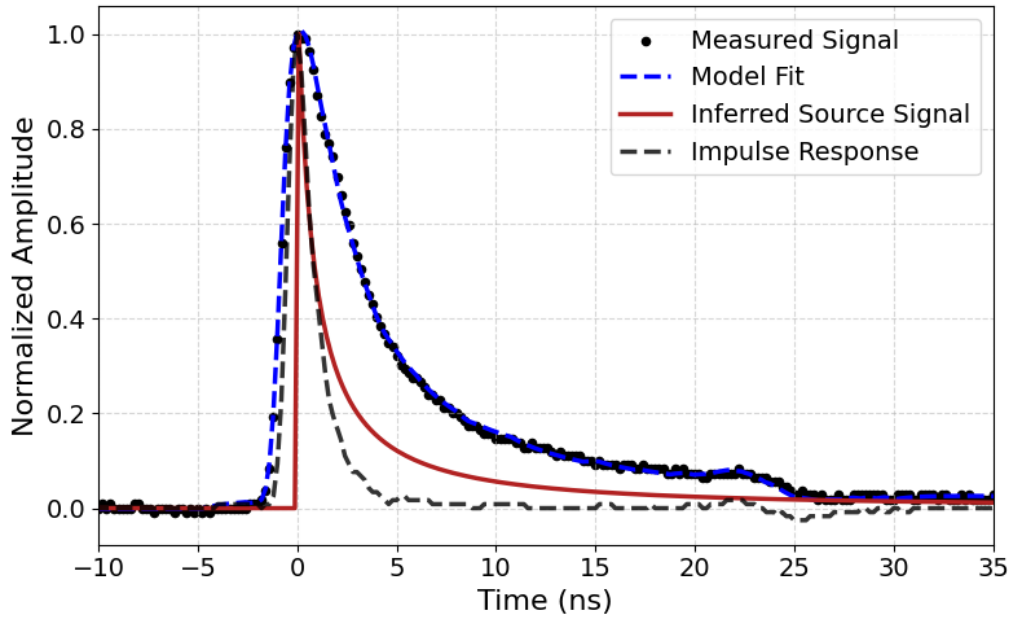


Figure A.2: The model fit compared to measured unfiltered signal data for 500 μJ pulse energy. Included as well is the impulse response and inferred source signal $f(\theta, t)$ for reference.

While the priors were informed, the posteriors could still significantly deviate from these if there was a mathematically superior solution. With this in mind, the results above show remarkable consistency between datasets considering the number of data points and free parameters. The $1\text{-}\sigma$ error bounds of every single parameter overlap, except for τ_{disc} that just barely does not. The p -value for this deviation is only 0.15, which is not statistically significant. That said, the characteristic decay constant τ_{cont} is consistent across all three datasets and always smaller than τ_{disc} despite no such constraint being enforced in the prior for the latter. This is consistent with the observations in figure 4.8 that the processes in the short-pass domain indeed decay faster on average than in the long-pass domain.

The bounds for b_{cont} and b_{disc} , while not overlapping, are still close enough to imply that they are governed by similar physical processes. The amplitudes A_{cont} and A_{disc} , despite having the largest uncertainties, overlap very well and clearly show additive linear behavior as expected ($A_i^{unfiltered} = A_i^{shortpass} + A_i^{longpass}$). Additionally, in the long-pass domain, their relative amplitudes are close to 1 despite no such constraint being enforced. This implies that there indeed are two different dominant physical processes as hypothesized, as otherwise one of them would have been suppressed by the inference model.

Although the physical motivation for this model is strong, it is still good practice to evaluate the statistical rigidity of it. 7 parameters (6 physical + 1 nuisance) is considered many for a 1-D signal regression of this type, and therefore it is entirely possible we are overfitting the data. To simplify the model, we keep the 3-step funnel

analysis structure, but we use only equation A.5 in all three steps. This reduces the total number of parameters down to 4 while still being physically motivated by virtue of being a master equation for monotonically decaying physical processes. The final posteriors are presented below in table A.2.

Table A.2: Parameter posteriors (median $\pm$ standard deviation) in the case of 500 μJ pulse energy for the unfiltered data, using equation A.5 as model.

Parameter	Shortpass	Longpass	No filter
τ (ns)	0.96 ± 0.04	1.45 ± 0.03	1.12 ± 0.02
b	1.41 ± 0.02	1.222 ± 0.007	1.293 ± 0.006
A_1	15.3 ± 0.2	19.3 ± 0.1	32.9 ± 0.2

Since step 1 is identical, the priors in step 2 are just as constrained as before, being informed by the step 1 posteriors. Despite this, the model converges to posteriors far outside the error bounds of the initial informed priors for every single parameter. From a physical perspective, this clearly implies that there are indeed different physical processes behind each wavelength domain and that the inference model is able to explore the parameter space and converge properly.

A.1.5 Benchmarking

In order to evaluate the models from a statistical perspective, a number of common goodness-of-fit tests were used to compare them. The coefficient of determination (R^2) test evaluates a general baseline quality of the fit, while the reduced Chi-squared (χ^2_ν) evaluates how well the model estimates the error variance. The Kolmogorov-Smirnov (KS) test, specifically its p -value, is used to evaluate whether or not the noise is Gaussian (as assumed in the likelihood function, see equation A.6), and can be used together with χ^2_ν to explain possible discrepancies compared to the R^2 value. Finally, the Bayesian Information Criterion (BIC) and Akaike Information Criterion (AIC) are used to compare the statistical validity of using 7 versus 4 parameters. The complete set of test scores is compiled below in table A.3.

Table A.3: Goodness-of-fit scores for the original 7-parameter model (2-process model) compared to the simpler 4-parameter model (1-process model). The best score for each test, whenever applicable, is in bold.

Test	7 parameters	4 parameters
R^2	0.99864	0.99864
χ^2_ν	2.04	2.03
KS p -value	5.3×10^{-18}	1.0×10^{-18}
BIC	-377	-396
AIC	-406	-413

Again, the results are very interesting. The R^2 is identical down to 5 significant digits, implying we are pushing the boundaries of how well the data can be modeled, and the reduced Chi-squared is also almost identical down to 3 significant digits. Because the 4-parameter model overall slightly outperforms the 7-parameter model in these categories, the BIC and AIC scores are unsurprisingly in its favor, albeit still relatively close because of how strong the overall fit was ($R^2 \approx 0.999$). From a statistical perspective, the 4-parameter, 1-process model is superior. It also shows that using a single master equation of the form in equation A.5 to model the combined effects from several nonlinear decay processes is mathematically robust.

From a physical perspective, and especially considering the consistency between datasets, the 7-parameter is still considered the better choice for this system. Statistical goodness-of-fit scores should not rule over physical intuition when the 7-parameter model categorically produces consistent parameter bounds whereas the 4-parameter categorically does not.

Another interesting observation is the discrepancy between the computed R^2 and χ^2_ν values for both models. An R^2 of >0.99 would imply a very good statistical fit, while $\chi^2_\nu \approx 2$ in isolation would be considered no more than acceptable. Because of the former, it is highly likely that the lower χ^2_ν score is due to non-Gaussian noise, rather than the model being wrong. A KS p -value of less than 10^{-17} in both cases (where $p < 0.05$ would be the typical threshold for statistical significance) confirms this is the case, and looking at the residuals over time for the 7-parameter model in figure A.3, it is immediately obvious why. Ignoring the residuals from the actual signal fit starting from around $t = 0$, it is clear that the noise floor in the beginning is not Gaussian, but seem to come in discrete steps of 0.2 mV. Additionally, they do not appear to be randomly distributed, but rather predictably oscillatory in nature.

This is in all likelihood due to hardware artifacts from the oscilloscope (Tektronix TDS 3054). It is an 8-bit digital oscilloscope, meaning it resolves the signal into 256 steps for any given magnification. In the case of the plasma emission signal, this means steps of 0.2 mV. The oscillatory nature is likely due to analog noise drifting over and under the rounding limit, centered at 0. With this in mind, it is still reasonable to use the Gaussian noise approximation for the likelihood function: for one, there is no simple model that would reliably predict these noise artifacts without extensive further testing, and secondly, the gaussian approximation still produces generally very good fits as confirmed by the high R^2 score.

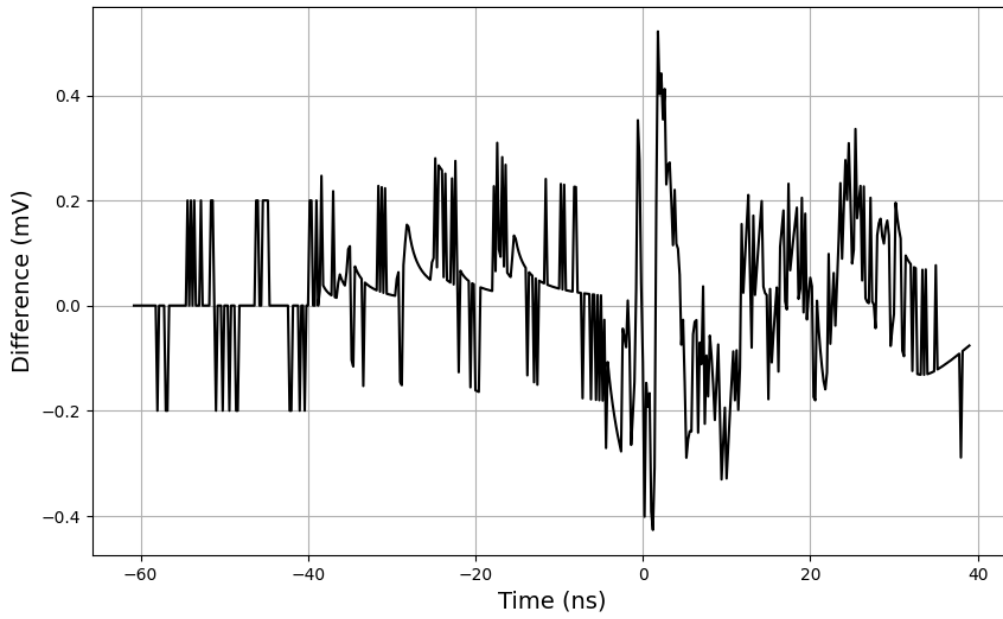


Figure A.3: Residuals for the inferred 7-parameter model for the unfiltered data at 500 μJ pulse energy.

As a final benchmark test for the results, one can try numerically computing the source signal and compare to the physically motivated 2-process (7 parameter) model. Currently, the model is not fitted directly to the data, but is passed through a forward-convolution filter (see equation A.1) and fitted to the measured signal data. Although the convolution process is linear and in principle reversible, it requires additional degrees of freedom even if the output and one of the sources are known. It is in theory possible, therefore, that the source signal has a noticeable different profile from the proposed theoretical model. Specifically, it is of interest to see if a numerically produced source signal also decays monotonically like the theoretical model, which if true would imply we have identified the correct family of equations.

In order to most efficiently reverse the signal convolution for the output data using the impulse response data, a Wiener filter is used. It introduces one degree of freedom, a 'frequency contribution floor', named simply SNR for *Signal-to-Noise Ratio*, in order to prevent frequencies with negligible contributions to the signal from blowing up the calculations. The signals, including the model, are normalized and time shifted with respect to peak amplitude, and evaluated for (Normalized) Root Mean Squared Error (NRMSE) for different SNR values. The results are presented below in figure A.4,

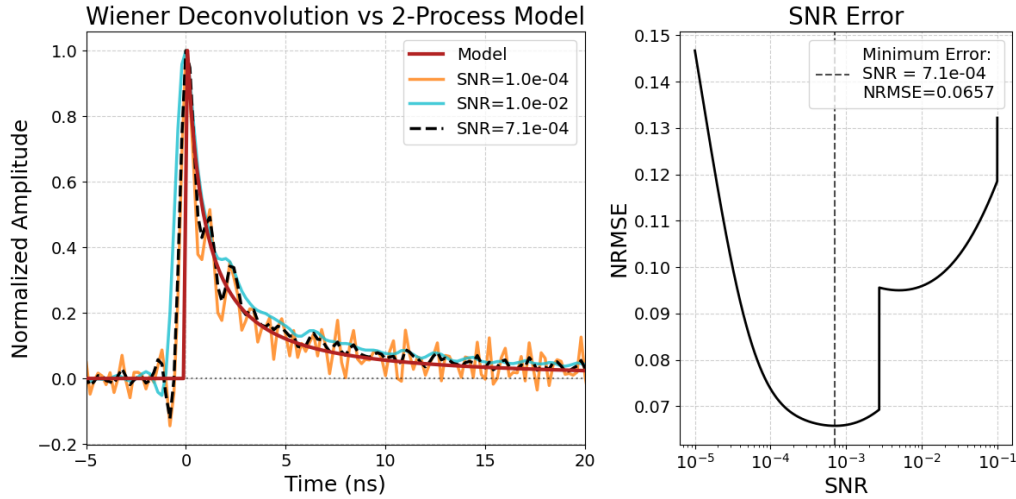


Figure A.4: Left: Deconvolution of the unfiltered signal for different SNR values, including the global minimum, compared to the inferred 2-process model. Right: The NRMSE of the inferred model and the deconvolved signal for a range of SNR values, including the global minimum.

The best SNR value produces an NRMSE of 0.0657, meaning the average variation of the two models is 6.67% of the peak signal amplitude. Considering this is a 1-parameter fit of a signal passed through a filter that notoriously amplifies noise, this is a promising result. Assuming local variations are due to noise amplification, no signs of non-monotonicity is found, further reinforcing the physical motivation of the 2-process model.

A.1.6 Conclusion

The IBD model successfully extracts the two emission process (continuum and discrete) from the captured photodiode data, and performs well during statistical and physical benchmarking. While the inferred parameters on their own do not contain much useful information, they can be used to compare different decay processes to get ballpark estimates for their temporal evolution. However, the model is very sensitive to noise and will not work on very weak signals due to its complex parameter space. Ultimately, we would recommend employing more advanced spectroscopic equipment and techniques to characterize the physical mechanisms directly rather than relying on a statistical model like IBD, but its ability to extract meaningful information from heavily compressed data (i.e. the 1-D photodiode signal) with next to no prior information other than physical intuition, makes it a good exercise in creative problem solving and a demonstration of the power of Bayesian inference.

A.2 Porcine Bone Spectrometry Measurements

A collection of 8 individual spectra captured during the cutting process of porcine bone, divided into 4 groups of similar overall shape, are shown in figure A.5. All individual spectra are averaged over 2 consecutive measurements of 1 second integration time each. The spectrally broadened laser signal was much stronger than any plasma emissions, so in order to get a well resolved plasma signal the integration time was by necessity much longer than the saturation limit for the laser signal.

Variations in relative size of spectral lines, as well as the observed plateaus, are attributed to differences in surface geometry and distance to the focus, which affects both the intensity of the plasma plume and the amount of reflected laser light.

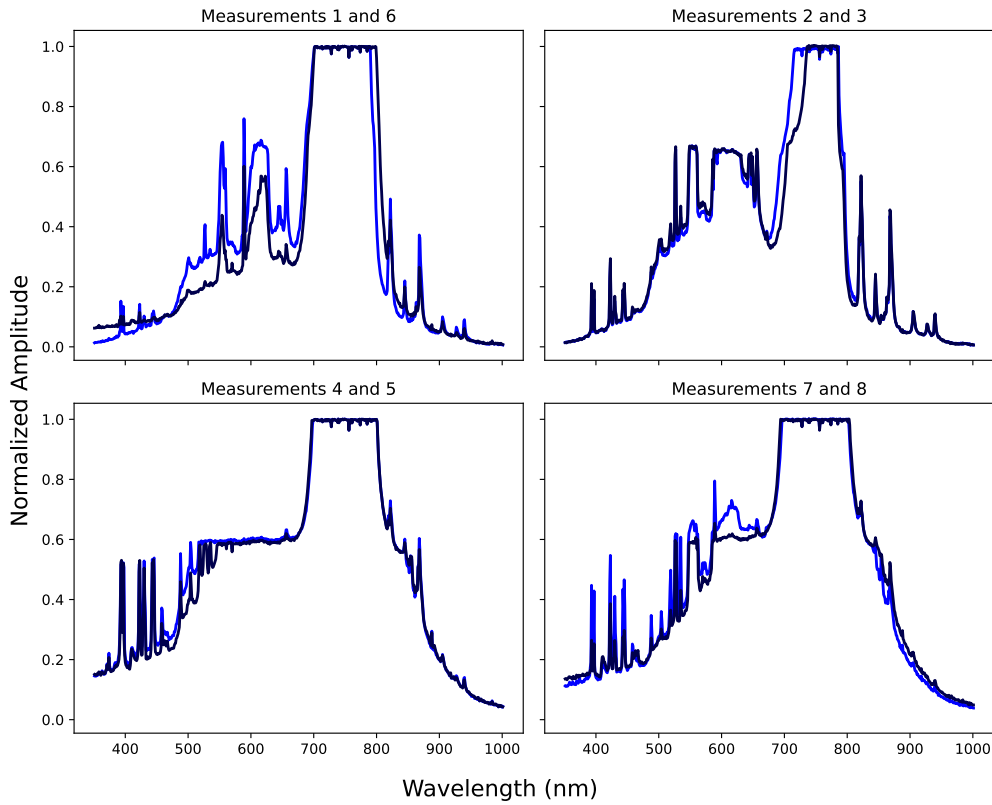


Figure A.5: Measurements taken at different times of the emission spectra generated by ablating porcine bone at at $500 \mu\text{J}$ pulse energy.

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