White Light Continuum for Broadband Nonlinear Spectroscopy

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WHITE LIGHT CONTINUUM FOR BROADBAND NONLINEAR SPECTROSCOPY

by

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Major Professors: David J. Hagan and Eric W. Van Stryland
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ABSTRACT

Supercontinuum (SC) generation, oftentimes referred to as white-light continuum (WLC), has been a subject of interest for more than 40 years. From the first observation of WLC in condensed media in the early 1970s to the first observation of WLC in gases in the mid-1980s, much work has been devoted to developing a framework for understanding the complex nature of this phenomenon as well as discovering its utility in various applications.

The main effort of this dissertation is to develop a WLC for the purpose of broadband nonlinear spectroscopy and use it in spectroscopic measurements. The ability to generate a high-quality, high-spectral-irradiance source of radiation confined in a single beam that spans the visible and near-infrared spectral regimes has great utility for nonlinear measurement methods such as the Z-scan technique. Using a broadband WLC instead of conventional tunable sources of radiation such as optical parametric generators/amplifiers has been shown to increase the efficiency of such measurements by nearly an order of magnitude.

Although WLC generation has many complex processes involved, and complete models of the process involve highly complex numerical modeling, simple models can still guide us in the optimization of systems for WLC generation. In this dissertation the effects of two key mechanisms behind WLC generation in gaseous media are explored: self-phase modulation (SPM) and ionization leading to plasma production. The effects of SPM are largely dependent upon the third-order nonlinear refractive index, $n_2$, of the gaseous medium whereas the effects of plasma production are dependent upon many parameters including the initial number density, ionization potential/energy, and the rate of ionization production. It is found that in order to generate a stable WLC suitable for nonlinear spectroscopy, the phase contributions from SPM and plasma
production should be nearly equal. This guided our experiments in inert gases using mJ level, 150 fs-FWHM (full-width at half-maximum) pulses at 780 nm as well as 40 fs-FWHM pulses primarily at 1800 nm to create a stable, high-spectral-irradiance WLC. The generated WLC is shown to have sufficient spectral energy and spatial quality suitable for nonlinear spectroscopic measurements.

In addition to extending the WLC bandwidth by using a long wavelength (1800 nm) pump source, it is found that by using a secondary weak seed pulse with a peak irradiance three orders of magnitude less than the main pulse, the spectral energy density is enhanced by more than a factor of 3 in Krypton gas for a WLC spectrum that spans over 2 octaves. Numerical simulations are presented which qualitatively describe the experimental results. The spectral enhancement of the WLC by seeding is also demonstrated for other inert gases and condensed media.

Other efforts described in this dissertation include the development of the Dual-Arm Z-scan technique and its extension to measuring thin film nonlinearities in the presence of large substrate signals as well as predicting the $n_2$ spectra of organic molecules (where we can approximate their behavior as if they were centrosymmetric) from knowledge of the one-photon and two-photon absorption spectra using a simplified sum-over-states quantum perturbative model by utilizing a quasi 3-level and quasi 4-level system.
This dissertation is dedicated to my family and in loving memory of my grandmother Annie Ensley, grandfather Howard Brooks, and great-aunt Nadine Ensley.
**ACKNOWLEDGMENTS**

**Faculty Advisors**

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Nearly every morning during the years of my Ph.D. studies, I woke up with one of the same prayers: asking God to use me in the best manner possible. There is a song lyric sung by one of my favorite musicians, Donny Hathaway, in which we says “Lord help me … to inspire those, that need inspiration. Let my life be a sign for the coming generation.” I understand that is/was a tall prayer to take upon, but one I innately inherited considering my chosen career path.

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CHAPTER 1 INTRODUCTION

1.1 Background and Motivation

Supercontinuum (SC) generation, oftentimes referred to as white-light continuum (WLC), is a complex process that is initiated when a laser pulse propagates in a nonlinear medium which leads to the generation of new frequencies. This process has garnered much attention ever since the first observation of small scale frequency shifts in the early 1960s. These effects are primarily due to the optical Kerr effect which results in an irradiance-dependent change in the refractive index whose third-order nonlinear refractive index coefficient is denoted as $n_2$, i.e. $n(I) = n_0 + n_2 I$ where $n_0$ is the linear refractive index. This change in index inherently leads to a lensing effect which can alter the focus of a beam. Additionally, this change in index inherently alters the phase of the beam which leads to instantaneous frequency shifts. In Ref. [1], frequency shifts in carbon disulfide (CS$_2$) and nitrobenzene were observed with an incident 100 kW ruby laser at 694 nm. In Ref. [2], similar frequency shifts in CS$_2$ were observed with respect to different polarization states with a 5 MW ruby laser operating with a pulse width of 50 ns. These early observations, amongst others such as in Ref. [3], prompted numerical studies to explore these frequency shifts where nonlinear effects such as self-phase modulation (SPM), the accumulation of phase arising from propagating through a nonlinear medium and self-steepening (discussed in a subsequent paragraph), which both are dependent on the magnitude of $n_2$, were examined in detail [4, 5].

The first observation of WLC in solid media is attributed to Alfano et al. [6] where ps pulses at 532 nm were focused into flint glass, quartz, and calcite. The observations made by Alfano et al. verified, to a certain extent, the linear relation of propagation distance in the medium to frequency shift with respect to SPM postulated by the authors of Refs. [7, 8]. SPM also predicts a
linear increase of the frequency broadening with respect to irradiance, but the observed broadening in Ref. [6] and many other works did not follow this trend, but was found to be asymmetrical in nature. The self-steepening effect, a distortion of the optical pulse as a result of propagation through a nonlinear medium, was introduced as a manner to describe the asymmetry in the spectral broadening in materials [5]. In self-steepening, the central portion of a pulse travels at a slower speed than the edges of a pulse due to the Kerr nonlinearity, i.e. \( n_2 \). Other efforts to describing asymmetry explored the balance of SPM and dispersion [9].

Fork et al. [10] observed an asymmetric spectrum extending from 410 nm to 909 nm when generating a WLC with 80 fs pulses at 627 nm in ethylene glycol. Thus, most of the broadening observed was to the anti-Stokes side of the pump wavelength. Fork et al. attributed this spectral broadening to SPM, group velocity dispersion (GVD), self-steepening, and possible four-photon parametric mixing which involves the parametric mixing of the pump pulse and frequencies contained in the generated continuum as described in Ref. [11]. This prompted the calculations of Yang et al. [12] which included contributions of SPM and non-resonant four-wave mixing (FWM) into the nonlinear wave equation. The first observations of WLC in gases were made by Corkum et al. [13] in which they also noted the asymmetry of the spectra.

Another important contributor to spectral broadening has been attributed to self-focusing. Self-focusing can be conceptualized as the spatial analog of SPM. Self-focusing is the collapse of a beam due to propagation in a nonlinear medium which has been an observed phenomenon since the mid-1960s [14, 15]. In other words, the focus spot of a light beam is altered compared with its geometrical focus. Much work has been devoted to study the effects of self-focusing with respect
to spectral broadening [16-19]. It is stated in these works that the precursor for WLC generation is beam collapse due to self-focusing.

Similar observations were made to verify self-focusing as a necessity for spectral broadening. Corkum et al. attributed self-focusing as a precursor to the spectral broadening seen in gases due to the dominance of $n_2$ in SPM prior to severe beam modification and the SC threshold being of the same magnitude as the self-focusing threshold [20]. The authors also noted that spectral broadening in gases below the self-focusing threshold is smaller than what is predicted from SPM alone. Others experiments have proven that self-focusing plays a significant role in spectral broadening process [21].

Shortly after Alfano et al.’s observations of SC generation in condensed media, it was hypothesized that one of the mechanisms responsible for halting beam collapse is plasma production [22]. Bloembergen proposed that the strong anti-Stokes broadening with respect to the pump pulse in condensed media was due to this effect. But, for the early studies of WLC generation in gases, it was believed that plasma production could not explain the anti-Stokes broadening [13, 20]. In Ref. [13], 70 fs and 2 ps pulses at 600 nm were used to generate WLC in various gases at different pressures in which the change in frequency on the anti-Stokes portion of the spectrum was nearly the same as the pump frequency. Based upon this, the authors calculated that the irradiance needed would be much larger than the multi-photon ionization threshold of most gases and concluded that plasma production could be eliminated as the direct cause of the blue spectral component and cannot account for a WLC spectrum predominantly Stokes shifted from the pump frequency. Of note, the authors acknowledged that their assumptions were based upon numbers that were not experimentally confirmed. The first observation of self-channeled pulses in air was
made by the authors of Ref. [23]. In their report, high intensity pulses (~10^{13} \text{ W/cm}^2) were propagated through atmospheric air which clamped into a single filament and generated a WLC. This WLC was attributed to the balance of self-focusing in air by plasma production along with natural diffraction. In their calculations, the generated electron density from plasma production was estimated to be ~10^{16} \text{ cm}^{-3} needed to balance the Kerr index change of ~10^{-5}. Numerical simulations performed by the authors of Ref. [24] confirmed the estimated plasma density from Ref. [23] within a factor of 2 thus establishing the balancing of the Kerr index change with the index from the plasma contribution. It was observed in Ref. [25] that rings would form during the filamentation process in air. The self-channeling process was described as a waveguide with the refractive index of the core due to plasma production and the refractive index of the cladding due to the Kerr index. Thus, the formation of rings were determined to be a result of the leaky propagation mode of the self-guiding structure between plasma production and self-focusing termed conical emission. Simulations performed by the authors of Ref. [26] confirmed this phenomenon by adding the plasma contribution into the nonlinear wave equation. They noted not only the inhibition of the self-focusing due to plasma production but the conical emission due to the abundance of plasma.

Self-steepening has been attributed as a major source of the anti-Stokes broadening with respect to the pump frequency for filamentation in gases in Ref. [27] by envokeing the moving-focus model presented in Ref. [28]. The moving-focus model states that a pulse can be viewed as a longitudinal stack of transverse slices each focusing according to the formalism of the critical self-focusing power given in Ref. [16]. Thus, when the Kerr index change equals that from plasma production, different portions of the pulse will travel at a different speeds as mentioned previously. The front part of the pulse would encounter self-focusing, but travel faster than the central part of
the pulse. The back part of the pulse encounters the plasma generated by the peak of the pulse where the intensity is less than the other slices. This leads to the back slice of the pulse traveling faster than the front part of the pulse and eventually catching up with the front part of the pulse. The effects of self-steepening were also presented in the context of filamentation in Refs. [29, 30]. In Ref. [30], the effects of group velocity dispersion (GVD) on the WLC generation were said to become important during the self-steepening process. Plasma production halting the Kerr nonlinearity and GVD being prominent with self-steepening in regards to filamentation have been observed in other works [19, 31].

In recent years, there has been much debate regarding higher order Kerr terms, i.e. related to the 5th, 7th, 9th, etc. order polarization responses, causing the arrest of self-focusing and thus producing plasma-free filamentation [32]. This effort was largely fueled by measurements of the higher-order Kerr coefficients of atmospheric air in Ref. [33]. The authors of Ref. [33] measured alternating signs of the Kerr coefficients such that
\[ n(l) = n_0 + n_2 l + n_3 l^2 + n_4 l^3 + \cdots + n_K l^{K-1} \]
where they determined the 5th order Kerr coefficient \( n_3 \) to be negative, the 7th order Kerr coefficient \( n_4 \) to be positive, etc. In their measurements, the higher-order Kerr coefficients of the constituents of air were measured at a pressure of 100 mbar with peak irradiances either equal to or exceeding 18 TW/cm². Thus, considering only the value of \( n_3 \), the negative change in index from the Kerr nonlinearity using their measured coefficient would range from \(-10^{-6}\) to \(-10^{-5}\). But at these irradiances and corresponding initial number density \(\sim 10^{24} \text{ m}^{-3}\), the plasma nonlinearity would still arise as measured by the authors of Ref. [34] in which they determined an electron density of \(\sim 10^{21} \text{ m}^{-3} - 10^{22} \text{ m}^{-3}\) using similar experimental parameters as Ref. [33] and those used in the simulations of Ref. [32]. The measured electron densities correspond to a change in index due to plasma formation of \(-10^{-7}\) to \(-10^{-6}\). Such magnitudes of the negative contribution from the plasma
are nearly similar to those proposed by the higher-order Kerr contributions. Thus, the measurements of Ref. [34] provided a contradiction to the conjecture and simulations provided in Refs. [32, 33] in that at the irradiances required to see a significant change in index from the higher-order Kerr terms, plasma would be generated which would dominate the nonlinearity. Other efforts such as in Refs. [35, 36] have been made to debunk the role of the higher-order Kerr coefficients being the main mechanism in arresting the self-focusing nonlinearity.

Filamentation and, thus, WLC generation has found utility in many applications such as remote sensing [37, 38] and pulse compression [39, 40]. For the purpose of this dissertation, the aim is to experimentally study WLC generation in gas media for the purpose of broadband nonlinear spectroscopy. By identifying the effects and relative magnitudes of the balancing mechanisms, a high-spatial-quality, high-spectral-irradiance WLC can be obtained for use in the nonlinear characterization of various materials using such methods as the Z-scan technique [41].

As mentioned in the previous paragraphs, there are many complex mechanisms involved in describing WLC. But since the 1990s, it has been established that WLC, specifically as it pertains to gaseous media, is primarily due to the arrest of self-focusing by the plasma nonlinearity. Thus, in this dissertation, the WLC generated by mJ-level, 150 fs-FWHM and 40 fs-FWHM laser sources will be investigated in the context of contributions from $n_2$ and the ionization-induced plasma. It will be shown that the generation of a WLC suitable for nonlinear spectroscopy occurs when the phase contributions from SPM and the plasma are nearly equal. Efforts to extend the usable WLC to longer wavelengths are explored with respect to using weak seed pulses and using a long wavelength pump source (1800 nm).
1.2 Dissertation Outline

Chapter 2 introduces the origins of the nonlinear refractive index and its effects upon SPM and self-focusing, particularly the critical self-focusing power. Chapter 3 introduces the plasma nonlinearity via ionization. It is shown that the plasma produces a negative refractive index change due to the generation of free electrons. The plasma nonlinearity is also discussed with respect to analytical models to predict the rate of ionization and the effects of the plasma on spectral broadening. Chapter 4 presents a derivation of the nonlinear wave equation including the contributions from the nonlinear refractive index and the plasma nonlinearity. The addition of terms via a change in the refractive index as well as various effects arising from nonlinear source terms are also discussed. Chapter 5 describes the laser sources that are used in this dissertation including the optical parametric devices. Chapter 6 briefly details the Z-scan technique and the recently developed dual-arm Z-scan technique. An extension to the dual-arm Z-scan technique for measuring thin film nonlinearities in the presence of large substrate backgrounds is discussed. Also, the modeling of organic molecules in which centrosymmetry is approximated is presented using a quantum perturbative sum-over-states model. Chapter 7 details the WLC experiments using mJ-level 150 fs-FWHM and 40 fs-FWHM laser sources. The spectral enhancement observed in Kr gas using a weak seed is discussed as well as the enhancement observed by using a weak seed in other inert gases and condensed media. Numerical simulations are presented that qualitatively describe the experimental observations of the seeding enhancement in Kr gas. The WLC generated from a long wavelength pump source (1800 nm) is also presented. Chapter 8 summarizes the results of this dissertation as well as proposes work for future research.
CHAPTER 2 THE NONLINEAR REFRACTIVE INDEX

2.1 Origins of the third-order nonlinear refractive index and its affect upon self-phase modulation

Third-order nonlinearities arising from bound-electronic interactions are responsible for such phenomena as third-harmonic generation, Raman scattering, two-photon absorption (2PA), four-wave mixing (FWM), and the optical Kerr effect which can affect WLC. The magnitude of these instantaneous processes depends on the strength of the applied optical field as well as the strength of the dipole response of the medium. For the purposes of this dissertation, there are a mixture of third-order processes as well as higher order processes that WLC is dependent upon. In this section, we derive an expression for the nonlinear refraction (NLR) coefficient describing the intensity dependent refractive index. As we’ll see, this material dependent NLR coefficient leads to effects that affect the propagation of light through media. We start with the time response of the polarization $P$ of a medium being, in general, written as an expansion such that:

$$P(t) = \varepsilon_0 \sum_n \chi^{(n)}(t)E(t)^n,$$

where $\varepsilon_0$ is the vacuum permittivity, $\chi^{(n)}(t)$ is the $n^{th}$ order susceptibility, and $E(t)$ is the electric field. The left-hand-side of Eqn. (2.1) is typically expressed as a power series such that

$$P(t) = P^{(0)}(t) + P^{(1)}(t) + P^{(2)}(t) + \cdots + P^{(n)}(t).$$

Hence, the superscripts denote the order of the response. Momentarily considering only the fields (that is, not considering spatial and temporal dependencies), the electric displacement $D$ is defined as:

$$D = \varepsilon E = \varepsilon_0 E + P,$$
where $\varepsilon = \varepsilon_0 \varepsilon_r$ is the total permittivity of the medium and $\varepsilon_r$ is the relative dielectric permittivity. We now only consider odd terms up to order 3 in Eqn (2.1) since these are the only terms that can have responses at the input frequency. Hence, these are the so-called self-action nonlinearities since they don’t necessitate responses at other frequencies. Considering this and substituting in the expression for the electric displacement $D$, we can solve for the relative dielectric permittivity yielding:

$$\varepsilon_r = 1 + \chi^{(1)} + \chi_{eff}^{(3)} E^2, \quad (2.4)$$

where $\chi_{eff}^{(3)}$ denotes the effective third-order response due to the tensor nature of the susceptibility which will be discussed in a later section. It can be shown that the relation between the refractive index $n$ and $\varepsilon_r$ is given as:

$$n = \sqrt{\varepsilon_r \mu_r}, \quad (2.5)$$

where $\mu_r$, the relative magnetic permeability, is unity for non-magnetic media. Note that the quantities $n$ and $\chi_{eff}^{(3)}$ are typically complex and, thus, have a real and imaginary component. The real and imaginary components correspond to the phase and loss in the medium, respectively. In general the total refractive index including both linear and nonlinear contributions can be expressed as:

$$n = n_0 + \Delta n, \quad (2.6)$$

where $n_0$ is the linear refractive index and $\Delta n$ is the change in index due to various response mechanisms such as cross-phase modulation (XPM) and plasma generation as will be discussed in the subsequent chapter. In the case of self-phase modulation (SPM), this change in index is a Kerr-
type effect and therefore depends on the intensity of the input light. Therefore, we assume a response of the form:

\[
\Delta n = n_2 I,
\]

where \(n_2\) is the third-order nonlinear refractive index and the irradiance \(I\) which is defined as the magnitude of the Poynting vector \(\vec{S} = (1/2)Re|\vec{E} \times \vec{H}^*|\) where \(H\) is the magnetic field can be expressed as:

\[
I = \frac{1}{2} n_0 c \varepsilon_0 |E|^2,
\]

with \(c\) and \(\varepsilon_0\) being the speed of light and vacuum permittivity, respectively. Squaring Eqns. (2.5) and (2.6) and substituting Eqn. (2.7) into the resultant expression allows the following relation to be obtained:

\[
n_0^2 + 2n_0 n_2 I + n_2^2 I^2 = 1 + \chi^{(1)} + \chi_{eff}^{(3)} |E|^2.
\]

where we have also used the expression given in Eqn. (2.4). Note that we are neglecting the imaginary component of \(n\). By equating like terms on both sides of Eqn. (2.9), we arrive at the following:

\[
n_0 = \sqrt{1 + Re(\chi^{(1)})}
\]

\[
n_2 = \frac{Re(\chi_{eff}^{(3)})}{c \varepsilon_0 n_0^2}.
\]

The exact form of \(\chi_{eff}^{(3)}\) in Eqn. (2.11) depends on the incident electric fields as well as the symmetry of the medium which will be discussed in Section 2.3. Hence \(n_2\) describes the change in refractive index of a material due to an increasing electric field strength and is directly proportional to the nonlinear polarization response of order 3. Since the nonlinear polarization is time-
dependent, it follows that Eqn.(2.7) has a time dependency of $\Delta n(t) = n_2 I(t)$ where, again, $I(t) \propto |E(t)|^2$. To get the frequency components of the electric field, we can take a Fourier transform defined as:

$$E(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E(t) e^{i\omega t} dt,$$

(2.12)

where $E(\omega)$ represents the electric field spectrum in terms of the angular frequency $\omega$. We can define our temporal envelope to have a carrier phase that propagates in the $z$-direction with a central frequency $\omega_0$ such that:

$$E(z, t) = A(t) e^{i(kz - \omega_0 t)},$$

(2.13)

where $A(t)$ is the envelope function, $k = k_0 n$ where $k_0$ is the vacuum wavenumber defined as $2\pi/\lambda_0$, $\lambda_0$ is the vacuum wavelength, $n$ takes the form of that given in Eqns. (2.6) and (2.7), and $\omega_0$ is defined as $2\pi c/\lambda_0$. If we assume a temporally Gaussian envelope function (which is the case for all experiments presented in this thesis) of the form $A(t) = e^{-t^2/2\tau^2}$, where $\tau$ is the temporal width at HW 1/e M of the irradiance, substitution of Eqn. (2.13) into Eqn. (2.12) leads to:

$$E(z, \omega) = \frac{e^{ik_0 n_0 z}}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-t^2/2\tau^2} e^{i[k_0 n_2 I(t)z]} e^{i(\omega - \omega_0)t} dt,$$

(2.14)

where $I(t)$ is of the form given in Eqn. (2.8) and we have substituted in the expression for $\Delta n$. Taking the squared modulus of Eqn. (2.14) leads us to the power spectrum, or spectral intensity, $S(z, \omega)$ of the pulse given as:

$$S(z, \omega) \propto \left| \int_{-\infty}^{\infty} e^{-t^2/2\tau^2} e^{i[k_0 n_2 I(t)z]} e^{i(\omega - \omega_0)t} dt \right|^2.$$

(2.15)
Thus we can observe the frequency dependence of a temporally Gaussian pulse as it propagates through a medium of length $z$. This phase accumulation through propagation through a nonlinear medium is referred to as self-phase modulation (SPM). Thus, for large $E$ field magnitudes, i.e. large irradiance, $\Delta n$ increases and the total phase accumulation due to propagation in the medium becomes appreciable which causes spectral broadening of the input pulse.

![Figure 2-1. Calculation of Eqn. (2.15) in terms of (a) the angular frequency and (b) the wavelength. The black and red solid lines represent the input pulse spectrum for a 150 fs and 40 fs pulse, respectively. The dotted lines represent the spectrum after phase accumulation through $z = 1$ m of a medium with $n_2 = 1 \times 10^{-23}$ m$^2$/W for the two different pulse width inputs. The phase term is defined as $\phi(z, t) = k_0 \Delta n(t) z$.](image)

The solid black and red lines in Figure 2-1 represent the initial pulse spectrum, with $\Delta n(t) = 0$, pulse inputs of 150 fs and 40 fs (FWHM), respectively. The width of the pulse in the frequency domain is related to the width of the pulse in the time domain meaning $\Delta \omega \sim 1/\Delta \tau$, i.e. the narrower the pulse in the time domain the broader the pulse is in the frequency domain. From Eqn. (2.12), the relation between the bandwidth and pulse width of a Gaussian beam can easily be derived and is given as:

$$12$$
Hence, the initial bandwidth is larger for the 40 fs pulse than the 150 fs pulse. As \( \Delta n(t) \) increases, the input spectrum broadens due to SPM which is shown as the dotted lines in Fig. 1.1. The phase accumulation, \( \phi(z, t) = k_0 \Delta n(t) z \), is calculated through a medium of length \( z = 1 \) m with \( n_2 = 1 \times 10^{-23} \) m\(^2\)/W using pulse energies of 120 \( \mu \)J and 400 \( \mu \)J for the 40 fs and 150 fs pulse, respectively, at a center wavelength of 780 nm. From Figure 2-1, the spectral broadening is much more significant for the short pulse input even though the phase accumulation is kept nearly the same. This is due to the difference in the initial bandwidths. Notice that plotting the broadening in terms of the angular frequency is symmetric with respect to the central frequency for a temporally Gaussian pulse. This phenomenon is due to the nonlinear phase function being symmetric, i.e. \( \Delta n(t) = \Delta n(-t) \). Therefore, SPM produces symmetric frequency broadening with respect to the central frequency for symmetric input pulses and response functions. As will be discussed in a subsequent chapter, the parameters used in these calculations are similar to those used to generate WLC in gas. Thus, the calculations presented here give an insight to how much spectral content is expected to be generated from SPM.

2.2 Self-focusing

Another important manifestation of the \( n_2 \) in materials can lead to a change in the spatial properties of an optical beam. Any material possessing an \( n_2 \) can undergo self-lensing, also known as a “Kerr-lens”, due to the formulism of Eqn. (2.6). At large enough irradiances, the Kerr-lensing effect can become quite large which can overcome the inherent diffraction of the beam resulting in the beam to collapse upon itself. This is referred to as critical self-focusing. In this section, we briefly
examine this phenomenon and arrive at an expression for this condition. We, thus, utilize Maxwell’s Equations to derive an appropriate wave equation as such:

\[
\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \tag{2.17}
\]

\[
\nabla \cdot \vec{D} = \vec{\rho} \tag{2.18}
\]

\[
\nabla \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t} \tag{2.19}
\]

\[
\nabla \cdot \vec{B} = 0, \tag{2.20}
\]

where \( \vec{B} \) is the magnetic flux density defined as \( \mu \vec{H} \) and \( \mu = \mu_0 \mu_r \) being the total magnetic permeability with \( \mu_0 \) being the permeability of free space, \( \vec{\rho} \) is the surface charge density, and \( \vec{J} \) is the current density. Taking the curl of Eqn. (2.17) and using the identity \( \nabla \times (\nabla \times \vec{E}) = \nabla (\nabla \cdot \vec{E}) - \nabla^2 \vec{E} \), the following is obtained:

\[
\nabla (\nabla \cdot \vec{E}) - \nabla^2 \vec{E} = -\left( \nabla \times \frac{\partial \vec{B}}{\partial t} \right). \tag{2.21}
\]

If the medium is isotropic, there are no source terms (i.e., \( \vec{\rho} = 0 \)), and under time harmonic conditions, i.e. \( \partial / \partial t \rightarrow -i\omega \), plugging Eqn. (2.19) into Eqn. (2.21) leads to:

\[
\nabla^2 \vec{E} = -\omega^2 \mu \varepsilon \vec{E} = -\omega^2 \mu_0 \mu_r \varepsilon_0 \varepsilon_r \vec{E}. \tag{2.22}
\]

Noting that \( n^2 = \varepsilon_r \mu_r, \varepsilon_0 \mu_0 \equiv 1/c^2 \), and \( k_0^2 = \omega^2 / c^2 \) we arrive at the so-called Helmholtz Equation:

\[
\nabla^2 \vec{E} + k^2 \vec{E} = 0, \tag{2.23}
\]

where \( k = k_0 n \). Assuming an electric field of the form:
\[ \vec{E}(x, y, z) = A(x, y, z)e^{ik_0n_0z}, \]  
(2.24)

where \( A(x, y, z) \) is the envelope, and substituting Eqn. (2.24) into Eqn. (2.23) leads to:

\[ \frac{\partial^2 A}{\partial z^2} + 2i k_0 n_0 \frac{\partial A}{\partial z} + \frac{\partial^2 A}{\partial x^2} + \frac{\partial^2 A}{\partial y^2} + (k^2 - k_0^2 n_0^2)A = 0. \]  
(2.25)

Invoking the slowly varying envelope approximation (SVEA), i.e. \( \frac{\partial^2 A}{\partial z^2} \ll 2i k_0 n_0 \frac{\partial A}{\partial z} \), and noting that \( k^2 = k_0^2(n_0 + \Delta n)^2 \), Eqn. (2.25) can be reduced to:

\[ i \frac{\partial A}{\partial z} + \frac{1}{2k_0 n_0} \nabla^2_\perp A + k_0 \tilde{n}_2 |A|^2 A = 0, \]  
(2.26)

where we have introduced the transverse Laplacian \( \nabla^2_\perp = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \), defined \( \tilde{n}_2 \equiv n_2 n_0^2 c \varepsilon_0 \), and neglected the \( \Delta n^2 \) term. The 2\textsuperscript{nd} term of Eqn. (2.26) describes diffraction effects and the last term represents SPM. We can write the Laplacian in cylindrical coordinates keeping only the radial components as \( \nabla^2_\perp = \frac{\partial^2}{\partial r^2} + (1/r) \frac{\partial}{\partial r} \) which yields:

\[ i \frac{\partial A}{\partial z} + \frac{1}{2k_0 n_0} \frac{1}{r} \frac{\partial A}{\partial r} + k_0 \tilde{n}_2 |A|^2 A = 0, \]  
(2.27)

where we have neglected the 2\textsuperscript{nd} order radial derivative since \( (1/r) \partial / \partial r \gg \partial^2 / \partial r^2 \). Following Yariv and Kelley [14, 42], an exact solution to Eqn. (2.27) is not possible. Therefore, we make the ansatz that in describing the initial focusing of a beam we may only consider the transverse dependence in the exponent of an assumed solution. We may then assume a solution as follows [42]:

\[ A(r, z) = \varphi(z)e^{ik_0n_0\tilde{n}_2|\varphi(r,z)|^2z}. \]  
(2.28)

Taking the radial derivative of Eqn. (2.28) yields:
\[
\frac{\partial A(r, z)}{\partial r} = (ik_0n_0\bar{n}_2 z)\phi(z) \frac{\partial|\varphi(r, z)|^2}{\partial r} e^{ik_0n_0\bar{n}_2|\varphi(r, z)|^2 z}.
\]

(2.29)

Defining the variable \( \frac{1}{\rho^2} = -\frac{1}{|A|^2} \frac{1}{r} \frac{\partial|\varphi(r, z)|^2}{\partial r} \) and substituting the resultant expression from Eqn. (2.29) into Eqn. (2.27) leads to:

\[
\frac{\partial A}{\partial z} = \frac{\bar{n}_2}{2\rho^2} |A|^2 Az + ik_0\bar{n}_2 |A|^2 A.
\]

(2.30)

For a Gaussian radial distribution, i.e. \( e^{-r^2/w^2} \) where \( w \) is the beam size at HW \( 1/e^2 \) M of the irradiance, the variable \( \rho \) is a constant which equals \( w/\sqrt{2} \) and the preceding result is valid. It’s clear that the 1\textsuperscript{st} term on the right hand side of Eqn. (2.30) grows with \( z \) while the 2\textsuperscript{nd} term on the right hand side acts upon the phase due to the imaginary component. Following [42], the focusing distance \( z_f \) is defined as the distance in which the change in \( A \) is comparable to \( A \). Thus, Eqn. (2.30) can be simplified to the following considering only the amplitude:

\[
1 \sim \frac{dA}{A} = \frac{\bar{n}_2}{2\rho^2} |A|^2 zdz = \frac{\bar{n}_2}{4\rho^2} |A|^2 z_f^2,
\]

(2.31)

and the focusing distance is, thus, determined to be:

\[
z_f \sim \frac{1}{\sqrt{\bar{n}_2 |A|}} \frac{2\rho}{\sqrt{\bar{n}_2}}
\]

(2.32)

The analysis thus far has neglected diffraction since the transverse dimensions in the assumed solution of Eqn. (2.28) is absent in the expression for the amplitude. We can reintroduce diffractive effects by equating Eqn. (2.32) to the characteristic diffraction length \( z_0 = \pi w^2/\lambda_0 \) of a Gaussian beam (of which this analysis is based). At this point, the focusing effect balances out that due to diffraction, and the beam begins to collapse upon itself. In the literature, this is mainly termed critical self-focusing or self-trapping. The critical power \( P_c \) at which this occurs can be found by
expressing the power in terms of the field amplitude. Since the power $P$ is defined as $\frac{\pi w^2}{2} I$ by use of Eqn. (2.8) and $|E|^2 = |A|^2$ from Eqn. (2.24), $z_f$ becomes:

$$z_f = w^2 \frac{\pi n_0 c \varepsilon_0}{\sqrt{2\tilde{n}_2 P}}.$$  \hspace{1cm} (2.33)

after substituting in the value of the variable $\rho$. Thus, we can find an expression for $P_c$ by equating Eqn. (2.33) with $z_0$:

$$P_c = \frac{n_0 c \varepsilon_0 \lambda_0^2}{2\pi \tilde{n}_2}.$$  \hspace{1cm} (2.34)

Substituting our previous definition of $\tilde{n}_2$, Eqn. (2.34) becomes:

$$P_c = \frac{\lambda_0^2}{2\pi n_0 n_2}.$$  \hspace{1cm} (2.35)

It is often noted that the initiation of WLC occurs when the optical beam power is greater than $P_c$. The experimental results presented in CHAPTER 7 will revisit this point. Note that the result derived in Eqn. (2.35) is nearly identical to that obtained in Ref. [16].

2.3 The nonlinear refractive indices of gases

In Section 2.1, we developed a general picture of the origin of the nonlinear refractive index and how it relates to the third-order susceptibility. We also observed how this nonlinear refractive index is responsible for spectral broadening and pulse collapse when high intense light propagates through certain media. In order to fully characterize the extent in which these phenomena occur, a more detailed description of the polarization response is needed. For the scope of this thesis, we’ll concentrate mainly on gaseous media. Thus, to determine the $n_2$ of a gas medium, we revisit the
polarization response terms of Eqns. (2.1) and (2.2) such that we can represent the 3rd order polarization response as a convolution of the form:

\[
P^{(3)}(t) = \varepsilon_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi_{i j k l}^{(3)}(t - \tau_1, t - \tau_2, t - \tau_3) E_j(\tau_1) E_k(\tau_2) E_l(\tau_3) d\tau_1 d\tau_2 d\tau_3,
\]  

(2.36)

where the subscripts \(i, j, k, l\) represent the polarizations of the incident electric fields and we note that the third-order susceptibility is a fourth rank tensor. We represent the third-order susceptibility in the frequency domain by the use of the following transform:

\[
\chi_{i j k l}^{(3)}(\omega_1, \omega_2, \omega_3) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi_{i j k l}^{(3)}(t_1, t_2, t_3) e^{i(\omega_1 t_1 + \omega_2 t_2 + \omega_3 t_3)} dt_1 dt_2 dt_3,
\]  

(2.37)

and we can represent the left hand side of Eqn. (2.36) in terms of the input frequency such that:

\[
P^{(3)}(t) = \varepsilon_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi_{i j k l}^{(3)}(\omega_1, \omega_2, \omega_3) E_j(\omega_1) E_k(\omega_2) E_l(\omega_3) e^{i(\omega_1 + \omega_2 + \omega_3) t} d\omega_1 d\omega_2 d\omega_3.
\]  

(2.38)

It follows from the Delta function Fourier transform that Eqn. (2.38) can be re-written as:

\[
P^{(3)}(\omega) = \varepsilon_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi_{i j k l}^{(3)}(\omega_1, \omega_2, \omega_3) E_j(\omega_1) E_k(\omega_2) E_l(\omega_3) \delta(\omega - \omega_1 - \omega_2 - \omega_3) d\omega_1 d\omega_2 d\omega_3.
\]  

(2.39)

In the general case, the frequencies can be different such that the incident electric field can be written as a superposition of monochromatic waves so that:

\[
E(\omega_i) = \frac{1}{2} \sum_n (E_{\omega n}(\delta(\omega_i - \omega_n)) + c.c.),
\]  

(2.40)
and \( c.c. \) stands for the complex conjugate. For the general case of 3 different input frequencies, there are 6 different terms in Eqn. (2.40). Thus, plugging these terms back into Eqn. (2.39) would yield 216 total terms coming from 6 terms each for the \( j,k, \) and \( l \) polarizations. Some major simplifications can be made by considering cases for when \( \omega_1, \omega_2, \) and \( \omega_3 \) are degenerate as well as considering the symmetry of the medium. The forms of the third-order susceptibility for various nonlinear phenomena are given in Table 2-1.

Table 2-1. The forms of the third-order susceptibility for various nonlinear processes. These are taken from Ref. [43].

<table>
<thead>
<tr>
<th>( \chi^{(3)}(3\omega; \omega, \omega, \omega) )</th>
<th>Third-harmonic generation (3HG or THG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi^{(3)}(\omega; \omega, -\omega, \omega) )</td>
<td>3rd order nonlinear refraction</td>
</tr>
<tr>
<td>( \chi^{(3)}(\omega_1; \omega_1, \omega_2, \omega_3) )</td>
<td>Self-phase Modulation (SPM)</td>
</tr>
<tr>
<td>( \chi^{(3)}(\omega; \omega, \omega, -\omega) )</td>
<td>Degenerate Four-Wave Mixing (DFWM)</td>
</tr>
<tr>
<td>( \chi^{(3)}(\omega_4; \omega_1, \omega_2, \omega_3) )</td>
<td>General Four-Wave Mixing (FWM)</td>
</tr>
<tr>
<td>( \chi^{(3)}(\omega; \omega, \omega, -\omega) )</td>
<td>Two-photon absorption (2PA)</td>
</tr>
</tbody>
</table>

For the scope of this thesis, we are concerned mostly with the polarization response at the same frequency as the input. Such responses are coined self-action nonlinearities. For the case of 3rd order nonlinear refraction, SPM, and degenerate four-wave mixing (DFWM), by using intrinsic permutation symmetry, it can be shown that we can express Eqn. (2.39) as [43]:

\[
P_x^{(3)}(\omega) = \frac{3}{4} \varepsilon_0 \chi_{xxx}^{(3)}(\omega; \omega, -\omega, \omega) |E_x(\omega)|^2 E_x(\omega),
\]

(2.41)
where we have assumed the polarization response is along one direction (here, we arbitrarily set this as the x-direction). This formulism leads to an expression for $n_2$ as [44]:

$$n_2 = \frac{3}{4n_0^2 c \varepsilon_0} Re \left( \chi^{(3)}_{xxxx} (\omega; \omega, -\omega, \omega) \right). \quad (2.42)$$

Notice that the more complete form of Eqn. (2.42) mimics the general form of Eqn. (2.11) except for the pre-factor determined by intrinsic permutation symmetry.

The determination of $n_2$ for various gases has been a widely studied topic [33, 45-47]. One of the most cited works has been that of Lehmeier et al. [48] in which they determined the nonlinear hyperpolarizability, $\gamma^{(3)}$, via 3rd harmonic generation (3HG) using picosecond pulses at 1055 nm. Note, however, that the polarization response from 3HG differs from that of degenerate NLR as given in Table 2-1. Thus, the deduction of the NLR coefficient can vary due to the difference in the susceptibility tensor. In order to deduce $n_2$, we need to convert the microscopic $\gamma^{(3)}$ to the macroscopic $\chi^{(3)}$ by the following relation [49]:

$$\chi^{(3)} = \varepsilon_0^{-1} N_0 f^{(3)} \gamma^{(3)}, \quad (2.43)$$

where $N_0$ is the number density of molecules and $f^{(3)} = \frac{1}{3^4} [\varepsilon_r(\omega_1) + 2][\varepsilon_r(\omega_2) + 2][\varepsilon_r(\omega_3) + 2] [\varepsilon_r(\omega_1 + \omega_2 + \omega_3) + 2]$ is the third-order local field correction. The values of $\gamma^{(3)}(3\omega; \omega, \omega, \omega)$ experimentally determined via 3HG for the inert gases are listed in Table 2-2.
Table 2-2. Experimental values of the nonlinear hyperpolarizability $\gamma^{(3)}$ for the inert gases via third-harmonic generation taken from Ref. [48].

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\gamma_{mks}^{(3)} (3 \omega; \omega, \omega, \omega)$ $(10^{-64} \text{Coulomb} \cdot \text{m}^4/\text{V}^3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.13</td>
</tr>
<tr>
<td>Ne</td>
<td>2.03</td>
</tr>
<tr>
<td>Ar</td>
<td>26.5</td>
</tr>
<tr>
<td>Kr</td>
<td>72.2</td>
</tr>
<tr>
<td>Xe</td>
<td>212</td>
</tr>
</tbody>
</table>

The experimentally obtained $\gamma^{(3)}(3 \omega; \omega, \omega, \omega)$ from Ref. [48] agreed with measurements performed by the dc Kerr effect in Ref. [50] which has the form of $\gamma^{(3)}(\omega; 0,0, \omega)$. Since these two measurements produced similar values, it can be assumed that there are no 0 frequency resonances that affect the spectral dispersion of $\gamma^{(3)}$, i.e. it is constant. Furthermore, the values obtained at the measured wavelengths can be considered the static limit values (sometimes referred to as the DC limit, $\omega \rightarrow 0$) which allows us to relate $\chi^{(3)}(3 \omega; \omega, \omega, \omega)$ and $\chi^{(3)}(\omega; \omega, -\omega, \omega)$. In the DC limit, the relation is as follows [51]:

$$3\chi^{(3)}(3 \omega; \omega, \omega, \omega) = \chi^{(3)}(\omega; \omega, -\omega, \omega).$$  \hspace{1cm} (2.44)

This allows us to determine $n_2$ with respect to $\gamma^{(3)}(3 \omega; \omega, \omega, \omega)$ via Eqns. (2.42), (2.43), and (2.44) as:
\[ n_2 = \frac{9N_0 f^{(3)}}{4ce\varepsilon_0^2 n^2} \text{Re} \left( \gamma^{(3)}(3\omega; \omega, \omega, \omega) \right) , \]  

(2.45)

where \( f^{(3)} \) can be simplified to \( \frac{1}{3^4} [\varepsilon_r(\omega) + 2]^3[\varepsilon_r(3\omega) + 2] \).

The linear refractive index for the inert gases can be expressed in a Sellmeier-type equation and the coefficients were determined in Ref. [52] and are displayed in Table 2-3.

\[ n_0^2(\lambda) - 1 = A_0 \left( 1 + \sum_{n=1} A_n \frac{1}{\lambda^{2n}} \right) . \]  

(2.46)

In Eqn. (2.46), \( \lambda \) is given in Angstroms.

<table>
<thead>
<tr>
<th>Gases</th>
<th>( A_0(10^{-4}) )</th>
<th>( A_1(10^5) )</th>
<th>( A_2(10^{11}) )</th>
<th>( A_3(10^{17}) )</th>
<th>( A_4(10^{24}) )</th>
<th>( A_5(10^{30}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.6927</td>
<td>2.24</td>
<td>0.594</td>
<td>0.172</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ne</td>
<td>1.335</td>
<td>2.24</td>
<td>0.809</td>
<td>0.356</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>5.547</td>
<td>5.15</td>
<td>4.19</td>
<td>4.09</td>
<td>0.432</td>
<td></td>
</tr>
<tr>
<td>Kr</td>
<td>8.377</td>
<td>6.7</td>
<td>8.84</td>
<td>14.9</td>
<td>2.74</td>
<td>5.1</td>
</tr>
<tr>
<td>Xe</td>
<td>13.66</td>
<td>9.02</td>
<td>18.1</td>
<td>48.9</td>
<td>14.5</td>
<td>43.4</td>
</tr>
</tbody>
</table>

The refractive index of gases is pressure \((P)\) and temperature \((T)\) dependent such that [48, 53]:

\[ n(\lambda, P, T) = \left( 2 \frac{n_0(\lambda)^2 - 1}{n_0(\lambda)^2 + 2 P_0 T} + 1 \right)^{1/2} \left( 1 - \frac{n_0(\lambda)^2 - 1}{n_0(\lambda)^2 + 2 P_0 T} \right)^{-1/2} , \]  

(2.47)
and $T_0$ and $P_0$ are defined as 273.15 K and 1 atm, respectively, i.e. the values at standard temperature and pressure (STP). It follows from the pressure and temperature dependence of Eqn. (2.47) that the $n_2$ given in Eqn. (2.45) follows the same dependency. This will be revisited in further detail in Section 7.1. Inherently, there is dispersion in $n_2$ due to the dispersion from the refractive index as well as $\gamma^{(3)}$, but far from resonances, the dispersion in both the refractive index and $\gamma^{(3)}$ is flat. Thus, the $n_2$ over a broad spectral range is essentially constant for a given pressure and temperature.

As mentioned briefly before, there has been much work in experimentally determining the nonlinear refractive index of gases. Various experimental measurements for the inert gases are listed in Table 2-4.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>3.40E-25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.20E-25</td>
<td>2.65E-25</td>
</tr>
<tr>
<td>Ne</td>
<td>1.80E-23</td>
<td>8.50E-25</td>
<td></td>
<td></td>
<td></td>
<td>1.40E-24</td>
<td>1.30E-24</td>
</tr>
<tr>
<td>Ar</td>
<td>1.94E-22</td>
<td>7.96E-24</td>
<td>2.00E-23</td>
<td>1.40E-23</td>
<td></td>
<td>1.74E-23</td>
<td>1.30E-24</td>
</tr>
<tr>
<td>Kr</td>
<td>1.89E-23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.03E-23</td>
<td>3.10E-23</td>
</tr>
<tr>
<td>Xe</td>
<td>8.43E-22</td>
<td>5.48E-23</td>
<td></td>
<td></td>
<td></td>
<td>1.12E-22</td>
<td>9.20E-23</td>
</tr>
</tbody>
</table>

The values listed herein were obtained with various methodologies at different wavelengths. Even so, the values are typically within the same order of magnitude, specifically for Kr for which a great deal of the experiments in this thesis are based. Therefore, for the purposes of discussing the WLC characteristic in inert gases as it pertains to the nonlinear refractive index, Eqn. (2.45) in conjunction with Eqns. (2.46) and (2.47) are utilized.
CHAPTER 3 IONIZATION AND THE PLASMA NONLINEARITY

3.1 Derivation of the plasma index

The stabilization of WLC is met by countering SPM with other nonlinear mechanisms. In the case of generation in gaseous media, the main stabilizing mechanism is plasma production through ionization. Ionization is the process by which an electron is removed from an atomic core or molecule, thus generating a charged particle. Thus, the plasma is the state of charged particles of both electrons and ions. As opposed to the increase in the refractive index due to SPM, ionization plays an opposite effect as it decreases the total refractive index. Since the ionization process generates free electrons, the refractive index change due to ionization can be modeled based on Drude theory for an electron gas. This change in refraction can be modeled with the 1st order polarization term of Eqns. (2.1) and (2.2).

To derive this expression, the individual forces acting on a single particle are incorporated into a single equation of motion: the electrical force, restoring force (of which invokes a “Hooke’s law” type expression), and friction/loss mechanisms. The electrical force is given by $-qE$ where $q$ is the electrical charge. The Hooke’s law restoring force is given by $-K\vec{r} = -m_e\omega_0^2\vec{r}$ where $K$ is the effective “spring constant”, $\vec{r}$ is the displacement vector, $m_e$ is the mass of the electron, and $\omega_0 = \sqrt{K/m_e}$ is the frequency of maximum displacement of the electron from the particle. Friction losses can be described by $-m_e\Gamma \vec{v}(t)$ where $\Gamma$ describes the damping rate resulting from radiation, scattering, and/or collision losses, and $\vec{v}(t)$ is the time derivative of the displacement vector. The equation of motion is then written as:

\[ 24 \]
To give the frequency dependence of the terms, we make use of the Fourier transform given in Eqn. (2.12) and the following relation:

\[ \Im \left[ \frac{\partial^n \tilde{r}(t)}{\partial t^n} \right] = (-i\omega)^n \tilde{r}(\omega). \]  

(3.2)

Using the relation of Eqn. (3.2) into Eqn. (3.1) leads to

\[-m_e \omega^2 \tilde{r}(\omega) - i m_e \Gamma \tilde{r}(\omega) + m_e \omega_0^2 \tilde{r}(\omega) = -qE(\omega). \]  

(3.3)

Solving for the displacement vector yields:

\[ \tilde{r}(\omega) = \frac{-q}{m_e} \frac{E(\omega)}{(\omega_0^2 - \omega^2 - i\omega\Gamma)}. \]  

(3.4)

For a molecule or atom, the total response of the polarization \( P \) is the sum over all dipole moments, \( \mu(\omega) = -q\tilde{r}(\omega) \), per unit volume such that \( P(\omega) = N_e \mu(\omega) \) where \( N_e \) is the number density of electrons. From Eqns. (2.1) and (2.2), the polarization can also be expressed as \( P(\omega) = \varepsilon_0 \chi^{(1)}(\omega) E(\omega) \) where we have taken a Fourier transform of the time dependence of the polarization to obtain the frequency dependence and have neglected higher order terms in the susceptibility while only looking at the linear term. We can use this expression along with Eqn. (3.4) to obtain the frequency dependent linear susceptibility:

\[ \chi(\omega) = \frac{N_e q^2}{m_e \varepsilon_0 (\omega_0^2 - \omega^2 + i\omega\Gamma)}. \]  

(3.5)

In the case of plasma generation, the electron can be considered a free particle, i.e. having no immediate restoring force to its parent ion and, thus, \( \omega_0 \to 0 \). By substituting this into Eqn. (3.5),
we arrive at the expression for the linear susceptibility in the presence of no restoring force, the so-called Drude model.

\[ \chi(\omega) = -\frac{N_e q^2}{m\varepsilon_0 (\omega^2 + i\omega\Gamma)}, \]  

(3.6)

If the approximation can be made that energy loss due to radiation and scattering and collisional losses are negligible (which is the case in dilute gases), then in the limit as \( \Gamma \to 0 \), Eqn. (3.6) can be further simplified to:

\[ \chi(\omega) = -\frac{\omega}{\omega^2}, \]  

(3.7)

where we have defined \( \omega_p = \sqrt{N_e q^2/m_e\varepsilon_0} \), as the plasma frequency. The plasma frequency is the natural oscillation of the free electron density and occurs when the real part of the dielectric function is zero. To determine the contribution from the plasma, or collective state that includes the free electrons generated as a result of the ionization process, to the total refractive index, the difference between indices can be found as

\[ n_0^2 - n_{pl}^2 = (1 + \chi_{host}) - (1 + \chi_{plasma}) = (n_0 + n_{pl}) (n_0 - n_{pl}) \approx 2n_0 \Delta n_{pl} \]  

where we have chosen \( n_0 \) as the index of the host medium (gas), \( n_{pl} \) is the index of the plasma whose susceptibility depends on the formalism of Eqn. (3.7), and \( \Delta n_{pl} \) is the change in index due to the plasma. To arrive at this conclusion, the index of the plasma is assumed to be similar in magnitude to that of the gas in equilibrium, i.e. \( n_0 \approx n_{pl} \). This is assuming that, specifically for low density plasmas in gaseous media, the plasma frequency is orders of magnitude less than the optical frequency and the dielectric function of the gaseous media is near unity (\( \chi_{host} \approx 0 \)). Using the free electron susceptibility given in Eqn. (3.7), the change in index due to plasma production can be expressed as:
\[ \Delta n_{pl} = \frac{\omega_p^2}{2n_0\omega^2}. \]  

(3.8)

From Eqn. (3.7) we observe that the plasma always contributes negatively to the total refractive index since the susceptibility arising from the free electrons is negative. To determine the magnitude of \( \Delta n_{pl} \) we must first determine the plasma frequency and, thus, the free electron density. This can be found by employing a rate equation as follows [59]:

\[ \frac{\partial N_e}{\partial t} = R(I)(N_0 - N_e), \]  

(3.9)

where \( R(I) \) is the ionization rate as a function of the irradiance \( I \), and \( N_0 \) is the original number density of atoms or molecules as defined in Section 2.3. For the scope of this thesis, the gas characteristics are such that we assume that all collisions are elastic such that no energy loss occurs in motion, gas motion is random, and there are no intermolecular forces from the gases except when they collide. These assumptions allow us to describe the gas as an ideal gas. Therefore, assuming an ideal gas relation, \( N_0 \) can be determined by the relation \( N_0 = P/k_bT \) where \( k_b \) is Boltzmann’s constant. The rate equation of Eqn. (3.9) assumes single ionization of a particle, i.e. one free electron per atom or molecule, which is valid in most instances since the electric field strengths that we use in our experiments are much less than that to doubly ionize a gas particle. There are other collisional dynamics that can alter the assumption of single ionization which will be discussed in the following section.

The plasma contributes to the overall phase of the medium and, thus, we can determine how the plasma affects spectral broadening as mentioned in Section 2.1. The spectral broadening from the plasma can be derived by expressing the phase incurred from the plasma as \( \phi_{pl} = \)
\( k_0 \Delta n_{pt} z \). Taking the derivative with respect to \( z \) leads to \( d\phi_{pt}/dz = k_0 \Delta n_{pt} \). Taking a time derivative and integrating with respect to \( z \) yields:

\[
\frac{\partial \phi_{pt}}{\partial t} = k_0 \int \frac{\partial \Delta n_{pt}}{\partial t} dz.
\] (3.10)

Since the derivative with respect to \( t \) of the phase incurred from the plasma is the change in frequency \( \Delta \omega_{pt} = -d\phi_p/dt \), substituting Eqns. (3.8) and (3.9) into Eqn. (3.10) leads to the following expression for the change in frequency due to plasma formation

\[
\Delta \omega_{pt} = \frac{k_0}{2n_0 N_c} \int R(I) (N_0 - N_e) \, dz,
\] (3.11)

where we have defined the critical density, \( N_c \equiv \omega^2 m_e \varepsilon_0 q^2 \). The critical density is the number density at which the gas becomes opaque and, hence, \( N_c \gg N_0 \).

Without knowledge of the ionization rate, we can qualitatively describe the spectral broadening due to the plasma by using the Fourier analysis presented at the end of Section 2.1. From Eqns. (3.8) and (3.9), the temporal dependence of \( \Delta n_{pt} \) is due to the temporal dependence of the free electron density \( N_e(t) \). Since \( N_e(t) \) is dependent upon the temporal profile of the input pulse, we can assume Gaussian pulses to determine the formalism for \( \Delta n_{pt}(t) \). Thus, the shape of \( \Delta n_{pt}(t) \) can be approximated by an error-function of the form \( \sim 1 + erf(t/\tau) \) for simplicity. The error function approximates the plasma production correctly because as a pulse propagates through a gaseous medium, the amount of generated free electrons is small far from the peak of the irradiance, increases through the pulse duration, and reaches a “steady-state” value as the irradiance of the pulse again becomes small. This long-lived steady-state is the result of the
electron-ion recombination time being on the order of nanoseconds and, thus, long compared to
the duration of femtosecond pulses [60, 61].

Figure 3-1. Calculation of Eqn. (2.15) in terms of (a) the angular frequency and (b) the wavelength. The black and red solid lines represent the input pulse spectrum for a 150 fs and 40 fs pulse, respectively. The dotted lines represent the spectrum after phase accumulation due to the plasma via Eqn. (3.8) while using the error function formalism to describe $N_e(t)$. The magnitude of the phase is kept the same as that for SPM in Figure 2-1. The phase term is defined as $\phi(z, t)_{PL} = k_0 \Delta n_{pl}(t)z$.

The solid black and red lines in Figure 3-1 represent the initial pulse spectrum for a 150 fs and 40 fs pulse, respectively. The inputs are shown along with the respective spectral broadening due to plasma generation with respect to frequency, Figure 3-1(a), and wavelength, Figure 3-1(b). The plasma generates frequencies that are primarily anti-Stokes shifted from the central frequency of the incident laser pulse. Thus, the argument can be made that plasma is primarily responsible for the higher frequency components in WLC generation. Note that the frequency broadening is asymmetric with respect to the input central frequency. This can be attributed to the response function of the plasma index being asymmetric. We also see a similar trend with respect to SPM.
as more spectral broadening from the plasma is expected to occur with short pulses than long
pulses. The magnitude of the phase is such that it is kept the same as it is in the case of Figure 2-1.

3.2 The Ionization Rate

Ionization can be described in various ways. For example, an electron can be removed from
its ion core via multiphoton ionization (MPI), tunneling, and/or collisional ionization. These
processes often occur concurrently and depends heavily on the magnitude, wavelength, and
duration of the incident pulse. For instance, collisional ionization is not expected to play a role in
ionization processes for pulses shorter than the collision time of the medium [24]. This collision
time, specifically for gases, is typically less than 1 ps. Since the experiments reported in this thesis
are performed with sub-picosecond pulses, the collisional contributions to ionization will be
neglected. To describe the regions in which MPI and tunneling exist in the realm of ionization, an
adiabatic parameter was first proposed by Keldysh [62]. To arrive at this parameter, the mean free
time of an electron passing through a barrier with width equal to the ionization potential \( I_p \) is
considered. The force acting on an electron equals to \( qE \). Thus, the width \( \ell \) of the barrier is defined
as:

\[
\ell = \frac{I_p}{qE} \tag{3.12}
\]

The velocity, \( v \), of an electron as it passes through the barrier is:

\[
\langle v \rangle = \frac{1}{2} \sqrt{\frac{2I_p}{m_e}} \tag{3.13}
\]
such that the mean free time is simply the ratio of Eqns. (3.12) and (3.13) and the bracketed quantity in Eqn. (3.13) represents the average electron velocity. Note that this mean free time is related to the oscillation frequency such that:

\[ f_t = \frac{\langle v \rangle}{\ell} = qE \frac{1}{\sqrt{2m_e I_p}}. \]  

(3.14)

At small frequencies up to \( f_t \), the electron is more probable to tunnel through the barrier within a half-cycle. But at higher frequencies, the tunneling effect, as was argued by Keldysh, should be accompanied by other mechanisms such as multiphoton absorption. Thus, this parameter, oftentimes referred to as the Keldysh parameter, is defined as [59, 62]:

\[ \gamma = \frac{f}{f_t} = \frac{1}{\lambda q} \sqrt{\frac{m_e n_0 c^3 \varepsilon_0 I_p}{I}}, \]  

(3.15)

where \( f = c/\lambda \) is the carrier frequency and we have substituted the irradiance defined in Eqn. (2.8) in place of the electric field. When \( \gamma \gg 1 \), the ionization is mainly MPI whereas for \( \gamma \ll 1 \) the ionization is mainly described by tunneling effects. From Eqn. (3.15), we observe that for short wavelengths, the Keldysh parameter can predict mostly MPI, but for large pulse irradiance, the Keldysh parameter predicts a tunneling effect. In cases when \( \gamma \) is near unity, the processes describing ionization are mixed existing of a mixture of MPI and tunneling.
Figure 3-2. Log-log plot of the calculation of the Keldysh parameter, Eqn. (3.15), for $I = 5 \text{ TW/cm}^2$ and $I_p = 14 \text{ eV}$ (Kr gas). The inset shows the main figure with axes expanded for visible and near-infrared wavelengths. The red dashed line in the inset represents when $\gamma = 1$.

Figure 3-2 shows the plot of Eqn. (3.15) with $I = 5 \text{ TW/cm}^2$ (pulse energy = 400 $\mu$J, beam waist = 180 $\mu$m (HW 1/$e^2$ M), and $\tau = 150$ fs-FWHM) and $I_p = 14$ eV, i.e. that for Kr gas. For this pulse irradiance, the ionization can be described by purely tunneling only for long wavelengths (THz regime) while at the very short wavelengths, the ionization can be described by purely MPI. Thus, for most wavelength regimes, the ionization is due to a mixture of both MPI and tunneling and models predicting ionization must incorporate both.

The ionization rate, as mentioned in Eqn. (3.9), can be found from different analytical theories such as the ADK model [63], barrier suppression model [64], Szöke’s model [65], Krainov
model [66], Keldysh model [62], and the PPT model [67]. The main premise in calculating this rate is determining the transition of an electron from its ground state to the free state either directly or through an intermediate state. Thus, the electronic wave functions of these states must be known. The full quantum mechanical derivation of the ionization rate is outside the scope of this thesis.

Verifying the validity of the aforementioned analytical theories involves experimentally observing the effects of ionization and comparing to theory. The direct observation of ionization is, thus, the detection of ions. Much work has been devoted to identifying the rates for various gases and determining which theories are best suited for the wavelength regime and irradiance levels used [64, 68, 69]. It is widely recognized that the PPT model, an extension of Keldysh theory which incorporates a correction to the Coulomb potential experienced by an electron in its free state as well as introduces non-monochromatic light and AC electric fields to the derivation, is most accurate in calculating the ionization rate in both tunneling and MPI regimes [59, 69-72]. The ionization rate according to the PPT model is written as [59, 67]:

\[ R(l) = \frac{I_p}{\hbar}|C_{nl}|^2 f_{lm} \sqrt{\frac{6}{\pi}} (2\xi)^{2n^*-3} (1 + \gamma^2)^{3/2} A_m(\gamma) \exp \left( -2\frac{\xi g(\gamma)}{3} \right). \] (3.16)

The terms within Eqn. (3.16) are expressed as follows:

\[ |C_{nl}|^2 = \frac{24n^*-2}{n^*\Gamma(n^* + l + 1)\Gamma(n^* - l)} \] (3.17)

\[ f_{lm} = \frac{(2l + 1)(l + |m|)!}{2^{|m|} |m|! (l - |m|)!} \] (3.18)

\[ g(\gamma) = \frac{3}{2\gamma^2} \left[ \left( \frac{1}{2\gamma^2} \right) \sinh^{-1}(\gamma) - \frac{1 + \gamma^2}{2\gamma} \right] \] (3.19)
\[ A_m(\gamma) = \frac{4\gamma^2}{\sqrt{3\pi}|m|!(1 + \gamma^2)} \sum_{n=K}^{\infty} \exp(-\alpha(n - K))W_m\left(\sqrt{\beta(n - K)}\right) \quad (3.20) \]

\[ \alpha(\gamma) = 2 \left[ \sinh^{-1}(\gamma) - \frac{\gamma}{\sqrt{1 + \gamma^2}} \right] \quad (3.21) \]

\[ \beta(\gamma) = \frac{2\gamma}{\sqrt{1 + \gamma^2}} \quad (3.22) \]

\[ W_m(x) = \exp(-x^2) \int_0^x \exp(y^2)(x^2 - y^2)^{|m|} dy, \quad (3.23) \]

where \( \xi = E_a/E \) and \( E_a \), the intra-atomic electric field, is defined as [73]:

\[ E_a = \frac{4}{3} \sqrt{2m_e} \frac{l_p^{3/2}}{q\hbar}, \quad (3.24) \]

where \( \hbar \) is the reduced Planck’s constant. The form of Eqn. (3.17) is a result of the asymptotic coefficient of the atomic wave function away from the nucleus [63, 74, 75] where \( n^* = Z(I_H/I_p)^{1/2} \) is the effective principal quantum number with \( Z \) being the effective charge of the atomic core and \( I_H \) is the ionization potential of the hydrogen atom (13.6 eV [76]). The value of \( Z \) is either 0, 1, or 2 for a negatively charged ion, neutral atom, or positively charged ion, respectively. By considering only integer values of \( Z \) and neglecting any correction factors, \( n^* \) is expected to deviate from the actual value by no more than \( \pm 30\% \) [74]. Eqn. (3.18) depends on the orbital angular momentum number \( l \) and projection on the field direction \( m \).
Figure 3-3(a) shows the calculation of Eqn. (3.16) for 400nm, 800nm, 1300nm, and 1800nm pulses. Note that the shorter the wavelength, the faster the rate increases for low pulse irradiance. This is mainly due to the effects of MPI which coincides with what the Keldysh parameter predicts. MPI corresponds to an absorption of 5-photons, 10-photons, 15-photons, and 21-photons in Kr gas for the 400nm, 800nm, 1300nm, and 1800nm pulse, respectively. In the large pulse irradiance regime, the rate converges to nearly the same value for the 400nm and 800nm pulse where tunneling starts to dominate. Similarly, for the 1300nm and 1800nm pulses, the rate approaches a static value in the large pulse irradiance regime.

Figure 3-3(b) shows the calculation of Eqn. (3.16) using an 800nm pulse for the noble gases Ne, Ar, Kr, and Xe. As expected, the rate increases faster at low pulse irradiance as the ionization energy decreases. For MPI of an 800nm pulse, this corresponds to 8-photon absorption,
10-photon absorption, 11-photon absorption, and 14-photon absorption for Xe, Kr, Ar, and Ne, respectively. Note that for $I \approx 10$ TW/cm$^2$, the rate is calculated to be 17 orders of magnitude larger in Xe than in Ne owing to the fact of the difficulty in ionizing atoms with large potentials. Additionally, we can confirm our initial assumption of single ionization as expressed in Eqn. (3.9). For example, the 2$^{nd}$ ionization energy of Kr is 24.36 eV [76] which would require a great deal more irradiance to ionize the 2$^{nd}$ electron. More precisely, to generate the same amount of Kr$^+$ ions at $I = 10$ TW/cm$^2$ would require an irradiance > 5$\times$ to generate the same amount of Kr$^{2+}$ ions.

Since the PPT model incorporates both MPI and tunneling regimes in the determination of the ionization rate, these regimes can be separated in the model. As stated previously, $\gamma \ll 1$ represents the tunneling regime whereas $\gamma \gg 1$ represents the MPI regime. Thus, the terms of Eqn. (3.16) can be amended appropriately in these limits. For MPI, the resultant rate is often represented in a power law form such that:

$$R(I) = \sigma_k I^k,$$  \hspace{1cm} (3.25)

where $\sigma_k$ is the $k$-photon absorption cross section and $k = \text{Int}\left[\left(I_p/h\omega\right) + 1\right]$. It follows that in this limit as $\gamma \gg 1$, $\sigma_k$ can be calculated by equating Eqn. (3.16) and Eqn. (3.25). The calculated cross sections are given in Table 3-1 for an 800nm pulse for Ne, Ar, Kr, and Xe gas.
Table 3-1. Calculated MPI cross sections from Eqn. (3.16) for $\gamma \gg 1$. The cross sections are given for Ne, Ar, Kr, and Xe gas for an 800nm excitation [69].

<table>
<thead>
<tr>
<th></th>
<th>$k$</th>
<th>$\sigma_k$ $(cm^2s^{-1}W^{-k})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>14</td>
<td>$1.55 \times 10^{-185}$</td>
</tr>
<tr>
<td>Ar</td>
<td>11</td>
<td>$5.06 \times 10^{-140}$</td>
</tr>
<tr>
<td>Kr</td>
<td>10</td>
<td>$4.35 \times 10^{-125}$</td>
</tr>
<tr>
<td>Xe</td>
<td>8</td>
<td>$2.40 \times 10^{-96}$</td>
</tr>
</tbody>
</table>

The manner in which the MPI cross section is calculated from Eqn. (3.25) has been shown to be relatively accurate using a variety of irradiance levels at different wavelengths experimentally [68, 77, 78].

Similarly for the tunneling regime, Eqn. (3.16) can be amended in the limit when $\gamma \ll 1$. In this limit, from Eqn. (3.19), $g(\gamma) \rightarrow 1$ and from Eqn. (3.20), $A_m(\gamma) \rightarrow 1$ such that the rate of Eqn. (3.16) has no frequency dependence. This leads to a modified rate of the form in the tunneling regime as:

$$R(I) \equiv \left(I_p/h\right)(2\xi)^{n^*-3}xexp\left(-\frac{2\xi}{3}\right).$$

3.3 The effects of plasma on the WLC

It was proposed by Bloembergen in the mid-1970s that plasma production could be a major component for the anti-Stokes spectral component of the WLC generated in condensed media [22].
But in the specific case of spectral broadening in gases, it was believed in early studies that the plasma could not explain the blue components observed in the WLC [13, 20]. In Ref. [13], it was argued that due to the formalism of Eqn. (3.11), it was impossible for plasma production to be primarily responsible for the blue-shifting of the WLC spectrum. In their experiments, 70 fs and 2 ps pulses at a wavelength of 600 nm were used to generate WLC in different gases where they observed $\Delta \omega \cong \omega_0$. Using this in Eqn. (3.11), the authors calculated an irradiance of $\approx 10^{15}$ W/cm$^2$ in order to satisfy the condition presented for direct anti-Stokes spectral broadening from the plasma alone. This irradiance was stated to be much higher than the MPI threshold of $\approx 10^{13}$ W/cm$^2$ specifically in the case for Xe gas although there was no direct experimental confirmation of the amount of plasma generated.

Self-guiding of light through filamentation was studied in reports such as Nibbering et al. [25] where the guiding was said to be due to the interplay of the increase in the refractive index from SPM and that of plasma generation. The irradiance contained in the pulse after filamentation and formation of a modulated pulse spectrum was measured to be $\approx 10^{14}$ W/cm$^2$ in their experiments. To estimate $N_e$ and $\Delta n_{PL}$, the authors of [25] set Eqn. (2.7) equal to Eqn. (3.8). Using the $n_2$ of atmospheric air of $3 \times 10^{-19}$ cm$^2$/W from Ref. [45], they calculated $N_e \approx 10^{16}$ cm$^{-3}$ leading to $\Delta n_{PL} \approx 10^{-5}$. From Eqn. (3.9), we can estimate the amount of generation such that $N_e \approx R(I)N_0\tau$ where $N_0 \cong 10^{19}$ cm$^{-3}$ for atmospheric gases. Hence, the rate can be estimated to be $R(I) \approx 10^{10}$ s$^{-1}$. Braun et al. [23] reported clamping of high intensity pulses ($\approx 10^{13}$ W/cm$^2$) in atmospheric air forming a single filament and, thus, generating a WLC. The authors also contributed this to the balancing of SPM and plasma and calculated $N_e \cong 4.5 \times 10^{16}$ cm$^{-3}$ leading to $\Delta n_{PL} \cong 3.5 \times 10^{-5}$. Their calculations included the effects of diffraction; nonetheless, the
magnitude of $\Delta n_{PL}$ obtained from theirs and Nibbering et al. is similar. In addition, the plasma density has been directly measured in the experiments of Chen et al. [34] and found to be $\sim 10^{16}$ cm$^{-3}$ for various focusing geometries.

As mentioned above, the generation of WLC requires a balance between phase incurred through SPM and that through ionization. Thus, using the aforementioned characteristics of this balance, we can get a simple, qualitative picture of this process using Fourier analysis.

Figure 3-4. Calculation of Eqn. (2.15) for (a) 150 fs and (b) 40 fs pulse inputs at a central wavelength of 780 nm. The solid black, red, blue, and green lines represent the case for when $\phi_{PL} = 0.5 \phi_{SPM}$, $\phi_{PL} = \phi_{SPM}$, $\phi_{PL} = 2 \phi_{SPM}$, and $\phi_{PL} = 4 \phi_{SPM}$, respectively.

Figure 3-4 shows the plot of the calculation of Eqn. (2.15) for various cases of the plasma nonlinearity being less than, equal to, and greater than that due to SPM. The results are shown for a 150 fs and 40 fs pulse input in Figure 3-4(a) and Figure 3-4(b), respectively. The trend follows that for increasing amounts of plasma nonlinearity, the spectrum shifts more towards the anti-Stokes side of the central frequency. Also, the amount of Stokes shift is decreased for increasing amounts of plasma nonlinearity. These simple calculations do not mimic what is observed in actual
experiments quantitatively, but qualitatively, this behavior is observed when solving an appropriate wave equation that correctly takes into account the influence of SPM and plasma nonlinearity as well as other appropriate terms.
CHAPTER 4 THE NONLINEAR WAVE EQUATION

4.1 Derivation of the Nonlinear Wave Equation for WLC processes

In Section 2.2, the wave equation was derived under time harmonic conditions, i.e. $\partial / \partial t \rightarrow -i\omega$, to describe self-focusing. In order to develop an appropriate wave equation to describe the WLC process, the temporal derivatives must be included to describe the necessary spatio-temporal characteristics. Thus, we start by revisiting Maxwell’s equations defined in Eqns. (2.17), (2.18), (2.19), and (2.20). Plugging Eqn. (2.19) into (2.21) leads to:

$$\nabla (\nabla \cdot \vec{E}) - \nabla^2 \vec{E} = -\mu \frac{\partial}{\partial t} \left( \vec{J} + \frac{\partial \vec{D}}{\partial t} \right),$$

(4.1)

Again, we assume an isotropic medium such that the 1st term on the left hand side of Eqn. (4.1) is zero. Thus, we can rewrite Eqn. (4.1) such that:

$$\nabla^2 \vec{E} = \mu \frac{\partial^2}{\partial t^2} \vec{D} = \mu \frac{\partial \vec{J}}{\partial t},$$

(4.2)

The current density $\vec{J}$ can be expressed as:

$$\vec{J} = qN_e \vec{v}_e,$$

(4.3)

where $\vec{v}_e$ is the drift velocity. Taking the partial derivative with respect to time of Eqn. (4.3) leads to an expression which allows us to express the time derivative of the drift velocity in terms of the electrical force and, thus,

$$\frac{\partial \vec{J}}{\partial t} = qN_e \frac{\partial \vec{v}_e}{\partial t} = -\frac{q^2 N_e \vec{E}}{m_e}.$$

(4.4)

Substituting Eqn. (4.4) into Eqn. (4.2) and using the expression of $\vec{D}$ from Eqn. (2.3), we obtain:
\[ \nabla^2 \vec{E}(r, t) + \frac{\partial^2 \vec{E}(z, t)}{\partial z^2} - \frac{n^2 \partial^2 \vec{E}(r, z, t)}{c^2 \partial t^2} + \frac{\mu_0 q^2 N_e \vec{E}(r, z, t)}{m_e} = 0, \]  

(4.5)

where we have explicitly written out the coordinate dependencies, separated the transverse coordinates from the longitudinal coordinate in the spatial derivative, and assumed non-magnetic media \((\mu_r = 1)\). To transform the field to the frequency domain, we make use of the Fourier Transform and use the relation from Eqn. (3.2) to arrive at the following:

\[ \nabla^2 \vec{E}(r, \omega - \omega_0) + \frac{\partial^2 \vec{E}(z, \omega - \omega_0)}{\partial z^2} + \frac{n^2 \omega^2}{c^2} \vec{E}(r, z, \omega - \omega_0) + \frac{\mu_0 q^2 N_e \vec{E}(r, z, \omega - \omega_0)}{m_e} = 0. \]  

(4.6)

Note that \(k^2(\omega) = n^2 \omega^2 / c^2 = k_0^2 n(\omega)^2\) and thus describes the frequency dependent wave-vector where \(n\) is a dispersive quantity. For some of the following analysis, we truncate the dispersive nature of the wave-vector such that \(k = k(\omega)\). We can assume a solution to Eqn. (4.6) of the form to that in Eqn. (2.24), i.e.:

\[ \vec{E}(r, z, t) = A(r, z, t)e^{i(k_0 n_0 z - \omega_0 t)}, \]  

(4.7)

and substitution of this, i.e. Eqn. (4.7), into Eqn. (4.6) while using SVEA (see Section 2.2) yields:

\[ \nabla^2 A(r, \omega - \omega_0) + 2i k_0 n_0 \frac{\partial A(z, \omega - \omega_0)}{\partial z} + (k^2 - (k_0 n_0)^2) A(r, z, \omega - \omega_0) + \frac{\mu_0 q^2 N_e A(r, z, \omega - \omega_0)}{m_e} = 0. \]  

(4.8)

The expression \((k^2 - (k_0 n_0)^2) = (k - k_0 n_0)(k + k_0 n_0)\). Since \(k \cong k_0 n_0\), the aforementioned expression can be approximated as:

\[ (k^2 - (k_0 n_0)^2) \cong 2k_0 n_0(k - k_0 n_0), \]  

(4.9)
and Eqn. (4.9) can be written as:

\[
\frac{\nabla^2 A(r, \omega - \omega_0)}{2k_0 n_0} + i \frac{\partial A(z, \omega - \omega_0)}{\partial z} + (k - k_0 n_0) A(r, z, \omega - \omega_0) \\
+ \frac{\mu_0 q^2 N_e A(r, z, \omega - \omega_0)}{2k_0 n_0 m_e} = 0. 
\]  

(4.10)

Typically, \( k(\omega) \) can be expressed as a power series expansion in a way that includes linear effects as well as nonlinear effects such that:

\[
k(\omega) = \Delta k_{NL} + \sum_{n=0}^{N} \frac{k_n}{n!} (\omega - \omega_0)^n. 
\]  

(4.11)

The \( \Delta k_{NL} \) term represents nonlinear effects associated with a change in index which will be discussed later. The last term represents a correction to the wavevector written in terms of \( k_n \) defined as such:

\[
k_n = \left. \frac{d^n k}{d \omega^n} \right|_{\omega = \omega_0} .
\]  

(4.12)

It is easy to see that the \( n = 0 \) term of Eqn. (4.11) represents \( k(\omega) = \Delta k_{NL} + k_0 n(\omega)|_{\omega = \omega_0} \) where the last term is simply \( k_0 n_0 \). The expression of Eqn. (4.11) also infers that taking \( n = 1 \) takes into account the group velocity whereas taking \( n = 2 \) accounts for group velocity dispersion (GVD), the spreading of the pulse in time due to different frequency components each travelling with its own group velocity. Thus, we can substitute Eqn. (4.11) into Eqn. (4.10) to obtain the following:
\[
\begin{align*}
\frac{\nabla^2_A(r, \omega - \omega_0)}{2k_0n_0} + i \frac{\partial A(z, \omega - \omega_0)}{\partial z} + \Delta k_{NL} A(r, z, \omega - \omega_0) \\
+ \sum_{n=1}^{N} \frac{k_n}{n!} (\omega - \omega_0)^n A(r, z, \omega - \omega_0) \\
+ \frac{\mu_0 q^2 N_e A(r, z, \omega - \omega_0)}{2k_0n_0m_e} = 0.
\end{align*}
\]

(4.13)

We now take an inverse Fourier Transform back into the time domain by use of the following relation:

\[
\mathcal{S}^{-1}[(\omega - \omega_0)^n A(r, z, \omega - \omega_0)] = i^n \frac{\partial^n A(r, z, t)}{\partial t^n}.
\]

(4.14)

Hence, Eqn. (4.13) can now be expressed as:

\[
\begin{align*}
\frac{\nabla^2_A(r, t)}{2k_0n_0} + i \frac{\partial A(z, t)}{\partial z} + \Delta k_{NL} A(r, z, t) + \sum_{n=1}^{N} \frac{k_n}{n!} i^n \frac{\partial^n A(r, z, t)}{\partial t^n} \\
+ \frac{\mu_0 q^2 N_e A(r, z, t)}{2k_0n_0m_e} = 0.
\end{align*}
\]

(4.15)

Revisiting the nonlinearity of the wavevector, we can express \(\Delta k_{NL} = k_0 \Delta n\) where \(\Delta n\) is of the form given in Eqn. (2.7). We can also express the last term on the left hand side of Eqn. (4.15) in terms of the change in index due to plasma formation given in Eqn. (3.8). Thus, Eqn. (4.15) can be re-written in the following form:

\[
\begin{align*}
\frac{\nabla^2_A(r, t)}{2k_0n_0} + i \frac{\partial A(z, t)}{\partial z} + k_0 \left( \frac{2}{\varepsilon_0} \right) A(r, z, t) |A(r, z, t)|^2 + \Delta n_{pl} A(r, z, t) \\
+ \sum_{n=1}^{N} \frac{k_n}{n!} i^n \frac{\partial^n A(r, z, t)}{\partial t^n} = 0,
\end{align*}
\]

(4.16)

where we have defined \(\bar{n}_2 \equiv n_2n_0^2 \varepsilon_0 c\) as it was in Section 2.2.
Eqn. (4.16) is termed the nonlinear wave equation and can, thus, describe the WLC generation process. The 1st term represents diffraction. The 3rd term represents the combined effects of spatial self-focusing effects, temporal SPM, and effects of the pulse due to plasma generation. The last term on the left hand side of Eqn. (4.16) represents dispersive characteristics of the WLC generation process. Typically, only 2nd order dispersion is considered in most WLC simulations which represents the effects of GVD. Also, of note is the fact that the plasma nonlinearity could have been lumped together with $\Delta k_{NL}$ in the initial derivation since it can be represented as a change in index, i.e. the $\vec{J}$ term could have been neglected in Eqn. (4.2) and still arrived at the same result. This fact leads to the extension of this nonlinear wave equation by the inclusion of other nonlinear terms whose formalism is derived from a change in refractive index. For example, the Raman contribution in non-inert gases can be accounted for by introducing a non-instantaneous component in Eqn. (2.7) so that [79]:

$$\Delta n(t) = n_2 I(t) + \int_{-\infty}^{\infty} R'(t - t') I(t') dt'$$

where $R'$ is the non-instantaneous component of the 3rd order nonlinear response. The non-instantaneous component is related to the 3rd order response via Eqn. (2.36) such that $R'(t)$ is directly proportional to $\chi^{(3)}_N(t)$ where the subscript $N$ denotes the non-instantaneous component of the 3rd order response. We can incorporate this time dependent change in index back into the wave equation so that Eqn. (4.16) includes the non-instantaneous response as:
\[
\n\n\frac{\nabla^2 A(r, t)}{2\kappa_0 n_0} + i \frac{\partial A(z, t)}{\partial z} \\
+ k_0 \left( n_2 |A(r, z, t)|^2 + \Delta n_{pt} \right) \\
+ \frac{1}{n_0^2 c \varepsilon_0} \int_{-\infty}^{t} R'(t - t') |A(r, z, t')|^2 dt' \right) A(r, z, t) \\
+ \sum_{n=1}^{N} \frac{k_n}{n!} \frac{\partial^n A(r, z, t)}{\partial t^n} = 0.
\]

(4.18)

The authors of Ref. [45] derived the response function for determining the rotational Raman contribution of the two main constituents of air. It is important to note that while including the Raman contribution for molecules such as air is important for filamentation studies, molecules having no asymmetry in its polarizability do not possess rotational contributions. Therefore, when discussing filamentation in inert gases where the polarizability is symmetric, the Raman contribution is neglected. An asymmetry can be obtained with a strong enough electric field, but for the scope of this thesis, the electric fields are not sufficient to generate such a response.

Note that a more rigorous wave equation can be derived by including the total polarization response given in Eqn. (2.2). In general, all order responses can be included in the wave equation. But as eluded to in the previous paragraph, for inert gases, only odd terms in the polarization are non-zero due to the symmetry of the medium. Thus, Eqn. (4.2) can be re-written as:

\[
\nabla^2 \vec{E} - \frac{n^2}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} - \mu_0 \frac{\partial \vec{J}}{\partial t} = \mu_0 \frac{\partial^2 \vec{p}^{(3)}}{\partial t^2},
\]

(4.19)

where we have taken the polarization up to the third-order response and neglected all higher-order odd terms. Now, we can substitute the expression of Eqn. (2.36) into the expression on the right
hand side of Eqn. (4.19). This directly allows for the inclusion of multiple third-order effects such as DFWM and general FWM as well as XPM whose susceptibility form is listed in Table 2-1.

4.2 The effects of nonlinear phenomena on wave propagation

The most basic linear and nonlinear terms describing the filamentation process in gaseous media, as discussed in the previous section, is SPM, ionization, dispersion, and self-focusing all of which are accounted for by Eqn. (4.16). Taking the a major source of contribution of the blue spectral shift of the pump frequency has been attributed to the temporal variation of the irradiance at the back part of the pump pulse with negative slope [27]. This can be envisioned by invoking the moving-focus model explained in Ref. [28]. The moving focus model states that a pulse can be viewed as a longitudinal stack of transverse slices each focusing with respect to the power obtained in that slice. When the intensity is clamped (the refractive index contribution from the plasma equals that from self-focusing) a central slice of the pulse would travel at the phase velocity, i.e. $c/n$. The front part of the pulse would encounter self-focusing, but travel faster than the central part of the pulse. The back part of the pulse encounters the plasma generated by the peak of the pulse where the intensity is less than the other slices. This leads to the back slice of the pulse traveling faster than the front part of the pulse and eventually catching up with the front part of the pulse. This qualitative process outlined in Ref. [27] is coined self-steepening and can lead to a blue-shifted spectrum.

Self-steepening in the context of the filamentation process was studied in Ref. [29] and Ref. [30]. By expressing the nonlinear source term on the right-hand side of Eqn. (4.19) in a similar form as the E-field given in Eqn. (4.7), it can be shown that an operator of the form $[1 + (i/\omega_0)\partial/\partial\tau_r]$ can arise where $\tau_r$ is the retarded time defined as $t - k_1z$ [80]. This operator
can then be implemented into the nonlinear wave equation in which effects such as self-steepening can be incorporated. In Ref. [29], the effects of self-steepening in sapphire were studied. From numerical simulations, it was found that as an intense pulse approaches collapse, the self-steepening process causes a large phase jump exhibiting a broad blue-shift with a sharp cutoff. Multi-photon excitation eventually leading to free electron generation, thus, was found to halt the collapse at powers higher than that of the critical power threshold in the case of sapphire. In Ref. [30], numerical simulations in air were performed in which it was found that plasma formation was the main contribution to defocusing leading to self-steepening. At that point, group-velocity dispersion and higher-order nonlinearities became important during the propagation of the pulse.

Prior to the simulations performed in Ref. [30], the filamentation process was attributed to the balance of SPM with plasma production and diffraction [23]. To estimate the amount of contribution from the plasma, the expression was written as:

\[
\Delta n_{spm} = \Delta n_{pl} + \frac{(1.22\lambda_0)^2}{8n_0\pi w_0^2}
\]

(4.20)

where the last term on the right represents the contribution from diffraction. With an intensity of 7 x 10^{13} W/cm^2 and the \( n_2 \) of air taken from Ref. [46] as 5.6 x 10^{-19} cm^2/W, the plasma density was estimated to be 4.5 x 10^{16} cm^{-3} needed to balance the self-focusing contribution of 3.5 x 10^{-5}. Kasparian et al. numerically determined the clamped intensity in air to be 4.5 x 10^{13} W/cm^2 by incorporating the ionization rates of both nitrogen and oxygen but disregarding diffraction [24]. In their simulations, they balanced self-focusing with the contribution from plasma. Their numerical result agreed with the experimental estimate of Ref. [23] within a factor of 2. Another consequence from the filamentation process in air was found to be conical emission, a leaky propagation mode of the self-generated guiding structure between ionization and self-focusing [25].
Other works have noted the importance of ionization on the spectral broadening process. Brodeur et al. conducted a systematic study of the bandgap dependence of the supercontinuum in various transparent media [19]. Since the generation of WLC in materials was found to occur above a certain threshold and the anti-Stokes broadening increased with an increase in the bandgap of the material, the intensities required for WLC produced significant multi-photon excitation rates in those materials which contribute to free electron generation. Along with the bandgap dependence, the authors concluded that multi-photon excitation leading to plasma in condensed media is an essential mechanism to explain the anti-Stokes shift in the WLC. Kolesik et al. simulated the effects of plasma formation in water and found that, along with chromatic dispersion, it was one of the factors that limited the spectral extent of WLC generation [31].
CHAPTER 5 DESCRIPTION OF LASER SOURCES

To perform the experiments described in this thesis, high intensity sources are required. This chapter describes in brief detail the types of sources that were used.

![Figure 5-1. General schematic of Clark-MXR laser system which outputs 1 mJ, ~150 fs (FWHM) pulses at 1 kHz repetition rate.](image)

In Figure 5-1, the general schematic of the Clark-MXR series CPA-2110 is shown. The laser system outputs pulses at 775 nm with ~1 mJ, ~140 fs (FWHM) pulses at a 1kHz repetition rate. This laser has a bi-level design such that the seed, oftentimes referred to as the oscillator, is produced in the bottom where it gets amplified in the top. From the figure, a 980 nm diode laser pumps an Erbium doped fiber producing 1550 nm pulses at a 40 MHz rep rate. The 1550 nm pulses are compressed and doubled in a PPLN (Periodically poled Lithium Niobate) crystal with tight
temperature control. The 775 nm pulses are then stretched such that the pulse width is on the order of 100s of picoseconds to reduce the peak irradiance in the amplification stage.

On the top portion of the laser system, 1064 nm pulses are generated by pumping a Nd:YAG rod with a flash lamp. The 1064 nm pulses are doubled by an LBO crystal and the resultant 532 nm pulses pump the Ti:Sapphire rod at a 1 kHz rep rate via acousto-optic modulated Q-switching. Typically, the nominal 532 nm power incident on the Ti:Sapphire is ~7.2 W. The pulse from the oscillator is injected into the cavity where it is directed via polarization in and out of the cavity by applying voltage to the Pockels cell which then passes through the Faraday rotator and finally to the pulse compressor after final amplification. Of note, the pulse compressor was positioned for the optimum energy output of the optical parametric generator (described below). Thus, the pulse width of the 775 nm directly from the output typically varied from ~140 fs (FWHM) to ~160 fs (FWHM).

Figure 5-2. (a) Typical second-order intensity autocorrelation of the 775 nm, 1 mJ Clark-MXR laser system. (b) Typical spectrum of the output 775 nm pulse measured by an Ocean Optics HR4000 spectrometer. The inset in (b) shows an image of the 775 nm pulse captured by a DataRay WinCamD Beam Profiler.
To generate the broadly tunable radiation used for nonlinear spectroscopy, typically an optical parametric generator / amplifier (OPG/A) is used.

Figure 5-3. General schematic of TOPAS-C. The “M” refers to mirrors, “B/S” refers to beam splitters, “DM” refers to a dichroic mirror, and “BD” is a beam dump. The 775 nm notch filter blocks the strong input from reaching the output.

Shown in Figure 5-3 is the general schematic of one of the OPG/As used in this thesis: the TOPAS-C model produced by Light Conversion. The 775 nm input is the 1 mJ system described in Figure 5-1. The TOPAS-C is a 3-stage amplification system. The 1st stage consists of generating a WLC (denoted by the white line) in a sapphire window with a small portion of the 775 nm. The 2nd stage is the pre-amplification stage in which a portion of the WLC is mixed in one of the BBO crystals along with another portion of the 775 nm input that was split via a beam splitter. This stage is responsible for amplification of the idler. The last stage involves mixing both signal and idler pulses from the pre-amp stage onto the 2nd BBO crystal with a majority of the 775 nm pulse that was split at the input. At the output, there is a movable notch filter to block the strong 775 nm pump. The spectrum generated from this OPG produced output signal + idler pulses ranging from 1100 nm – 2640 nm. Frequency mixing at the output allowed us to obtain the second harmonic of either the signal (SHS) or idler (SHI), i.e. 550 nm – 1100 nm. Since the energy output of the idler near the edge of the tuning range is weak, the SHI in the range of ~900 nm – 1100 nm is also weak. Therefore, there was a wide gap in available energy when approaching the spectral region from
900 nm – 1100 nm. To ascertain wavelengths from ~ 510 nm to 600 nm, i.e. wavelengths shorter than SHS, the 775 nm notch filter was removed to allow sum-frequency generation of the 775 nm pump and the idler wavelengths. It’s important to note that the signal and idler have orthogonal polarizations and, thus, the positions of the mixer crystals on the output must be oriented properly to achieve maximum efficiency. See Figure 5-4 for the typical energy output and spectrum of TOPAS-C.

![Figure 5-4](image)

Figure 5-4. (a) Typical energy output of TOPAS-C by pumping with 1 mJ from the laser system described in Figure 5-1. The wavelength range is 1100 nm – 1620 nm for the signal, 1500 nm – 2640 nm for the idler, 550 nm – 810 nm for the second-harmonic of the signal (SHS), 750 nm – 1100 nm for the second-harmonic of the idler (SHI), and 511 nm – 600 nm for the sum-frequency of the idler (SFI). (b) Typical spectrum of the output of the TOPAS-C for a 1300 nm signal with corresponding 1920 nm idler. The solid red line is a Gaussian fit to obtain the bandwidth of the 1300 nm (Δλ = 38 nm – FWHM) and the solid blue line is a fit of the 1920 nm (Δλ = 70 nm – FWHM). The spectrum is measured with an Ocean Optics NIRQuest256-2.5 spectrometer.

A similar laser system to the one described in Figure 5-1 with higher energy output was also used in the experiments of this thesis. The difference between the higher energy system and that described in Figure 5-1 is primarily the amount of pump power incident on the Ti:Sapphire. For
the higher energy laser system, the 532 nm pump power was ~11 W. The other difference is, instead of a 40 MHz oscillator, the higher energy laser system’s oscillator operated at 27 MHz. This system produced ~2mJ, ~150 fs (FWHM) pulses at a 1 kHz repetition rate. Of note, this higher energy system was a factory upgraded option from the laser system used in previous group members’ theses, e.g. see Ref. [81].

For the higher energy ~150 fs – FWHM laser system, the OPG/A used is the TOPAS-800 model produced by Light Conversion as shown in Figure 5-5. It is a 5-pass system in which all nonlinear phenomena occur on one BBO (Beta-BaB₂O₄) crystal. The first stage is responsible for the generation of the superfluorescence (SFL) denoted by the thin red line in the figure. The output SFL (denoted by the white line in the figure) is amplified by a portion of the 775 nm input in the 2nd pass. The diffraction grating (DG) reduces the spectral width and stabilizes the shape. The 3rd pass involves another reflection from the grating while the 4th pass again amplifies the weak SFL. The 4th pass amplification is commonly referred to as the pre-amp stage. The 5th pass is the main amplification stage with the pre-amp light being passed through the BBO crystal with a majority of the initially split 775 nm pump. At the output, there is a movable notch filter to block the strong 775 nm pump. The spectrum generated from this OPG produced output signal + idler pulses.

Figure 5-5. General schematic of TOPAS-800. The “M” refers to mirrors, “B/S” refers to beam splitters, and “DG” refers to a diffraction grating. The 775 nm notch filter blocks the strong input from reaching the output.
ranging from 1140 nm – 2400 nm. Frequency mixing at the output allowed us to obtain the SHS, SHI, and SFI (by removing the notch filter). At the time of the experiments utilizing this system, there were 2 similar TOPAS-800 models being pumped by the ~2 mJ laser source: the one depicted in Figure 5-5 and the other one being identical except for the diffraction grating being replaced by a translatable mirror. The TOPAS-800 with the translatable mirror was pumped with a small portion of the 775 nm (~0.4 mJ) such that the energy output was much less than typical (see Figure 5-4(a)). Furthermore, the available energy at the edge of the tuning range decreased more drastically compared with that shown in Figure 5-4(a).

Figure 5-6. General schematic of Coherent Legend Elite Duo HE+ which outputs ~12 mJ, ~40 fs (FWHM) pulses at 1 kHz repetition rate. SPA stands for single-pass amplifier and REGEN stands for regenerative cavity. The “M” refers to mirrors and “BD” refers to a beam dump.

Another laser source utilized in this thesis is the Coherent Legend Elite Duo HE+ whose general schematic is shown in Figure 5-6. The 800 nm seed (or oscillator) is generated from the Vitara-T model which produces 500 mW pulses at a 80 MHz repetition rate. These pulses have a
bandwidth of ~70 nm (FWHM) and have a temporal width of ~20 – 30 fs (FWHM). The pulses are stretched and then injected into the REGEN cavity pumped by the Evolution 45 at 20 W. After amplification in the REGEN cavity, the pulses are then amplified further in the single-pass amplifier (SPA) by the Evolution HE at 45 W. The amplified pulses are then compressed to a temporal width of ~40 fs (FWHM) with an energy of 12 mJ. See Figure 5-7 for the typical intensity autocorrelation and spectrum of the output pulse.

For the 12 mJ laser system, the OPA used is the TOPAS-HE model produced by Light Conversion. This system is identical to the TOPAS-C model with the addition of an extra, high-energy amplifier stage. The typical energy output and spectrum is shown in Figure 5-8.

Figure 5-7. (a) Typical second-order intensity autocorrelation of the 800 nm, 12 mJ Coherent Legend Elite Duo HE+ laser system. (b) Typical spectrum of the output 800 nm pulse measured by an Ocean Optics HR4000 spectrometer. The inset in (b) shows a CCD image of the 800 nm pulse provided by the Coherent service engineer.
Figure 5-8. (a) Typical energy output of TOPAS-HE by pumping with \(~10\) mJ from the laser system described in Figure 5-6. The wavelength range is 1140 nm – 1600 nm for the signal and 1600 nm – 2550 nm for the idler. (b) Typical spectrum of the output of the TOPAS-HE for a 1300 nm signal and 1800 nm idler. The solid red line is a Gaussian fit to obtain the bandwidth of the 1300 nm pulse (\(\Delta \lambda = 80\) nm – FWHM) and the solid blue line is a fit of the 1800 nm (\(\Delta \lambda = 157\) nm – FWHM). The spectrum is measured with an Ocean Optics NIRQuest256-2.5 spectrometer.
CHAPTER 6 THIRD-ORDER NONLINEAR CHARACTERIZATION OF MATERIALS

Materials exhibiting large third-order nonlinearities are useful in various applications. For example, a large imaginary component of the third-order nonlinearity, i.e. 2PA ($\alpha_2$), is necessary in micro-fabrication [82, 83], optical data storage [84, 85], bio-imaging [86, 87], and optical power limiting [88, 89] while a large real component of the third-order nonlinearity, i.e. $n_2$, is sought for applications such as all optical switching [90-92]. One of the quickest and most efficient means of characterizing these materials has been to study their optical properties using the Z-scan technique which can simultaneously measure nonlinear absorption (NLA) and NLR utilizing a single Gaussian beam [41]. This technique has shown to be widely used and very popular evidenced by the over 3,970 citations in peer-reviewed journals per Web of Science at the time of this chapter’s writing. It is also the most cited journal article in the history of IEEE Journal of Quantum Electronics. Considering the magnitude of literature published using this technique, only a brief overview will be given related to third-order nonlinearities.

6.1 Z-scan Technique

![Figure 6-1. General schematic of the Z-scan technique.](image)

Shown in Figure 6-1 is the general schematic of the Z-scan technique. The sample is scanned along the axis of a focusing beam, while measuring the transmittance $T(Z)$ through a
slightly closed aperture placed in the far field. As described in [41], NLR results in self-lensing, causing changes in the far field beam radius, so that the aperture transmittance is sensitive to NLR. We refer to this as a closed aperture (CA) Z-scan. Removal of the aperture causes the Z-scan to be only sensitive to 2PA, in which case, we refer to the Z-scan as an “open-aperture” (OA) Z-scan. Inherently, the CA Z-scan will be sensitive to both 2PA and NLR. The following analysis assumes a “thin” sample in which the Rayleigh range \( z_0 \) is larger than the sample thickness. This allows the assumption that the beam waist doesn’t change within the sample which significantly simplifies the computation. The electric field of light after propagating through a thin sample exhibiting both 2PA and NLR is expressed as [93]:

\[
E_e(z, r, t) = E(z, r, t) e^{-\frac{\alpha_0 L}{2}} (1 + q(z, r, t) )^{(l k_0 n_2/\alpha_2 - 1/2)}
\]

\[
E(z, r, t) = \frac{E_0}{\sqrt{1 + (z/z_0)^2}} \text{Exp} \left[-\frac{r^2}{w_0^2 (1 + (z/z_0)^2)} - \frac{t^2}{2\tau^2} \right. \\
\left. - i \left( \frac{kr^2 z}{2(z^2 + z_0^2)} + \phi(z, t) \right) \right]
\]

where \( \alpha_0 \) is the linear absorption coefficient, \( L \) is the sample thickness, \( q(z, r, t) = \alpha_2 l(z, r, t) L_{eff} \) describes the transmission loss due to 2PA where \( L_{eff} = (1 - e^{-\alpha_0 L})/\alpha_0 \), and \( \phi(z, t) \) describes phase variations which, for the scope of this thesis, are related to the 3\(^{rd}\) order response. Free-space propagation of \( E_e(z, r, t) \) in Eqn. (6.1) via a Huygens-Fresnel integral allows us to obtain the field distribution at the aperture which we will denote as \( E_{ap} \). The transmitted power through the aperture is obtained by performing a spatial integral of Eqn. (2.8) up to the aperture radius \( r_a \) such that:

\[
P_T(z, t) = \frac{1}{2} c \varepsilon_0 n_0 \int_0^{2\pi} \int_0^{r_a} |E_{ap}(z, r, t)|^2 r dr d\theta.
\]
To obtain the normalized $T(z)$, we perform a temporal integral of Eqn. (6.2) and divide by the total energy throughput in the absence of the sample which leads to:

$$T(z) = \frac{\int_{-\infty}^{\infty} P_T(z, t) \, dt}{S \int_{-\infty}^{\infty} P_l(z, t) \, dt},$$

(6.3)

where $S$ is the linear transmittance of the aperture and $P_l(z, t)$ is the instantaneous power input to the sample.

Figure 6-2. $T(z)$ plotted for a hypothetical sample exhibiting both 2PA and NLR for OA and CA scans as well as the divided result CA/OA.

Figure 6-2 shows Z-scans for a hypothetical sample exhibiting both 2PA and NLR. In the case of OA Z-scans, in which the Z-scan is insensitive to phase variations, $T(z)$ will be a symmetric function of $z$, where $z = 0$ is defined at the minimum beam waist. In the case where 2PA coexists with NLR, the CA Z-scan exhibits features due to both 2PA and NLR, as can be seen from the CA Z-scan in Figure 6-2. However, it is found that dividing the OA scan by the CA scan (CA/OA)
yields a result that is similar to that which would have been obtained for pure NLR. Hence, in the absence of 2PA, \( T(z) \) for the CA scan (or for the divided result CA/OA) will be an antisymmetric function of \( z \), showing a peak in transmittance prior to focus and a valley after focus for a negative \( n_2 \), with the order of the peak and valley being reversed for a positive \( n_2 \). The parameter \( q_0 \) describes the maximum transmission loss due to 2PA whereas \( \Delta \phi_0 = k_0 n_2 I_0 L \) describes the maximum phase shift in a nonlinear medium.

Some simplifications in computation can be made for analyzing \( T(z) \) in the absence of 2PA. In the absence of 2PA, Eqn. (6.1) reduces to

\[
E_e(z, r, t) = E(z, r, t)e^{-\frac{\alpha_0 L}{2}} e^{i\Delta \phi(z, r, t)}
\]

\[
\Delta \phi(z, r, t) = \frac{k_0 n_2 l(t) L_{eff}}{1 + (z/z_0)^2} \exp \left[ \frac{-2r^2}{w_0^2 (1 + (z/z_0)^2)} \right]. \tag{6.4}
\]

The phase variations contained in Eqn. (6.4) can be expressed through a Taylor series expansion and, thus, can be decomposed into a summation of Gaussian beams which is referred to as the Gaussian Decomposition (GD) method [94]. Hence, each Gaussian beam of Eqn. (6.4) can be propagated to the aperture plane where they are re-summed to obtain the total complex field. Eqns. (6.2) and (6.3) are then applied to the re-summed electric field. The term by term expressions for the GD method are explicitly written out in Ref. [93].
Figure 6-3. Comparison of peak-to-valley transmission changes for different amounts of nonlinear phase shifts calculated by using a full Huygens-Fresnel integral and 5 terms in the Gaussian Decomposition method.

Figure 6-3 shows the agreement between using the GD method to 5 terms and the full Huygens-Fresnel integral to calculate the peak-to-valley transmission change, $\Delta T_{p-v}$, for different amounts of phase shifts. There is less than 5% difference between the methods for $\Delta \phi_0 \leq \pi$. Thus the GD method presents major ease in computation for scans that only include NLR contributions. For $\Delta \phi_0 \leq 0.5$, the GD method to 2 terms, i.e. $m=0$ and $m=1$, is also in good agreement with the full Huygens-Fresnel integral. Furthermore, a simple analytical expression can be derived based upon the 2-term GD expansion which calculates $\Delta T_{p-v}$ as a function of $S$ and $\Delta \phi_0$ [41]

$$\Delta T_{p-v} \approx 0.406(1 - S)^{0.25}\Delta \phi_0.$$

(6.5)

The numerical coefficient is roughly constant in the small aperture limit ($S \leq 0.5$), but for large $S$, it can slightly deviate from the value.
In determining material nonlinearities, many of the synthesized materials of interest are compounds that need to be measured in solution. Therefore, two separate Z-scans must be performed: one on the solution and another on the solvent. To extract $n_2$ and/or $\alpha_2$, either the values obtained from the fitting of each individual scan must be subtracted or each scan is subtracted from its respective analog, i.e. the solvent scan is subtracted from the solution scan, and the resultant curve is fit.

Figure 6-4. (a) CA/OA Z-scans of a 1.2 mM solution of a quinolinium heptamethine organic dye (AJBC 3701 from Alex Jen’s group at the University of Washington) dissolved in the neat solvent dimethylformamide (DMF) and that of the pure solvent. (b) The subtracted curve of the solvent Z-scan from the solution Z-scan. The Z-scans were performed at 1120nm and the aperture transmittance was set to 0.33. The solution and solvent were both placed in 1 mm thick quartz cuvettes. The inset in (a) shows the structure of the molecule.

Figure 6-4(a) shows the divided CA/OA Z-scan of a 1.2 mM solution of a quinolinium heptamethine dye dissolved in dimethylformamide (DMF) and the CA Z-scan of the solvent itself. The $\Delta T_{p-v}$ of the solution is less than that of the solvent which indicates that the dye has negative NLR. At this wavelength, extraction of the signal of the dye is straightforward since
the signal is easily discernable above the noise. Hence, the $n_2$ can be readily found using the Z-scan analysis mentioned above.

Figure 6-5(a) shows CA Z-scans of a 0.5 mM solution of a commercially available dye (3,3'-Diethylthiadicarbocyanine iodide) dissolved in the neat solvent acetonitrile (ACN) and that of the pure solvent. (b) The subtracted curve of the solvent Z-scan from the solution Z-scan. The Z-scans were performed at 900 nm with a minimum beam waist and pulse width of 20 μm (HW 1/e² M) and 120 fs (FWHM), respectively. The aperture transmittance was set to 0.33. The solution and solvent were both placed in 1 mm thick quartz cuvettes. The inset in (a) shows the structure of the molecule.

Figure 6-5(a) shows CA Z-scans of a 0.5 mM solution of a commercially available dye in acetonitrile (ACN) and that of the solvent itself. Since there is negligible amount of 2PA from the dye, the curve is dominated by NLR, and thus only information about $n_2$ can be extracted. The $\Delta \gamma_p - \nu$ of the solution is similar in magnitude to that of the solvent. Therefore, extracting the signal of the dye becomes difficult since the determination of the NLR depends on the the difference between the solution and solvent scans. Figure 6-5(b) shows the subtraction of the solvent scan from the solution scan. Note that the signal is buried within the noise. Accurate extraction of the $n_2$ cannot be obtained and only an “upper-limit” can be expressed. This “upper-
limit” depends on the magnitude of the noise and can yield $n_{2\text{-max}}$ from Eqn. (6.5). From Figure 6-5(b), $\Delta T_{p-v} \cong 1.7\%$ corresponding to $n_{2\text{-max}} = 0 \pm 0.1 \times 10^{-15}$ cm$^2$/W using $I_0 = 97$ GW/cm$^2$ after taking into account Fresnel reflections from the cuvette front surface. Hence, neither the magnitude nor sign of the NLR can be extracted in such instances. Thus, conventional Z-scans are limited in determining small solute nonlinearities in the presence of large solvent nonlinearities.

6.2 Dual-Arm Z-scan

The difficulty in extracting the NLR of materials largely arises from the uncorrelated noise found in the two separate Z-scans. To overcome this problem, we have developed the Dual-arm (DA) Z-scan technique in which two Z-scans are performed simultaneously: one of the solution and one of the solvent [95]. Since now the Z-scans of the solvent and solution are performed simultaneously, the noise in both Z-scans is correlated. Most noise sources are correlated, e.g. energy fluctuations, beam pointing instabilities, pulse width, etc., between each arm and this greatly enhances the sensitivity in extracting the $n_2$ of the solute. This expands upon the previous work of Ma et al. [96], where a reference arm with a focusing lens and aperture matched to the signal arm was used to increase the signal-to-noise ratio (SNR).

The experimental configuration is shown in Figure 6-6. A pulse, either directly from the laser source or generated by an OPG/A, is expanded through a 2-lens telescope and an aperture is placed in the beam such that the most intense portion of the beam passes through the aperture. This process is known as “top-hat” and provides a flat-top pulse which aids in reducing pointing instability of the pulse. It then passes through a half-wave plate and polarizer (not shown) to provide attenuation, then is spatially filtered and re-collimated to obtain an approximately
Gaussian beam. Approximately 10% of the energy is split off by a beam sampler (not shown) used to monitor the input energy. The remaining 90% is evenly split between two arms (Arm A and Arm B) using a 50/50 dielectric beam splitter. Since the reflection/transmission percentage of beam splitters is highly dependent upon the incident polarization and wavelength and, hence, only 50/50 for very specific configurations, on one of the arms (here arm B in Figure 6-6), a continuously variable neutral density (ND) filter is introduced for energy equalization, which will be discussed later.

Figure 6-6. Schematic of dual-arm Z-scan. The items labeled CA and OA represent the closed aperture and open aperture detectors for each arm, respectively. The reference beam used for energy monitoring is not shown.

In order to ensure that the signal from the solvent can be properly removed, it is essential that the two arms be equalized. This requires that the pulse width, beam waist, pulse energy, relative Z-position of the two samples, aperture linear transmittance, and distance from each sample to its respective aperture are matched. In addition to matching the irradiance parameters, the equipment in each arm is also matched, i.e. photodetectors, sample cuvettes matched to within tight tolerances [97], and corresponding matched optics. The pulse widths in both arms will be identical so long
as the dispersion in the optical components is the same in each arm. This is typically not a problem for pulse widths greater than 100 fs (FWHM), but for short pulse width excitation, a compensation plate is placed in the reflected arm of the DA Z-scan to compensate for the thickness of the 50/50 beam splitter. Typically, the input polarization is set such that the reflected arm has a higher percentage of the incident radiation so that the variable ND filter can also be placed on the reflected arm. This reduces the thickness of added material needed to compensate for chirp effects. Matching the beam waists is done by collimating the beam prior to the first beam splitter, using matched optics in each arm, and equalizing the arm path lengths. To ensure that signal fluctuations due to pointing instability of the laser are correlated between the arms, the number of mirror reflections beyond the 50/50 beam splitter shown in Figure 6-6 is matched so that any asymmetries in the beam profile are clipped in the same manner by the apertures placed after the samples.

Once the beam waists and pulse widths along each arm have been equalized, the pulse energy can then be equalized. Attempts to do so using energy meters failed as the accuracy is not sufficient for our purposes. Instead, this is accomplished by scanning two cells filled with the same solvent, preferably with large NLR, e.g. carbon disulfide (CS$_2$), and attenuating one of the beams using the continuously variable ND filter until $\Delta \Gamma_{p-v}$ on each arm is equal as shown in Figure 6-7. The continuously variable ND filter (Thorlabs – Part No. NDC-100C-4M) was chosen to be 100 mm in diameter with an optical density (OD) ranging from 0 to 2 so that the transmission gradient on the outer circumference of the filter would induce a negligible energy gradient on the incident pulse. Note that this is only valid for incident pulses that are relatively small in size.
Figure 6-7. Z-Scan signals for CS2 at $\lambda = 780$ nm, $\tau = 115$ fs (FWHM), $w_0 = 17$ $\mu$m and $E = 14$ nJ for energy equalization. The green triangles show the subtraction of the two scans and, hence, how well the two arms of the DA Z-scan are matched in irradiance.

To ensure that the two samples experience the same irradiance and noise simultaneously at all points along the Z-axis, the relative Z-position of the samples is adjusted until the CA signals from both arms lie directly on top of each other. When subtracting the two curves from each arm, the resultant signal (green triangles in Figure 6-7) should yield a curve whose nonlinear effects are minimized to below the noise floor, a value that can vary with different experimental apparatuses. This can be checked by increasing the pulse energy and verifying that the resultant signal does not change.
Figure 6-8. Procedure of processing DA Z-scan data using the low-energy background (LEB(Z)) and the corresponding Z-scan curves of the solution and solvent at low energy and their subtraction, high energy scan of solution and solvent and their subtraction, and direct comparison of the uncorrected and corrected signal from the solute and fit with $\Delta \phi_0 = -0.06$, $q_0 = 0.03$, using $S = 0.33$. This particular data set is of a squaraine molecule dissolved in toluene [95, 98].

Once the difference between CA signals of both arms has been minimized, in the case of solution measurements, the cells used for alignment are replaced with cells containing the solution in one arm and the solvent in the other arm. Following Figure 6-8, a scan is performed at a low irradiance where the nonlinear signal from either arm is less than the noise level, to correct for any remaining systematic differences in the arms due to linear effects e.g. cell mismatch, etc. This is similar to the procedure of background subtraction described in [41]. The subtraction of the solvent CA signal from the solution CA signal at this low energy yields a signal that we refer to as the Low Energy Background $LEB(Z)$ (Eqn. (6.6), where the subscripts $S$ and $V$ denote the solution and solvent, respectively) which is the residual signal due to linear differences between the two arms.
This is primarily due to variations in the linear transmittance of the two cells. For solution measurements, the \( LEB(Z) \) can be minimized by using a set of high quality matched cells whose manufacturing tolerances have been tightly controlled as mentioned previously and the expression is given as:

\[
LEB(Z) = T_S(V)|_{E=0} - T_V(Z)|_{E=0}. \tag{6.6}
\]

We have found that smoothing the \( LEB(Z) \) using a Savitzky-Golay algorithm [99] as implemented by Origin 8.6.0 [100] reduces the noise injected into the final CA signal. This algorithm is based on a least squares methodology for specific user-specified interval ranges. The pulse energy is then increased and the samples are scanned to measure their nonlinear properties. The solvent CA signal is then subtracted from the solution CA signal to yield the uncorrected transmittance for the solute

\[
T_{U,uncorr}(Z) = 1 + (T_S(Z) - T_V(Z)), \tag{6.7}
\]

where the subscript \( U \) denotes the solute and the addition of unity normalizes the signal. Subtracting \( LEB(Z) \) from \( T_{U,uncorr}(Z) \) yields the corrected solute CA signal as:

\[
T_U(Z) = T_{U,uncorr}(Z) - LEB(Z). \tag{6.8}
\]

This is equivalent to a CA Z-scan performed on the solute itself, i.e. \( n_{2,V} = 0 \). For solutes exhibiting small to negligible 2PA with respect to NLR (i.e. \( 2k_0n_2/\alpha_2 \geq 1 \)), the analysis to determine \( n_{2,U} \) from Eqn. (6.5 is valid for small \( \Delta \phi_0 \) is valid when fitting CA/OA. For the situation shown in Figure 6-8, the 2PA is a major component in the CA Z-scan; therefore, the analysis using the Huygens-Fresnel propagation integral must be used. The OA Z-scan signal simultaneously obtained at this irradiance and at subsequent higher irradiances can be used to determine \( \alpha_{2,U} \). This allows a one-parameter fit for determining \( n_{2, U} \) when analyzing the CA Z-scan signal. Alternately,
a two-parameter fit to the corrected signal in Figure 6-8 can be used to determine the nonlinear parameters and can give similar results for $\alpha_{2,U}$ along with determining $n_{2,U}$.

As mentioned previously, the enhancement of the SNR from the DA Z-scan technique is due to the overall reduction of the noise in the solute signal. To quantify this reduction in noise, we can study the error due to the fitting presented in each individual scan. Typically, as briefly mentioned in the previous section, there are two different approaches to analyzing the solute data using the conventional Z-scan method. First, there is the method of subtracting $T_V(Z)$ from $T_S(Z)$ independently and fitting the respective $n_{2,U}$ value which we refer to as the subtract-fit method. Since we typically restrain our fits to within one standard deviation $\sigma$ from the peak and the valley, following Refs. [95, 101] we can write the error in $\Delta\gamma_{p-v}$ as

$$\Delta\gamma_{p-v} \pm \delta = (T_p \pm \sigma) - (T_V \pm \sigma).$$

(6.9)

In this case, $\delta = \sqrt{2}\sigma$ where we have added in quadrature. To calculate the fitting error we apply a digital high-pass filter on $T_V(Z)$ and $T_S(Z)$ for the conventional Z-scans and $T_U(Z)$ for the DA Z-scans with a cutoff frequency of $\sim 1/z_0$ to calculate the respective $\delta$’s. This cutoff frequency works well in extracting the high frequency noise components. We determine $\Delta n_2$ by calculating $n_2$ for $\Delta T_{p-v} \pm \delta$ with the usual Z-scan theory. The second method involves fitting $n_{2,V}$ and $n_{2,S}$ separately and then subtracting to find $n_{2,U}$. We refer to this as the fit-subtract method where $\Delta n_{2,U}$ now becomes $\delta_S + \delta_V$.

To experimentally investigate this technique, we compare the use of the conventional Z-scan method to the DA Z-scan technique to measure the NLR of a squaraine molecule, SD-O 2405 [98], in toluene solution in a 1 mm quartz cuvette. We perform both conventional and DA Z-scans
on this solution at wavelengths from 695 nm to 920 nm, using pulses of duration 115 fs (FWHM) generated from TOPAS-C described in Figure 5-3.

Figure 6-9. (a) Sequential CA Z-scans of the solvent toluene (open red triangles) and the solution SD-O 2405 in toluene (closed black squares) at 695 nm with a concentration $C = 47 \, \mu m$, the pulse energy $E = 31 \, nJ \, (I_0 = 51 \, GW/cm^2)$ and (b) the subtraction of the solvent CA signal from the solution CA signal (open green squares); (c) Simultaneous CA DA Z-scans of the solvent toluene (open red triangles) and the solution SD-O 2405 in toluene (closed black squares) at 695 nm using the same pulse and (d) the subtraction of the solvent CA signal from the solution CA signal after LEb(Z) subtraction (open green squares) and corresponding fit of both 2PA and NLR (solid blue line) with $\Delta \phi_0 = -0.16$, $q_0 = 0.077$, using $S = 0.33$. [95].
Figure 6-9(a) shows sequential Z-scans of the solution at 695nm using a peak irradiance of 51 GW/cm². At this pulse energy ($E$) of 31 nJ and corresponding irradiance and concentration ($C$) of 47 μM, the differences between the Z-scan signals of the solvent and solution are just barely distinguishable from each other. Also, notice the level and uncorrelated nature of the noise between the two scans. Applying a high-pass filter to the individual Z-scans in Figure 6-9(a) yields $\delta_S = 1.2\%$ and $\delta_V = 1.3\%$. This translates to $\Delta n_{2,S} = 0.10 \times 10^{-15}$ cm²/W and $\Delta n_{2,V} = 0.11 \times 10^{-15}$ cm²/W, which yields $\Delta n_{2,U} = 0.15 \times 10^{-15}$ cm²/W using the irradiance parameters listed in Figure 6-9(a). Subtracting $T_V(Z)$ from $T_S(Z)$ yields the signal shown in Figure 6-9(b). Taking a high-pass filter of the curve in Figure 6-9(b) yields the same result, $\delta = 1.8\%$ corresponding to $\Delta n_{2,U} = 0.16 \times 10^{-15}$ cm²/W. Because of the uncorrelated nature and amplitude of the noise between the two Z-scans, the total signal of the solute is nearly the same as the noise so that $n_{2,U}$ cannot be accurately determined. With the respective signal and noise values for this case, the conventional Z-scan technique cannot accurately determine $n_{2,U}$, regardless of which of the two methods is used.

Next, we perform a DA Z-scan with the same experimental parameters as in Figure 6-9(a). Figure 6-9(c) shows $T_V(Z)$ and $T_S(Z)$ measured simultaneously using the DA Z-scan technique and Figure 6-9(d) shows the corrected CA signal of SD-O 2405 after solvent subtraction. Because most of the noise is correlated between the arms, the correlated noise is cancelled out and the SNR is increased, thus reducing the fitting error. In this case $\delta = 0.19\%$ which corresponds to a $\Delta n_{2,U} = 0.016 \times 10^{-15}$ cm²/W, more than a 9 times reduction in $\Delta n_{2,U}$ compared to the conventional Z-scan method and hence a $9.3\times$ enhancement in SNR when using the DA Z-scan technique. Again
at this wavelength there is some NLA in addition to the NLR and the same comments as for Figure 6-8 apply. Here $\alpha_{2, U} = 0.015$ cm/GW.

### 6.3 Dual-arm Z-scan to measure thin film nonlinearities

The DA Z-scan method has also been extended to measure the nonlinearities of thin films on thick substrates [102]. The same energy, pulse width, and beam waist equalization procedures apply as mentioned in the above section. But in the case of films, the relative sample Z-positions are found by performing Z-scans of the bare substrates. To fabricate the films for DA Z-scan measurements, substrates from the same lot are cleaved in two, yielding one blank reference substrate and another on which the film is deposited (see Figure 6-10(a) inset).

![Figure 6-10](image_url)

**Figure 6-10.** Scan procedure of thin films for DA Z-scan by (a) scanning bare area of the film and substrate and by (b) translating the sample to the “film” area and scanning at high energy.
This serves a dual purpose: one to safeguard against thickness irregularities between substrates and the other to collocate the sample Z-positions. The cleaved halves reserved for deposition can be coated by different methodologies with organic molecules or with semiconductor material. To match sample Z-positioning, the cleaved half containing the film and the other blank half are placed on their own 3-D stage mounted on top of the Z-scan stage and scanned together. The half containing the film is translated to the “Bare Area” (see Figure 6-10a) so only the substrate is measured. The z-positions are matched by observing a flat line subtraction of the CA signals on both arms (identical to the subtraction shown in Figure 6-7 for solvents).

![Figure 6-11.](image)

Figure 6-11. (a) LEB(Z) and high energy scan of a 3 μm thick ZnO film deposited on a 1 mm thick quartz substrate. (b) The subtraction of the curves in (a) along with the fit. The gold shaded region in (a) depicts the nonlinear signal on top of the large linear background.

The process of background subtraction is essential for thin film measurements as the linear background, a major byproduct of the sample inhomogeneity, is oftentimes larger than the signal due to the film. Shown in Figure 6-11(a) is LEB(Z) for a ZnO film (thickness = 3 μm) deposited on a 1 mm thick quartz substrate. In this case, the linear background is ~4× than that due to the
nonlinear signal which if not accounted for, could lead to vastly different determinations of the NLR.

Figure 6-12. Comparison of the CA Z-scan presented in Figure 6-11(b) with its respective 1 mm thick quartz substrate. The measurements were performed using 780nm pulses at a pulsewidth of 170 fs (FWHM) using $I_0 = 260$ GW/cm$^2$. The fit obtained for the film was $n_{2,U} = 1.0 \pm 0.25 \times 10^{-14}$ cm$^2$/W. The film was fabricated by the Kippelen group at Georgia Institute of Technology [102].

Figure 6-12 shows Z-scans of the 1 mm thick quartz substrate and ZnO film (from Figure 6-11) at 780 nm excitation and 170 fs (FWHM) pulse width with an energy of 370 nJ ($I_0 = 260$ GW/cm$^2$). At this wavelength and irradiance, there are no nonlinear absorption signals observed from the film or substrate. Using the same notation in the above section where the subscripts $S$, $V$, and $U$ represent the film plus substrate, substrate, and film, respectively, $\Delta T_{p-v,U} = 7 \cdot \Delta T_{p-v,U}$. The value of $n_{2,V}$ measured for the quartz is $0.24 \pm 0.05 \times 10^{-15}$ cm$^2$/W and agrees with previously reported literature values [103]. The value of $1.0 \pm 0.25 \times 10^{-14}$ cm$^2$/W obtained from the ZnO film agrees within error with our measurements of bulk ZnO (thickness of 530 μm) of $1.24 \pm 0.31 \times$
10^{-14} \text{ cm}^2/\text{W} using the same experimental configuration and also agrees with the literature value [104]. Although \( n_{2, U} \) is 40 times larger than \( n_{2, V} \), the thickness of the substrate is > 300× that of the film making the overall nonlinear phase shift of the film small. Hence, the DA Z-scan method was essential in determining the NLR of the film.

Figure 6-13 shows Z-scans of an organic thin film (whose structure is shown as an inset) after substrate and low-energy background subtraction as well as the substrate itself at 45 fs (FWHM), 1400 nm excitation with an energy of 66 nJ \( (I_0 = 125 \text{ GW/cm}^2) \). In this case, there is an appreciable OA signal which contributes significantly to the CA signal. The \( \alpha_{2, U} \) value determined from the OA signal is 5.6 ± 1.4 cm / GW and the CA signal is then fit with an \( n_{2, U} \) of -2.5 ± 0.63 × 10^{-13}
cm$^2$/W and the corresponding $\alpha_{2,U}$ value. The $n_{2,V} = 0.24 \pm 0.05 \times 10^{-15}$ cm$^2$/W. Considering the signals from the film and substrate, conventional Z-scans would be adequate in determining the nonlinearity. But ultimately, the DA Z-scan technique still significantly reduces the noise present allowing for the enhancement of the SNR ratio.

6.4 Quasi 3-level modeling of organic molecules

As mentioned briefly in the introduction, organic molecules have been widely studied for their applicability for nonlinear optical devices such as all-optical switching (AOS) [106-110]. For efficient operation, these devices require a large NLR while minimizing linear and nonlinear optical losses. We have recently shown that we can predict the dispersion of $n_2$ of various organic molecules in which the main polarizability is along one molecular axis such that we can approximate them as being centrosymmetric. This can be achieved from knowing only its linear absorption and 2PA spectrum by utilizing a simplification to a quantum mechanical perturbation model [111]. Since the spectrum of 2PA can be measured quite rapidly by using such methods as two-photon induced fluorescence spectroscopy and white-light pump probe spectroscopy [112, 113], this enables the determination of NLR to be rapid as well where experimentally obtaining values of $n_2$ can be time consuming. We also noted that the 2PA contribution in the model only needs to be included when modeling the 2PA spectra in regions outside of the linear absorption bandwidth. This gives better representation of the modeling with the experimentally obtained spectra. The following paragraphs describe this work and the next section will present another level of sophistication to predict the NLR of centrosymmetric organic systems.

The sum-over-states (SOS) model, first proposed in Ref. [114] and expounded upon in Ref. [115], is a quantum-mechanical perturbation model that takes into account a molecule’s ground
state along with all possible excited states and their corresponding transition dipole moments. Of note, this model has been studied in greater detail by previous group members than what will be presented here [116-118]. Organic systems contain a great number of excited states making the full perturbation theory model computationally intensive and difficult to implement [107]. This model can be simplified by accounting for only the most important states. Thus, a simplification to the full SOS model, named the essential-state model, was presented in Ref. [119] to describe the nonlinear behavior of these systems by utilizing the smallest number relevant energy states, which are critical in determining the 2PA spectrum and NLR dispersion of a molecular system. It has been shown that the spectral behavior of many organic systems can be described by as few as two states [91, 120, 121]. But the 2-level essential-state model breaks down for organic systems in which the electronic cloud distribution is symmetric, and thus possessing zero permanent dipole moment. In this case, at least a third energy state is required to describe the third-order nonlinearity of the molecules [122]. The second hyperpolarizability \( \gamma^{(3)} \) (defined for gases in Section 2.3) of an organic system can be written in terms of \( \omega \) as [121, 123, 124]:
\[ \gamma_{ijk}^{(3)}(\omega) = \{\omega_p + \omega_q + \omega_r; \omega_p, \omega_q, \omega_r \} \]

\[
\frac{1}{\hbar^3} \sum_{v,n,m} \left\{ \frac{\mu_{gv}^l (\mu_{vn}^l - \mu_{gg}^l) (\mu_{nm}^k - \mu_{gg}^k) \mu_{mg}^j}{(\bar{\omega}_{vg} - \omega_p - \omega_q - \omega_r)(\bar{\omega}_{ng} - \omega_q - \omega_r)(\bar{\omega}_{mg} - \omega_p)} + \frac{\mu_{gv}^l (\mu_{vn}^l - \mu_{gg}^l) (\mu_{nm}^k - \mu_{gg}^k) \mu_{mg}^j}{(\bar{\omega}_{vg}^* + \omega_p)(\bar{\omega}_{ng}^* - \omega_q + \omega_p)(\bar{\omega}_{mg} - \omega_r)} \right. \\
+ \frac{\mu_{gv}^l (\mu_{vn}^l - \mu_{gg}^l) (\mu_{nm}^k - \mu_{gg}^k) \mu_{mg}^j}{(\bar{\omega}_{vg}^* + \omega_p)(\bar{\omega}_{ng} - \omega_q + \omega_p)(\bar{\omega}_{mg} - \omega_p)} \left. \right\} \\
- \sum_{n,m} \left\{ \frac{\mu_{gn}^l \mu_{ng}^k \mu_{gm}^j \mu_{mg}^j}{(\bar{\omega}_{ng} - \omega_p - \omega_q - \omega_r)(\bar{\omega}_{ng} - \omega_r)(\bar{\omega}_{mg} - \omega_p)} + \frac{\mu_{gn}^l \mu_{ng}^k \mu_{gm}^j \mu_{mg}^j}{(\bar{\omega}_{ng}^* + \omega_q)(\bar{\omega}_{ng} - \omega_r)(\bar{\omega}_{mg} - \omega_p)} \right. \\
+ \frac{\mu_{gn}^l \mu_{ng}^k \mu_{gm}^j \mu_{mg}^j}{(\bar{\omega}_{ng}^* + \omega_r)(\bar{\omega}_{ng}^* + \omega_p)(\bar{\omega}_{mg} - \omega_q)} \left. \right\} \\
+ \frac{\mu_{gn}^l \mu_{ng}^k \mu_{gm}^j \mu_{mg}^j}{(\bar{\omega}_{ng}^* + \omega_r)(\bar{\omega}_{ng}^* + \omega_p)(\bar{\omega}_{mg}^* + \omega_q + \omega_r)} \right\}
\]

where \( i,j,k \), and \( l \) are the molecular axis coordinates. The subscripts \( p,q, \) and \( r \) represent the frequencies of the applied electric fields and thus describe the photon energies. The complex frequency \( \omega_{\ell g} = \omega_{\ell g} - i \Gamma_{\ell g} \) defines the resonant transition frequency between states \( g \) and \( \ell \) (i.e. \( \ell = v, n, \) or \( m \)) where \( \omega_{\ell g} \) is the central frequency and \( \Gamma_{\ell g} \) is the damping factor related to the linewidth of the transition with the \( \ast \) denoting the complex conjugate. The transition dipole
moments $\mu_{g\ell}$ and $\mu_{\ell\ell'}$ are defined as $\langle g | \mu | \ell \rangle$ and $\langle \ell | \mu | \ell' \rangle$, respectively, and describe the transition between $g$ and $\ell$ and the transition between the different states $\ell'$, respectively.

For the 3-level model, we consider a minimum of 3 essential states. Therefore, the states corresponding to subscripts $v, n$, and $m$ refer to either the first excited state which will be denoted as $e$ or the 2PA state denoted as $e'$. For symmetric molecules, the ground state $g$ has either even or odd symmetry, the 1st excited state has the opposite symmetry of the ground state, and the 2PA state has the same symmetry as the ground state. Thus, the normal dipole allowed selection rules apply and the symmetry of the states is well described by even and odd parity. The transition from the ground state $g$ to the 1st excited state $e$, and from $e$ to the 2PA state $e'$, are electric dipole allowed due to the selection rule (even$\leftrightarrow$odd); while the direct transition between the ground state and 2PA state with the same symmetry (even$\rightarrow$even or odd$\rightarrow$odd) is forbidden. This well-defined symmetry applies only to the case of purely symmetric molecules. But for molecules possessing a permanent dipole, the states have mixed parity and thus self-transitions and transitions from the ground state to 2PA state are allowed, i.e $g \to g$, $e \to e$, and $g \to e'$. It thus follows that the transition dipole moments are defined as $\mu_{ge}$ and $\mu_{ee}$, for the transition between the ground state $g$ and first excited state $e$ and states $e$ and 2PA state $e'$, respectively, and for the mixed parity case $\mu_{ge'}$ describing the transition from the ground state $g$ to the 2PA state $e'$. The complex frequency $\tilde{\omega}_{\ell g}$ can now be re-defined in terms of the states $e$ and $e'$ where $\tilde{\omega}_{eg}$ and $\tilde{\omega}_{eg'}$ defines the frequency and damping related with the transition between the ground and intermediate state and ground and 2PA state, respectively. Note that for molecules having multiple 2PA resonances, additional transitions from the intermediate state to each additional 2PA state are included in Eqn.
Thus, when describing systems with multiple 2PA states, we term this the quasi 3-level model.

The first summation of Eqn. (6.10) involves the sum over all possible ways to arrange the states \( u, n, \) and \( m \). Therefore, since there are two possibilities for each state, i.e. each state can either occupy the intermediate state \( e \) or the 2PA state \( e' \), there are 8 total cases contributing to the summation. In general, all 8 cases are non-zero when considering molecules with permanent dipole moments. But if we only consider purely centrosymmetric molecules (this becomes an approximation when considering molecules without a strong permanent dipole moment), the number of non-zero cases reduces to 1. The terms corresponding to each case for the first summation of Eqn. (6.10) are listed in Table 6-1.
Table 6-1. The terms existing in the numerator of the 1st summation of Eqn. (6.10) for the cases corresponding to all possible transitions of purely centrosymmetric molecules and those with permanent dipole moments. The cases are given for each permutation of states \((v, n, m)\). The state vectors are defined so that \(|1\rangle = |e\rangle\) and \(|2\rangle = |e'\rangle\). For example, Case I has the form \((1,1,1)\) corresponding to \((v = e, n = e, m = e)\). The form \((1,2,2)\) of Case III corresponds to \((v = e, n = e', m = e')\).

<table>
<thead>
<tr>
<th>Case</th>
<th>Purely Centrosymmetric</th>
<th>Molecules with Permanent Dipole Moments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case I (1,1,1)</td>
<td>N/A</td>
<td>(\Delta \mu^2 \mu_{ge}^2)</td>
</tr>
<tr>
<td>Case II (1,2,1)</td>
<td>(\mu_{ge}^2 \mu_{eer}^2)</td>
<td>(\mu_{ge}^2 (\mu_{eer} - \mu_{gg})^2)</td>
</tr>
<tr>
<td>Case III (1,2,2)</td>
<td>N/A</td>
<td>(\mu_{ge} (\mu_{eer} - \mu_{gg}) (\mu_{eer} - \mu_{gg}) \mu_{ger})</td>
</tr>
<tr>
<td>Case IV (1,1,2)</td>
<td>N/A</td>
<td>(\mu_{ge} \Delta \mu (\mu_{eer} - \mu_{gg}) \mu_{ger})</td>
</tr>
<tr>
<td>Case V (2,1,1)</td>
<td>N/A</td>
<td>(\mu_{ge} \Delta \mu (\mu_{eer} - \mu_{gg}) \mu_{ger})</td>
</tr>
<tr>
<td>Case VI (2,2,1)</td>
<td>N/A</td>
<td>(\mu_{ge} (\mu_{eer} - \mu_{gg}) (\mu_{eer} - \mu_{gg}) \mu_{ger})</td>
</tr>
<tr>
<td>Case VII (2,1,2)</td>
<td>N/A</td>
<td>(\mu_{ger}^2 (\mu_{eer} - \mu_{gg})^2)</td>
</tr>
<tr>
<td>Case VIII (2,2,2)</td>
<td>N/A</td>
<td>(\mu_{ger}^2 (\mu_{eer} - \mu_{gg})^2)</td>
</tr>
</tbody>
</table>

The permanent dipole moment difference between the ground and first excited state is defined as \(\Delta \mu = \mu_{ee} - \mu_{gg}\). Typically, the strength of the ground to intermediate state transition dipole moment is much greater than the ground to 2PA state dipole moment for molecules of mixed parity.
such that $\mu_{ge} \gg \mu_{g'e}$. Thus, the dominant cases for molecules possessing a permanent dipole moment are Case I and Case II listed in Table 6-1 whereas the only non-zero case for purely symmetric molecules is that of Case II.

For the 2nd summation of Eqn. (6.10), the transitions involve those only to the ground state. For the case of mixed parity, it follows that there are 4 ways to arrange the states $n$ and $m$ so that they either correspond to the intermediate state $e$ or the 2PA state $e'$. In the case of purely symmetric molecules, there is only one case that is pertinent. The terms in the numerator of the 2nd summation are shown in Table 6-2.

Table 6-2. The terms existing in the numerator of the 2nd summation of Eqn. (6.10) for the cases corresponding to all possible transitions of purely centrosymmetric molecules and those with permanent dipole moments. The cases are given for each permutation of states $(n,m)$. The state vectors are defined so that $|1\rangle \equiv |e\rangle$ and $|2\rangle \equiv |e'\rangle$. For example, Case I has the form $(1,1)$ corresponding to $(n = e, m = e)$. The form $(1,2)$ of Case II corresponds to $(n = e, m = e')$.

<table>
<thead>
<tr>
<th></th>
<th>Purely Centrosymmetric</th>
<th>Molecules with Permanent Dipole Moments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case I (1,1)</td>
<td>$\mu_{ge}^4$</td>
<td>$\mu_{ge}^4$</td>
</tr>
<tr>
<td>Case II (1,2)</td>
<td>N/A</td>
<td>$\mu_{ge}^2\mu_{g'e}^2$</td>
</tr>
<tr>
<td>Case III (2,1)</td>
<td>N/A</td>
<td>$\mu_{ge}^2\mu_{g'e}^2$</td>
</tr>
<tr>
<td>Case IV (2,2)</td>
<td>N/A</td>
<td>$\mu_{g'e}^4$</td>
</tr>
</tbody>
</table>
Note that in the case of molecules with permanent dipole moments, Case II and Case III of Table 6-2 yield the same numerator but have different denominators. In the case for purely symmetric molecules, there exist one non-zero case which is when state $n = m = e$. Similar to the terms in the 1$^{st}$ summation, if we assume that $\mu_{ge} \gg \mu_{ger}$ the dominant case for molecules possessing a permanent dipole moment is Case I.

From the two dominant cases listed in Table 6-1, the first summation includes contributions from the permanent dipole moment difference $\Delta \mu$ as well as transitions to the 2PA final state, $\mu_{eer}$. Thus, terms involving $\Delta \mu$ are referred to as Dipolar terms (D-terms) and terms involving $\mu_{eer}$ are referred to as two-photon terms (T-terms). Since $\Delta \mu$ is only retained when the states $v, n,$ and $m$ all represent the intermediate state $e$, the D-terms can be derived from the 2-level model [123]. The terms involving $\mu_{eer} - \mu_{gg}$ have mixed D-term and T-term qualities. For slightly asymmetric molecules, $\mu_{gg} \ll \mu_{eer}$ and the mixed terms vanish leaving just the T-terms.

The second summation of Eqn. (6.10), see Table 6-2, whose terms always show a negative contribution represent the “Negative terms” (N-terms) corresponding to the transition between states $g$ and $e$ for purely symmetric molecules, i.e. not involving the 2-photon final state or corresponding to the transition between states $g$ and $e$ and/or $e'$ for molecules of mixed parity. To describe systems with multiple 2PA resonances, additional T-terms with dipole allowed transitions between states $e$ and $e'$ are included in Eqn. (6.10), i.e. the same intermediate state is used. Thus, this model is referred to as a quasi 3-level model when accounting for multiple 2PA states.

The experimentally measured $n_2$ and $\alpha_2$ are macroscopic quantities. To relate $n_2$ and $\alpha_2$ to $\gamma^{(3)}$, we use the following relations [111]:

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\[ n_2 = \frac{1}{5} \cdot \frac{3Nf^{(3)}}{4\varepsilon_0^2 c n_0^2} \text{Re}\hat{\gamma}^{(3)} \]  \hspace{1cm} (6.11) \\
\[ \alpha_2 = \frac{1}{5} \cdot \frac{3\omega Nf^{(3)}}{2\varepsilon_0^2 c^2 n_0^2} \text{Im}\hat{\gamma}^{(3)}_T, \]

where \( \hat{\gamma}^{(3)} \) is a dispersive quantity to describe the averaging due to the permutations of the fields for self-action nonlinearities, i.e. \( \omega = \omega_p + \omega_q + \omega_r \), and the subscript \( T \) denotes that only the T-terms are kept and the N-terms are excluded from the calculation (described later). Of note is that \( f^{(3)} \), previously defined in Section 2.3, is defined with respect to the subscripts \( p, q, \) and \( r \) representing 1, 2, and 3, respectively. The formulism of Eqn.(6.11) assumes that we are describing highly symmetric organic systems as described in the above reference. \( \hat{\gamma}^{(3)} \) is defined so that:

\[ \hat{\gamma}^{(3)}(\omega) = \frac{y^{(3)}_{xxx}(\omega; \omega, -\omega) + y^{(3)}_{x,xxx}(\omega; \omega, -\omega, \omega) + y^{(3)}_{xx,xxx}(\omega; -\omega, \omega, \omega)}{3}. \]  \hspace{1cm} (6.12)

Note that \( \hat{\gamma}^{(3)} \) is only defined along one molecular coordinate axis since we are considering molecules in which the main polarizability lies in one direction which implies that the transition dipole moments are also defined along the same axis, i.e. \( \mu \equiv \mu^x \).
Figure 6-14. 3-level essential-state model calculation, Eqn. (6.12), of the spectrum of the real (dashed black line) and imaginary (solid red line) components of $\gamma^{(3)}$, including (a) T-terms, (b) N-Terms, and (c) their sum as a function of the input photon frequency normalized by $\omega_{eg}$. The dotted blue line in (c) is $\gamma^{(3)}_T$, i.e. the imaginary component of the T-terms. The green dashed line in (a), (b), and (c) represents $\gamma^{(3)} = 0$. The D-terms are neglected in these calculations. The parameters used are $\omega_{e'g} = 1.6 \omega_{eg}$, $\Gamma_{eg} = \omega_{eg}/300$, $\Gamma_{e'g} = 4 \Gamma_{eg}$, and $\mu_{ge} = \mu_{e'e} = 5 D$.

Figure 6-14 shows a plot of the real (dashed black line) and imaginary (solid red line) components from Eqn. (6.12) for the general case of a centrosymmetric molecule. The T-terms are shown in Figure 6-14(a), the N-terms are shown in Figure 6-14(b), and the total response is shown in Figure 6-14(c). The Re$\gamma^{(3)}$ is directly proportional to $n_2$ while the Im$\gamma^{(3)}_T$ is directly proportional to $\alpha_2$. Thus, the peak of Im$\gamma^{(3)}_T$ corresponds to a 2PA resonance and, from the input parameters given in the caption of Figure 6-14, is observed at $\omega_{e'g}/2$. The D-terms (although not included in the calculations) mimic the T-terms with resonances at both $\omega_{eg}/2$ and $\omega_{eg}$. When describing $n_2$ via Re$\gamma^{(3)}$, both T-terms and N-terms are used. When describing $\alpha_2$ via Im$\gamma^{(3)}_T$, the N-terms are neglected as discussed in Ref. [111].

The linear parameters used in the calculation of Eqn. (6.10) can be extracted from the linear absorption spectrum, i.e. $\omega_{eg}, \Gamma_{eg}$, and $\mu_{ge}$.
Figure 6-15. Normalized linear absorption of YZ-V-69 dissolved in carbon tetrachloride. The red line is the Lorentzian fit to the spectrum to obtain the width and peak of the linear absorption band. The structure is shown in the inset. This molecule was provided by Marder’s group at Georgia Institute of Technology.

Figure 6-15 shows the normalized linear absorption spectrum of YZ-V-69 dissolved in carbon tetrachloride. The peak of the main absorption band corresponds to $E_{ge} = \hbar \omega_{eg}$ and the half-width half-maximum of the Lorentzian fit corresponds to $\Gamma_{eg}$. Thus, for YZ-V-69 $\omega_{eg} = 1.27 \text{eV}/\hbar$ and $\Gamma_{eg} = 0.044 \text{eV}/\hbar$. The ground state dipole moment can be determined using the following relation [125, 126]:

$$\mu_{ge} = 3.563 \cdot 10^{-33} \sqrt{\frac{1}{E_{ge}} \int \frac{\varepsilon(\nu)d\nu}{f^{(1)}}},$$

(6.13)

where $E_{ge}$ is the peak photon energy in eV, $\varepsilon(\nu)$ is the molar absorbance spectrum in units of cm$^{-1}$M$^{-1}$ where M is the molarity and $\nu$ is the wavenumber (cm$^{-1}$), and $f^{(1)} = (n_0^2 + 2)/3$ is the 1st-order local field correction. For YZ-V-69, $\varepsilon_{max} = (2.6 \pm 0.26) \cdot 10^5$ cm$^{-1}$M$^{-1}$. The integral of
Eqn. (6.13) is performed over the main absorption band. The units of $\mu_{ge}$ is given in Coulomb·m. Oftentimes, the units of the transition dipole moments are given in Debye (D) where $1\text{D} \cong 3.33 \cdot 10^{-30}$ Coulomb·m. For YZ-V-69, $\mu_{ge}$ is equal to 14 D.

Shown in Figure 6-16 is the spectrum of 2PA of YZ-V-69 in carbon tetrachloride. The measured $\alpha_2$ coefficients are expressed in terms of the 2PA cross-sections defined as [127]:

$$\delta_{2PA} = 10^{58} \frac{\hbar \omega \alpha_2}{N},$$  \hspace{1cm} (6.14)

where $\delta_{2PA}$ is in units of GM defined as $10^{-50}\text{cm}^4\cdot\text{s}\cdot\text{molecule}^{-1}\cdot\text{photon}^{-1}$. Thus, using Eqn. (6.11) we can express $\delta_{2PA}$ in terms of the quasi 3-level model as:

$$\delta_{2PA}(\omega) = \frac{1}{5} \cdot 3 \cdot 10^{58} \hbar \omega \frac{f(3)}{2 \epsilon_0 c^2 n_0^2} \text{Im} \hat{g}_T^{(3)}(\omega).$$ \hspace{1cm} (6.15)
The 2PA spectrum of YZ-V-69 was measured via Z-scans as outlined in Ref. [111]. Two 2PA bands are observed at $0.56\omega_{eg}$ and $0.75\omega_{eg}$ corresponding to $\hbar\omega_{erg} = 1.43$ eV and $\hbar\omega_{erg} = 1.91$ eV, respectively. Notice that the width centered at $0.56\omega_{eg}$ was not resolved with Z-scans due to limitations with detection at the time of measurements. But the non-degenerate 2PA spectrum was measured in chloroform by Joel Hales of Joseph Perry’s group at the Georgia Institute of Technology which confirmed not only the peak of this 2PA band but also the width. It’s important to note that the linear absorption spectrum in chloroform is slightly red-shifted and narrower than that in carbon tetrachloride, but we assume that the 2PA spectral shape is similar. Thus, the widths of the 2PA bands at $0.56\omega_{eg}$ and $0.75\omega_{eg}$ are fit with $\hbar\Gamma_{erg} = 0.06$ eV and $\hbar\Gamma_{erg} = 0.03$ eV, respectively, while $\mu_{eer}$ is fit with 6.1 D and 0.5 D, respectively.

![Figure 6-17. NLR spectrum in units of GM (see text) along with quasi 3-level model prediction (solid black line) of YZ-V-69 in carbon tetrachloride. The green dashed line represents $\delta = 0$.](image-url)
Figure 6-17 shows the NLR spectrum of YZ-V-69 in carbon tetrachloride along with the predicted dispersion from the quasi 3-level model. The measured $n_2$ coefficients are expressed in terms of the NLR cross-sections defined as [128]:

$$\delta_{NLR} = 10^{58} \frac{\hbar \omega^2 n_2}{c N},$$

(6.16)

where $\delta_{NLR}$ is also in units of GM. Thus, using Eqn. (6.11) we can express $\delta_{NLR}$ in terms of the quasi 3-level model as:

$$\delta_{NLR}(\omega) = \frac{1}{5} \cdot \frac{3 \cdot 10^{58} \hbar \omega^2 f^{(3)}}{4 \varepsilon_0^2 c^2 n_0^2} \Re \hat{\rho}^{(3)}(\omega).$$

(6.17)

Using the nonlinear parameters obtained from the 2PA spectrum, we find good qualitative and quantitative agreement between experimental values and that predicted by the quasi 3-level model. The measured quantities are within a factor of ~1.5 with the quasi 3-level model. We revisit the fact that $\Re \hat{\rho}^{(3)}$ is largely dependent upon the 2nd summation of Eqn. (6.11) and, thus, $\mu_{ge}^4$. So any inaccuracy in the determination of $\mu_{ge}$ from Eqn. (6.13) could lead to discrepancies in the predicted magnitude of NLR. In the next section, we extend the number of essential states to 4 to model the linear absorption more precisely.

### 6.5 Quasi 4-level modeling of organic molecules

In the quasi 3-level model, we considered only 3 essential states, i.e. 2 dipole allowed transitions: the ground state, one intermediate state, and the possibility of multiple 2PA states. For YZ-V-69, the linear absorption is not accurately modeled by a single Lorentzian corresponding to the intermediate state transition as shown in Figure 6-15. Note from the figure that there is a significant vibronic shoulder that is not included in the linear absorption determination even
though it is a one-photon allowed transition. Thus, if we extend the number of essential states to 4, we can include the vibronic shoulder as an intermediate state and model the linear absorption more precisely. Including this additional intermediate state extends the dipole allowed transitions to 4.

Extending the number of essential states to four to include 2 intermediate states increases the permutations to assign the states \( \nu, n, \) and \( m \) in Eqn. (6.11). Therefore, states \( \nu, n, \) and \( m \) can refer to the 1st intermediate state (denoted as \( e^{(1)} \) in Figure 6-18), the 2nd intermediate state (denoted as \( e^{(2)} \) in Figure 6-18), or the 2PA state \( e' \). For simplicity, we’ll assume that these states have well-defined symmetry such that the dipole allowed transitions occur for states with opposite parity. Thus, the transitions from one intermediate state to the other intermediate state are forbidden. Furthermore, there are no permanent dipole moments.

Figure 6-18. Schematic of the quasi 4-level model showing the allowed transitions between the various levels. For simplicity, we assume purely centrosymmetric molecules so that all permanent dipole moments are zero and the transition between the two intermediate states is forbidden.
In terms of the quasi 4-level model, the first summation of Eqn. (6.10) has 27 total possibilities to arrange the states \(\nu, n,\) and \(m\). Since we only consider centrosymmetric molecules whose states have well-defined symmetry, there are 4 non-zero cases which contribute. The numerators are listed in Table 6-3.

Table 6-3. The terms existing in the numerator of the 1st summation of Eqn. (6.10) for the cases corresponding to the non-zero transitions of purely centrosymmetric molecules for the quasi 4-level model. The cases are given for the permutations of states \((\nu, n, m)\). The state vectors are defined so that \(|1\rangle \equiv |e^{(1)}\rangle\), \(|2\rangle \equiv |e^{(2)}\rangle\), and \(|3\rangle \equiv |e'\rangle\). For example, Case I has the form \((1,3,1)\) corresponding to \((\nu = e^{(1)}, n = e', m = e^{(1)})\). The form \((2,3,1)\) of Case III corresponds to \((\nu = e^{(2)}, n = e', m = e^{(1)})\).

<table>
<thead>
<tr>
<th>Case</th>
<th>Purely Centrosymmetric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case I (1,3,1)</td>
<td>(\mu_{ge^{(1)}}^2\mu_{e^{(1)}e'\nu}^2)</td>
</tr>
<tr>
<td>Case II (1,3,2)</td>
<td>(\mu_{ge^{(1)}}\mu_{ge^{(1)}e}\mu_{ge^{(2)}}\mu_{e^{(2)}e'\nu}^2)</td>
</tr>
<tr>
<td>Case III (2,3,1)</td>
<td>(\mu_{ge^{(1)}}\mu_{ge^{(1)}e}\mu_{ge^{(2)}}\mu_{e^{(2)}e'\nu}^2)</td>
</tr>
<tr>
<td>Case IV (2,3,2)</td>
<td>(\mu_{ge^{(2)}}\mu_{e^{(2)}e'\nu}^2)</td>
</tr>
</tbody>
</table>

Note that Case II and Case III listed in Table 6-3 have the same functional form but have different denominators such that these 2 cases are, indeed, different.

For the 2nd summation of Eqn. (6.10), the transitions involving those to the ground state produce 4 total permutations of states \(n\) and \(m\) for the case of the quasi 4-level model with all cases...
being non-zero. The terms appearing in the numerator of the 2\textsuperscript{nd} summation are shown in Table 6-4.

Table 6-4. The terms existing in the numerator of the 2\textsuperscript{nd} summation of Eqn. (6.10) for all cases of a purely centrosymmetric molecules for the quasi 4-level model. The cases are given for the permutations of states \((n, m)\). The state vectors are defined so that \(|1\rangle \equiv |e^{(1)}\rangle\) and \(|2\rangle \equiv |e^{(2)}\rangle\). For example, Case I has the form \((1,1)\) corresponding to \((n = e^{(1)}, m = e^{(1)})\). The form \((2,1)\) of Case III corresponds to \((n = e^{(2)}, m = e^{(1)})\).

<table>
<thead>
<tr>
<th></th>
<th>Purely Centrosymmetric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case I (1,1)</td>
<td>(\mu_{ge^{(1)}}^4)</td>
</tr>
<tr>
<td>Case II (1,2)</td>
<td>(\mu_{ge^{(1)}}^2\mu_{ge^{(2)}}^2)</td>
</tr>
<tr>
<td>Case III (2,1)</td>
<td>(\mu_{ge^{(1)}}^2\mu_{ge^{(2)}}^2)</td>
</tr>
<tr>
<td>Case IV (2,2)</td>
<td>(\mu_{ge^{(2)}}^4)</td>
</tr>
</tbody>
</table>

Note that Case II and Case III listed in Table 6-4 have the same functional form but have different denominators such that these 2 cases are, indeed, different.
Figure 6-19. Normalized linear absorption (dashed black line) of YZ-V-69 dissolved in carbon tetrachloride along with two Lorentzian fits to model the linear absorption band. The solid red line is the Lorentzian fit of Figure 6-15 which refers to the 1st intermediate state for the quasi 4-level model whereas the solid blue line is the Lorentzian fit of the vibronic shoulder referring to the 2nd intermediate state.

Figure 6-19 shows the fit of the vibronic shoulder with a Lorentzian (solid blue line) to represent the 2nd intermediate state of the quasi 4-level model along with the fit of the main linear absorption band (solid red line). Using Eqn. (6.13), we obtain $\mu_e^{(2)} = 5.1D$. This value is obtained from subtracting the integrated molar absorbance of the 2nd intermediate state (vibronic shoulder) from the overlapping integrated region from the 1st intermediate state (main absorption band) and using the subtracted integrated value in Eqn. (6.13). Additionally from the Lorentzian fit, we obtain $\omega_e^{(2)}g = 1.40\ eV/\hbar$ and $\Gamma_e^{(2)}g = 0.08\ eV/\hbar$. For the 1st intermediate state, we use the same parameters from the quasi 3-level model, i.e. $\mu_e^{(1)} = 14D$, $\omega_e^{(1)}g = 1.27\ eV/\hbar$, and $\Gamma_e^{(1)}g = 0.044\ eV/\hbar$. 

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Figure 6-20. 2PA spectrum of YZ-V-69 in carbon tetrachloride along with quasi 4-level model fit (solid red line). The green dashed line represents $\delta = 0$.

Figure 6-20 shows the 2PA spectrum of YZ-V-69 along with the quasi 4-level model using Eqn. (6.15). The addition of the 2nd intermediate state increases the number of terms to 48 for each 2PA band so there are 96 terms contributing to the fit in Figure 6-20. Since we don’t know the individual strengths from each intermediate state to the respective 2PA state, it is assumed that

$$\mu_e^{(1)} = \mu_e^{(2)}$$

where the superscripts (1) and (2) represent the lower-lying 2PA state and higher-lying 2PA state, respectively. Thus, to fit the 2PA spectrum the values of $\mu_e^{(1)} = 4.8 \, D$ and $\mu_e^{(2)} = 0.44 \, D$ were used. As expected, the peaks and widths of the two 2PA bands are the same as for the quasi 3-level fits.
Figure 6-21. NLR spectrum of YZ-V-69 plotted along with the predicted dispersion of NLR from the quasi 3-level fit (solid black line) and quasi 4-level fit (dashed red line). The green dashed line represents $\delta = 0$.

Figure 6-21 shows the predicted NLR dispersion of YZ-V-69 using the quasi 4-level model as a dashed red line. For comparison, the predicted dispersion from the quasi 3-level fit is shown as a solid black line. The introduction of the 2nd intermediate state allows for better modeling of the linear absorption band. This, in turn, gives a more precise accounting of the N-terms which dominate the magnitude of NLR. The quasi 4-level model matches slightly better the NLR data for the 3 smallest photon energies and 2 largest photon energies when the magnitudes are smaller and when the magnitudes become large, respectively. Whereas the quasi 3-level model marginally undershoots the measured magnitude of NLR for the 2 largest photon energies, the quasi 4-level model matches better the measured magnitudes within error.
In Ref. [111], it was argued that in describing the 2PA coefficient $\alpha_2$ via the SOS model, that the imaginary component of the N-terms should not be included outside of the linear absorption bandwidth. These terms correspond to absorption saturation and produce a strong negative contribution to the imaginary component of the nonlinear response. Shown in Figure 6-22 are the fits to the 2PA spectrum of YZ-V-69 using the quasi 3-level model and quasi 4-level model while including the imaginary component of the N-terms. Notice how with the quasi 4-level fit and its inclusion of the 2nd intermediate state (and, thus, the inclusion of additional N-terms), the model tends negative more quickly than the quasi 3-level fit. Thus, we can make the inference that with the inclusion of additional intermediate states, the fit will tend more and more negative. In describing organic systems by utilizing tens or hundreds of intermediate states that are strongly coupled to the ground state, as often done by quantum-chemists, large discrepancy in the 2PA...
spectrum arises due to their inclusion of the imaginary component of the N-terms in spectral regions of transparency where, in real systems, the linear absorption is negligible.

From the linear absorption and 2PA spectrum, we can extract all necessary parameters to use a simplified essential state model to predict the dispersion of NLR. The quasi 3-level model qualitatively follows the trend of the experimentally obtained NLR data. Furthermore, the magnitudes are shown to differ by no more than a factor of 2. The magnitude of NLR is dominated by the N-terms and, thus, the magnitude of $\mu_{ge}$ to the fourth power. Therefore, an inaccurate determination of $\mu_{ge}$ can undershoot or overshoot the measured results. By introducing a second intermediate state, i.e. using a quasi 4-level system, the linear absorption can be more precisely modeled and a better representation of the N-terms can be obtained. This, in turn, allows for a better quantitative description of the measured results. It must be noted, however, that the complete physics behind adding the vibronic band as an intermediate state in the quasi 4-level model is not fully understood regarding the strengths of the dipole moments from the vibronic band to each 2PA state. Further study should commence regarding this issue.
A WLC has been shown to be useful in a wide variety of fields. For instance, a WLC was introduced as a source in the LIDAR (light detection and ranging) technique to monitor water vapor content and pollutants in the atmosphere [129]. Pulse compression ranging from the few fs to attosecond regime has been observed through filamentation [130-134]. More importantly for the scope of this thesis, a WLC has great utility in nonlinear spectroscopy.

Transient absorption spectroscopy, also known as the pump-probe technique, allows for such measurements as degenerate and non-degenerate 2PA spectra [112, 135, 136] and excited state absorption (ESA) cross-sections [137]. In the case of the pump-probe technique, the “strong” pump pulse stimulates the excitation of an electron into an excited state while the probe is used to gauge the population of that excited state in transmission. Depending on the spectral region of excitation, an instantaneous or cascaded nonlinearity can occur. For a cascaded nonlinearity, usually two types of processes can occur: $\chi^{(1)}: \chi^{(1)}$ or $\chi^{(3)}: \chi^{(1)}$. The first type involves linear absorption of the pump followed by absorption of the probe. The second type involves 2PA of the pump followed by absorption of the probe. A full description of the corresponding rate equations that govern the populations of the excited states is outside the scope of this thesis but can be found in references such as [138, 139]. The conventional means of generating the probe pulses is by using either a small portion of the laser source or an OPG/A as a tunable source. A WLC probe was utilized as early as the 1980s by pumping a water filled cuvette with sub-picosecond pulses [140]. This allowed a broadband probe with wavelengths ranging from 350 nm – 900 nm to be obtained. To extend the wavelength range of the probe, 2200 nm pulses were focused into a 1 mm...
thick sapphire window to generate a spectrum ranging from 450 nm to greater than 1700 nm in Ref. [141]. A WLC generated by focusing 1300 nm pulses into a 2.5 mm thick piece of calcium fluoride was shown to produce probe pulses spanning the visible and near-IR regime [142, 143]. The WLC generated in the aforementioned materials is sufficient for using as a probe as the required energy, or spectral energy density, does not need to be high. For instance, in Ref. [112], the WLC generated by focusing 1400 nm pulses into a 1.5 mm thick piece of fused silica allowed the determination of the non-degenerate 2PA spectrum of ZnS and an organic compound.

As described in Section 6.1, the Z-scan is a widely used technique to measure nonlinear absorption and refraction. To ascertain the full spectra of materials, an OPG/A is typically used to generate the wavelengths needed. In Ref. [144], a WLC was generated by focusing \( \sim 10 \mu J \), 775 nm, 150 fs (FWHM) pulses into a 3 cm cuvette filled with distilled water to be used for Z-scan measurements. This produced spectral energy densities of 10 pJ/nm – 25 nJ/nm over the range of 650 nm – 900 nm. To spectrally separate the WLC, 10 nm (FWHM) bandpass interference filters were used of varying peak transmittances which resulted in near transform-limited pulses. This allowed the measurement of 2PA coefficients of ZnSe where the measured coefficients were determined to range from \( \sim 3.5 \) cm/GW to \( \sim 5.5 \) cm/GW which agreed with the theoretical prediction from a 2-band model [145]. This technique was extended to measuring the NLR coefficients of ZnSe by using the same WLC generated in water but using a linearly variable bandpass filter in Ref. [146]. Although the WLC spectral energy density was adequate to ascertain the 2PA spectrum of ZnSe in the above range, it would not be sufficient to measure many organic materials as they are usually in solution at relatively low concentrations and typically have much smaller nonlinearities than semiconductors.
To address the problem of insufficient spectral energy density, the WLC was extended to generation in a noble gas in Refs. [81, 128]. Since the pump energy is much higher to produce WLC in gaseous media as than in condensed media, it was hypothesized that there would be an increase in the spectral energy density due to the increase in pump energy. The WLC generated in Ref. [128] was sufficient to measure the 2PA and NLR spectra of ZnSe, ZnS, as well as an organic molecule whose 2PA data had previously been determined in Ref. [147]. The authors generated this WLC in a 125 cm chamber filled with Kr gas at a pressure of 2.4 atm. The temporal width of the pulses after traversing through 10 nm (FWHM) bandwidth interference filters were determined to range from ~80 fs (FWHM) to ~140 fs (FWHM) which resulted in a time-bandwidth product of ~0.47 to 1.3. The VIS-NIR WLC pulses were shown to be closer to transform-limited than the UV-VIS portion of the WLC. The following section is presented to reproduce the aforementioned experiments with a focus on the generation characteristics presented in CHAPTER 2 and CHAPTER 3.
7.1 780nm Pumped WLC

Figure 7-1 shows the schematic of the WLC which is similar to the one used in Ref. [128]. An input pulse is incident on the lens (in figure above, the pulse comes from the left) and is weakly focused into a 125 cm chamber filled with Krypton (Kr) gas at various pressures. The chamber windows used in this experiment were 3 mm thick fused silica windows. The pulse is generated from a Clark-MXR CPA 2110 which outputs 780 nm, 1 mJ, ~150 fs (FWHM) pulses at a 1kHz repetition rate (see CHAPTER 5 for description of the laser system). The $\lambda/2$ waveplate and polarizer pair is used to attenuate the energy. The $\lambda/4$ waveplate is used to change the polarization state of the pulse from linear to different ellipticities. The output spectrum is then re-collimated with a lens and passes through a notch filter which blocks the 780 nm pump pulse leaving only the generated portion of the WLC spectrum as will be discussed in a subsequent paragraph. The WLC then passes through various narrow bandpass interference filters ($\Delta \lambda \sim 10$ nm FWHM) to determine the spectral irradiance in the specified spectral regions.
Figure 7-2. Transmission of different optical elements used to block the 780 nm pump from the WLC. The solid blue line is the spectrum of a 780 nm dielectric mirror at a 45 degree angle of incidence (AOI). The solid red line is the notch filter from TOPAS-C at a 0 degree AOI. The solid green line is a Semrock (Part No. NF03-785E-25) notch filter at a 0 degree AOI. The solid black line is the laser spectrum measured by an Ocean Optics HR4000 spectrometer. The offset inset shows the main figure with the horizontal axis expanded.

Figure 7-2 shows the transmission spectra of different optical elements that were used to block the 780 nm laser from the resultant WLC measured using a Cary 500 spectrophotometer. The solid blue line represents the spectrum of a 780 nm dielectric mirror at a 45 degree angle of incidence. The reflectance bandwidth of the mirror is sufficient in blocking the entire spectral bandwidth of the 780 nm laser pulse at a blocking OD $> 2$. Note that due to the sensitivity limitations of the Cary 500 spectrophotometer, a more accurate determination of the blocking OD could not be obtained. The transmission in the visible spectral region (450 nm – 650 nm) is relatively flat with a transmission greater than 85%. The transmission spectrum suffers drastically
in the near-IR spectral region (not shown), but since the WLC generated in Ref. [128] was mostly usable in the visible, it was determined that it wouldn’t pose a major problem. The solid red line in Figure 7-2 is the spectrum of the TOPAS-C notch filter used in the OPG/A. This notch filter is designed to have a large blocking OD covering the 780 nm laser spectrum while allowing the signal and idler pulses (1160 nm – 2600 nm) to be transmitted through. Unfortunately, the visible spectral region is not adequately transmitted. The solid green line is the transmission spectrum of the Semrock notch filter (Part No. NF03-785E-25). This filter has the flattest transmission outside of the blocking OD range which makes it ideal for WLC spectroscopy. But the blocking OD range is not sufficient to completely block the 780 nm laser spectrum from being transmitted. The offset inset of Figure 7-2 shows the main figure with the horizontal axis expanded. There is a small amount of the laser spectrum that is not blocked by the Semrock filter. Since the pump energy for the WLC is quite large, as will be shown later, there would be significant leakage of the laser on the bandpass filters (see Figure 7-1) which could cause damage. Therefore, it was decided to use the 780 nm dielectric mirror at 45 degree angle of incidence as a notch filter to block the strong pump from the WLC.
To spectrally separate the WLC, we use narrow ($\Delta \lambda \sim 10$ nm FWHM bandwidth) bandpass interference filters. Some of the spectra are shown in Figure 7-3. In the WLC setup, the interference filters are positioned such that most of the rejected bandwidth is reflected. As shown, the peak transmittance of each filter is different and dictates the available energy for WLC spectroscopy. For most of the filters used, the blocking OD is greater than 2 and the rejection bandwidth extends from ~200 nm to ~2000nm.

Figure 7-3. Transmission spectrum of the bandpass interference filters used to spectrally separate the WLC.
Figure 7-4. Output energy at 400 nm versus the input 780 nm pump energy. The red shaded regions represent the energies in which no WLC was observed. The white shaded regions indicate when a flickering of the WLC was observed. The cyan shaded regions represent the range where a “stable” WLC was observed by eye. The yellow shaded regions represent the energy range where multiple filamentation was observed. $\Delta n_{pl}$ and $\Delta n_{SPM}$ are described by Eqn. (3.8) and Eqn. (2.7), respectively.

Figure 7-4 shows the plots of the output energy at 400nm (± 5 nm) with respect to the input 780nm pulse energy. These data were taken using a lens with a focal length $f_L$ of 1 m yielding a minimum spot size $w_0 \approx 100 \mu m$ (HW 1/e² M) near the middle of the chamber. In each graph, the red shaded region represents the energy range where there was no WLC generation observed; the white region represents the range where flickering is observed (or unstable generation); the cyan
region represents the range in which a stable WLC is observed (where the output at 400nm is the most stable); and the yellow region represents the energy range where there is multiple filamentation clearly seen by eye. It is important to note that the labeled pressure on the graphs is the pressure read off the pressure gauge on the chamber. Thus, the actual pressure inside the chamber is 1 atm above the reading. All calculations presented hereafter take this into effect.

In Section 3.3, it was stated that the WLC is initiated by the balance of SPM and plasma specifically in gases. Thus, we can determine $\Delta n_{SPM}$ from the relations found in Eqn. (2.43) and Eqn. (2.45) and $\Delta n_{pl}$ from Eqn. (3.8). As mentioned in Section 2.3, the magnitude of $n_2$ of gases can be determined with knowledge of $\gamma^{(3)}$. This was determined experimentally obtained in Ref. [48] by measuring 3HG in gases using picosecond pulses at 1055nm. As mentioned in Section 2.3, the index of refraction in gases is dependent upon its pressure $P$ and temperature $T$ as [48]:

$$n(\lambda, P, T) = \left(2 \frac{n_0(\lambda)^2 - 1}{n_0(\lambda)^2 + 2 P T_0} + 1\right)^{1/2} \left(1 - \frac{n_0(\lambda)^2 - 1}{n_0(\lambda)^2 + 2 P T_0}\right)^{-1/2}. \quad (7.1)$$

This means that $n_2$ is spectrally dispersive and depends also upon $T$ and $P$ such that:

$$n_2(\lambda, P, T) = \frac{9 N_0 f^{(3)}}{4 c \epsilon_0^2 n(\lambda, P, T)^2} Re \left(\gamma^{(3)}(3 \omega; \omega, \omega, \omega)\right), \quad (7.2)$$

where the spectral dependence comes from the dispersion relation found in Ref. [52] as mentioned in Section 2.3. To determine $\Delta n_{PL}$, we use the relation of Eqn. (3.8) and calculate $R(I)$ given in Eqn. (3.16) for the various pump energies. To determine the irradiance distribution through the chamber, we use spatially and temporally Gaussian beams and, for simplicity, consider only the peak on-axis field distribution ($r = 0$). Therefore, the electric field is written as:
\[ E(z, t) = A(z)e^{-\frac{1}{2}(\frac{z}{z_0})^2} \]

\[ A(z) = \frac{2I_0}{c\varepsilon_0} \sqrt{1 + \left( \frac{z - f_L}{z_{0,l}} \right)^2}, \tag{7.3} \]

where \( z_{0,l} \) is the characteristic Rayleigh range given as \( \pi w_{0,I}^2 / \lambda \) with \( w_{0,I} = \lambda f_L / \pi w_I \) and \( w_I \) is the input beam size incident on the lens.

Figure 7-5. Beam profile of 780 nm pump pulse along with Gaussian fits provided by the DataRay WinCamD Beam Profiler. Note that to achieve this profile from the laser, there was an aperture placed inside the laser cavity. The two fits are from the x and y cross-sections of the beam.

From the profile obtained in Figure 7-5, the beam diameter is \( \sim 4 \text{ mm} \) FW 1/e² M of irradiance, thus making \( w_f \approx 2.0 \text{ mm} \) (HW 1/e² M of irradiance) in these experiments. The electric field, and thus the irradiance profile, is defined in this way to easily model changes in beam focusing due to using different focusing lenses. As can be inferred from Eqn. (7.3), the peak electric field occurs at the focus of the lens which is expected. We use the parameters for Kr gas in which the ionization potential is 14 eV [148] for single ionization of an electron lying in its outer most electron shell.
(i.e. n = 4). Revisiting Figure 3-3, the ionization rate is highly dependent upon the electric field strength, i.e. the irradiance. Several orders of magnitude increase in the rate can be calculated for just one order of magnitude increase in irradiance, which has been observed experimentally [59, 70]. By using Eqn. (7.3) in Eqn. (3.16), we can analyze the experimental results presented in Figure 7-4.

Table 7-1 shows the SPM and plasma contributions using the average input energy for generating a stable WLC (cyan shaded regions in Figure 7-4) for the gas pressures of 35 psi, 45 psi, 55 psi, and 65 psi. The input energies used to tabulate the constants are 950 µJ, 750 µJ, 550 µJ, and 400 µJ, respectively.

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>( n_2(\lambda, P, T) ) ( (m^2/W) )</th>
<th>( \Delta n_{SPM} )</th>
<th>( \frac{N_e(P,J)}{N_0(P)} )</th>
<th>( \Delta n_{PL} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>( 5.7 \times 10^{-23} )</td>
<td>( 1.4 \times 10^{-5} )</td>
<td>( 1.7 \times 10^{-2} )</td>
<td>( -3.8 \times 10^{-4} )</td>
</tr>
<tr>
<td>45</td>
<td>( 6.9 \times 10^{-23} )</td>
<td>( 1.3 \times 10^{-5} )</td>
<td>( 1.3 \times 10^{-3} )</td>
<td>( -3.5 \times 10^{-5} )</td>
</tr>
<tr>
<td>55</td>
<td>( 8.0 \times 10^{-23} )</td>
<td>( 1.1 \times 10^{-5} )</td>
<td>( 3.8 \times 10^{-5} )</td>
<td>( -1.2 \times 10^{-6} )</td>
</tr>
<tr>
<td>65</td>
<td>( 9.2 \times 10^{-23} )</td>
<td>( 9.5 \times 10^{-6} )</td>
<td>( 8.6 \times 10^{-7} )</td>
<td>( -3.1 \times 10^{-8} )</td>
</tr>
</tbody>
</table>

For the two middle pressures, \( \Delta n_{SPM} \) and \( \Delta n_{PL} \) are similar in magnitude where they considerably diverge at the lowest and highest pressures (see Table 7-1). For the highest pressure (and, thus, lowest needed input energies), \( \Delta n_{PL} \) is calculated to be 2 orders of magnitude less than
whereas at the lowest pressure (corresponding to the highest input energy), $\Delta n_{pl}$ is calculated to be 2 orders of magnitude more than $\Delta n_{SPM}$. This can be explained, in part, by the ionization rate model that was employed. Although the model has been shown to model experimental data quite well, the free electron density predicted can change by orders of magnitude with a small difference in input energy. In fact, the ionization rate is calculated to be 4 orders of magnitude larger for a 950 $\mu$J pulse than a 400 $\mu$J pulse, i.e. only $2.4 \times$ in irradiance. This, correspondingly, reduces the plasma contribution by 4 orders of magnitude. In addition to the ionization rate changing drastically with incident energy, we have neglected a host of other mechanisms which will be discussed in subsequent sections. Even so, qualitatively, the extracted values from our experiments agree with what is expected. The conditions for stable WLC generation include balancing out the contributions from both SPM and plasma generation. In addition, the experiments presented in Figure 7-4 were performed with various sets of lenses, i.e. focusing geometries, with the focal length of 1 m being the optimum for the given laser pulse characteristics.
In Section 2.2, we mentioned that at the critical power a pulse can overcome its inherent spreading due to diffraction and collapse upon itself. It is said, thus, that as a pre-cursor to filamentation or WLC generation, the optical pulse must be above this threshold power. To map our experimental data with these conditions, we have utilized Eqn. (2.35) along with Eqn. (7.2) such that the critical power is pressure dependent. Thus, we can express the energy in which we start to see flickering, $E_C$, in terms of its power by using the expression $E_C/\sqrt{\pi \tau}$ and compare it to the pressure dependent critical power. The results are shown in Figure 7-6. For increasing pressures, i.e. increasing $n_2$ since the nonlinearity of the gas increases with pressure, the power required for self-trapping decreases. Note that the trend of our experimental data agrees with what is predicted by Eqn. (2.35) as shown in Figure 7-6. The discrepancies in the absolute magnitude can be attributed to not precisely knowing the beam energies in which we initiate critical self-
focusing inside our gas chamber. There is external focusing from our lens along with the self-focusing induced by propagating inside the pressurized gas medium. For higher input energies, we can also initiate a lensing effect, albeit small, from the input fused silica window on the gas chamber coupled along with the external lensing and propagation through the gas which can alter the location of the minimum focus due to the power for critical self-focusing in the window and gas medium.

The most stable WLC occurred for an input energy of 750 $\mu$J at a gauge pressure reading of 45 psi. With $f_L$ of 1 m, $w_i = 2$ mm (HW 1/e² M), and $\tau = 150$ fs (FWHM), this corresponds to a peak irradiance of $\sim 19 \text{ TW/cm}^2$ which is similar to the irradiance used to generate a WLC in previous experiments [81, 128].

Figure 7-7. Images of the stable WLC observed at a distance of 5 m from the output of the WLC chamber. The upper right inset shows the diffracted white light from a grating.

Figure 7-7 shows the images of the stable WLC as well as images of the spectrally filtered WLC at a distance of 5 m from the output of the WLC chamber. The inset to the figure shows the
spectrum obtained by diffracting the WLC by a course grating. The beam profiles of the WLC taken by a DataRay WinCamD profiler are shown in Figure 7-8.

![Figure 7-8. Beam profiles taken with the DataRay WinCamD of the spectrally filtered WLC.](image)

The beam profiles of the visible portion of the 780 nm pumped WLC are primarily dependent on the pump profile. Since the pump beam profile was fairly circular and symmetric and, thus, resembled a Gaussian-like spectrum, the visible WLC displayed similar characteristics. Thus, the visible portion of the WLC was verified to be adequate for WLC spectroscopy. The Stokes side of the pump frequency displayed beam profiles of a “ring” pattern not suitable for WLC spectroscopy.
Figure 7-9. The usable energy of the WLC generated from the optimum parameters discussed above. The solid red line shows the transmission spectrum of the 780 nm dielectric mirror used as a “notch” filter (same as in Figure 7-2).

Figure 7-9 shows the usable energy of the WLC after traversing through the notch filter and each bandpass interference filter. Throughout the visible regime, we can access tens of nJ’s for WLC spectroscopy. As the spectrum is shifted more and more to the anti-Stokes side of the pump, the available WLC energy drops compared to the middle portion of the visible spectrum. On the Stokes side of the 780 nm pump, the available energy drops substantially. Furthermore, as mentioned in the preceding paragraph, the beam profiles in this regime indicate that WLC spectroscopy could not be performed. Note the drop in WLC spectral energy approaching the pump bandwidth. Since the available WLC energy is a product of the transmission of both the notch filter and bandpass filter, the drop in energy is not indicative of the “true” WLC energy. Here, “true” means the measured energy divided by the transmittance of both filters. For example, at 730 nm the measured energy was 5 nJ whereas the transmission of the 780 nm dielectric mirror is 0.72%.
Thus, correcting by just the notch filter yields an energy of ~690 nJ. The actual energy is indeed higher since this energy is not corrected by the transmission of the bandpass filter.

It was observed in Ref. [149] that the WLC generated in condensed media could be suppressed by changing the polarization state of the incident laser pulse. By changing the state to circularly polarized light, the authors noted an increase in required incident pulse energy while also noticing a change in the output WLC spectrum. This was later confirmed in reports studying WLC suppression in anisotropic and chiral media [150]. The polarization dependence was studied for WLC generated in air in Ref. [151]. The authors observed that the visible portion of the WLC was enhanced when using circularly polarized light and the efficiency of transferring energy from the pump to the visible spectral components was increased. Furthermore, numerical simulations conducted by the authors of Ref. [152] showed that filament formation for linearly polarized light differed substantially from that of nearly circular polarized light with that of nearly circular polarized light producing more uniform filaments.

One of the factors contributing to the increase in the pulse energy needed when changing to circular polarization is the decrease in $n_2$ which is 1.5 times smaller than for linearly polarized light [79]. Note that this factor is only relevant to isotropic materials for bound-electronic nonlinearities. That inherently leads to an increase in the critical power according to Eqn. (2.35). Furthermore, the authors of Ref. [153] experimentally observed a reduction in the ion yield of fragments when using circularly polarized light with respect to linearly polarized light, i.e. more energy is required to create the same ion yield. Taking note of the aforementioned work, we set out to try to improve the spectral intensity of the visible portion of our WLC by changing the polarization state of the incident pulse.
Figure 7-10. Spectral intensity versus wavelength for WLC generated using linearly polarized and different elliptically polarized 780 nm pump pulses. The intensity was measured by an Ocean Optics HR4000 spectrometer.

Figure 7-10 shows two cases where the pressure inside the WLC chamber was held fixed while the $\lambda/4$ waveplate in Figure 7-1 was rotated to achieve different ellipticities. The ellipticity is defined as $\sqrt{P_{\text{min}}/P_{\text{max}}}$ where $P_{\text{min}}$ and $P_{\text{max}}$ are the minimum and maximum power detected, respectively, through a polarizer. For the case shown in (a), the pressure was set to a gauge reading of 40 psi with an input energy of $\sim 705 \mu J$. The ellipticities were varied from 0.07 to 0.16. Larger ellipticities could not be obtained due to the WLC disappearing completely. We observed the same trend as in Ref. [149] of suppressed WLC for varying degrees of ellipticity. For the case in (b), the pressure was set to a gauge reading of 45 psi with an input energy of $\sim 580 \mu J$. In this case, larger values of ellipticity could be obtained up to 0.28. Furthermore, we observe the same trend as in (a) of decreased WLC output with increased ellipticity. In both cases (a) and (b), we observed a flattening of the spectrum in the visible spectral region with the reduction of the total output. But,
unfortunately, we did not observe a large enhancement of the available energy at the output. This was performed for other pressures and the same trend was observed.

For the scope of this work, it is essential to know what parameters are needed such that we can generate high-spectral-irradiance WLC. Note that the measured spectrum shown in Figure 7-9 extends to more than twice the frequency of the input pulse, i.e. > 1 octave in bandwidth, with strong anti-Stokes shifting and relatively weak Stokes shift with respect to spectral energy density. This trend follows the Fourier analysis presented at the end of Section 3.3 for similar phase contributions from SPM and plasma. The spectral flatness of the available WLC is a result of the interplay of various nonlinear mechanisms as well as the notch filter used, as the transmission of the notch filter has transmission modulations. Many materials such as semiconductors and organics with moderately large nonlinear coefficients can be measured with the spectral energy densities provided by this WLC. But for most molecules of interest used in solution, this output is insufficient, especially when trying to measure organics and semiconductors which have linear absorption in the near-infrared (NIR). The following section presents efforts on trying to extend the spectral bandwidth and energy density for broadband WLC nonlinear spectroscopy.

7.2 Seeded WLC in Kr gas

Of interest to the scope of this work, WLC can be used for nonlinear spectroscopy, as discussed in the introduction to this chapter, where the high spectral irradiance, ultra-broadband source of radiation confined in a single beam can replace conventional tunable sources of radiation such as OPGs. As stated at the end of the previous section, we would like to expand our spectrum into the NIR wavelengths in order to characterize more materials of interest. Spectral expansion of the WLC in air to the mid-IR (4.5 μm) has been demonstrated by using long focal length geometries.
Spectral expansion into the near-IR recently was achieved by using different focusing geometries in condensed media [155]. But as mentioned in the introduction to this chapter, generation in condensed media is limited by the input pump energy which causes damage. The lack of high-energy WLC sources in practical laboratory environments has limited the ability to use single beam sources of radiation as an alternative to OPGs/OPAs for rapid nonlinear optical characterization.

Spectral extension of the WLC by introducing a weak secondary pulse, i.e. seed pulse, has been demonstrated in various condensed media [156-159] with high energy terahertz and visible radiation by pump-seed pulse interactions in gases being also investigated [160-164]. Since WLC generated in gases is not limited by the same energy restrictions of optical damage thresholds as condensed media, it is advantageous to use gases for high energy WLC generation.

Our initial thoughts into using a seed pulse were to bridge the gap between the WLC generated from our fundamental 780 nm pulse and a near-IR seed pulse mainly through four-wave mixing (FWM) along with other nonlinear processes that occur in the generating medium. We then witnessed experimental evidence of large energy enhancement and spectral broadening of a single filament, WLC source of radiation by using visible, weak (∼ μJ) fs seed pulses to stimulate the nonlinearity generated from the fs pump beam. For different seed wavelengths, we observe strong Stokes and anti-Stokes broadening with spectral energy seen as part of the filament [165].

The experimental configuration is presented in Figure 7-11. A Ti:Sapphire laser system, different from that used in Section 7.1, thus having different pulse characteristics, e.g. temporal and spatial pulse chirp, beam shape, etc., producing ∼1.4 mJ, ∼150 fs (FWHM), 780 nm pulses at a 1 kHz repetition rate is used in our seeded WLC studies (the higher energy laser system similar
to the one depicted in Figure 5-1 and used in Section 7.1). The output of the laser system is divided into two pulses by a beam splitter. The pump pulse (~ 0.4 – 0.6 mJ) is temporally delayed on an optical delay line and weakly focused, \( f_L = 1.5 \) m, into the WLC chamber, labeled noble gas chamber, filled with krypton gas (pressure gauge reading of 40 psi). The energies used to generate a stable, single-filament, un-seeded WLC (similar to that shown in Figure 7-7) resulted in peak irradiances of \(~10^{12} \text{ W/cm}^2\). The same notch filter used in Figure 7-9 was used to block the pump from the resultant WLC at the output of the gas chamber.

![Figure 7-11. Experimental configuration of seeded WLC.](image)

The seed pulses were generated by pumping an OPA with ~0.4 mJ of the laser output. The wavelengths of the seed pulses ranged from 500 nm to 1300 nm. The seed pulses were weakly focused \((f_L = 0.75)\) with the lens placed before the dichroic mirror and overlapped spatially and temporally with the pump. The combination of \(\lambda/2\) waveplates and polarizers were used to attenuate both the energies of the pump and seed pulses.
Knife edge scans were taken along the position of the chamber for the 780 nm pump and for a 650 nm seed pulse as shown in Figure 7-12. To determine the focusing characteristics of the pump and seed, we used the following relation:

$$w(z) = w_0 \sqrt{1 + M^2 \left( \frac{z}{z_0} \right)^2},$$  \hspace{1cm} (7.4)

where $M^2$ describes the value of divergence from an ideal Gaussian beam. For the 780 nm pump pulse and 650 nm seed pulse, $M^2$ is fit to 1.4 and 1.5, respectively, with a minimum spot size $w_0$ at focus of 150 \(\mu\text{m}\) (HW $1/e^2$ M) and 260 \(\mu\text{m}\) (HW $1/e^2$ M), respectively. We use Eqn. (7.4) to determine $w_f$ for the 650 nm seed of 775 \(\mu\text{m}\) (HW $1/e^2$ M). For the other seed pulses at different wavelengths, we assume that $w_f$ and $M^2$ is the same. This allows us to estimate the minimum $w_0$.
for the other seed wavelengths of 195 µm (HW 1/e² M) which allows us to infer that the spot size of the pump pulse is always smaller than any of the seed pulses near the initiation of WLC.

The WLC was spectrally analyzed by the use of bandpass interference filters at 40 - 50 nm increments similar to the ones shown in Figure 7-3. In all experiments the seed pulse energy did not exceed 1 µJ to ensure that the irradiance of the seed (∼10⁹ W/cm²) was much less than that of the pump. Such low irradiances for the seed pulses by themselves are insufficient to induce critical self-focusing nor lead to filamentation.

The typical spectra of the seeded and unseeded WLC are shown in Figure 7-13 for (a) the 600 nm and (b) 1300 nm seed pulse energy of 1 µJ and pump pulse energy of ∼0.4 mJ. In (a), the presence of the seed pulse results in a dramatic enhancement of the spectral irradiance. For WLC Z-Scans, the values given are representative of the actual spectral energy densities available for measurements since the values are not corrected by the transmission of the notch filter.
Figure 7-13. Comparison of spectral output energy density of unseeded WLC (closed black squares) with seeded WLC (closed red circles) using (a) 600 nm seed and (b) 1300 nm seed of energy 1 µJ and pump energy of ~0.4 mJ. The dark green vertical line in (a) represents the 600 nm seed bandwidth and in (b) the 1300 nm seed bandwidth. The magenta horizontal dotted line denotes the typical energy density necessary to perform WLC Z-scans. The vertical shaded area in both figures represents wavelengths cut off by the 780 nm notch filter. The inset of (a) plotted on a log scale shows the extension of the WLC spectrum on the Stokes side of the 780 nm pump. The inset of (b) also plotted on a log scale shows the slight enhancement and broadening around the 1300 nm seed pulse. The spectral energy density shown is that which is available for measurement, i.e. it is not corrected by the transmission of the notch filter or each bandpass filter [165].

Without the seed pulse, the typical WLC spectrum has an integrated energy of ~1250 nJ (area under the black curve of Figure 7-13). The stimulation by weak seed pulses of wavelengths within the unseeded WLC (visible seed pulses) results in an increase of the total integrated energy to ~5800 nJ (area under the red curve of Figure 7-13), i.e. more than 360 % enhancement for this seeding wavelength. In the case of WLC Z-Scans, the unseeded WLC typically yields a usable wavelength range (denoted by the magenta line in Figure 7-13 representing the spectral energy density of 1 nJ / nm) of 400 nm – 800 nm for nonlinear optical characterization. The introduction
of the weak seed pulse extends the usable energy range from 300 nm to > 1100 nm (see Figure 7-13(a) inset). At 1000 ± 7 nm (the typical cutoff of our unseeded WLC), we measure the largest enhancement utilizing a 650 nm seed resulting in 14.2 ± 0.6 nJ / nm versus ~0.17 nJ / nm, i.e. an 83x increase. The enhancement at this particular wavelength can be attributed to FWM with the FWM wavelength relation given as:

$$\lambda_{FWM}^{-1} = 2\lambda_{pump}^{-1} - \lambda_{seed}^{-1}. \quad (7.5)$$

We also observe significant enhancement at wavelengths not directly associated with FWM. For instance, the 600 nm seeded WLC yields nearly 10 nJ / nm output at 532 ± 4 nm compared to 1.5 nJ / nm output for an unseeded WLC, resulting in more than 6x enhancement with a seed pulse energy ~0.3% that of the 780 nm pump. As stated previously, the spectral energy densities presented in Figure 7-13 have not been corrected by the transmission of the notch filter. Doing so would give a more accurate representation of the “true” WLC shape.
Figure 7-14. Corrected seeded WLC spectra. The data in Figure 7-13 have been corrected by the transmission of the notch filter to obtain the “true” WLC shape.

Shown in Figure 7-14 is the corrected spectra from Figure 7-13. That is, the data have been corrected by the transmittance of the notch filter (see Figure 7-9). Note that by this correction, the spectral energy density at 300 nm increases to ~10 nJ / nm from less than 2 nJ / nm. Similarly, the energy density near the bandwidth of the notch filter are significantly enhanced. By correcting, we can ascertain the “true” shape of the WLC spectra.

From the dispersion relation given in Eqn. (2.46), we can calculate the phase matching condition for FWM as:

\[ \Delta k = 2k_{\text{pump}} - k_{\text{seed}} - k_{\text{FWM}}, \]  

(7.6)

for the various seed wavelengths used. The calculations are presented in Table 7-2.
Table 7-2. FWM phase mismatch for various seed wavelengths for a pump wavelength of 780 nm calculated from Eqn. (7.6).

<table>
<thead>
<tr>
<th>Seed wavelength (nm)</th>
<th>$\lambda_{FWM}$ (nm)</th>
<th>$\Delta k$ (m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>1772</td>
<td>-97.4</td>
</tr>
<tr>
<td>550</td>
<td>1340</td>
<td>-54.1</td>
</tr>
<tr>
<td>600</td>
<td>1114</td>
<td>-27.8</td>
</tr>
<tr>
<td>650</td>
<td>975</td>
<td>-12.3</td>
</tr>
<tr>
<td>710</td>
<td>865</td>
<td>-2.99</td>
</tr>
<tr>
<td>1150</td>
<td>590</td>
<td>-32.0</td>
</tr>
<tr>
<td>1200</td>
<td>578</td>
<td>-37.8</td>
</tr>
<tr>
<td>1240</td>
<td>569</td>
<td>-42.5</td>
</tr>
<tr>
<td>1300</td>
<td>557</td>
<td>-49.5</td>
</tr>
</tbody>
</table>
Figure 7-15 provides the experimental map of the WLC spectrum seeded with different wavelengths with the same seed pulse energy (1 µJ). As was stated previously, the largest enhancement and spectral broadening occurs for seeding in the visible range. Seed wavelengths slightly above and below that of the pump could not be utilized due to the limitations of the energy output of the OPA and/or the broad bandwidth of our highly reflective dichroic mirror cutting off wavelengths close to that of the pump (see Figure 7-11). Therefore, no information could be obtained from the “experimental gap” region in Figure 7-15. Additionally, the WLC may extend further into the UV region below 300 nm but due to the notch filter’s cutoff in the UV this could not be determined.
Figure 7-16. (a) Energy within an 8 nm FWHM bandwidth centered at 532 nm using seed pulses at 600 nm and 1300 nm versus time delay between the pump and seed pulse, and (b) differential spectral energy density map of WLC spectrum using a fixed 600 nm seed and recording the temporal behavior of the white-light spectrum at different time delays between pump and seed pulses. The large shaded area, labeled “experimental gap”, in (b) represents spectral regions that could not be measured due to the cutoff of the notch filter. The small shaded area represents the 600 nm seed bandwidth [165].

We also measured the dependence of the WLC enhancement on the time delay between pump and seed pulses as shown in Figure 7-16. The output light was collected onto either a silicon or germanium photodiode covering a range from ~200 nm to ~1800 nm, respectively. In Figure 7-16(a), the irradiance at 532 ± 4 nm is shown for seed wavelengths of 600 nm and 1300 nm. The enhancement for each seeded wavelength occurs at the zero delay between the seed and pump pulse, which was determined by sum frequency generation on a ~200 µm thick Type-I BBO crystal. For fixed seed wavelengths, the overall behavior of the spectral enhancement has similar dynamics as shown in Figure 7-16(b). The data presented in Figure 7-16(b) is the difference
between when the pump and seed pulses are temporally overlapped or not, i.e. the enhancement. The broadening is seen to follow the cross-correlation of the pump and seed pulse. Moreover, the peak of the spectral enhancement occurs near zero delay which implies that the stimulated generation and energy enhancement occur near the initiation of filamentation for all wavelengths.

Table 7-3. Output WLC energy density for different seed wavelengths. The unseeded output WLC energy density is given in parenthesis for comparison. In the case of “Total WLC Energy”, the seed pulse energy (~ 1 µJ) transmitted in the absence of the pump (~ 0.4 mJ) was subtracted from the total reading.

<table>
<thead>
<tr>
<th>Seed wavelength (nm)</th>
<th>@ 532 nm (nJ / nm)</th>
<th>@ 1000 nm (nJ / nm)</th>
<th>Total WLC Energy (µJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>3.6 ± 1.2 (1.5)</td>
<td>3.9 ± 0.4 (0.17)</td>
<td>3.1 (1.2)</td>
</tr>
<tr>
<td>550</td>
<td>7.5 ± 2.1 (1.5)</td>
<td>2.3 ± 0.1 (0.17)</td>
<td>2.8 (1.2)</td>
</tr>
<tr>
<td>600</td>
<td>9.5 ± 2.2 (1.5)</td>
<td>7.2 ± 0.9 (0.17)</td>
<td>3.7 (1.2)</td>
</tr>
<tr>
<td>650</td>
<td>6.7 ± 1.2 (1.5)</td>
<td>14.2 ± 0.6 (0.17)</td>
<td>3.8 (1.2)</td>
</tr>
<tr>
<td>710</td>
<td>4.0 ± 0.7 (1.5)</td>
<td>1.1 ± 0.02 (0.17)</td>
<td>1.9 (1.2)</td>
</tr>
<tr>
<td>1150</td>
<td>2.5 ± 0.8 (1.5)</td>
<td>0.9 ± 0.3 (0.17)</td>
<td>1.3 (1.2)</td>
</tr>
<tr>
<td>1200</td>
<td>1.6 ± 0.2 (1.5)</td>
<td>0.3 ± 0.01 (0.17)</td>
<td>1.21 (1.2)</td>
</tr>
<tr>
<td>1240</td>
<td>1.5 ± 0.1 (1.5)</td>
<td>0.2 ± 0.01 (0.17)</td>
<td>1.3 (1.2)</td>
</tr>
<tr>
<td>1300</td>
<td>1.5 ± 0.1 (1.5)</td>
<td>0.17 ± 0.01 (0.17)</td>
<td>1.21 (1.2)</td>
</tr>
</tbody>
</table>
Table 7-3 shows the WLC energy densities at 532 ± 4 nm and 1000 ± 7 nm with and without the seed (500 nm to 1300 nm). For example, a 500 nm seed yields an energy density at 1000 nm of 3.9 nJ / nm compared to 0.17 nJ / nm unseeded, i.e. an enhancement of 23. The largest enhancement at 532 nm and 1000 nm occurs with seed inputs in the visible spectral range with a peak near 600 nm at 532 nm and 650 nm for 1000 nm. Also shown (last column) is the overall enhancement of the total WLC energy with different seeds.

Figure 7-17. (a) Output energy at 532 ± 4 nm as a function of seed pulse energy in the case of the 600 nm seed pulse. Enhancement was observed with a seed pulse energy less than 10 nJ. The unseeded output energy (seed pulse energy of 0 nJ) was 3 nJ and is shown as a cross. An aperture was used to observe the energy confined in the single filament WLC as opposed to any possible scattered radiation from the seed-plasma interaction. (b) Observed signal of the different spectral components of the WLC as a function of the input pump energy.

Figure 7-17(a) shows the output energy at 532 nm with respect to the input seed energy for a seed pulse at 600 nm. The unseeded output corresponding to 0 nJ seed pulse energy (shown as a cross in the figure due to the log scale) results in an energy of 3 nJ. Thus, with as low as 10 nJ of seed pulse energy, we are able to observe WLC enhancement and the total seeded WLC output
energy is ~3 times greater than that of the unseeded WLC. For seed pulse energies greater than 100 nJ, the enhancement begins to saturate. Figure 7-17(b) shows the output signal at different spectral components of the WLC with respect to 780 nm pump pulse energy. The black squares show the output signal at the near the FWM wavelength of 980 nm for a 650 nm seed. The blue triangles show the output signal at 550 nm, and the red circles show the output signal at 550 nm without the presence of the seed pulse. The generation of the WLC spectral components was initiated at lower pump energies in the presence of the seed pulse. Furthermore, at 980 nm and hence near the FWM wavelength, the generation started with 75 μJ less energy of the 780 nm pump. Of importance, the FWM enhancement can be attributed mostly to the $\chi^{(3)}$ of the gas medium, i.e. we observed FWM without filamentation at pump energies much less than that required to see observe WLC. But the FWM is enhanced as the filamentation progresses as shown by the black squares in Figure 7-17(b). This feature of controlling the output WLC via a second pulse has been observed in Ref. [166] but in condensed media using a much larger seed to pump pulse ratio.
Figure 7-18. Beam profiles of the anti-Stokes side of the 780 nm pump pulse with and without the 650 nm seed pulse.

As mentioned in Section 7.1, the WLC should have high quality spatial profiles to be useful for nonlinear spectroscopy. Figure 7-18 shows beam profiles of the anti-Stokes side of the 780 nm pump with and without the 650 nm seed pulse. The seed pulse is observed to have a significant impact on the spatial characteristics of the generated WLC. A major observation is the significant size difference when the WLC is seeded. For each wavelength in Figure 7-18, the seed pulse causes the beam to shrink. This is an indication that the seed pulse is causing a change in the beam divergence. But in each case, the seed pulse preserves the circular profile of the generated WLC for most wavelengths.
As mentioned in Section 7.1, the beam profiles on the Stokes side of the 780 nm pumped WLC showed “ring” structures in some of the profiles making it non-conducive for nonlinear spectroscopy. Figure 7-19 shows beam profiles of the Stokes side of the 780 nm pump with and without the 650 nm seed pulse. As with the anti-Stokes side of the 780 nm pump, the seed pulse is observed to have an impact on the spatial characteristics of the generated WLC. For the 900 nm and 950 nm portion of the WLC, the seed pulse retains the “ring” structure of the unseeded case. Again, the major observation is the size difference when the WLC is seeded. For each wavelength in Figure 7-19, the seed pulse causes the beam to shrink. This is an indication that the seed pulse is causing a change in the beam divergence on the Stokes side of the WLC. Only for certain
wavelengths on the Stokes side of the pump is the WLC, either seeded or unseeded, are the beam profiles adequate for nonlinear spectroscopy.

7.3 Seeded WLC in other inert gases and condensed media

Since enhancement was observed in Kr gas for low seed pulse energies, we decided to investigate this same phenomenon for other inert gases and condensed media. In this section, we present data on seeding in liquid media as well as Argon and Xenon.

![Normalized spectral intensity of the 780 nm pumped WLC generated in (a) ethanol, (b) tetrahydrofuran, and (c) water with and without a 650 nm seed pulse. This data was measured with an Ocean Optics HR4000 spectrometer.](image)

To investigate the WLC enhancement in liquid media, we utilized a 10 cm path length cell and filled it with various solvents. Figure 7-20 shows the normalized intensity spectra for the 780 nm pumped WLC generated in (a) ethanol, (b) tetrahydrofuran, and (c) water. The energy used to generate a stable WLC for ethanol was 2.6 µJ in which the 650 nm seed pulse energy was set to 0.52 µJ in order to avoid any filamentation from the seed pulse alone. For tetrahydrofuran, the pump energy was set to 1.6 µJ with a seed pulse energy of 0.52 µJ and for water, the pump energy was set to 4.8 µJ with a seed pulse energy of 1 µJ. The 10 cm path length cell was positioned near
Position 40 (see Figure 7-12) after taking out the WLC chamber (see Figure 7-11). This ensured that the geometric focus was similar for both the pump and seed pulse, i.e. $w_{\text{pump}} \approx w_{\text{seed}} \approx 300 \mu\text{m}$ (HW $1/e^2$ M). This, in turn, gives the ratio between the irradiance of the pump and seed pulse ($I_{\text{pump}}/I_{\text{seed}}$) of 4, 2.5, and 3.8 for ethanol, tetrahydrofuran, and water, respectively. Although the ratio is less for tetrahydrofuran than for ethanol, there is more enhancement observed. Taking the integrated spectrum, i.e. the area under curve, yields an enhancement of 1.3 for tetrahydrofuran compared to 1.2 for ethanol. The largest enhancement occurs for water where the integrated spectrum yields an enhancement of 2. From Ref. [167], the $n_2$ for ethanol, tetrahydrofuran, and water is $0.65 \cdot 10^{-15}$ cm$^2$/W, $0.69 \cdot 10^{-15}$ cm$^2$/W, and $0.5 \cdot 10^{-15}$ cm$^2$/W, respectively. Note that the $n_2$ for water is smaller than that of ethanol and tetrahydrofuran whose $n_2$ is similar. From this limited set of data, we observe a small trend of increased enhancement in media with smaller nonlinearities with the largest enhancement occurring in gaseous media as described in Section 7.2.
Figure 7-21. (a) Comparison of the available energy for spectroscopy of unseeded WLC (closed black squares) with seeded WLC (closed red circles) in Ar gas at a gauge pressure of 60 psi using a 650 nm seed pulse of energy 2 µJ and pump energy of ~0.81 mJ. The orange shaded region and gray shaded region in (a) represent the 650 nm seed pulse and notch filter, respectively. (b) Comparison of the available energy for spectroscopy of unseeded WLC (closed black squares) with seeded WLC (closed red circles) in Xe gas at a gauge pressure of 40 psi using a 680 nm seed pulse of energy 4.2 µJ and pump energy of ~0.145 mJ. The orange shaded region and gray shaded region in (b) represent the 680 nm seed pulse and notch filter, respectively.

Figure 7-21(a) shows the available energy from seeded WLC in Ar gas at a gauge pressure 60 psi. The seed pulse wavelength is 650 nm at an energy of 2 µJ. Just as in Kr gas, we observe similar enhancement on the anti-Stokes and Stokes side of the 780 nm pulse. The energy in the visible spectral region is enhanced at least by a factor of ~2. The near-IR spectral enhancement is observed mostly near the FWM peak. It is important to note that although there is significant enhancement observed across the WLC spectrum due to the seed pulse, the enhancement is not as much as that described in Section 7.2. This is, in part, possibly due to the change in pump and seed focusing through the WLC chamber. Prior to these measurements, there was a visit from the service engineer to repair the laser system. Therefore, the output divergence from the OPG was measured to be different than the case presented in Section 7.2. We placed an expansion telescope
of 1.5 before the seed focusing lens (see Figure 7-11). This, in turn, reduced the beam size at the minimum focus, and the new minimum spot sizes for the pump and seed pulse were determined to be 180 µm and 120 µm, respectively (HW 1/e² M). For all positions inside the WLC chamber, the seed pulse had a geometric focus smaller than that of the 780 nm pump. In Figure 7-21(b) the available energy from seeded WLC in Xe gas at a gauge pressure of 40 psi is shown with respect to the unseeded case. The seed pulse is 680 nm with an energy of 4.1 µJ. As with Ar gas, we observe spectral enhancement not only in the visible but extending into the near-IR. Compared with Ar, the enhancement near the FWM bandwidth is larger. Whereas we observe an enhancement in Ar gas near the corresponding FWM wavelength of ~27, in Xe gas the enhancement near the corresponding FWM wavelength is more than 2 orders of magnitude. The focusing geometry of the pump and seed pulse is similar to that for Ar gas.

![Figure 7-22](image)

**Figure 7-22.** The critical power (black squares) and $n_2$ (red triangles) plotted for the inert gases as a function of the ionization potential. These calculations are performed for $P = 40$ psi and a wavelength of 780 nm at $T = 300$ K.
To observe stable WLC in the studied gases, we used energies of 145 µJ, 400 µJ, and 810 µJ in Xe, Kr, and Ar, respectively. Plotted in Figure 7-22 is the critical power (see Eqn. (2.35)) for each of the inert gases calculated from the second hyperpolarizabilities listed in Table 2-2 at a pressure of 40 psi, temperature of 300 K, and wavelength of 780 nm. The ionization potentials are taken from Ref. [76]. The trend of increased energy input versus ionization potential for the gases is observed experimentally. From the calculated \( n_2 \)'s, the critical power for Xe, Kr, and Ar is 1.98 GW, 5.93 GW, and 15.8 GW, respectively. With respect to Kr, the required energy from experiments to generate WLC is -64% for Xe and 103% in Ar. From the calculations of the critical power, the power difference with respect to Kr is -67% for Xe and 166% for Ar. From the experimental data in Figure 7-13 and Figure 7-21, we observe that for unseeded WLC, the amount of spectral energy in the near-IR increases with the pump energy. Thus, there is more available energy in the near-IR when using Ar gas than using Xe gas. This brings an important strategy in extending the spectral range when generating WLC in noble gases. The larger the pump energy, the more extension into the near-IR spectral region. Thus, we can increase the necessary pump energy by either reducing the pressure thereby reducing the \( n_2 \) and increasing the required critical power and/or generating in a gas with a larger ionization potential. But revisiting the discussion in Section 7.1, the two dominant characteristics for stable WLC generation is nearly equal contributions from the plasma nonlinearity and SPM. From Eqn. (3.16), the ionization rate is highly dependent on the ionization potential and from Eqn. (3.8) the change in index due to plasma is dependent on the initial pressure. For example, to generate \( \Delta n_{pl} \cong 10^{-6} \) for an arbitrary focusing geometry and pressure of 1 atm at a wavelength of 780 nm, the required energy would be 0.356 mJ, 0.690 mJ, 1.13 mJ, 3.78 mJ, and 5.61 mJ for Xe, Kr, Ar, Ne, and He, respectively. Thus, adjusting one parameter in the generation process can have drastic effects in both the amount
of $\Delta n_{SPM}$ and $\Delta n_{pl}$ generated. While it may be more beneficial in terms of spectral extension into the near-IR to generate in a gas with a large ionization potential, there may arise limitations in producing the necessary amount of $\Delta n_{pl}$ depending on the energy limitations of the laser system and/or focusing geometries incorporated.

With respect to seeding the WLC, we observed large enhancement near the FWM peak. In Figure 7-23, the absolute magnitude of Eqn. (7.6) is plotted with respect to various seed wavelengths. Thus, we can calculate the FWM efficiency (the minimum of $|\Delta k|$ represents the largest efficiency) associated with the seed wavelengths and pressures used in our experiments. At a fixed pressure of 1 atm (Figure 7-23(a)), $|\Delta k|$ is smallest in Ar and largest in Xe for all seed wavelengths. For all gases, the largest efficiency occurs when $k_{pump} = k_{seed}$. But, as described earlier, utilizing a seed wavelength close to the wavelength of the pump could not be done due to the dichroic mirror in Figure 7-11 having a broad reflective bandwidth centered at the pump

Figure 7-23. The magnitude of the phase matching for FWM (Eqn. (7.6)) as a function of the seed wavelength at a pressure of (a) 1 atm and (b) the pressures used in the experiments of Figure 7-13 and Figure 7-21.
wavelength. In Figure 7-23(b), $|\Delta k|$ is plotted for the pressures used in the experiments. As is the case in (a), the calculated minimum $|\Delta k|$ occurs for Ar with Xe having the largest. From these calculations, it is difficult to extract the trend that is observed in experiments, i.e. in terms of the largest to smallest FWM enhancement observed in Xe, Kr, and Ar, respectively. Thus, it is speculated that while FWM has a large impact on the seeded WLC spectrum, there are a multitude of other processes that may cause the large spectral energy enhancement not only around the FWM peak but across the entire visible and near-IR spectrum.

7.4 Numerical Simulations of Seeded WLC in Kr gas

As briefly mentioned in the previous section, the FWM between the pump and visible seed may help to explain the extension of the WLC to longer wavelengths in the near IR, but it does not explain the enhancement observed across the visible. In Ref. [73], numerical simulations were performed to describe the effects of a strong pump pulse on a seed beam. The authors showed that the ionization front induced by the pump causes a frequency blue-shift of the seed pulse when its maximum irradiance lies at the same position as the ionization front. We note that this may be one of the effects in our observations, but we also observe strong transfer of the pump energy to both the anti-Stokes and Stokes spectrum of the WLC which is not accounted for in the authors’ simulations. To model the WLC numerically, we have collaborated with the authors of Ref. [168] and utilized their nonlinear envelope equation (NEE). The NEE in normalized units is written as:
\[
\frac{\partial \psi}{\partial \zeta} = i \left( 1 + \frac{i \partial}{\omega \tau_p \partial \tau_R} \right)^{-1} \nabla_\perp^2 \psi \\
+ i L_{df} \sum_{n=2}^{NN} \frac{\beta_n}{n!} \left( \frac{i \partial}{\tau_p \partial \tau_R} \right)^n \psi + i \left( 1 + \frac{i \partial}{\omega \tau_p \partial \tau_R} \right) \frac{L_{df}}{L_{nl}} \frac{|\psi|^2 \psi}{2} \\
- \frac{L_{df}}{2L_{mp} |\psi|^2} \frac{\partial \eta}{\partial \tau_R} - \frac{L_{df}}{L_{pl}} \left( i + \frac{1}{\omega \tau_c} \right) \eta \left( \psi + \frac{\tau_c \partial \psi}{\tau_p \partial \tau_R} \right) \\
\]

\[
\psi = \exp(-t^2) + \frac{E_{\text{seed}}}{E_{\text{pump}}} \exp[-i(\omega_{\text{seed}} - \omega_{\text{pump}})t_0 t] \exp(-t^2),
\]

where the initial field condition normalized by the peak input field amplitude \( \psi \) is also given in Eqn. (7.7), \( \zeta \) is the propagation normalized to the diffraction length \( L_{df} \), \( \tau_R \) is the retarded time normalized by the pump pulse width \( \tau_p \), \( \beta_n \) is \( k_n \) of Eqn. (4.12), \( L_{nl} \) is the nonlinear length, \( L_{mp} \) is the \( m \)-photon absorption length, \( \eta \) is the normalized electron density, \( L_{pl} \) is the plasma length, and \( \tau_c \) is the electron-ion collision time. The parameter \( t \) in Eqn. (7.7) is normalized to the pump pulse duration and \( t_0 \) is the seed pulse width. The terms are explicitly defined in Ref. [168] and references therein. The first term describes space-time focusing associated with diffraction, the second term describes group velocity dispersion (\( NN=3 \) for these simulations), the third term describes self-steepening along with cross-phase and self-phase modulation, and the fourth and fifth term describes plasma generation via multi-photon absorption. Note that nearly the same effects are described by Eqn. (4.16). Eqn. (7.7) is solved as a broadband, single-field propagation code with the seed pulse implemented as a perturbation to the pump pulse field amplitude since the seed field amplitude is much less than that of the pump for all cases. Eqn. (7.7) omits the Raman response function (see Eqn. (4.18)) given in Ref. [168] due to Kr being an inert gas and the \( E \)-field strength not being strong enough to distort the atom to produce a response of that form.
Figure 7-24 shows the simulated evolution of the 780 nm pump and 600 nm seed pulse at various positions in the WLC chamber filled with 3.7 atm of Kr gas. In Figure 7-24(a), the seed and pump pulse initial intensity is given with respect to the beam size of the 650 nm seed pulse given in Figure 7-12; therefore, although the peak irradiance at focus is nearly 3 orders of magnitude different, the relative intensity difference at the chamber input is less due to the pump beam spot size being much larger than the seed spot size. Figure 7-24(b) shows the evolution at 2.5 cm inside the chamber. We start to see both FWM peaks, i.e. $\lambda_{FWM}^{-1} = 2\lambda_{pump}^{-1} - \lambda_{seed}^{-1}$ and $\lambda_{FWM}^{-1} = 2\lambda_{seed}^{-1} - \lambda_{pump}^{-1}$, due to the inherent $\chi^{(3)}$ of the medium. Near the minimum focus, shown in Figure 7-24(c), we observe the formation of the WLC and the broadening of the spectrum beyond both FWM peaks. As the filament propagates to the chamber output, the spectrum on the Stokes side of the pump increases in magnitude and the spectrum flattens out.
Figure 7-25. (a) Numerical simulation (same as Figure 7-24(d) for the black curve) and (b) experimental results of WLC generated with a 780 nm pump with and without a 600 nm seed pulse (black and red, respectively). The axis titles on (a) are the same as (b).

Figure 7-25 shows the comparison of (a) the numerical simulation and (b) the experimental results of the WLC generated from the 780 nm pump pulse with and without the inclusion of a 600 nm seed pulse. The experimental results and simulation agree qualitatively using the given input pulse parameters with the simulation showing roughly an order of magnitude increase in the spectral energy density for most of the wavelengths on the anti-Stokes side of the pump. There were no energy enhancement measurements performed near the 600 nm seed pulse due to the strong intensity of the initial pulse. Also, there is an experimental gap near the notch filter bandwidth in which no measurements were performed. The dominant mechanism as far as the spectral extension and broadening on the Stokes side of the pump appears to be due to FWM as hypothesized earlier.
Figure 7-26. Pump and seed pulse (1300nm) evolution in 3.7 atm of Kr gas at (a) $z = 0$, corresponding to the chamber input, (b) $z = 2.5$ cm, (c) $z = 55$ cm, near the minimum focus, and (d) at the chamber output.

Figure 7-26 shows the evolution of the 780 nm pump and 1300 nm seed pulse at various positions in the chamber. Again, the seed and pump pulse initial intensity is given with respect to the beam sizes given in Figure 7-12. To obtain the 1300 nm spot size and subsequent focusing, we have assumed the same divergence as the 650 nm seed pulse and used Gaussian matrix transformations to propagate through the chamber. Figure 7-26(b) shows the evolution at 2.5 cm inside the chamber. We only show one of the FWM peaks corresponding to $\frac{1}{\lambda_{FWM}} = 2\frac{1}{\lambda_{Pump}} - \frac{1}{\lambda_{Seed}}$ since the other peak occurs at a wavelength of 3.9 µm which is outside the range of numerical simulation. Again this peak at 0.56 µm is due to the inherent $\chi^{(3)}$ of the medium. Near the minimum focus, shown in Figure 7-26(c), we observe the formation of the WLC and the broadening of the spectrum to the short wavelength FWM peak. As the filament propagates to the chamber output, the spectrum on the anti-Stokes side flattens out and there is broadening around the seed pulse wavelength.
Figure 7-27 shows the comparison of (a) the numerical simulation and (b) the experimental results of the WLC generated from the 780 nm pump pulse with and without the inclusion of a 1300 nm seed pulse. The experimental results and simulation agree qualitatively on the anti-Stokes side of the pump. Both show relatively no enhancement in the visible portion of the spectrum. The trend continues to agree for both experiment and numerical simulation on the Stokes side of the pump until near the 1300 nm seed bandwidth. The intensity of the 1300 nm seed pulse disallowed for any measurements to be taken near the bandwidth so an exact comparison at the seed wavelength was unable to be obtained. The discrepancy arises with the broadening around the seed bandwidth. The numerical model predicts that the bandwidth broadens to $\Delta \lambda_{FWHM} \sim 200$ nm, while the experimental data shows a very narrow broadening around the seed wavelength.
7.5 Near-IR Pumped WLC with ultrashort pulses

In Section 7.2 and Section 7.3, we discussed spectral extension of the 780 nm pumped WLC into the near-IR by using a weak seed and by using higher energy pulses in other gaseous media. But the energy was not sufficient for nonlinear spectroscopy. Generating a low spectral energy density, broadband WLC in condensed media that covers multiple octaves has not been problematic. For example, multiple octave WLC has been observed by using near-IR pump pulses in tellurite fibers [169] and fluoride fibers [170] at 1550 nm and 1450 nm, respectively. Recently, it has been shown that continua spanning from the visible regime to 5 \( \mu \text{m} \) could be obtained in CaF\(_2\), BaF\(_2\), and ZnS by pumping with 27 fs pulses at 2.1 \( \mu \text{m} \) [171]. But as is the case for 800 nm pumped WLC in fibers regarding limitations in pump power input, the output WLC energy density is not sufficient for nonlinear spectroscopy.

Pertaining to gaseous media, in Ref. [154], it was found that the WLC could extend into the mid-IR, i.e. > 4 \( \mu \text{m} \), by pumping high power (2 TW) pulses at 800 nm into atmospheric air. In Ref. [172], near-IR continua was produced in Xe gas by pumping with 55 fs pulses at 2 \( \mu \text{m} \). This work was mainly aimed at observing pulse compression but also proved the possibility of extending the WLC into the near-IR. A similar pulse compression experiment was performed by the authors of Ref. [173] when using 1550 nm pump pulses in ~5 atm of Ar. In Ref. [174], the extension of the WLC from 350 nm to 5 \( \mu \text{m} \) was observed in Ar gas by using 80 fs pulses at 3.9 \( \mu \text{m} \). This work was extended to observing filamentation in molecular gases in Ref. [175] in which the authors noted a vast difference in the spectra generated in Ar and the molecular gases. Modest broadening spanning from 1100 nm to 1700 nm in highly pressurized nitrogen (~ 30 atm – 70 atm) was observed by the authors of Ref. [176] by using mJ level, 110 fs pulses at 1240 nm. Most recently,
the authors of Ref. [177] published their work on filamentation in the atmosphere spanning 400 nm to 4 µm by using 90 fs pulses at 3.9 µm.

Of note, we had performed preliminary work in 2011 regarding the extension of the WLC by utilizing near-IR pump pulses which preceded much of the initial work of producing WLC in gases in that spectral range discussed in the previous paragraph. The preliminary work utilized signal pulses from a TOPAS-C (see CHAPTER 5) at 1200 nm and 1500 nm to generate a broadband, yet unstable, WLC that spanned from 400 nm to > 1600 nm in ~7.4 atm of Kr gas. This work provided the proof of concept of extending the WLC to the near-IR for nonlinear spectroscopy in which we had prepared a proposal for funding. This funding allowed the purchase of the Coherent Legend Elite Duo HE+ as well as the TOPAS-HE described in CHAPTER 5. Furthermore, observations such as those of Ref. [178] in which a flattening of the visible portion of the generated WLC in condensed media was observed by utilizing 45 fs pulses compared to 300 fs pulses, prompted the purchase of the ultrashort pulse width option. Thus, the experiments presented in this section detail the extension of the WLC in the near-IR by utilizing the 40 fs (FWHM), 12 mJ Coherent laser system described in Figure 5-6.

Figure 7-28. Schematic of the WLC generated with the laser system described in Figure 5-6. “BD” stands for beam dump, “DSP” stands for dichroic short-pass (described in the main text), and “LVFs” are linearly variable short-pass and long-pass filters.
Figure 7-28 shows the schematic of the WLC pumped by the 40 fs (FWHM), 12 mJ Coherent laser system described in Figure 5-6. The input pulse is incident on the lens (note that in Figure 7-28, the pulse comes from the left) and is weakly focused into a 183 cm chamber filled with Kr gas at various pressures. For the experiments with ultrashort pulses, the chamber windows were chosen to be 2 mm thick sapphire windows (Meller Optics – Part No. MSPW200/020M). Since sapphire is a naturally birefringent material, the windows were cut so that the c-axis was perpendicular to the faces. This, in turn, minimizes changes in polarization due to the birefringence, thus preserving the polarization state of the incident pulse. Sapphire was also chosen for its broad transparency region. The transmission region for sapphire is from 150 nm to 5 μm. This allows not only for the entire generated WLC to lie in the transparency region but also for longer wavelength pump pulses to be utilized in future experiments. The thickness of 2 mm was chosen so that the windows could withstand moderate to high pressures as well as to minimize the effects of pulse chirp due to the large bandwidths of the incident pulses (see Figure 5-8b). For example, the 1800 nm idler pulse from TOPAS-HE has a bandwidth of ~160 nm (FWHM). Thus, in sapphire, the group delay dispersion (GDD) is less than 10 fs / mm across the bandwidth of the pulse for both the o- and e-wave (dispersion curves for the calculation of the GDD obtained from Ref. [179]). The λ/2 waveplate was used to rotate the linearly polarized pulses according to the choice of notch filter (discussed below). The only observed drawback to using sapphire windows stems from the material’s relatively large refractive index which inherently causes a great deal of Fresnel losses. There was dialogue to place an anti-reflection coating on the input window to minimize the reflection losses. But it was later decided against due to the typically low damage thresholds of these types of coatings and the inability to have use longer wavelength pump pulses in the future whose bandwidth necessarily wouldn’t lie within the anti-reflection range.
Attenuation of the incident pulses was achieved via neutral density filters as opposed to polarizers. The polarizers used in previous experiments that were discussed in prior sections are > 20 mm thick and have a clear aperture of ~10 mm in diameter. Thus, the thickness of the polarizer would induce chirp of the incident pulses and due to the high peak power of the pulses could induce self-focusing which could lead to unwanted filamentation in the calcite. Furthermore, the pulses leaving the TOPAS-HE are ~ 10 mm (FW 1/e^2 M) which would impinge on the clear aperture of the polarizer. The output pulse from the chamber traverses through either a dichroic short-pass filter or a 1 cm water cuvette which are used as notch filters for the input pulses. To spectrally separate the WLC, a linearly variable short-pass filter is used with a linearly variable long-pass filter to create a tunable bandpass filter with varying bandwidths (discussed later).

![Figure 7-29](image)

Figure 7-29. (a) Transmission of the dichroic short-pass filter (Thorlabs – DMSP1500) at 45 deg AOI for horizontally (solid black line) and vertically (solid red line) polarized light. (b) Transmission of 1 cm of water at normal incidence. The green dashed line in (a) and (b) shows the spectrum of the incident 1800 nm pulse. These are used as a notch to block the strong pump pulse from the resultant WLC. Note the difference in tick marks on the horizontal axis for (a) and (b).
Figure 7-29(a) shows the transmission spectrum for the dichroic short-pass filter (labeled DSP in Figure 7-28). This spectrum was measured using a Cary 500 spectrophotometer. The solid red line in (a) represents the transmission of vertically polarized light whereas the solid black line in (a) represents the transmission of horizontally polarized light. The blocking bandwidth for both orientations of the polarization are sufficient for reflecting the total bandwidth of the 1800 nm pulse. But the transmission differs drastically for the two orientations. Remember that the polarization of the WLC follows that of the pump. So, depending on the polarization of the incident pulse, there could be less energy available for spectroscopy due to the transmission of the dichroic mirror for different polarizations. Therefore, the $\lambda/2$ waveplate in Figure 7-28 (Thorlabs – Part No. AHWP05-1600) was inserted to rotate the horizontally polarized pulses from TOPAS-HE to the vertical polarization to allow for maximum energy throughput for spectroscopy. This achromatic waveplate was purchased due to the relatively flat retardance from 1100 nm to 2000 nm.

In Figure 7-29(b), the transmission spectrum for 1 cm of water is shown. To calculate the transmission, the real and imaginary component of the linear refractive index was taken from Ref. [180]. From the calculated transmission spectrum, 1 cm of water blocks the bandwidth of the 1800 nm pulse with an OD greater than 4. The transparency region is calculated to be from 300 nm to 900 nm, i.e. having a transmission greater than 90%.

For the near-IR pumped WLC at 1800 nm, the dichroic mirror and 1 cm water cuvette were used to block the 1800 nm pump from the resultant WLC. For the near-IR wavelengths (1000 nm – 1450 nm), the dichroic mirror was used as a notch since the transmission in that region is spectrally flat. For the VIS-NIR portion of the generated WLC, i.e. 400 nm to 900 nm, the 1 cm
water cuvette was used since the transmission is high across that bandwidth. It’s important to note that the induced chirp on the WLC from traversing the dichroic mirror is expected to be minimal since the total thickness of the mirror is 3.2 mm and the dichroic coating typically has minimal GVM in regions of spectral flatness. To calculate the chirp from the 1 cm water cuvette, we use the following relation:

\[
g(z) = \tau \sqrt{1 + \left(\frac{z}{z_d}\right)^2}
\]

where the function \( g \) describes the output pulse width after propagation through a medium of length \( z \) and \( k_2 \) is defined in Eqn. (4.12) where we have taken the dispersion relation of water from Ref. [181] at a temperature of 293 K. As an example, for an incident 50 fs-FWHM pulse, the chirp through 1 cm of water reaches a maximum at 400 nm of 60 fs-FWHM. Thus, for the wavelengths spanning the transparency region of 1 cm of water, the induced chirp is calculated to range from 50 fs-FWHM to 60 fs-FWHM. Note that this formalism only assumes that the initial pulse isn’t chirped.
Figure 7-30. Transmission spectra of the (a) linearly variable short-pass and long-pass filters shown in Figure 7-28. The dashed lines represent certain locations along the short-pass filter and the solid lines represent certain locations along the long-pass filter. (b) Some of the near-IR bandpass interference filters used to spectrally separate the WLC generated by the near-IR pump. The transmission spectra in (a) was provided by the filter supplier Delta.

Figure 7-30(a) shows some of the transmission spectra of the LVFs depicted in Figure 7-28 at certain positions along the filter. The dashed lines in the figure represent certain locations along the short-pass filter whereas the solid lines represent certain locations along the long-pass filter. As mentioned briefly before, the LVFs consist of a linearly variable short-pass filter and a linearly variable long-pass filter. The two LVFs work in conjunction to produce a tunable bandpass filter with varying bandwidth. The usable range for the variable short-pass and long-pass filters is stated to be 350 nm – 850 nm. Although the company states this to be the range, in practice, it was found that the best range was between 400 nm – 800 nm. Therefore, these LVFs were used with the 1 cm water cuvette being the “notch” filter. Also of note is that the blocking OD far away from the transmission band is not sufficient to block unwanted radiation. For example, positioning the LVFs to allow a 10 nm bandwidth centered at 400 nm would block out of band visible radiation to around
700nm, but radiation in the near-IR would be transmitted through to a certain extent. Therefore, it was found that, specifically on the UV-VIS portion for the LVFs, additional short-pass filters were needed to block the near-IR portion of the WLC that was not blocked by the 1 cm water cuvette. In addition to using the LVFs in the VIS-NIR, we also used the narrow bandpass filters depicted in Figure 7-3.

Figure 7-30(b) shows some of the individual bandpass interference filters used to spectrally separate the near-IR portion of the WLC. Accordingly, the dichroic mirror shown in Figure 7-29(a) was used as a notch in this range. The narrow bandpass filters (~10 – 12 nm FWHM) depicted are from Edmund Optics whereas the wider bandwidth filters, i.e. ~54 nm-FWHM for the 1242 nm filter and ~81 nm-FWHM for the 1424 nm filter, are from PixelTeq. Of note, the blocking OD outside of the transmission band for certain interference filters is not sufficient for portions of the unwanted, generated WLC. For instance, the blocking range of the 1150 nm bandpass filter only extended to 1400 nm. Therefore, generated WLC from 1400 nm to the edge of the blocking range of the dichroic mirror (~1550 nm) is not sufficiently blocked by using the 1150 nm bandpass filter. Thus, it must be emphasized the importance of checking the linear spectrum of these interference filters periodically since they can degrade substantially over time.
Figure 7-31. (a) The corrected power at certain bandwidths of the WLC generated by an 1800 nm pump pulse where corrected indicates that the measured power was divided by the transmittance of the notch filters used but not for the transmission of each individual bandpass filter. The data point at 1800 nm is the input pump power. (b) The normalized intensity spectrum of the WLC measured by an Ocean Optics NIRQUEST-512-2.5. The green dashed line in (b) is the typical spectrum of the 1800 nm pump pulse. The spectra in (b) was measured without the dichroic notch filter.

Figure 7-31(a) displays the corrected power output of the WLC generated with 690 µJ pulses at 1800 nm using a lens with focal length 1.5 m. Here, corrected means that the measured power was divided by the transmittance of the respective notch filters used. The energy is that incident on the input window; therefore, it is not corrected by reflection losses. The gauge pressure was set to 56 psi of Kr gas. The WLC generated spans the entire visible regime and the near-IR regime up to the pump pulse bandwidth. The WLC power on the Stokes side of the pump bandwidth was not measured due to limitations with detection. Note that the laser operates at 1 kHz so the energy per pulse is simply the average power divided by the repetition rate, e.g. 100 µW equals 100 nJ. Comparing the visible portion of the generated WLC in Figure 7-31(a) to that obtained in Figure 7-9, we observe similar energy across that range. Furthermore, there is a great
deal more available energy in the near-IR spectral region as compared to the 780 nm pumped WLC.

Figure 7-31(b) shows the normalized intensity spectrum of the generated WLC measured with an Ocean Optics NIRQUEST-512-2.5. It’s important to note that this spectrometer was a loaner unit which preceded our purchase of the NIRQUEST 256-2.5. Note that the spectra was taken in the absence of the dichroic notch filter. Also shown in the figure is a typical spectrum of the 1800 nm pump pulse. We observe the generated frequencies on the anti-Stokes side of the pump pulse as shown in (a), but of interest is the noticeable generation of frequencies on the Stokes side of the pump pulse. The extent of the Stokes generated WLC was not determined due to limitations in detection at the time.

Of the utmost importance for the scope of this thesis is how suited the generated WLC pulses are for nonlinear spectroscopy. For the 780 nm pumped WLC, it was observed that the beam profiles of the WLC largely depended upon the input pump profile. By obtaining good pump profiles, the WLC, specifically on the anti-Stokes side of the pump, was shown to mimic, for the most part, that of the pump.
Figure 7-32. (a) Beam profile of the 1800 nm pump pulse when TOPAS-HE is set for maximum energy output. (b) Corresponding beam profiles of the VIS-NIR spectral regions of the WLC at the maximum position of TOPAS-HE. The beam profile in (a) was taken with a Spiricon Pyrocam III profiler while the beam profiles in (b) were taken with a Cinogy CinCam beam profiler.

As stated in CHAPTER 5, the TOPAS-HE is identical to the TOPAS-C except for an additional high-energy amplifier stage. Typically, OPG/As produce beam profiles that are not suitable for nonlinear spectroscopy which is why we always spatially filter our beams for measurements such as Z-scan. With the addition of the high-energy amplifier in TOPAS-HE, there was a chance that the beam profiles could become worse than typical OPG/As such as TOPAS-800 or TOPAS-C. Shown in Figure 7-32(a) is the beam profile of the 1800 nm pump pulse with TOPAS-HE set to produce the highest energy output. This profile was measured with a Spiricon Pyrocam III. Notice how the beam profile is not only elliptical but that the central portion is spotty. Due to this beam profile, the 1800 nm pulse would not focus well. That is, during the initial WLC generation, the 1800 nm pulse would not generate a clean filament in which the wavelengths could be generated cleanly.
Shown in Figure 7-32(b) are the resultant beam profiles of the visible portion of the WLC generated by the 1800 nm pump pulse at 400 nm, 520 nm, 600 nm, 710 nm, 800 nm, and 950 nm. Obviously, these pulses would not be conducive for nonlinear spectroscopic measurements. Compared to the beam profiles of the visible WLC generated by the 780 nm pump pulse in Figure 7-8, the visible WLC energy obtained from this 1800 nm pulse is not centrally contained as seen by the spotty nature of the profiles. For this set of data, wavelengths greater than 950 nm were not investigated since the visible profiles produced such results. Therefore, it was decided to try and improve the visible portion of the WLC by improving the 1800 nm pulse beam profile.

Figure 7-33. Second order intensity autocorrelation of the 1800 nm pump pulse when the high-energy amplifier stage of TOPAS-HE is (a) set for the maximum output energy and (b) detuned by 17 steps from the maximum output. In TOPAS-HE, 2 steps equal 1 µm of linear translation. The insets in (a) and (b) show the corresponding beam profile measured by a Spiricon Pyrocam III.

To improve the quality of the beam output from TOPAS-HE, we first tried to manipulate the 1st amplification stage of the OPA, i.e. the pre-amp, by reducing the power incident on the 1st BBO crystal and by adjusting the spatial overlap of the 800 nm pulse. Afterwards, we tried to adjust spatial overlap on the 2nd and 3rd stages (for TOPAS-HE, the 3rd stage is the high-energy
amplifier), but to no avail. Finally, it was found that by detuning the temporal overlap on the 3rd stage, the spatial beam quality changed drastically, but the energy output and stability was affected. One of the biggest concerns was the effect that this detuning would have on the temporal characteristics of the output beam. Figure 7-33 shows the second order intensity autocorrelation of the 1800 nm pulse for (a) the position of the 3rd stage such that there is maximum energy output and (b) the detuned 3rd stage position for the best looking beam profile. As shown, the detuned 1800 nm pump pulse has a smaller measured pulse width than the 1800 nm pump at the peak position of the high-energy amplifier. Also, it was observed that there was a small effect on the bandwidth of the 1800 nm pulses measured by an OceanOptics NIRQUEST 256 spectrometer when detuning the high-energy amplifier (not shown). The insets to both (a) and (b) show the corresponding beam profiles of the 1800 nm pump pulse for the max position and detuned position, respectively. Note there is still a slight ellipticity in the case for a detuned 1800 nm pulse but the profile is much more circular than in (a). Furthermore, the beam energy is concentrated in one spot and does not possess the spotty characteristics of that shown in (a). Earlier in this paragraph it was stated that the detuned position affected the energy output and stability of the 1800 nm pulse. At just 17 steps detuned from the maximum position (for TOPAS-HE, 2 steps equal 1 µm of linear translation) the energy output dropped by nearly a factor of 2 and the instability increased by a factor of 3. Even so, it was decided that the decrease in energy and increase in instability could be tolerated for a better beam profile. It’s important to note that there were discussions to spatially filter the 1800 nm pulse as is done with Z-scans. It was decided against due to the similar loss in energy that would result from the spatial filtering process as well as the added complexity in experimental design.
Figure 7-34 shows knife edge scans of the 1800 nm pump with respect to the position along the chamber to determine the $M^2$ value (see Eqn. (7.4)). These scans were performed on the beam depicted in the inset of Figure 7-33(b). The $M^2$ was determined to be $1.1 \pm 0.02$ with a minimum spot size at the focus of a 1 m lens of 355 μm (HW 1/e² M).
Figure 7-35. The usable power (energy) of the WLC generated by the 1800 nm pulse depicted in the inset of Figure 7-33(b). The open symbols depict measurements obtained with the 1 cm water cuvette used as a notch filter. The closed symbols depict measurements obtained when using the dichroic mirror (DMSP1500) as a notch filter. LVF stands for linearly variable filter and BF stands for bandpass filter.

Figure 7-35 shows the available power (energy) of the WLC generated by the 1800 nm pulse detuned from the maximum position on the high-energy amplifier stage as shown in the inset of Figure 7-33(b). The energy of the 1800 nm pulse used to generate this WLC was 620 µJ before the input to the chamber. Taking into account Fresnel losses from both surfaces of the input window, the actual energy was 530 µJ at the exit of the input window (the refractive index of sapphire is ~1.74 at 1800 nm [179]). The position of the 1 m lens was positioned such that the
minimum focus occurred near the middle of the 183 cm long chamber, i.e. position 900 of Figure 7-34. The gauge pressure was 40 psi of Kr gas.

The open symbols indicate that the 1 cm water cuvette was used as the notch filter while the closed symbols indicate the dichroic mirror being used as the notch filter. The open red circles are measurements taken with narrow bandpass filters of width ~10 nm-FWHM (similar to the ones depicted in Figure 7-3). The open black squares are measurements taken with the linearly variable filters with the filters positioned to allow a 10 nm-FWHM bandwidth at the specified center wavelength and the open blue triangles are the same except for the filters being positioned to allow a 20 nm-FWHM bandwidth. The closed green circles are measurements taken with bandpass filters for the near-IR wavelengths. Note that the bandpass filters with center wavelengths at 850 nm, 950 nm, and 1000nm have FWHM bandwidths of 40 nm, 40 nm, and 70 nm, respectively.

Comparing the available energy in the visible portion of the WLC by pumping with 1800 nm pulses and 780 nm pulses (see Figure 7-9), we observe similar magnitudes for the bandpass filters, but larger energies when using the LVFs. The trend observed with the 780 nm pumped WLC of decreasing energy in the NUV-VIS region with respect to the VIS-NIR portion is repeated for the 1800 nm pump pulse. Another observation is the flatness of the spectrum when the LVFs are utilized instead of the fixed bandpass filters. This is due to the typically flat transmission of the short-pass and long-pass filters across their respective transparency bands. Positioning the filters for 20 nm-FWHM bandwidths nearly doubles the available energy when compared to allowing for 10 nm-FWHM bandwidths at the same wavelength. Note that the energy measurements for the LVFs increase for wavelengths shorter than 550 nm. This is most probably due to the leakage of
near-IR wavelengths that lie outside of the blocking bandwidth. At the time of these measurements, there was not a short-pass filter positioned to block the leakage radiation.

Comparing the available energy in the near-IR portion by pumping with 1800 nm pulses as opposed to 780 nm pumped WLC, we observe a drastic difference. When pumping with 780 nm pulses, the available energy at wavelengths longer than 900 nm was well below 10 nJ. For the 1800 nm pumped WLC, we observe at least tens of nJ’s of available energy from 900 nm up to the edge of the dichroic mirror blocking range. Although not shown in Figure 7-30(b), some of the wide bandwidth filters allow hundreds of nJ’s to be utilized from the generated WLC. Hence, the WLC generated from the 1800 nm pump pulses spans the visible to near-IR wavelength range with adequate energy available for nonlinear spectroscopy.

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Figure 7-36. Beam profiles of the WLC generated by the 1800 nm pulse when the high-energy amplifier is detuned from the maximum position. These profiles were taken with a Cinogy CinCam beam profiler.
Shown in Figure 7-36 are the beam profiles of the WLC generated by the 1800 nm pump pulse with the profile shown in the inset of Figure 7-33(b). In the VIS-NIR spectral region, the WLC profiles are fairly symmetric and mimic that of the input pump pulse. For the WLC below 600 nm, the profiles show some asymmetry and are spotty in nature. Thus, even with a near-IR pump with a circular beam profile, the WLC generated on the blue-side of the visible spectrum are not conducive for nonlinear spectroscopy. Wavelengths longer than 1100 nm could not be measured since the beam profiler was silicon-based, thus having low spectral response beyond 1100 nm.

Figure 7-37. (a) Schematic of the experimental configuration to determine the pulse widths of the WLC. (b) The extracted pulse widths for various spectral components of the WLC. (c) Typical cross-correlations of the WLC with 1420 nm pulses and the corresponding fits. The cross marks in (b) are the calculated transform limit pulse widths (see Eqn. (2.16)). Note the unphysical result at 1100 nm is discussed in the text.
To determine the pulse widths of the WLC generated by the 1800 nm pump pulse, we performed cross-correlations using an experimental configuration as shown in Figure 7-37(a). The corresponding signal pulse from TOPAS-HE when set for an 1800 nm idler pulse, i.e. 1420 nm, was overlapped spatially and temporally in a 100 µm thick BBO crystal to detect the SFG from the cross-correlations. For the WLC below 800 nm, the LVFs were used for spectral separation while for wavelengths greater than 800 nm, the bandpass filters were used. Also of note, the measurements for the 850 nm, 950 nm, 1000 nm, 1242 nm, and 1424 nm bandpass filters had bandwidths of 40 nm, 40 nm, 70 nm, 54 nm, and 81 nm, respectively, all of which are given in FWHM. The pulse widths were extracted via the typical convolution integral expressed as:

\[ h(t) = \int_{-\infty}^{t} I_{1420\text{nm}}(\tau)I_{WLC}(t-\tau)d\tau \]  

(7.9)

where \( I_{1420\text{nm}} \) and \( I_{WLC} \) are the irradiance distributions, i.e. proportional to the squared modulus of Eqn. (7.3), for the 1420 nm signal pulse and spectrally filtered WLC pulse, respectively. The width of the resultant function, \( h(t) \), is simply \( \sqrt{\tau_{WLC}^2 + \tau_{1420\text{nm}}^2} \). Autocorrelations were performed for the 1420 nm signal pulse which yielded \( \tau_{1420\text{nm}} = 54 \) fs (FWHM).

Shown in Figure 7-37(b) is the extracted \( \tau_{WLC} \) via the cross-correlations with the 1420 nm signal pulse with some of the typical scans shown in (c). The orange triangles in (b) represent measurements with the 1 cm water cuvette used as a notch filter while the blue circles represent measurements with the dichroic mirror used as a notch filter. The black crosses in (b) are the transform limit pulse widths calculated based upon the bandwidth of the WLC (refer back to Eqn. (2.16)). The measured pulse widths were determined to be \(~100\text{ fs-FWHM}\) covering the visible to near-IR spectral regions. Large discrepancies between the transform limit pulse width and
measured pulse width were found for 450 nm and 500 nm. This could be attributed to leakage of the near-IR radiation when using the LVFs. Large discrepancies were also found for the 40 nm-FWHM bandwidths of the 850 nm and 950 nm filters as well as for the 70 nm-FWHM bandwidth filter at 1000 nm. Note that the result for the 1100 nm filter revealed an unphysical characteristic, i.e. the measured pulse width is less than the transform limit. The cross-correlation at 1100 nm revealed features that indicated multiple frequencies were present during the scan. Therefore, it is assumed that this measurement was not indicative of the true pulse width measurement of 1100 nm. It was found later that the 1100 nm bandpass filter had degraded such that the blocking OD was insufficient at the longer wavelengths. Even though we observed that the WLC was chirped in certain spectral regions, for the purposes of nonlinear spectroscopy, so long as the pulse width is known, it does not disallow for measurements to be conducted.

In addition to the 1800 nm pumped WLC, we conducted preliminary measurements utilizing other pump wavelengths from the 40 fs-FWHM laser system to determine how it affects the amount of available energy.
Figure 7-38. The available energy from the WLC generated with (a) 800 nm pulses and (b) 1300 nm pulses from the 40 fs-FWHM laser source. The blue dotted lines in (a) and (b) represent the spectrum of the 800 nm pulse and 1300 nm pulse, respectively.

Figure 7-38(a) shows the available energy from the WLC generated with 800 nm, 40 fs-FWHM pulses. The pulse energy was measured to be 103 µJ before the input to the chamber. A 2 m focusing lens was placed such that the minimum spot size was close to the middle of the chamber (Position ~900 of Figure 7-34). Using the fitting function from the Cinogy CinCam beam profiler, it was determined that the minimum spot size was ~210 µm (HW 1/e² M). The gauge pressure reading was set to 38 psi. The black squares in (a) represent measurements that were taken with the LVFs while the red triangles represent measurements taken with fixed bandpass filters. The blue dashed line represents the spectrum of the input pulse and the gray area represents the notch filter bandwidth. In general, the amount of energy available from the 800 nm pump pulse while using the LVFs was found to be slightly less to that generated by the 1800 nm pump pulse. Compared to the ~150 fs-FWHM pumped WLC at a similar wavelength (see Figure 7-9), the available energy is nearly similar. This is an indication that by using shorter pulses, i.e. 40 fs-
FWHM compared to ~150 fs-FWHM, the efficiency of the WLC might be enhanced in the visible portion of the WLC spectrum as found in Ref. [178] and briefly mentioned in the beginning of this section. The available energy on the Stokes side of the 800 nm pump pulse was found to be small with the amount of energy in a 70 nm-FWHM bandwidth filter at 1000 nm being only ~1 nJ.

Figure 7-38(b) shows the available power (energy) from the WLC generated with 1300 nm pulses from the TOPAS-HE. Typical second-order intensity autocorrelations determined that the temporal width of the 1300 nm pulse was ~45 fs-FWHM. The pulse energy was measured to be 348 µJ before the chamber. The same 2 m focusing lens was positioned such that the minimum focus occurred near the middle of the chamber. The gauge pressure reading was set to 29 psi. The beam waists near focus nor along the position of the chamber were not measured at this time. For the wavelengths measured below 800 nm, fixed bandpass filters of bandwidth 10 nm-FWHM were used. For the measurements at 850 nm, 950 nm, and 1000 nm, the bandwidths were 40 nm, 40 nm, and 70 nm, respectively. All measurements on the Stokes side of the 1300 nm pulse were taken with fixed bandpass filters of bandwidth 12 nm-FWHM. Additionally, for the measurement of energies on the anti-Stokes side of the 1300 nm pump pulse, an 1100 nm short-pass filter was used to block the pump. For energy measurements on the Stokes side of the 1300 nm pump pulse, a 1350 nm long-pass filter was used. For the 1300 nm pumped WLC, we observed more energy available in the visible portion than that from the 800 nm pumped WLC. Compared to the 1800 nm pumped WLC, the available energy in the visible portion was found to be similar. On the Stokes side, the energy measurements taken at 1400 nm and 1500 nm could be influenced due to the 1350 nm long-pass filter not adequately blocking the 1300 nm pump sufficiently. Still, we should expect that the energy would drop on the Stokes side as observed with the 780 nm and 800 nm pumped WLC.
We observed that the 1800 nm pump produced the most energy spanning the visible and near-IR regimes. This could be the result, in part, of two effects: the ability to increase the pump power to create a stable WLC and the usage of short pulses to generate WLC more efficiently. With the 800 nm, ~40 fs-FWHM pumped WLC, the amount of available energy was found to be comparable to that of the 780 nm, ~150 fs-FWHM pumped WLC although much less energy was used for generation. Unfortunately, a direct comparison for the near-IR pumped WLC using longer pulses (~150 fs-FWHM) was not able to be completed due to limitations of the output power of the ~150 fs-FWHM laser source.
CHAPTER 8 CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

The main effort in this dissertation involved generating a WLC in inert gases for the purpose of nonlinear spectroscopy using such methods as the Z-scan technique and utilizing this WLC to perform spectroscopic measurements. By using 150 fs-FWHM pulses at 780 nm and 40 fs-FWHM pulses at 1800 nm, it was shown that a WLC could be generated that spanned multiple octaves with high-spatial-quality and high-spectral-irradiance. Another effort discussed in this dissertation was the extension of the dual-arm Z-scan technique to measuring thin film nonlinearities in the presence of large substrate signals. By using a simplified quantum mechanical perturbative model, it was found that the $n_2$ spectra of organic molecules approximated as centrosymmetric could be predicted with knowledge of just the one-photon and two-photon absorption spectra.

Two key mechanisms were found to be responsible for WLC generation one of which being SPM. The effects of the third-order nonlinear refractive index $n_2$ was examined in the context of WLC in which the initial spectral broadening occurred due to SPM. The extent of SPM is the result of the irradiance of the incident pulse, the magnitude of $n_2$, as well as the propagation distance in the medium. Thus, as it pertains to the inert gases, the amount of irradiance needed to produce sufficient SPM is much larger than in condensed media where the pressure and temperature dependent $n_2$ for gases can be nearly 3 orders of magnitude less than the $n_2$ in condensed media. Also in order to offset the small magnitude of $n_2$, we utilized long path length chambers of 125 cm and 183 cm in which we could accumulate more phase due to SPM leading to more spectral broadening. Furthermore, the positive phase accumulation due to the positive $n_2$ gives rise to a positive change in index and self-focusing which has an important effect upon the WLC generation
process. Thus, the critical power for self-focusing, the spatial analog to SPM, was derived for which the Kerr-lensing (self-lensing) effect became large enough to overcome the inherent diffraction of the pulse which resulted in beam collapse. This power is often said to be a precursor to filamentation and WLC generation. Thus, the critical power for the inert gases was determined to be GW-level for the incident wavelengths used in this thesis, i.e. primarily 780 nm and 1800 nm, due to the small magnitude of $n_2$.

The other key mechanism in the WLC process explored in this dissertation was ionization-induced plasma production. The plasma was found to produce a negative contribution to the total refractive index. This negative change in refractive index arising from the plasma was derived and was found to depend on the amount of free electrons generated through the ionization process as well as the incident wavelength. The PPT model [67] for calculating the ionization rate was used to determine the amount of free electrons generated and, thus, gave the magnitude of the negative contribution to the refractive index.

The knowledge that the phase accumulation from plasma and SPM should be nearly the same to generate WLC aided our efforts in determining the parameters needed to achieve a stable WLC suitable for nonlinear spectroscopy. The first set of WLC experiments described in this dissertation used a Ti:Sapphire laser system which output mJ level, 150 fs-FWHM pulses at 780 nm to determine the exact parameters necessary for the initiation of WLC as well as the parameters necessary for stable WLC. Experimentally, it was found that the initiation of WLC occurred when the power of the incident pulse was similar to the calculated critical self-focusing power. Stable WLC was observed for power levels slightly larger than the calculated critical self-focusing power and when the change in index from SPM was nearly identical to that calculated from the plasma.
The usable range of this WLC was found to be from 400 nm to 710 nm and produced tens of nJs with high spatial quality beam profiles necessary for nonlinear spectroscopy. On the longer wavelength side of the 780 nm pump pulse, the WLC spectral energy density dropped drastically and the spatial profiles for some of the wavelengths produced ring-like structures unsuitable for nonlinear spectroscopy.

It was found by utilizing a secondary weak seed pulse co-propagating spatially and temporally with the 780 nm pulse, the spectral energy contained in the WLC could be enhanced by more than a factor of 3 in Kr gas. The enhanced WLC also was found to span more than 2 octaves. The largest amount of enhancement occurred for seed pulses lying in the visible regime with only modest enhancement when using near-IR pulses. This enhancement by using a weak seed pulse was observed in Ar and Xe gas as well as condensed media. A collaboration was formed with members of Prof. Alex Gaeta’s group (Bonggu Shim and Samuel E. Schrauth) at Cornell University to provide numerical simulations in modeling our experimental results. The numerical simulations utilized a broadband code in which the seed pulse was implemented as a perturbation to the 780 nm pulse. By using an appropriate nonlinear envelope equation, the numerical simulations were found to agree qualitatively with our experimental results. It is of note that efforts to use a two-color code in describing the seeded WLC were not successful. Although the spectral energy was enhanced across the visible and near-IR regimes, the seeding process was shown to change the spatial characteristics of the WLC. Furthermore, some of the near-IR wavelengths still revealed a ring-like structure not conducive for nonlinear spectroscopic measurements.

The bandwidth of the WLC was extended by using a high energy Ti:Sapphire laser system producing 40 fs-FWHM pulses with the ability to produce mJ level pulses in the near-IR. Thus,
1800 nm pulses were used to generate a WLC spectrum that covered more than 2 octaves and spanned from 400 nm to greater than 2000 nm. By adjusting the OPA in order to achieve a high-spatial-quality 1800 nm pump pulse, the resultant WLC in the near-IR and portions of the visible displayed high-spatial-quality characteristics as well. The available energy was measured to be in the tens of nJ in the visible portion of the generated WLC and increasing to hundreds of nJ in certain parts of the near-IR region. The ability to use high-energy pump pulses at longer wavelengths than 780 nm enabled the extension of the WLC into the near-IR regime where many materials of interest, specifically for all-optical switching applications in the telecommunications window, are transparent. Comparisons of the 150 fs-FWHM and 40 fs-FWHM pumped WLC at 780/800 nm revealed preliminary indications that using ultrashort pulses may improve the efficiency of WLC generation.

In another effort of this dissertation, the dual-arm Z-scan technique was extended to measuring thin film nonlinearity in the presence of large substrate backgrounds. By correlating the noise sources on both arms, i.e. pulse energy, beam pointing instability, etc., thin film nonlinearities of ZnO as well as an organic thin film were extracted from their respective 1 mm thick substrates. It was also presented in this dissertation that a simplified quantum mechanical perturbative model (sum-over-states) could be used to predict the dispersion of $n_2$ of organic molecules (which are approximated as centrosymmetric) with knowledge of just the one-photon and two-photon absorption spectra. By utilizing a minimum of 3 essential states, i.e. the ground state, intermediate state, and two-photon absorption state, the model can qualitatively and, for some molecules, quantitatively match that which was experimentally obtained. In Ref. [111], it was argued that saturation terms which predict a strong negative imaginary component to the third-order response
near the one-photon absorption edge should be neglected when modeling the two-photon absorption spectra. Additionally, extending the number of essential states to 4 allowed the linear absorption spectrum to be modeled more precisely which, in turn, allowed the prediction of the magnitude of $n_2$ to better match the experimental results.

8.2 Future Work

In Sections 7.2 and 7.3, it was observed that the WLC generated from a 780 nm pump pulse could be enhanced by a weak seed pulse which not only enriched the visible portion of the spectrum but extended the spectrum further into the near-IR. The same mechanisms that are responsible for the spectral enhancement for the 780 nm pulse should be the same for that of the 1800 nm pump pulse and other near-IR pulses used in Section 7.5. Thus, experiments should be carried out to map out the spectral enhancement with respect to visible and near-IR seed pulses and the necessary focusing geometry required to see such enhancement.
Preliminary measurements of seeding the 1300 nm pumped WLC are shown in Figure 8-1. Clearly, the ability to enhance the 1300 nm pumped WLC by secondary pulses is evident. Thus, to determine what extent this enhancement occurs, the full seeded WLC map, as was done in Figure 7-15, needs to be completed for the 1800 nm pumped WLC. Of major importance is to observe how the seeding affects the spatial quality of wavelengths longer than 1100 nm, i.e. outside of the sensitivity range of our silicon-based beam profilers. Furthermore, seeding the 40 fs-FWHM, 800 nm pumped WLC with visible and near-IR seed pulses should be explored. Note that the decrease in spectral intensity at wavelengths longer than the reflectance bandwidth of the notch filter is most likely due to the decreased sensitivity of the spectrometer and is not typical of 1300 nm pumped WLC, i.e. the spectrometer was not calibrated at the time of measurement and could provide only a relative measurement.
Figure 8-2. Numerical simulations of a 40 fs-FWHM, 800 nm pumped WLC seeded with a 40 fs-FWHM pulse at 1800 nm. These simulations were performed by members of Prof. Alex Gaeta’s group at Cornell University.

In addition to the experimental investigations of seeding the 40 fs-FWHM laser sources, numerical simulations such as that presented in Figure 8-2 will need to be performed along with the experimental investigations.

In Section 7.5, it was observed that a high-spatial-quality 1800 nm pulse generated high-spatial-quality WLC pulses throughout the spectrum down to ~600 nm (see Figure 7-36). But below 600 nm, the WLC beam profiles appeared to be spotty and not conducive for nonlinear spectroscopy. It was also mentioned that the 40 fs-FWHM, 800 nm pumped WLC produced spectral energy similar to that for the 1800 nm pump pulse.
Figure 8-3 shows typical beam profiles of the WLC generated with 40 fs-FWHM pulses at 800 nm. In (a), the typical beam profile of the 800 nm is displayed and in (b), various spectral components of the WLC are displayed. These profiles were taken with the Cinogy CinCam beam profiler. Since the available energy from the 800 nm pumped WLC is similar to the energy available in the visible from the 1800 nm pumped WLC and the NUV-VIS profiles of the 800 nm pumped WLC are high-spatial-quality, it may be beneficial to employ a 2-pump method for nonlinear spectroscopy.

Figure 8-4. Schematic employing a 2-pump method for nonlinear spectroscopy. The “BD” stands for beam dump and “TM” stands for translatable mirror.
A schematic of a proposed 2-pump WLC is shown in Figure 8-4. Since it was shown that the spatial beam profiles of the 1800 nm pumped WLC was adequate in the wavelength range from 700 nm to longer than 1100 nm and for the 800 nm pumped WLC it is assumed from below 400 nm to the edge of the 800 nm notch filter bandwidth, a WLC that covers the entire visible to near-IR spectral range with high-spatial-quality and high-spectral-irradiance could be obtained by using a 2-pump system. The “TM” in Figure 8-4 stands for a translatable mirror that could be moved in and out depending on the spectral range of measurement.
APPENDIX A: DERIVATION OF THE COMPARISON OF THE IMAGINARY COMPONENT OF THE N-TERMS TO SATURATION OF A 2-LEVEL SYSTEM
In Ref. [111] and Section 6.4, it was discussed that the imaginary component of the N-terms of the SOS model should not be included in describing the 2PA of organic molecules outside of the linear absorption bandwidth. It was argued that these terms represent saturation of absorption and since the linear losses are negligible in the transparency regions of measurement, these terms should be neglected. In this appendix, it will be shown that the saturation described by a 2-level system is mathematically equivalent to the imaginary component of the N-terms of the 3-level essential states model. We start by writing the propagation equation describing the saturation of linear absorption and 2PA given by:

$$\frac{dI}{dz} = -\frac{\alpha_0}{1 + I/I_{sat}}I - \alpha_2 I^2,$$

(A.1)

where $I_{sat}$ is the saturation irradiance in which the first term on the left-hand side of Eqn. (A.1) describes the reduction of the absorption with increasing irradiance. We expand the first term on the left-hand side to third-order to obtain:

$$\frac{dI}{dz} \approx -\alpha_0 \left( 1 - \frac{1}{I_{sat}} \right)I - \alpha_2 I^2 = -\alpha_0 I + \frac{\alpha_0}{I_{sat}}I^2 - \alpha_2^T I^2$$

(A.2)

where $\alpha_2^N$ and $\alpha_2^T$ are the effective 2PA coefficients from the N-terms and T-terms, respectively. From the second to last equality of Eqn. (A.2), we’ll need to express the $\alpha_0/I_{sat}$ term in terms of the parameters used in the essential-state model (refer back to Eqn. (6.10)). Thus, it can be shown that [123]:

$$\frac{1}{I_{sat}} = \frac{\sigma_{eg} \tau_I [f^{(1)}]^2}{\hbar \omega},$$

(A.3)
where $\sigma_{eg}$ is the 1PA cross section, $\tau_L$ is the lifetime, and $f^{(1)}$ is the 1st order local field correction defined as $(\varepsilon_r(\omega) + 2)/3$. The linear absorption coefficient is defined as:

$$\alpha_0 = \sigma_{eg} N. \quad (A.4)$$

Including the linear absorption coefficient in Eqn. (A.3) leads to:

$$\frac{\alpha_0}{I_{\text{sat}}} = \frac{\sigma_{eg}^2 N \tau_L [f^{(1)}]^2}{\hbar \omega}. \quad (A.5)$$

The relation between $\alpha_0$ and the linear susceptibility $\chi^{(1)}$ is given as:

$$\alpha_0 = \frac{\omega}{2n_0 c} Im \chi^{(1)}. \quad (A.6)$$

In terms of the SOS model, $\chi^{(1)}$ can be expressed as [123, 124]:

$$\chi^{(1)}(-\omega_p; \omega_p) = \frac{N f^{(1)}}{\hbar \varepsilon_0} \sum_m \left\{ \frac{\mu_{gm} \mu_{mg}}{\omega_{mg} - \omega_p} + \frac{\mu_{mg} \mu_{gm}}{\omega_{mg}^* + \omega_p} \right\}. \quad (A.7)$$

As stated in Section 6.4, since state $m$ represents the intermediate state, we’ll call this complex frequency $\bar{\omega}_{eg}$. Also, there is only one input field such that $\omega_p = \omega$. By substituting the expression of Eqn. (A.7) into Eqn. (A.6) and equating the result with Eqn. (A.4), we can obtain an expression for $\sigma_{eg}$ in terms of the parameters of the SOS model. And we can, thus, express Eqn. (A.5) as:

$$\frac{\alpha_0}{I_{\text{sat}}} = \frac{\omega N [f^{(1)}]^4 \tau_L}{4n_0^2 c^2 \hbar^3 \varepsilon_0^2} Im \left[ \frac{\mu_{ge}^4}{(\bar{\omega}_{eg} - \omega)^2} \right]. \quad (A.8)$$

Note that we have only used the resonance term of Eqn. (A.7) when describing the linear susceptibility. We will revisit including the non-resonant condition as a comparison towards the end of this section. The lifetime “$\tau_L$” can be represented as the detuning of the frequencies so that:
\[ \tau_L = \frac{2}{\omega_{eg} - \omega}, \quad (A.9) \]

where the quantum zero point energy is defined as \( E = (1/2)\hbar\omega \) and we use the uncertainty relation \( \Delta E \Delta \tau \geq \hbar \). Thus, we can express Eqn. (A.8) as:

\[ \frac{\alpha_0}{I_{sat}} = \frac{\omega N \left[ f^{(1)} \right]^4}{2n_0^2 c^2 \hbar^2 \epsilon_0} \frac{1}{(\omega_{eg} - \omega)} Im \left[ \frac{\mu_{ge}^4}{(\omega_{eg} - \omega)^2} \right]. \quad (A.10) \]

Now we need to find the expression for \( \alpha_2^N \). Recall that the 2nd summation of Eqn. (6.10) represented the N-terms for the second hyperpolarizability \( \gamma^{(3)} \). Thus, combining the 2nd summation of Eqn. (6.10) with Eqn. (2.43) allows us to express the N-terms in terms of \( \chi^{(3)} \) as:

\[ \chi_N^{(3)}(\omega) = [\omega_p + \omega_q + \omega_r; \omega_p, \omega_q, \omega_r] \]

\[ = - \frac{NF^{(3)}}{\hbar^3 \epsilon_0} \left[ \frac{\mu_{ge}^i \mu_{eg}^l \mu_{ge}^k \mu_{eg}^j}{(\omega_{eg} - \omega_p - \omega_q - \omega_r)(\omega_{eg} - \omega_r)(\omega_{eg} - \omega_p)} \right. \]

\[ + \frac{\mu_{ge}^i \mu_{eg}^l \mu_{ge}^k \mu_{eg}^j}{(\omega_{eg}^* + \omega_q)(\omega_{eg} - \omega_r)(\omega_{eg} - \omega_p)} \]

\[ + \frac{\mu_{ge}^i \mu_{eg}^l \mu_{ge}^k \mu_{eg}^j}{(\omega_{eg}^* + \omega_r)(\omega_{eg}^* + \omega_p)(\omega_{eg} + \omega_p + \omega_q + \omega_r)} \]

\[ \left. + \frac{\mu_{ge}^i \mu_{eg}^l \mu_{ge}^k \mu_{eg}^j}{(\omega_{eg}^* + \omega_r)(\omega_{eg} + \omega_p)(\omega_{eg} + \omega_p + \omega_q + \omega_r)} \right] \]

where the subscript \( N \) denotes the N-term contribution. We don’t consider any orientational averaging as was done in Section 6.4. But we will assume the directional dipole moments are the same in all directions, i.e. \( \mu_{ge}^l = \mu_{ge}^i = \mu_{ge}^k = \mu_{ge}^j \). The strong resonant condition of Eqn. (A.11)
occurs when $\omega_p = \omega_r = \omega$ and $\omega_q = -\omega$. We will consider the non-resonant terms later in this section. The 2PA coefficient is related to $\chi^{(3)}$ by the following relation [44]:

$$\alpha_2 = \frac{3\omega}{2n_0^2 c^2 \varepsilon_0} Im \chi^{(3)}.$$  \hspace{1cm} (A.12)

By using Eqn. (A.12) and Eqn. (A.11), we find:

$$\alpha_2^N = -\frac{\omega N f^{(3)}}{2n_0^2 c^2 \hbar^3 \varepsilon_0^2} Im \left[\left(\frac{\mu_{ge}^4}{(\bar{\omega}_{ge} - \omega)(\bar{\omega}_{ge} - e)(\bar{\omega}_{ge} - \omega)}\right) + \frac{\mu_{ge}^4}{(\bar{\omega}_{ge} - \omega)(\bar{\omega}_{ge} - \omega)(\bar{\omega}_{ge} - \omega)}\right].$$  \hspace{1cm} (A.13)

Note that the factor of 1/3 due to the permutations of the fields from Eqn. (6.12) has been kept for self-consistency in the DC-limit. From the last equality of Eqn. (A.2), we intended to show, when outside the linear absorption bandwidth, that:

$$\alpha_2^N \approx -\frac{\alpha_0}{I_{sat}}.$$  \hspace{1cm} (A.14)

In this region, we can assume that $|\bar{\omega}_{ge}| \approx |\bar{\omega}_{ge}^*| \approx \omega_{ge}$ such that Eqns. (A.13) and (A.10) can be re-written as:

$$\alpha_2^N \approx -\frac{\omega N f^{(3)}}{n_0^2 c^2 \hbar^3 \varepsilon_0^2} Im \left[\frac{\mu_{ge}^4}{(\bar{\omega}_{eg} - \omega)^3}\right]$$  \hspace{1cm} (A.15)

$$\alpha_0 \approx \frac{\omega N f^{(1)}}{2n_0^2 c^2 \hbar^3 \varepsilon_0^2} Im \left[\frac{\mu_{ge}^4}{(\bar{\omega}_{eg} - \omega)^3}\right].$$  \hspace{1cm} (A.16)

For self-action nonlinearities, $f^{(3)} = [f^{(1)}]^4$ and the form of Eqn. (A.15) is mathematically equivalent within a factor of 2 to Eqn. (A.16). Since $\alpha_0$ can be set to zero in the transparency regions of measurement, the right-hand side of Eqn. (A.16) vanishes, thus making $\alpha_2^N$ equal to
zero in this region as well. Therefore, as discussed in Sections 6.4 and 6.5 and in Ref. [111], the imaginary component of the N-terms should not be included in describing 2PA in regions of transparency.

Figure A-1. Plot of $\alpha_2^N$ (solid red line) and $-\alpha_0/I_{sat}$ (solid black line) when including both resonant and non-resonant terms found in Eqn. (A.11) and Eqn. (A.7). The parameters used were those for the molecule YZ-V-69 discussed in Section 6.4, i.e. $\omega_{eg} = 1.27 \text{eV}/\hbar$, $\Gamma_{eg} = 0.044 \text{eV}/\hbar$, and $\mu_{ge} = 14 \text{D}$. The right-axis shows the ratio (dashed blue line) of $\alpha_2^N$ to $-\alpha_0/I_{sat}$.

Figure A-1 shows the plot of $\alpha_2^N$ (solid red line) and $-\alpha_0/I_{sat}$ (solid black line) as a function of the input frequency normalized to the peak of the 1PA resonance of the molecule YZ-V-69. The parameters are the same as that stated in Section 6.4. For these plots the resonant and non-resonant terms were included, i.e. all terms from Eqn. (A.7) and Eqn. (A.11). This plot confirms the mathematical equivalency of Eqn. (A.15) and Eqn. (A.16) even when including the non-resonant contributions. The right-axis of the figure shows the ratio of $\alpha_2^N$ to $-\alpha_0/I_{sat}$ as a dashed blue line. The ratio is less than 2 for the entire range of 2PA measurements presented in Figure 6-16. So as stated previously, it is valid to neglect the imaginary component of the N-terms.
in this spectral range. It must be noted that within the bandwidth of the 1PA resonance, $\tau_L$ should not be substituted by Eqn. (A.9).
APPENDIX B: TIPS AND TRICKS TO SET UP AND FIT
Z-SCANS
Figure B-1. Another schematic detailing DA Z-scan (see also Figure 6-6). In the figure, “L” stands for lens, “ID” stands for iris diaphragm, “PH” stands for pinhole, “SF” stands for spatial filter, “BS” stands for beamsplitter, “M” stands for mirror, “Ref” stands for reference, “OA” stands for open-aperture, and “CA” stands for closed-aperture. The 3D Cartesian axis means that the object is placed on a 3D-stage whereas the 2D Cartesian axis means that the object is placed on a 2D-stage.

Figure B-1 shows a slightly more detailed schematic of the DA Z-scan compared to Figure 6-6. For the following context concerning the figure, “L” stands for lens, “ID” stands for iris diaphragm, “PH” stands for pinhole, “SF” stands for spatial filter, “BS” stands for beamsplitter, “M” stands for mirror, “Ref” stands for reference, “OA” stands for open-aperture, and “CA” stands for closed-aperture. In the figure, PH, the sample on Arm-A, and the sample on Arm-B are placed on 3D-stages. The irises for the closed-aperture detectors on Arm-A and Arm-B (ID3 and ID4) are placed on 2D-stages.
The front portion of the schematic, i.e. L-1 and L-2, represents a beam expansion telescope. The expansion telescope is particularly useful for laser sources/systems with a large amount of pointing instability. To reduce the noise from pointing instability, the expansion telescope is used in conjunction with an iris diaphragm (ID1 in the figure). This process is called “top-hatting” the beam and only allows for the expanded central portion of the beam to pass. The “top-hat” has a near uniform energy density in a given cross-section. Thus, to achieve a proper “top-hat”, L-1 and L-2 should have sufficient focal lengths such that the magnification of the beam is many times the size of the diameter of ID1. This ensures that fluctuations due to pointing instability are not as pronounced since the central portion of the beam that passes through ID1 has a relatively flat fluence distribution and, thus, any movement on the aperture would cause minimal loss in signal. Typically, the diameter of ID1 is set to ~2 mm for the resultant spatial filtering. Note that this process wastes a considerable amount of energy, but is deemed necessary for laser sources with significant pointing instability. It was observed that the signal and idler pulses from the TOPAS-HE did not suffer from significant pointing instability and, for that reason, there was no expansion telescope placed before ID1.

Not shown in the figure is where beam attenuation and spectral filtration is usually performed, i.e. between ID1 and L-3. Typically, beam attenuation is done by a half-waveplate and polarizer pair. For the 150 fs-FWHM laser system (and the ps and ns laser sources as well), this pair did not pose any major concerns. For the 40 fs-FWHM laser system, care had to be taken as to not generate a filament inside the polarizer due to the high peak power of the pulses. The other concern was the broad bandwidth of the signal and idler pulses coming from the TOPAS-HE. Typically, the extinction ratio of the polarizers (calcite from Newport; Part No. 10GL08) is ~10^5, but this is only for cross-polarizer pairs not with using half-waveplates. The typical retardance of
the achromatic half-waveplates we use ranges from 0.46 to 0.52 and 0.485 to 0.54 for the 400-700 nm waveplate and 700-1550 nm waveplate, respectively. Thus, for the broad bandwidth signal and idler pulses, the retardance varies quite substantially over the bandwidth of the pulse. The result is that the extinction ratio suffers drastically when using the half-waveplate and polarizer pair. It was found that the addition of ND filters was necessary to achieve the range of energies for Z-scan measurements. In addition to beam attenuation, other spectral separation filters are typically required. For example, when measuring with the signal pulses, there is residual SFS and SFI generated on the last stage of the OPG/A’s that propagate with the signal pulse. Thus to block the residual light, long-pass filters are used such that the visible leakage radiation is blocked while the near-IR signal pulses are transmitted. Furthermore, when measuring with the SHS, e.g. 650 nm, long-pass filters need to be used in conjunction with short-pass filters to block not only leakage SFS and SFI but leakage signal radiation as well. In some instances when using the 40 fs-FWHM laser source, it may be useful to use a bandpass interference filter to narrow the spectrum accordingly, e.g. using a bandpass interference filter of width $\Delta \lambda = 10 \text{ nm-FWHM}$ at 1300 nm. The narrow bandpass filter, if desired, should be placed after all beam attenuation and spectral filtration optics, i.e. just before L-3.

L-3 and PH along with L-4 consist of the spatial filtering of the beam. Spatial filtering allows high spatial frequencies to be removed through Fourier optics. For a more physical explanation, see texts such as Ref. [182]. PH represents a diamond pinhole which we typically order from Fort Wayne Wire Die. These pinholes are actually fabricated for the purposes of wire extrusion in which the diameter of the hole must be precise. For this reason, and the fact that they are made from single crystal diamond, is the reason we use these as pinholes for spatial filtering. The focal length of L-3 is chosen such that we don’t focus too tightly into the pinhole.
Gaussian ABCD matrices, we can calculate the beam size at the pinhole for a given focal length of L-3 as:

\[ w_0 = \frac{\lambda f_L}{\pi w_{in}}, \]  

(B.1)

where \( w_{in} \) and \( w_0 \) is the beam size incident on the lens (in this case, L-3) and the beam size at the pinhole, respectively, both given in HW \( \frac{1}{e^2} \) M. This formula assumes an \( M^2 \) of 1 (see Eqn. (7.4)) which is obviously not true or else we wouldn’t be spatially filtering our beam. But using this formula will provide a close approximation to choosing an adequate diameter pinhole. For example, in a previous paragraph it was stated that the diameter of ID1 is typically ~2 mm, thus, making \( w_{in} \cong 1 \) mm. If L-3 is 15 cm, for an 800 nm beam, the diameter of the pinhole should be ~80 \( \mu \)m. Obviously, the diameter of the pinhole chosen is the result of a combination of the size of ID1, the wavelength of the beam, and the focal length of L-3. But for a set focal length of L-3, the beam size at the pinhole can be tuned by slightly adjusting the diameter of ID1. This has multiple effects as well. By slightly decreasing the size of ID1, the beam size at the pinhole would increase but the total energy available would decrease and the beam size at the input lenses before the sample (L-6 and L-7) would be smaller, resulting in a larger beam size at focus on the sample (the importance of this will be discussed in a subsequent paragraph).
Figure B-2 shows images of a beam on a screen placed after the pinhole. In (a), the image is due to a misalignment on the transverse dimensions of the pinhole. By slight adjustment of the transverse dimensions on the 3D-stage, the beam will elope into one central lobe as shown in (b). In (b), we observe the diffraction patterns from the circular pinhole due to the misalignment along the z-axis. By properly adjusting the z-axis of the 3D-stage and tweaking the input beam size on L-3, an image such as in (c) can be obtained. In practice, there may be faint diffraction rings visible that still exists. If the diffraction rings are not so severe, an additional iris diaphragm can be placed after L-4 to block these faint rings. These rings, if not blocked, can produce artifacts on the Z-scan signal. A good quality beam is observed to have a bright central lobe, minimal diffraction rings, and an ellipticity as close to 1 as possible (purely circular). It is strongly advised to check the spatial quality of the beam going into the sample by placing a beam profiler (either the Cinogy CinCam or DataRay WinCamD) just before L-6 and L-7 to ensure that the beam is not perturbed by any of the optics placed after the spatial filter. L-4 is placed on a 1D-stage to easily collimate the resultant beam after spatial filtering simply due to dispersion. The focal length of L-4 is chosen.
to either produce a magnification of 1 or close to it. Typically, we do not magnify or reduce the spatially filtered beam a great deal before the focus to the sample.

BS-1 is chosen to be a wedged piece of fused silica such that the secondary reflection from the back surface is spatially separated from the first reflection of the front surface. This reflected line from BS-1 serves as the reference for the Z-scan and only requires around 4% to 8% of the total energy. The incident polarization is typically chosen to be vertical, or s-polarized, since Brewster’s angle for fused silica is a few degrees different from the 45 deg AOI depicted in Figure B-1, thus reducing the reflected energy for horizontal, or p-polarized, light. The depicted reflected line is chosen to be an exact duplicate of Arm-A and Arm-B. This is done in the instance that the DA Z-scan is converted to the conventional Z-scan technique by either replacing BS-2 with a mirror or simply removing BS-2. In this manner, the reference arm can still provide an ideal closed-aperture reference to either one of the arms in the conventional Z-scan methodology. To achieve this, the distance between BS-1 and L-5 should be equal to the distance between BS-1 and L-6 and BS-1 and L-7. Furthermore, the distance between L-5 and ID2 should be identical to the distance between L-6 and ID3 and L-7 and ID4.

BS-2 is chosen to be a broadband 50:50 plate beamsplitter such as BSW24 or BSW27 from Thorlabs. For these beamsplitters, the reflectance percentage is larger than the transmission for s-polarized light. Therefore, the continuously variable ND filter (not shown in Figure B-1 but discussed in Section 6.2) is placed in the reflected arm, i.e. Arm-A. This serves a dual purpose: achieving identical energy and compensating, in part, for the thickness of BS-2 that the transmitted beam traverses. Additionally, there is a 6 mm thick fused silica window to completely compensate for the thickness of BS-2 which is 8 mm thick. M3 and M4 are placed on a 1D-stage to make sure
the distance between BS-2 and L-6 is the same as between BS-2 and L-7. In reality, it is difficult to get the exact distances to be the same as could be ensured if a cross-correlation of some sort was performed. But as long as these two distances are within one mm of each other, as measured by a measuring tape, the beam sizes incident on L-6 and L-7 should be nearly the same. Of note, for a perfectly collimated beam, equating the distances between BS-2 and L-6 and BS-2 and L-7 is not necessary, but since there is no such perfectly collimated beam, these distances must be as close to equal as can be.

For Z-scan measurements, the irradiance must be sufficient to measure the materials of interest (this seems like an obvious statement, but read on …). We are usually fixed with the total amount of energy available after spatial filtering. The pulse width is fixed as well unless placing a pulse width compressor/stretcher before L-1 (for experimental details, see Section 5.2.2 and Ref. #160 of Ref. [118]). Thus, the biggest variable for adjusting the maximum total peak irradiance available is by manipulating the minimum beam size due to L-6 and L-7. From Eqn. (2.8) and the definition of the E-field given in Eqn. (6.1), it can be shown that the peak irradiance is given by:

\[ I_0 = \frac{2\text{Energy}}{\pi^{3/2} w_0^2 \tau_{HW} 1/e}. \]  

(B.2)

The focal length of L-6 and L-7 is 10 cm in the Z-scan experiments discussed in this dissertation. So, without changing lenses, the only manner in adjusting \( w_0 \) is by changing \( w_{in} \) incident on L-6 and L-7. This can be done by translating L-4 so as to slightly de-collimate the beam after spatial filtering. Recall from the previous paragraph that the distance in Arm-A and Arm-B is set to be equal. Thus, the de-collimation should not result in a different beam size on L-6 than on L-7 and \( w_0 \) will be the same in each arm. Typically, \( w_{in} \) is adjusted to produce a \( w_0 \) that results in a free-space Rayleigh range \( z_0 = \pi w_0^2 / \lambda_0 \), i.e. not including the refractive index) of \(~1.2\) times the
thickness of the sample. This ensures the smallest $w_0$ possible while staying well within the thin sample approximation (assuming small nonlinear phase shifts). As an example, for performing Z-scans on a 1 mm thick sample of fused silica at a wavelength of 800 nm, $w_0$ should be $\sim 17.5 \mu m$ (HW $1/e^2 M$) which makes $w_{in} \sim 1.5$ mm (HW $1/e^2 M$).

Both samples on Arm-A and Arm-B are placed on their own respective 3D-stage on top of the main Z-scan stage as described in Section 6.2. This allows for the sample Z-positioning to be matched as described by Figure 6-7. BS-3 and BS-4 are chosen to be the same as BS-2. The distance between L-6 and ID3 should be identical to the distance between L-7 and ID4. ID3 and ID4 are each placed on its own 2D-stage. Note that the initial beam alignment for Arm-A and Arm-B should always be with respect to the stage and not the closed apertures (ID3 and ID4). ID3 and ID4 are centered along the beam path via the 2D-stages they are mounted upon. Equating the distances from L-6 to ID3 and L-7 to ID4 can be done with a measuring tape. As long as the distances are within one mm, this should be sufficient.

Before starting measurements on the desired samples, the irradiance parameters must be known. Obviously, the energy is directly measured by an energy/power meter. The energy/power meters used in our group typically have a measurement uncertainty of $\pm 3.5\%$ as stated on the certificates of calibration provided to us by the company. But this uncertainty can vary quite drastically when measuring the energy/power close to the edge of the responsivity of the detector. For example, using one of our Silicon photodiode-based energy/power meter at a wavelength of 1100 nm could yield a measurement uncertainty of $\pm 20\%$ as communicated to us by a technical support engineer.
To determine the other parameters used in Eqn. (B.2), it is best to perform individual measurements to ascertain the values. The minimum beam waist can be experimentally determined via knife-edge scans whereas the pulse duration can be experimentally determined via autocorrelations. In lieu of these individual measurements to determine $w_0$ and $\tau$, Z-scans of reference materials can be performed. The FWHM of an OA Z-scan is $2 \cdot z_0$. Thus, a material exhibiting a large OA signal, i.e. large $\alpha_2$, can yield the magnitude of $w_0$ quite well. We typically use semiconductors since they a) typically have large $\alpha_2$ and b) are well-characterized materials. Some experimental and theoretical $\alpha_2$ coefficients are shown in Figure B-3 for common semiconductors used in our laboratory.

![Figure B-3. 2PA coefficients of common semiconductors used in our group as reference materials. The solid lines represent the theoretical prediction of 2PA using the 2-band model given in Ref. [145]. The solid symbols represent Z-scan measurements of bulk semiconductors taken in our laboratory except for the data points at 1064 nm for CdSe and 532 nm for ZnS which were taken from Ref. [183].](image-url)
A common reference material to extract $\tau$ is fused silica. The $n_2$ of fused silica is largely independent of the pulse-width such that the electronic nonlinearity dominates the NLR spanning from the ns to fs temporal excitation regimes. Furthermore, the dispersion of $n_2$ is relatively flat from $\sim$400 nm to the DC limit having a value of $(0.27 \pm 0.04) \cdot 10^{-15} \text{ cm}^2/\text{W}$ [103]. It is of note that CS$_2$ has long been used as a reference to determine $\tau$ due to its relatively large NLR. But the $n_2$ of CS$_2$ depends largely on the pulse-width for temporal excitations $> 20$ fs (FWHM) [79]; therefore, it is not advised to rely solely on CS$_2$ to extract $\tau$.

**Figure B-4.** (a) OA Z-scan of a 0.5 mm thick bulk sample of GaAs and (b) CA Z-scan of a 1 mm thick sample of fused silica at 1300 nm which are used as reference samples. The OA Z-scan of GaAs mainly gives $w_0$ while the CA Z-scan of fused silica mainly yields $\tau$. For these experiments, the values were fit to be $w_0 = 22.5 \mu\text{m}$ (HW 1/e$^2$ M) and $\tau = 130$ fs (FWHM).

Shown in Figure B-4 are Z-scans of reference materials (a) GaAs and (b) fused silica to ascertain $w_0$ and $\tau$, respectively. The first step in fitting $w_0$ for GaAs is to fix the $\alpha_2$ value to that of the prediction from the 2-band model, i.e. see Figure B-3. By doing so, this mandates a 2-parameter fit of $w_0$ and $\tau$ since we already know the energy from the energy/power meter reading.
But remember, the width of the OA Z-scan is solely determined by $w_0$ whereas the magnitude of the fit is determined by both. Thus, there is only a very narrow range of $w_0$ values that will fit the OA Z-scan. For the case shown in Figure B-4(a), the best-fit for $w_0$ yielded 22.5 $\mu$m (HW 1/e² M) which required $\tau$ to be fit with 120 fs (FWHM) when setting the $\alpha_2$ value to be 25 cm / GW, i.e. the theoretical value from the solid black line of Figure B-3 at 1300 nm. We, then, fit $n_2$ from the CA Z-scan of the fused silica sample by using the beam waist and pulse width found from the OA Z-scan of GaAs. By setting $n_2 = 0.27 \cdot 10^{-15}$ cm²/W for fused silica, we re-fit $\tau$ such that the $\Delta T_{p-v}$ of the fit matches the experimental data and determine the value to be 130 fs (FWHM). We also need to check and make sure $w_0$ extracted from the OA Z-scan agrees with that of the CA Z-scan. The $w_0$ from the CA Z-scan can be checked by observing the fit at the peak and valley of the transmittance. Furthermore, the distance between the peak and valley of the transmittance is approximately equal to 1.7 $z_0$. This entails not only should the shape of the curve at the peak and valley fit but the positions of the peak and valley should be the same as the data. For the case shown in Figure B-4(b), $w_0$ did not have to be adjusted. Therefore, the $\tau$ fit from the CA Z-scan is then used to re-fit the magnitude of the OA Z-scan of GaAs. Using this new $\tau$, the $\alpha_2$ of GaAs was determined to be 27 cm/GW which is 8% different than the theoretical value, i.e. good agreement between measured and theoretical value. Typically, the 2-band model can predict the measured value of $\alpha_2$ for some semiconductors within ± 30% in spectral regions near the peak 2PA. Note that the required irradiance to obtain an adequate signal from the OA Z-scan of a semiconductor is much lower than the signal from the CA Z-scan of fused silica. For the case in Figure B-4, the irradiance used for GaAs was 0.77 GW / cm² whereas for fused silica the irradiance used was 117 GW / cm² (the Fresnel reflection from the front surface is included in these irradiance calculations).
Previously, it was noted that CS$_2$ is often used as a reference due to its relatively large $n_2$ but it is not ideal due to the pulse-width dependence of $n_2$. Figure B-5(a) shows the CA Z-scan of CS$_2$ at 1300 nm measured concurrently with the GaAs and fused silica sample in Figure B-4. Using the extracted parameters, the peak irradiance was 36 GW/cm$^2$ (including Fresnel reflection from front surface) which gave a best-fit for $n_2$ of $3.4 \cdot 10^{-15}$ cm$^2$/W. This value agrees with the predicted $n_2$ dependence on pulse-width from Ref. [79] and shown as a solid green line in Figure B-5(b). Thus, CS$_2$ can be utilized as a secondary reference to verify the irradiance parameters extracted from GaAs and fused silica. Furthermore, the typical errors associated with extracting $w_0$ and $\tau$ via reference Z-scans are $\pm \sim 10\%$ each. With an energy/power measurement uncertainty of $\pm 3.5\%$, the total error bars due to irradiance uncertainty can range from $\pm 20\%$ to $\pm 25\%$ (see Section 2.2.4 in Ref. [101]).
APPENDIX C: IMAGES OF UCF AND LABORATORY
It is often interesting to re-visit how much things change over time. Thus, this Appendix contains pictures of how the campus and laboratory looked at the time of writing this dissertation.
LIST OF REFERENCES


100.*OriginLab 8.6.0*, 2012, OriginLab: Northhampton, M.A.


