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Generation and Characterization of Coherent Soft X-Ray Light with High Harmonic Generation

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Generation and Characterization of Coherent Soft X-Ray Light with High Harmonic Generation

by

Paul Christopher Arpin

B.S., Harvey Mudd College, 2006

A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
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Doctor of Philosophy
Department of Physics

2011
This thesis entitled:
Generation and Characterization of Coherent Soft X-Ray Light with High Harmonic Generation
written by Paul Christopher Arpin
has been approved for the Department of Physics

Henry Kapteyn

Prof. Margaret Murnane

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
High order harmonic generation (HHG) is a source of bright, ultrafast, fully spatially coherent, extreme ultraviolet (EUV) light with applications in ultrafast molecular and materials spectroscopy, element selective ultrafast magnetic dynamics, nano-thermal heat transport and high-resolution imaging. Harmonics have been generated up to a few keV, but the flux has been very low past 100 eV. Thus, applications of HHG have focused on the EUV region. By enhancing the brightness of harmonics at higher energies, we can expand the applications of HHG to the soft x-ray region of the spectrum.

The “water window” is a particularly important region of the spectrum for high resolution biological imaging. In this region, between 284 and 540 eV, water is an order of magnitude more transparent than carbon, providing contrast between various biological materials.

This thesis presents two methods to improve the brightness of harmonics in the water window. In the first, harmonics were generated from doubly ionized argon, which extended the cutoff photon energy to 540 eV, 200 eV higher than previously demonstrated from argon. The second method used the recently developed mid-infrared phase-matching technique to fully phase match the harmonic process at soft x-ray photon energies up to 540 eV which increased the brightness of harmonics in the water window by three orders of magnitude. This source was then characterized with the first spatial coherence measurement of any compact light source in this spectral range. In the future, this source can be used for high resolution, element specific, coherent imaging in the water window and ultrafast transient absorption spectroscopy in molecules and materials.
Dedication

For Carolynn.
Acknowledgements

There are many people who have helped along the way with the work presented in this thesis. First, I'd like to thank Margaret and Henry Kapteyn who have been great advisers all the way along.

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Finally, I would like to thank my friends and family, in particular my wife Carolynn Arpin.
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1.1 Applications of Bright, Coherent, Ultrafast, Soft X-Rays

Soft X-ray (SXR) radiation, with wavelengths spanning from 5 nm to 0.3 nm [15], is an important tool for a broad range of applications in science and technology owing to a few key properties. First, the short wavelength of the light allows very high spatial resolution, on the order of the wavelength. Second, throughout the soft X-ray region of the spectrum most elements exhibit inner shell absorption resonances which allow experiments with elemental and chemical sensitivity. Despite being useful in many applications, sources in this spectral range have been developed more slowly than sources at longer (visible and infrared) or shorter (hard X-ray) wavelengths. Many applications at the nanoscale require not only the spatial and spectral properties of soft X-rays, but also the ability to monitor the dynamics of very fast processes as the timescales of motion on the nanoscale can range from picoseconds [16] to femtoseconds [17].

Figure 1.1 shows examples of transitions in an element that occur at X-ray photon energies. Two important applications of these absorption edges in materials are as a quantitative contrast mechanism for imaging and as a spectroscopic tool. These two applications are introduced in section 1.1.1 and 1.1.2 respectively.

1.1.1 Coherent Imaging in the Water Window

One of the important spectral ranges of soft X-ray wavelengths is called the “water window”, a region of the spectrum between the carbon K-shell absorption edge at 284 eV and the oxygen
Figure 1.1: Characteristic energy level diagram for an atom. X-ray absorption edges correspond to resonances between inner electron shells and the continuum. On the right, the orbitals are labeled, and on the left, the standard X-ray notation for the transitions is indicated. For example, the K edge refers to a transition that excites an electron from the 1s shell into the continuum. Figure from ref [1].

K-edge at 543 eV. In this window of the spectrum, carbon is 10 times more absorbing than water as shown in figure 1.2, providing inherent amplitude contrast for imaging biological samples without the need for labeling [2,18]. Furthermore, because the scattering only depends on the density of carbon in the sample, it is possible to obtain quantitative data on the densities of materials in the image [2,19]. Finally, near the oxygen edge, the wavelength of the illuminating radiation is less than 3 nm, meaning that it is possible to do full field imaging with 10 nm resolution.

Imaging in the soft X-ray region of the spectrum, however, is challenging since traditional lenses cannot be manufactured for these wavelengths. This is because the index of refraction, \( n \), of materials in the soft X-ray region is very close to 1 (\( \delta < 10^{-2} \), where \( n = 1 - \delta \)), which would
Figure 1.2: Absorption length as a function of photon energy for a typical protein compared with the absorption length of water. Between the carbon k-edge at 284 eV and the oxygen k-edge at 540 eV, proteins are about 10 times more absorbing than water which provides an inherent contrast mechanism for imaging biological samples. (Inset) Three-dimensional, tomographic reconstruction of a cell, imaged with soft X-ray light in the water window. Image from ref [2].

require a short radius of curvature to focus the light. However, this requires a thick lens and soft X-ray radiation has very short absorption depths in materials (< 1 µm). There is some variability in these parameters and it is possible to optimize either the absorption length or index but it is always at the expense of the other. For example, light atoms, in general, are less absorbing but have an index closer to 1 and heavier atoms have a larger index change, but are more absorbing. As a result, a traditional lens with any significant refraction for SXR will strongly absorb in the SXR and no light will pass through the material.

Imaging techniques similar to traditional lens based imaging have been developed in the soft X-ray by fabricating zone plate objectives [15, 20]. However, this technique is inherently lossy — zone-plates image about 10 % of the light incident upon them. Furthermore, the limitation on the imaging resolution comes from the geometry and fabrication processes used to produce the objectives and not from the wavelength of the radiation used to image the sample.

An alternative to traditional imaging optics in the soft X-ray region of the spectrum is
coherent diffractive imaging, where a coherent source is used to illuminate the sample, and no optical element is used to reform the image. Instead, only the diffraction pattern of the object is measured and computational techniques are used to calculate an image of the object from the measured intensity pattern of the scattered light. This is appealing because it eliminates the need for the fabrication and alignment of complicated optics, and it eliminates any aberrations due to the optics used to reform the image. In fact, because the image is “formed” computationally, certain aberrations can be corrected for computationally, and near wavelength limited resolution is possible [21,22].

Figure 1.3 shows an example of coherent diffractive imaging of a frozen, hydrated cell using water window radiation from the Advanced Light Source at Lawrence Berkeley National Laboratory where the authors achieved an image with better than 25 nm spatial resolution [3]. The reconstruction process reproduces both the phase and amplitude contrast of the object, where bright field techniques can only provide amplitude contrast.

![Figure 1.3: Images of yeast cells. On the left is an image from a visible light microscope using differential interference contrast (DIC) microscopy. On the right, is a reconstructed image of the same type of cell using soft X-ray, coherent diffractive imaging with water window light. In the reconstructed image, color represents phase and brightness represents amplitude. From ref [3].](image)

An important requirement for the reconstruction algorithms in diffractive imaging is that the radiation illuminating the sample must be fully spatially coherent in order to have interference in the far field where the scattered light is detected. In addition to the spatial coherence, the
algorithms require that the sample is isolated, but this can be accomplished by placing a pinhole immediately in front of the sample.

### 1.1.2 Ultrafast, Soft X-Ray Spectroscopy

Section 1.1.1 discussed the abrupt drop in transmission above an element’s absorption edge and how this can be used to provide contrast between different elements. A more careful analysis of the absorption process shows that in fact, absorption edges in materials and molecules have structure, both near and far above the edge. For photon energies well above the edge, a photoelectron wave is released from the atom which can scatter off surrounding atoms, as shown in figure 1.4. Whether the scattered waves returning to the original atom add constructively or destructively affects the probability of ionization and consequently modulates the probability of absorbing the photon. Thus the structure 50 – 1000 eV above the edge, referred to as the extended X-ray absorption fine structure (EXAFS), provides information on the location of the atoms surrounding the atom from which the electron is ionized. EXAFS is a well developed, static technique for determining the structure of neighboring atoms surrounding an element [23], and it has been used in a pump-probe geometry with femtosecond resolution to watch lattice vibrations in dynamic measurements [24].

![Figure 1.4: Pattern of a spherical outgoing and backscattered photoelectron wave in the case of EXAFS (single scattering) and XANES (multiple scattering). Figure from ref [1].](image-url)

A more challenging, but rapidly developing technique is the interpretation of structure near the edge, referred to as X-ray absorption near-edge spectroscopy (XANES) or near-edge X-ray absorption fine structure (NEXAFS) [25]. A number of effects can change the structure near an
absorption edge, both above and below the edge. Below the edge, there can be resonances between the inner shell electron being excited and unoccupied orbitals, and above the edge, similar to EXAFS, the electron wave can scatter off of surrounding atoms affecting the probability of escape. This is a more complicated process than for the high energy photoelectrons in EXAFS because the low energy photoelectrons can scatter multiple times before returning to the initial atom. This leads to more complicated structure near the edges which requires more sophisticated theoretical analysis accompanying experimental data in order to provide a clear interpretation of the results. However, because it is sensitive to the local electronic structure, XANES is a powerful tool to better understand ultrafast charge transfer processes, and is actively being developed from a theoretical standpoint [26]

Figure 1.5 shows an example of X-ray transient absorption spectroscopy done using a synchrotron X-ray source. In this experiment, the authors resolved the transient spectrum due to the charge redistribution after photoexcitation. However, the limited time resolution prevented monitoring the initial fast dynamics that occur as the electronic structure evolves over the first $\approx 100$ fs after the initial excitation, see figure 1.5 (b).

1.2 High Harmonic Generation

Based on the discussion in sections 1.1.1 and 1.1.2, many of the exciting applications for soft X-ray sources require spatial coherence and $\approx 10$ fs temporal resolution. In the extreme ultraviolet (EUV) region of the spectrum, high harmonic generation (HHG) has been developed as a source of ultrafast [27,28], spatially-coherent [29,30] radiation. In the high harmonic process, an intense femtosecond laser pulse is nonlinearly upconverted from photons in the visible or infrared to much higher photon energies spanning from the EUV into the soft X-ray region of the spectrum. Extreme ultraviolet sources based on HHG have been used for diffractive imaging with near wavelength limited resolution [21,22] and as a tool to understand ultrafast dynamics on the nanoscale in magnetic structures [17], molecular systems [31–33], and nano-thermal heat transport [16].

However, the bright spectral range of high harmonic generation has been limited to wave-
Figure 1.5: (a) The \( [\text{Ru}(\text{bpy})_3]^{2+} \) complex is a commonly studied model system for metal to ligand charge transfer processes [1,4,5]. (b) Energy level diagram of charge transfer process in photoexcited \( [\text{Ru}(\text{bpy})_3]^{2+} \). An electron is photoexcited and removed from the ruthenium core. Initially it is uniformly distributed between the ligands and on a 100 fs timescale, it localizes to one of the ligands. (c) Static X-ray absorption spectrum of the L\(_3\) edge of ruthenium in the ground-state of \( [\text{Ru}(\text{bpy})_3]^{2+} \) (black trace R), and excited state absorption spectrum (red trace P). There is a visible shift in the location of the peaks of the pre-edge features B and C to B’ and C’ due to the change in the oxidation state shift of the ruthenium atom, as well as a new peak which appears at A’ corresponding to a transition into the previously occupied state which is photoexcited by the pump pulse. (d) Transient absorption spectrum 50 ps after laser excitation [1]. Figure from refs [1,4].
lengths above 10 nm. The goal of the work in this thesis is to extend the bright region of high harmonic generation to shorter wavelengths, which would enable applications of the spatial coherence and ultrafast time resolution of HHG in the soft X-ray region of the spectrum where many of the important inner shell absorption edges lie. Two different methods to extend bright harmonics into the water window are explored, and it is demonstrated that one of these approaches improves the brightness of high harmonic generation in the water window by over three orders of magnitude.

1.3 Thesis Overview

In this thesis, chapter 2 provides an overview of the high harmonic process and describes properties of sources based on HHG. It also introduces the physical limitations which have, historically, prevented applications of high harmonics at shorter wavelengths than 10 nm. Based on the discussion in this chapter, it will be clear that extending the high harmonic process from the EUV to the higher photon energies in the SXR can be done in one of two ways, increasing either the laser intensity or the laser wavelength used to drive the process. The two main experimental results presented in this thesis separately address these two approaches to generate harmonics in the water window.

Chapter 3 describes harmonics in the water window generated by high intensity lasers. This chapter will describe that above a certain photon energy, harmonics are necessarily generated from ions, and presents the first demonstration of high harmonics generated from a doubly ionized species.

Chapter 4 describes results of generating harmonics in the water window with an alternative method — increasing the wavelength of the laser used to drive the process. This chapter will discuss the first full phase-matching of the high harmonics process spanning the water window which allowed the harmonic brightness in this region of the spectrum to be improved by three orders of magnitude. Furthermore, this chapter describes how the improved brightness in this region of the spectrum allowed the first spatial coherence measurement in the water window using any compact light source. Based on the results presented here, in the future, this source can be
used for nano-scale imaging and spectroscopy throughout the soft X-ray region of the spectrum.

Chapter 5 describes initial progress in extending the results of chapter 4 to applications in transient absorption spectroscopy as well as briefly describing future plans for the experiment.
Chapter 2

High Harmonic Generation: Background and Theory

2.1 Introduction

This chapter provides an introduction to the high harmonic generation process, focusing, in particular, on the aspects that contribute to the results presented in chapters 3 and 4. In the high harmonic process there are always two scales that need to be understood in order to describe the process. From a microscopic perspective it is necessary to describe and understand how one single atom interacts with a strong laser field to generate harmonics. From a macroscopic perspective, it is necessary to understand how the laser and harmonic fields propagate in the gas medium, and how this extended medium made up of many atoms acts to build up the high harmonic signal. This chapter is broken into two major sections which separately address these two scales to build a complete picture of high harmonic generation.

2.2 Three Step Model

From a microscopic perspective, the high harmonic process is typically described by a semiclassical approximation known as the “three step model” [34,35]. This description has been particularly useful because it provides both a straightforward approach to make approximate calculations and also physical insight into the process. Figure 2.1 shows a schematic of the three-step process where (1) an electron is ionized from an atom, (2) accelerated in a laser field, and (3) then recombines with the parent ion releasing the excess energy it gained in the laser field in the form of a high energy photon. Each of these three steps will be developed separately in more detail in sections
Section 2.2.1 to 2.2.3. Section 2.2.4 discusses the consequences of the three step model on the structure of the radiation produced.

Figure 2.1: The three step model. The Coulomb potential of an atom with an electron initially in its ground state is perturbed by a strong laser field, leading to tunnel ionization of the electron. The electron is then accelerated away from the ion until the laser field switches direction, accelerating it back towards the ion. Once the electron returns to the parent ion it can recombine, giving off excess energy in the form of a high energy photon. Figure from ref [6].

2.2.1 Step 1: Ionization

In the first step of high harmonic generation, an atom or ion is ionized in the presence of a strong laser field. This section describes the standard approximation used to calculate the probability of ionization during the first step of the high harmonic process. The results in chapter 3 discuss high harmonic generation in a different regime, where the standard approximations no longer hold. As a result, this section also presents a correction to the standard approximation, which allows calculations to be extended into the high intensity regime of chapter 3 with more accurate results.

At the laser intensities and wavelengths typically used for high harmonic generation (1 – 5 \times 10^{14} \text{ W/cm}^2 and > 0.8 \text{ µm respectively}) the ionization process is well described by tunnel
ionization. In this picture, the laser field is considered to be a quasi-static perturbation to the Coulomb potential of the atom or ion, which allows the electron wavepacket to tunnel into the continuum as shown in figure 2.2(a).

Figure 2.2: (a) Potential for an electron in an atom in the presence of a strong electric field (black). The potential of the electric field (red) significantly distorts the Coulomb potential of the atom (green), allowing an electron to tunnel through the potential into the continuum. (b) At high electric fields, the Coulomb potential is sufficiently suppressed that there is no barrier for the electron to tunnel through. This is known as barrier suppression ionization.

In the tunnel ionization regime, the ionization rates are often approximated by the rates derived by Ammosov, Delone and Krainov for ionization due to a static electric field [34,36]. These ionization rates (referred to as the ADK rates) are a good approximation for the ionization process during an alternating electric field as long as the oscillation of the field is slow compared to the rate of ionization. Under these assumptions the ADK rate ($\omega_{\text{ADK}}$) is given by [34]:

$$
\omega_{\text{ADK}}(t) = \omega_p |C_{n^*l^*}|^2 G_{lm} \left( \frac{4\omega_p}{\omega_t} \right)^{2n^*-m-1} \exp \left( -\frac{4\omega_p}{3\omega_t} \right),
$$

(2.1)

where

$$
\omega_p = \frac{I_p}{\hbar},
$$

$$
\omega_t = \frac{e |E_l(t)|}{\sqrt{2m_e I_p}}.
$$
\[ n^* = Z \sqrt{\frac{I_p^h}{I_p}}. \]
\[ G_{lm} = \frac{(2l + 1)(l + |m|)!}{2^{[m]!} |m|!(l - |m|)!}, \]
\[ |C_{n^*l^*}|^2 = 2^{2n^*} [n^* \Gamma(n^* + l^* + 1) \Gamma(n^* - l^*)], \]

where \( l \) is the orbital angular momentum quantum number and \( m \) its projection, \( \hbar \) is Planck’s constant divided by \( 2\pi \), \( e \) and \( m_e \) are the charge and mass of the electron respectively, \( E_l(t) \) is the electric field of the laser at time \( t \), \( I_p \) is the ionization potential of the atom or ion, \( I_p^h \) is the ionization potential of the hydrogen atom, \( Z \) is the charge of the ion after tunnel ionization, \( l^* = 0 \) for \( l << n \) and \( l^* = n^* - 1 \) otherwise, and \( \Gamma(x) \) is the Gamma function. The ionization levels can be calculated as a function of time during a laser pulse by solving the coupled first order differential equations:

\[
\frac{dn_0}{dt} = -\omega_0(t)n_0(t) \\
\frac{dn_1}{dt} = \omega_0(t)n_0(t) - \omega_1(t)n_1(t) \\
\hspace{1cm} \ldots \\
\frac{dn_j}{dt} = \omega_{j-1}(t)n_{j-1}(t) - \omega_j(t)n_j(t) \\
\hspace{1cm} \ldots \\
\frac{dn_k}{dt} = \omega_k(t)n_k(t),
\]

where \( n_j \) is the fraction of the species that is \( j \) times ionized from its initial state and the \( k^{th} \) ionization state is the highest available to the species.

Figure 2.3 shows a typical calculation using the ADK rates. The exponential dependence of the ionization rate on the strength of the electric field is visible in the sharp increases in ionization during every half cycle when the laser field is high enough to ionize the species, followed by a flat region as the electric field approaches 0 before switching directions. In this model the ionization rates are almost 0 until the field strength crosses a threshold where they rapidly increase, giving the “step-like” structure seen in the sample calculation.
Figure 2.3: Sample calculation based on ADK rate equations shows the fraction population of Ar neutral (solid black) and Ar\(^+\) (red) as a function of time during a 15 fs laser pulse with a central wavelength of 800 nm and a peak intensity of \(3 \times 10^{14} \text{ W/cm}^2\) (laser electric field shown in dashed black).

The ADK rates provide a quick and relatively simple method to numerically estimate the ionization level of a gas in a strong laser field. However, due to the simple nature of the model, it should in general be applied with care — recognizing the regime where it is valid. One of the important corrections to the ADK rates comes at higher intensities where the barrier is suppressed below the ionization potential of the atom so that the electron is no longer bound (see figure 2.2(b)). An estimate of the peak intensity where this becomes significant can be derived by assuming a Coulomb potential which is instantaneously perturbed by a quasi-static laser field:

\[
V(\vec{r}, t) = V_{\text{Coulomb}} + V_{\text{laser}} = -\frac{Ze^2}{4\pi\varepsilon_0 r} - e\vec{r} \cdot \vec{E}_l(t) \tag{2.3}
\]

where \(V\) is the potential for the electron, \(V_{\text{Coulomb}}\) is the Coulomb potential of the atom or ion, \(V_{\text{laser}}\) is the potential due to the laser field, \(Z\) is the effective charge of the ion with the electron removed, \(e\) is the electron charge, \(\varepsilon_0\) is the permittivity of free space, \(\vec{r}\) is the spatial coordinate and
$\vec{E}_l(t)$ is the instantaneous electric field due to the laser. From equation (2.3), a threshold intensity can be calculated from the laser field strength, $E_{BSI}$, at which the barrier is suppressed below the ionization potential of the species:

$$E_{BSI} = \frac{\pi \epsilon_0 I_p^2}{Ze^3}. \quad (2.4)$$

Above $E_{BSI}$, the ADK rate overestimates the ionization rate [7, 37] because it still assumes an exponential dependence of the ionization rate on the electric field strength. In general, it is difficult to write a rate equation which accounts for the effects of barrier suppression ionization (BSI) and maintains the simplicity and convenience of the ADK rates. Several attempts since the publication of the ADK rates have improved the calculations over the ADK rates when compared with the exact calculations based on numerically integrating the Schrödinger equation [38, 39] but in most cases, the error of these models compared with the exact calculations was still quite large [7, 39].

Recently Tong and Lin [7] proposed a relatively simple correction factor that they claim gives consistent ionization rates with those calculated directly from the Schrödinger equation with an error $< 50\%$ for a static electric field over a broad range of intensities, where ADK rates can overestimate the ionization rate by an order of magnitude or more in the same range of intensities. Furthermore, they demonstrate that when this rate (which I will refer to as the BSI corrected ADK rate) is applied to a laser pulse, the results are consistent with exact calculations as shown in figure 2.4. For hydrogen, the BSI threshold occurs at a peak intensity around $1.4 \times 10^{14}$ W/cm$^2$ according to equation (2.4), above this intensity, the exact calculations deviate from the standard ADK rates and match up well with the BSI corrected rates. The figure shows that while the standard ADK rate calculations are more accurate below the critical field, over the whole intensity range, the BSI corrected results are more accurate. Two additional features to note from figure 2.4 are: 1) the exact ionization levels, in general, fall somewhere between the ADK rate calculations and the BSI corrected calculations and 2) for longer wavelengths, where the static field approximation is more accurate, the BSI corrected results are more accurate.
Throughout this thesis, the BSI corrected ADK rate ($\omega_{\text{BSI}}$) is given by [7]:

$$\omega_{\text{BSI}}(t) = \omega_{\text{ADK}}(t)e^{-\alpha(Z^2 t^6_p/I_p)(\omega_l/\omega_p)}$$

(2.5)

where $\alpha$ is an empirical parameter varying from 6 to 9 depending on the species. The authors recommend using $\alpha = 6$ for electrons ionized from an $l = 0$ state and $\alpha = 9$ for electrons ionized from $l > 0$ state.

### 2.2.2 Step 2: Acceleration in the Laser Field

In the second step of the high harmonic process, the ionized electron is accelerated in the laser field, first away from the ion, until the laser field switches direction. Then the electron is accelerated back towards the parent ion. Classical trajectories for the electron in this acceleration process can be obtained from Newton’s Second Law for a free electron in an oscillating laser field, $F = eE_l(t) = eE \cos(\omega_l t) = m_e a(t)$ where $\omega_l$ is the angular frequency of the laser field in rad/s and
$a(t)$ is the acceleration of the free electron in the field [34]. Integrating for electrons released at different phases in the laser field gives different classical trajectories that the electron will traverse before returning to the ion, each of which returns, in principal, with a different kinetic energy ranging from 0 up to a maximum return kinetic energy of $3.17U_p$ [34]. $U_p$, which is known as the ponderomotive potential, gives the average kinetic energy of a free electron oscillating in a laser field and is given by:

$$U_p = \frac{e^2 E_0^2}{4m_e \omega_l^2} = 9.33 \times 10^{-14} I_l \lambda_l^2,$$

(2.6)

where $E_0$ is the electric field at the peak of the oscillation and the second equation gives $U_p$ in eV, where $I_l$ is the peak intensity of the laser in W/cm$^2$, and $\lambda_l$ is the laser wavelength in µm. The maximum return kinetic energy occurs for electrons released at a phase of 18° in the laser field.

The classical considerations provide much insight into the physical process and accurately predict the kinetic energies of the returning electrons. However, quantum mechanical considerations are important in this step for understanding the brightness of the detected spectrum, and in particular how the brightness scales with driving laser wavelength. In the quantum mechanical picture, the electron has a wavefunction, which is initially confined in a bound state due to the potential of the nucleus. As soon as part of that wave function tunnels into free space, the initially well confined wavefunction begins spread out spatially. The discussion will return to this effect in section 2.2.4 where the scaling of the single atom effect with wavelength is considered.

### 2.2.3 Step 3: Recombination

Upon returning to the parent ion, the electron can recombine to its initial ground state releasing the excess energy in the form of a high energy photon. The total energy that can be released is given by the kinetic energy of the returning electron plus the energy of the bound state for the electron. In general this gives:

$$h\nu = I_p + KE_r$$

(2.7)
where $h$ is Planck’s constant, $\nu$ is the frequency of the photon released, and $KE_r$ is the kinetic energy of the returning electron.

As in the case of the second step, the classical picture misses some of the physics which is important to the scaling of the efficiency of the high harmonic process with laser wavelength. The recombination probability depends on the overlap of the returning electron wavefunction with the wavefunction of the electron in the bound state of the ion.

### 2.2.4 Properties of High Harmonics

The semi-classical three step model provides insight into many properties of the radiation produced in the high harmonic generation process.

One of the most important consequences of the three-step model is derivation of the cutoff rule. By combining the maximum return kinetic energy of $3.17U_p$ from section 2.2.2 and the photon energy released from equation 2.7 in section 2.2.3 gives a maximum photon energy that can be generated in the high harmonic process ($E_c$) as:

$$E_c = h\nu_c = I_p + 3.17U_p,$$

where $\nu_c$ is the frequency of the highest photon energy generated. From the cutoff rule, there are three parameters that can be manipulated to change the cutoff energy for high harmonics - (1) the ionization potential of the medium, (2) the intensity of the laser field used to drive the process, and (3) the wavelength of the laser field. All three of these approaches are addressed in this thesis. The laser intensity and ionization potential of the harmonic medium, which are inherently coupled, are varied at a constant wavelength in chapter 3. In chapter 4, the laser wavelength is varied to increase the cutoff photon energy.

In addition to the cutoff rule which gives the highest photon energy that can be generated, the three-step model provides information about the structure of the spectrum up to the cutoff. First, once the peak intensity of the laser is high enough to ionize the atom, there are many possible trajectories that the electron can travel before returning to the parent ion, as described in section
2.2.2. Each of these trajectories returns to the parent ion with a different kinetic energy, as a result, all photon energies up to the cutoff are generated with approximately equal probability. This is in sharp contrast to the case of low order nonlinear optics where the single atom intensity of harmonics falls off exponentially with harmonic order.

In the time domain, this process occurs for every half cycle of the laser field leading to a train of attosecond bursts of EUV and soft x-ray light. The Fourier transform of a periodic train of bursts of light separated by half the laser period in the time domain gives a periodic train of harmonics at twice the laser frequency. Because of this, the process only produces odd order harmonics of the fundamental laser frequency.

2.2.5 High Harmonic Single Atom Efficiency Scaling

The last property discussed in this section which arises from the three step model is the single atom efficiency scaling with driving laser wavelength. This is particularly relevant for the results presented in chapter 4 which analyzed experimental properties of harmonics generated with a long (2 µm) wavelength laser. In the simple picture, there are two effects that allow a “back of the envelope” estimate of the scaling.

The first effect comes from the quantum mechanical contributions to the propagation (section 2.2.2) and recombination (section 2.2.3) of the electron wavefunction. Assuming that the wavefunction spreading is proportional (in all 3 spatial dimensions) to the time that the electron spends in the continuum and that the recombination probability scales like one over the size of the electron wavefunction, there is a $\lambda_i^{-3}$ scaling of the single atom harmonic efficiency due to the spreading of the electron wavepacket in the continuum.

The second effect comes from the $\lambda_i^2$ scaling of the cutoff rule with wavelength. Assuming that the total single atom conversion efficiency from fundamental to harmonic light is approximately constant regardless of driving wavelength, the harmonic energy is distributed over a broader range so that the conversion efficiency into a single harmonic is reduced by an additional factor of $\lambda_i^{-2}$.

These two effects predict an unfavorable single atom efficiency scaling of $\lambda_i^{-5}$ for a single har-
monic moving towards longer wavelengths to drive the harmonic process. While this approximation is overly simplified, both detailed calculations based on the nonlinear Schrödinger equation and experimental results have shown that the single atom scaling for the efficiency of a single harmonic at a fixed harmonic energy and driving laser intensity is \( \lambda_l^{-5.5} \) to \( \lambda_l^{-6.5} \) [40, 41].

2.3 Macroscopic Effects

The previous section described the response of a single atom to a strong laser field and how this can lead to the generation of high energy harmonics of the fundamental laser field. While the single-atom picture accurately predicts many of the properties high harmonics, in order to generate an appreciable harmonic signal, \( 10^{13} \) – \( 10^{14} \) atoms must be used in the process. There are several macroscopic effects that arise from the propagation of the fundamental and harmonic fields in a gas medium. Perhaps the most important arises because this process is coherent. This means that the many atoms must emit the harmonic radiation in phase in order to generate an appreciable signal. As in the case of low order nonlinear optics, we define the phase mismatch [42]:

\[
\Delta k = qk_l - k_q,
\]

(2.9)

where \( \Delta k \) is the phase mismatch between the fundamental and \( q^{\text{th}} \) harmonic field, \( k_l \) is the wave vector of the fundamental laser, and \( k_q \) is the wavevector of the harmonic field. As the fundamental laser propagates in the medium, at each point in space it generates harmonics with a constant phase. The relative phase of the harmonics generated at position \( z \) and \( z + \Delta z \) in the medium is given by \( \phi(z + \Delta z) - \phi(z) = \Delta k \Delta z \). The output at the end of the harmonic medium will be the superposition of the harmonics generated every spatial position along the harmonic medium, given in integral form as:

\[
E_{\text{HHG}}(L) = \int_0^L E_{\text{HHG}}^0 \exp(i\Delta k z)dz,
\]

(2.10)
where $E_{HHG}(L)$ is the amplitude of the harmonics after a harmonic medium of length $L$, $E_{HHG}^0$ is the amplitude of the harmonics emitted between position $z$ and $z + dz$, where $z$ is the spatial position along the length of the harmonic medium. $E_{HHG}^0$ is assumed to be constant along the length of the medium.

There are three possible cases for the growth of the harmonic intensity according to equation 2.10, coherent growth with $\Delta k = 0$, coherent growth with $\Delta k \neq 0$, and incoherent growth which are plotted in figure 2.5. For coherent growth with $\Delta k = 0$, the intensity of the harmonic is given by $I_{HHG}(L) = |E_{HHG}(L)|^2 \propto L^2$ and grows quadratically with the length of the medium. In the second case, $I_{HHG}(L) \propto 1/\Delta k^2 \sin^2(\Delta k L/2)$ so that the harmonic intensity oscillates with a period $2L_c$ where $L_c = \pi/\Delta k$ is known as the coherence length - the distance over which the harmonic intensity grows coherently. The third case is that of incoherent growth, where the intensity of the harmonics at different points in the medium are added instead of the field (with amplitude and phase) so that $I_{HHG} \propto L$. The incoherent case is shown as a reference, falling between the phase matched and non-phase matched cases. These simple calculations show that phase-matching is critical to efficiently convert energy into the harmonic field.

Depending on the specific geometry used for phase-matching, different physical effects contribute to the phase mismatch. In the waveguiding geometry used throughout this thesis, the dominant contributions to $\Delta k$ arise from a geometrical correction for the propagation of the guided laser mode, the dispersion of the neutral gas medium, and the dispersion due to the free electron plasma which is created during the high harmonic process. These three contributions will be developed separately in sections 2.3.1 to 2.3.3, and the resulting contributions will be combined in section 2.3.4 where phase-matching in a hollow core waveguide will be discussed.

### 2.3.1 Laser Coupling and Propagation in a Hollow Core Waveguide

For all experiments discussed in this thesis, high harmonics are generated in a gas filled, hollow-core waveguide to guide the fundamental laser as harmonics are generated. An important distinction between the hollow waveguides used in this work and standard optical fiber is that the
Figure 2.5: Harmonic intensity as a function of the length of the harmonic medium for three cases: incoherent growth (black) and coherent growth with $\Delta k = 0$ (red) and $\Delta k = \pi/L_c$ (blue). For $\Delta k \neq 0$, the harmonic intensity oscillates with a period $2L_c$. The growth is plotted as a function of $L/L_c$ where $L_c$ refers to the coherence length of the $\Delta k \neq 0$ case. The coherent, $\Delta k = 0$, case is characterized by a quadratic growth with medium length in contrast to the linear growth of the incoherent case.

In high harmonic generation, the high peak laser intensities ($> 10^{14}$ W/cm$^2$) would damage any material used as the high index core and any harmonics generated would be immediately

index profile is reversed. In optical fiber, the light propagates in a high index medium surrounded by a low index cladding, allowing total internal reflection at the boundary. In contrast, hollow core waveguides have a low index in the core ($\approx 1$) and a high index in the cladding ($\approx 1.5$). Hollow core waveguides have a reflection at the boundary, but there is no total internal reflection, instead they rely on the high reflectivity of near glancing incidence reflections. For optical fiber, the total internal reflection leads to guided modes which are transmitted efficiently over very long distances, hundreds of meters to many kilometers and are primarily insensitive to bends in the guiding fiber. Hollow core waveguides, on the other hand, have in general, more lossy modes which are extremely sensitive to any bend or distortion to the straightness of the waveguide.

In high harmonic generation, the high peak laser intensities ($> 10^{14}$ W/cm$^2$) would damage any material used as the high index core and any harmonics generated would be immediately
reabsorbed by the material, so it is necessary to use a hollow core waveguide. Details of the
guided modes in a hollow core waveguide are discussed in detail in ref [43]. The authors derive the
propagation constant, \( k_{nm} \), in the waveguide, where \( n \) and \( m \) refer to the order of the mode:

\[
k_{nm}(\lambda) = \frac{2\pi}{\lambda} \left[ 1 - \frac{1}{2} \left( \frac{u_{nm}\lambda}{2\pi a} \right)^2 \right],
\]

where \( a \) is the radius of the hollow core of the waveguide and \( u_{nm} \) is the \( m \)th zero of the \( n - 1 \) Bessel
function of the first kind, such that \( J_{n-1}(u_{nm}) = 0 \). It is often assumed that the majority of
the energy of the laser field is propagating in the lowest order, \( EH_{11} \), mode where \( u_{11} = 2.4048 \).
The first term is the propagation constant in-vacuum and the second term is the correction for
propagation in the guided mode. The harmonics are generated in a high intensity region near the
center of the waveguide and have a relatively low divergence. As a result, they will not interact
with the walls of the waveguide, so it is assumed that the phase-matching term for the waveguide,
\( \Delta k_w \), is given by:

\[
\Delta k_w = qk_l = -\frac{u_{nm}^2 \lambda}{4\pi a^2}
\]

It is interesting to note that the sign of \( \Delta k_w \) is negative — meaning that the geometrical correction
increases the phase velocity of the light propagating in the guided mode. The other thing to note
at this stage is that there is a \( 1/a^2 \) dependence on the waveguide radius. For a large waveguide,
this term goes to 0 as one would expect for a geometry approaching that of free propagation.

2.3.2 Neutral Gas Dispersion

The dispersion due to propagation in the neutral gas is given by:

\[
\Delta k_n = \frac{2\pi q}{\lambda_l} \left( n(\lambda_l) - n(\lambda_l/q) \right),
\]

where, here, \( n \) refers to the index of refraction of the neutral gas medium. The index of refraction
for the noble gases is very close to 1 for the wavelengths typically used in the high harmonic process,
both at the fundamental and harmonic wavelengths. As a result, the index is often cited in terms of
\( \delta = n_n - 1 \). Some care should be taken here as the index of refraction in the soft x-ray and extreme
ultraviolet is \(< 1\) so numbers are often published with the opposite sign of \( \delta \). For consistency, in
this thesis, positive \( \delta \) refers to an index greater than 1 and negative values of \( \delta \) refer to an index
less than 1.

The index of refraction is commonly given at 1 atm, so the index is rescaled by the pressure
of the neutrals in the waveguide giving

\[
\Delta k_n(t) = \frac{2\pi q}{\lambda_l} \frac{P}{P_{atm}} (1 - \eta(t)) \Delta \delta, \tag{2.14}
\]

where \( P/P_{atm} \) is the ratio of the pressure in the waveguide to 1 atm, \( \eta \) is the fraction of the
atoms that have been ionized so that \( P/P_{atm} (1 - \eta) \) gives the pressure of the neutrals, and \( \Delta \delta = \delta(\lambda_l) - \delta(\lambda_l/q) \). The ionization fraction, \( \eta \), is written as a function of time because it is a dynamic
quantity that rapidly changes throughout the laser pulse, as described in section 2.2.1.

Typical values of \( \delta \) for the fundamental wavelengths are on the order of \( 10^{-4} \) to \( 10^{-5} \). For
the high photon energy harmonics (\( > 100 \text{ eV} \)), \( |\delta| \) is on the order of \( 10^{-5} \) or less, and is typically
at least an order of magnitude lower than for the fundamental wavelength. Consequently the index
of the harmonics is often assumed to equal one, giving \( \Delta \delta = \delta(\lambda_l) \).

\subsection*{2.3.3 Plasma Dispersion}

The previous section described the contribution of the neutral atoms to the relative dispersion
of the harmonics and fundamental light. The high harmonic process inherently ionizes many of the
neutral atoms creating ions and a free electron plasma that each have different contributions to the
overall dispersion. The dispersion of the ions is neglected here because at high ionization levels,
it is assumed that the low mass free electron density will have a much larger contribution to the
dispersion than the ions. The dispersion of the free electron plasma, however, cannot be neglected.

The refractive index of a plasma is given by \cite{44}:
\[ n_p = \sqrt{1 - \left( \frac{\omega_p}{\omega} \right)^2}, \tag{2.15} \]

with

\[ \omega_p = \sqrt{\frac{e^2 N_e}{\epsilon_0 m_e}}, \tag{2.16} \]

where \( \omega = 2\pi c/\lambda \) is the angular frequency of the radiation propagating in the plasma, \( c \) is the speed of light, \( \omega_p \) is the plasma frequency, and \( N_e \) is the free electron density. At a pressure of 1 atm, assuming 100% ionization, \( \omega_p = 2.8 \times 10^{14} \) rad/s for an ideal gas at room temperature. For a central wavelength of 800 nm, \( (\omega_p/\omega)^2 = 1.4\% \) and is even lower for the harmonic frequencies. This pressure and ionization level are both high for typical high harmonic geometries so \( (\omega_p/\omega)^2 \ll 1 \) can usually be assumed. This gives:

\[ n_p(\lambda) \approx 1 - \frac{1}{2} \left( \frac{\omega_p}{\omega} \right)^2 = 1 - \frac{e^2 N_e \lambda^2}{8\pi^2 c^2 \epsilon_0 m_e}. \tag{2.17} \]

It should be noted that for the results presented in chapter 4 a longer wavelength (2 µm) and very high pressures (>10 atm) are used, which could lead to a breakdown of this approximation. However, it turns out that a very low ionization level is required for the harmonics driven by 2 µm light, so the approximation is still valid. Care should still be taken when working in new regimes for HHG as the approximation will not necessarily hold in all cases. Equation 2.13 can be applied again with \( n \) here referring to the plasma index giving the plasma dispersion, \( \Delta k_p \), as

\[ \Delta k_p(t) = -qr_e \eta(t) N_{atm} \lambda t \frac{P}{P_{atm}} \left( 1 - \frac{1}{q^2} \right), \tag{2.18} \]

where \( r_e = (1/4\pi \epsilon_0)e^2/m_e c^2 \) is the classical electron radius and \( N_{atm} \) is the number density of atoms in the gas at 1 atm so that \( N_e = \eta N_{atm} P/P_{atm} \) is the free electron density. In this thesis, the results that will be discussed show very high-order harmonics, with \( q >> 100 \), so the \( 1/q^2 \) term is often neglected.
With the development of the three terms described in the previous sections, we can now write down the full phase-matching equation for a given harmonic (\(\Delta k_q\)):

\[
\Delta k_q = \Delta k_w + \Delta k_n + \Delta k_p = -\frac{q u_{nm} \lambda_l}{4 \pi a^2} + \frac{2 \pi q}{\lambda_l} \frac{P}{P_{atm}} [1 - \eta(t)] \Delta \delta - q r_e \eta(t) N_{atm} \lambda_l \frac{P}{P_{atm}} \left(1 - \frac{1}{q^2}\right).
\]  

(2.19)

The three terms have different signs, specifically \(\Delta k_w\) and \(\Delta k_p\) are both negative — meaning they increase the phase velocity of the fundamental relative to the harmonic radiation. In contrast, \(\Delta k_n\) is positive — meaning the neutrals decrease the phase velocity of the fundamental light. Phase-matching, then, is a matter of balancing the contributions of the different terms so that \(\Delta k_q = 0\).

In the waveguiding geometry, this is experimentally achieved by tuning the pressure of the gas in the waveguide. In the equation, there is a pressure dependent term \(\Delta k(P) = \Delta k_n + \Delta k_p\) and a pressure independent term \(\Delta k_0 = \Delta k_w\). As long as \(|\Delta k_n| > |\Delta k_p|\), there is a relative sign difference between the pressure dependent and pressure independent terms and by tuning the pressure, perfect phase-matching is possible.

The observation that \(|\Delta k_n| > |\Delta k_p|\) is necessary for phase-matching is important as it allows a definition for a regime where pressure tuned phase-matching is possible. We define a critical ionization \(\eta_c\), above which HHG cannot be phase-matched with pressure tuned phase-matching, by equating the neutral and plasma dispersion and obtain:

\[
\eta_c = \left[1 + \frac{\lambda_l^2 r_e N_{atm}}{2 \pi \Delta \delta} \left(1 - \frac{1}{q^2}\right)\right]^{-1}.
\]  

(2.20)

Because the ionization level is dependent on the intensity of the laser used to drive the harmonics, the critical ionization places a limit on the laser peak intensity that can be phase-matched, and consequently a limit on the harmonic photon energy that can be phase-matched according to the cutoff rule in equation 2.8. As an example, with helium as a harmonic medium driven by 0.8 µm
light the critical ionization is 0.5%. Figure 2.6 (a) plots the ionization fraction of He as a function of time during 25 fs laser pulse. Near the peak of the pulse the ionization level reaches the critical ionization. For a higher peak intensity pulse, the ionization fraction will cross the critical level before the peak of the pulse giving two regions of harmonics generated during the pulse: harmonics generated before the laser pulse reaches the critical ionization which can be phase-matched and harmonics generated later in the pulse which will have a higher single atom cutoff, but cannot be phase-matched. For helium this gives the highest photon energy that can be phase-matched as about 150 eV, when driven by 0.8 \( \mu m \) light.

![Figure 2.6: (a) Semilog plot of the results of an ADK calculation for helium in a 25 fs, 800 nm, laser pulse with a peak intensity of \( 6.6 \times 10^{14} \) W/cm\(^2\) and a cutoff photon energy of 150 eV. The dashed black line shows the critical ionization level 0.5%. At the peak of the pulse, the ionization level crosses the critical ionization, meaning that harmonics generated later in the pulse will not be phase-matched. (b) Plot of a similar calculation with a 5 fs FWHM pulse and a peak intensity of \( 8 \times 10^{14} \) W/cm\(^2\) and a cutoff photon energy of 180 eV. Showing that the critical ionization is reached for higher peak intensities when the laser pulse is shorter.](image)

Using a shorter laser pulse does make it possible to reach a higher intensity before reaching the critical ionization. Figure 2.6 (b) plots a similar calculation for a 5 fs pulse with a higher peak intensity. In this case, the critical ionization is not crossed until a laser peak intensity that corresponds to a cutoff of 180 eV, meaning that the phase-matching region can be extended, but only slightly.
The phase-matching discussion in this section has focused on pressure tuned phase-matching in a waveguide. In principal, there are other geometries that can be used to efficiently generate harmonics in the EUV from an 800 nm laser pulse. The two most popular geometries, in addition to waveguiding, are free focusing through a gas jet [45, 46] and free focusing through a gas cell [47]. These geometries will have different contributions to the phase-matching equation which are relevant, but ultimately the conclusions are similar to the case of harmonics generated in a waveguide. In all three cases efficient generation of harmonics is limited to, at best, about 200 eV when driven by a Ti:Sapphire laser.

From a single atom perspective, harmonics well into the keV region have been demonstrated [48, 49] but very few applications have been demonstrated above \( \approx 150 \) eV because the lack of phase-matching limits the flux at higher photon energies. Balancing the disparity between the highly favorable scaling of the single atom cutoff with the rigid limitations of phase-matching has been one of the major challenges in high harmonic generation. Because of this, many promising quasi-phase matching techniques have been developed in an attempt to extend the bright region of the high harmonic spectrum. Chapter 4 discusses a new approach, which allowed the first demonstration of pressure tuned phase-matching throughout the water window. More recent results have even shown phase-matching at photon energies above 1 keV [14].

### 2.3.5 Absorption Limited Harmonic Generation

Even when perfect phase-matching is achieved, there are limitations on the distance over which the harmonic intensity coherently increases, and, ultimately, this constrains the conversion efficiency of the process. One of the most significant limitations on the harmonic medium length is the reabsorption of the harmonics in the gas medium. Typical absorption lengths for harmonics generated in the EUV range from a couple hundred microns to a couple millimeters so it is important to understand how this affects the generated harmonics, both to make predictions about the harmonic efficiency and also to understand how to optimize the geometry for the harmonics. Simple calculations can be carried out along the lines of equation 2.10 with the addition of a term
of the form \( \exp(-z/2L_a) \) into the integral to account for the reabsorption of the harmonics, where \( L_a \) is the absorption length of the medium for a given harmonic energy at a given pressure.

Figure 2.7 plots the resulting harmonic output as a function of the length of the medium in terms of the absorption length \([8]\). For the case of fully phase-matched harmonic generation, \( L_c \gg L_a \), the harmonic flux grows rapidly but saturates after a few absorption lengths. This shows that the absorption length of the harmonic medium is an important property in determining the achievable flux when the geometry and phase-matching are fully optimized. It also provides information on the optimal geometry for high harmonic generation. Because the harmonic flux reaches 90\% after 6 absorption lengths, the optimized geometry will have a harmonic medium length of about 6\( L_a \).

![Figure 2.7: Harmonic output flux as a function of medium length for different ratios of the coherence length and absorption length: \( L_c \gg L_a \), \( L_c = 10L_a \), \( L_c = 5L_a \), \( L_c = L_a \) and \( L_c, L_a \gg L \). When perfectly phase-matched, the absorption limited harmonic growth(\( L_c \gg L_a \)), grows rapidly for a few absorption lengths and then asymptotically approaches a saturation value. The output reaches 90\% of the saturation value after 6 absorption lengths. Figure adapted from ref [8].](image)

2.4 Conclusions

This chapter introduced the basic concepts in high harmonic generation which will be important throughout this thesis. In particular, the high harmonic process was discussed on two scales:
1) at the microscopic level where the semi-classical three-step model describes the process that a single atom or ion can undergo in the presence of a strong laser field to generate very high order harmonics of the fundamental laser and 2) at the macroscopic level, the propagation of both the fundamental field and the harmonic fields through a gas medium have important consequences on the signal which reaches a detector. In any regime of high harmonic generation, both of these two perspective must be addressed, both to understand the process and to understand how to best optimize the harmonic signal being generated.
Chapter 3

Harmonics From a Highly Ionized Medium

3.1 Introduction

The cutoff rule for high harmonic generation gives a maximum photon energy that can be generated as $h\nu_{\text{cutoff}} = I_p + 3.2U_p$, where $I_p$ is the ionization potential of the generating medium and $U_p \propto I_l \lambda_l^2$ is the ponderomotive potential which characterizes the average kinetic energy an electron gains in an oscillating electric field and $I_l$ and $\lambda_l$ are the driving laser intensity and wavelength, respectively. The cutoff rule applies whether the harmonic medium is a gas of neutral atoms [50] or ions [9, 10]. From the cutoff rule, it is clear that there are three main parameters that can be manipulated to increase the harmonic photon energies that are generated: the driving laser wavelength, the driving laser intensity and the ionization potential of the nonlinear medium. In this chapter, I discuss a series of experiments where we change the last two parameters, the intensity and the ionization potential to explore how the high harmonic process is affected by using very high peak laser intensities to increase the harmonic cutoff. As I will show, this approach inherently requires the use of ions as the high harmonic medium, and therefore a change in the ionization potential of the harmonic medium. Increasing these two parameters led to the first demonstration of harmonics with photon energies $> 500$ eV from argon, an 200 eV extension beyond the previous highest published result [51].

Peak intensities in the range of $1 - 5 \times 10^{14}$ W/cm$^2$ efficiently generate harmonics in the extreme ultraviolet (EUV) from around 30 – 150 eV. Generating harmonics into the soft X-ray (SXR), and in particular into the water window, requires peak intensities above $10^{15}$ W/cm$^2$. 
There are three major challenges to using these high peak intensities to efficiently generate high photon energies with high harmonic generation.

1. The saturation effect due to the complete ionization of the high harmonic medium early in the laser pulse requires ions with a high ionization potential as the harmonic medium.
2. Ionization induced defocusing and ionization loss limit the peak intensity of the driving laser.
3. The high free electron density prevents phase-matching over extended distances.

Sections 3.2.1 - 3.2.3 introduce these three respectively and describe the challenges and opportunities they present to high harmonic generation at high peak laser intensities. Then a brief history of prior results generating harmonics from ions is provided in section 3.2.4. After introducing the problem and describing prior results, section 3.3 describes the current experimental results which were able to address issues (1) and (2) from above by combining laser pulse self compression and high harmonic generation from ions in a single gas filled waveguide. Section 3.4 describes briefly how issue (3) can be addressed in the future by combining the current results with experimentally demonstrated [52] and theoretically proposed quasi-phase matching techniques [53].

3.2 Background

3.2.1 Saturation Effect

The high harmonic process is always driven by a laser pulse with a finite rise time. Because of this, it is possible to fully ionize the harmonic medium prior to reaching the peak of the laser pulse. At high laser intensities, this leads to a saturation effect in the high harmonic cutoff where the highest harmonic generated no longer increases linearly with the peak laser intensity [50,54,55]. As I will describe in this section, this can be overcome by generating harmonics from ions which makes it possible to extend to higher cutoffs than the saturation intensity for harmonics from a neutral medium would allow for a given laser wavelength, pulse duration and harmonic medium.
It is instructive to consider calculations based on the ADK rates given in section 2.2.1 in equations (2.1) and (2.5). Figure 3.1 shows the results of integrating the ADK rate equation for argon at varying peak laser intensities. Here we use the BSI corrected ADK rates, which will, in general, slightly underestimate the ionization level [7]. For a given species, in order to generate harmonics at the peak intensity of the laser and maintain the cutoff rule it is necessary for that laser intensity to be sufficiently high to ionize that species. However, it is also necessary for a significant population of the atoms or ions to still be present in that state. For example, in order to generate harmonics from neutral argon, the peak intensity of the laser must be greater than about $1 \times 10^{14}$ W/cm$^2$ where neutral argon begins to be ionized which appears in figure 3.1 as a depletion of the neutral argon population and an increase of the $\text{Ar}^+$ population. Near a peak intensity of $6 \times 10^{14}$ W/cm$^2$, the neutral argon population is almost fully depleted by the peak of the pulse. Harmonics will be generated from neutral argon early in the pulse, but the cut-off will be ultimately limited by the intensity of the laser at the time when the neutral argon is fully depleted.

In order to generate harmonics from argon at a higher peak laser intensity, there are two main options. The first is to use shorter duration laser pulses, and the second is to generate the harmonics from ions. A shorter pulse duration has a much shorter rise time, allowing it to reach a higher peak intensity before the harmonic medium is depleted. Figure 3.2 shows that shorter pulse durations allow the neutral argon to survive to higher peak intensities and therefore higher harmonic cutoffs, but even with a 5 fs pulse the saturation cutoff approaches only 400 eV, an extension of 2 times. Furthermore, this is likely an overestimate as the BSI corrected ADK rate will underestimate the ionization level and the approximation becomes worse for shorter laser pulses where the quasi-static approximation breaks down [7].

While short laser pulses do enable the generation of harmonics from a neutral species with a high saturation cutoff, the improvement in the saturation cutoff, as seen in figure 3.2, is not necessarily significant. It is clear that to generate harmonics with very high peak laser intensities, it is necessary to generate the harmonics from ions.
Figure 3.1: Fractional populations for neutral Ar (dashed black), Ar$^+$ (black), Ar$^{2+}$ (red), Ar$^{3+}$ (blue) and Ar$^{4+}$ (green) at the peak of a 20 fs FWHM gaussian laser pulse with a central wavelength of 800 nm are plotted as a function of the peak intensity. For any given species, in order to generate harmonics at the peak of the pulse, it is necessary not only for the peak intensity to be high enough to ionize the species, but also necessary for the species to make up a significant fraction of the population at the peak of the pulse. This gives intensity ranges where the species can undergo the high harmonic process. For example, this window for ionizing Ar neutral at the peak of a 20 fs pulse is around $1 - 6 \times 10^{14}$ W/cm$^2$ and for Ar$^+$ it is around $6 - 20 \times 10^{14}$ W/cm$^2$. 
Figure 3.2: Argon neutral fractional population at the peak of a 50 fs (blue), 20 fs (red) and 5 fs (black) pulse as a function of peak laser intensity. The x-axis is rescaled to show the corresponding cutoff energy ($E_c$) for an electron ionized from neutral argon at the peak of the laser pulse.
3.2.2 Ionization Induced Defocusing and Ionization Loss

The previous section described that ions are a promising medium for high harmonic generation. The considerations so far have been primarily from a single atom perspective. From a macroscopic perspective, there are several effects that make harmonics from ions experimentally difficult to observe. This section describes two consequences of focusing a high peak intensity laser into an initially neutral gas medium.

As a high intensity laser propagates in a neutral gas medium, ionization of the gas in the leading edge of the pulse can impact the propagation of the remainder of the pulse. One of the consequences of this that can significantly impact high harmonic generation is an effect called ionization induced defocusing [56].

Referring to equation 2.17 we see that the index of refraction of a free electron plasma well below the critical density is given by:

\[ n(r) = 1 - \frac{N_e(r)}{2N_{\text{crit}}}, \tag{3.1} \]

where \( r \) gives the radial, spatial dependence of the index of refraction on the free electron density and \( N_{\text{crit}} \equiv \frac{\varepsilon_0 \omega^2 m_e}{e^2} \) is the critical density. The electron density will be highest on axis, where the laser is most intense, and will fall off rapidly with the intensity profile of the laser. Assuming that the electron density has a Gaussian profile gives,

\[ N_e(r) \approx N_e^0 \exp \left( -\frac{r^2}{r_0^2} \right), \tag{3.2} \]

\[ n(r) = 1 - \frac{N_e^0}{2N_{\text{crit}}} \exp \left( -\frac{r^2}{r_0^2} \right), \tag{3.3} \]

where \( N_e^0 \) is the electron density on axis and \( 2r_0 \) is the 1/e width of the density distribution. By defining \( n_0 \) as the on axis index of refraction and Taylor expanding the exponential term, an approximate scaling of \( n(r) \) can be shown to be
\[ n(r) \approx n_0 \left( 1 + \frac{N_e^0}{n_0 N_c r_0^2} r^2 \right), \quad (3.4) \]

which is the index profile of a negative gradient index (GRIN) lens [57] which acts to defocus the laser, preventing it from reaching the peak intensity it would in vacuum.

More detailed calculations, such as the one shown in figure 3.3 [56], demonstrate that ionization induced defocusing places a limit on the peak intensity that can be achieved focusing an intense pulse into an initially neutral gas. In high harmonic generation, long focal lengths are commonly used with f-numbers around f/100 where the effects of ionization induced defocusing are significant.

Figure 3.3: Peak intensity as a function of gas pressure for a different focal geometries for a 1 µm laser pulse with a 1 ps, Gaussian envelope and a vacuum peak intensity of \(10^{15}\) W/cm². Figure from [56].

Furthermore, as a neutral medium is ionized, energy from the driving laser pulse is lost to the ionization process. As a result, the laser loses energy during propagation which further limits the high harmonic cutoff. These two effects — ionization induced defocusing and ionization loss — make it experimentally challenging to maintain a high peak intensity and a high harmonic cutoff in a rapidly ionizing medium.
3.2.3 Phase-Matching Harmonics from Ions

In a highly ionized medium, the dispersion of the fundamental beam due to the free electron plasma becomes very large and the coherence lengths become quite short. As an example, for the 290th harmonic of an 0.8 μm laser, generated by ionizing 4 Torr of Ar$^{2+}$ in a 150 μm waveguide, equation 2.19 gives a coherence length of $L_c = \pi/\Delta k \approx 11 \mu m$. As a reference, when generating harmonics from neutral gases in the range of 50–100 eV, typical absorption limited harmonic medium lengths are $\approx 5–30$ mm.

3.2.4 Prior Results on Harmonics from Ions

Given the challenges of generating harmonics from ions, there have been only a few published results on harmonics from ions to date [9, 10, 51, 54, 58]. In references [9, 10, 51, 58], a waveguiding geometry is used which reduces the effects of ionization induced defocusing.

Gaudiosi and Reagan used a capillary discharge where a current pulse pre-ionizes the harmonic medium [9,10]. Using this technique they were able to strongly suppress the effects attributed to rapidly ionizing an initially neutral medium. Figure 3.4 shows that pre-ionizing the gas medium significantly improves the spatial mode of the fundamental beam after propagation throughout the gas filled capillary.

In addition to the improvement of the spatial mode, pre-ionizing the gas reduces other complications in the propagation of the laser pulse, such as self phase modulation. Figure 3.5 shows the spectrum of the fundamental laser pulse after the waveguide [10]. It is clear that the current pulse reduces distortions to the laser pulse as it propagates through the harmonic medium.
Figure 3.4: Image of the spatial mode of the fundamental laser pulse at the output of a waveguide filled with 6 Torr Ar as the time delay between a pre-ionizing current pulse is varied relative to the laser pulse. The laser pulse had a FWHM duration of 28 fs and a pulse energy of 8.5 mJ [9]. When the laser pulse arrives before the current pulse (−100 ns) the mode is significantly distorted due to ionization induced defocusing. When the current pulse arrives first and pre-ionizes the medium, ionization induced defocusing is significantly reduced and the spatial profile of the transmitted laser pulse is significantly improved (ie +1500 ns). Figure from ref [9].

Figure 3.5: Spectrum of the fundamental laser pulse after the waveguide when the waveguide is evacuated (dashed black), with gas and no discharge (dashed red), and gas filled with discharge (blue). Figure from ref [10].
3.3 Experimental Results

The results described in section 3.2.4 demonstrated that by pre-ionizing the harmonic medium it is possible to reduce the effects of rapidly ionizing the harmonic medium with the laser pulse itself, and made it possible to generate harmonics from ions in a controlled way. In contrast, the results presented in the remainder of this chapter are the first to monitor the effects of the highly nonlinear propagation on the laser field while generating harmonics from a medium, rapidly ionized during the laser pulse. These results show that there are strong effects which significantly modify both the spectrum and the temporal structure of the pulse which cannot be neglected when analyzing harmonics driven by a very high intensity laser field. In particular, these results demonstrate that the nonlinear evolution of the driving pulse is not always detrimental but can actually enhance the peak intensity in the harmonic medium leading to a higher harmonic cutoff. In addition, these are the first results to demonstrate harmonics from a doubly ionized species.

3.3.1 Pulse Self-Compression

Section 3.2.2 describes a macroscopic process that limits the peak intensity of a laser field propagating in a rapidly ionizing gas medium. This section describes laser pulse self-compression, a nonlinear effect which can occur for a high intensity laser field propagating in a rapidly ionizing medium, that can make it possible to maintain or even increase the peak intensity of a laser field in a rapidly ionizing medium.

Laser pulse self-compression has been observed in both short, gas-filled, hollow waveguides [59,60] and in filaments [61,62]. In both cases, nonlinear processes, such as self-phase modulation, broaden the spectrum of the pulse, while spatiotemporal effects compress the pulse in space and time without the need for external dispersion compensation. Past work that first investigated self-compression in a hollow waveguide observed a reduction in pulse duration from 30 to 13 fs [59]. This scheme was then used to enhance the flux of selected harmonics generated in neutral Ar at photon energies near 95 eV, using a self-quasiphase matching process [60]. The use of near-
single-cycle pulses, compressed in a filament, to generate harmonics has also been theoretically investigated [63]. No work to date has explored how the pulse self-compression mechanism can extend the HHG cutoff photon energies or to generate harmonics from multiply-charged ions.

### 3.3.2 Experimental Setup

In this experiment, 3 mJ pulses from a Ti:Sapphire laser amplifier system with a transform-limited pulse duration of 24 fs, at a repetition rate of 1 kHz, were focused into a 150 μm diameter, 2 cm long, hollow-core waveguide. The gas was inserted into the waveguide through a small hole placed 5 mm from the entrance of the waveguide. A pressure gradient was maintained in the waveguide by evacuating through another hole placed 5 mm from the exit of the waveguide, in addition to the differential pumping to vacuum at both ends of the waveguide. This resulted in an interaction region of 1 cm with a pressure ramp, where the laser entered through the high pressure end.

The laser pulse was characterized both before and after the waveguide using second-harmonic frequency-resolved optical gating (SHG-FROG) [64]. FROG measurements were deconvolved using commercial software (Femtosoft Technologies) to an error below 1% for a 256 x 256 sampling grid. In order to generate the brightest harmonics, the laser pulse width was adjusted by varying the spacing of the gratings in the compressor to optimize the flux of the highest harmonics generated in argon. Under these conditions, the pulse width measured after the waveguide was 38 fs with no gas in the waveguide, which was chirped from the transform limit of 24 fs. (The additional linear chirp required to optimize the harmonics may improve the self pulse compression process by increasing the spectral broadening [65].) The pulse spectrum and duration did not change significantly when low pressure helium was introduced into the waveguide (10 Torr). In helium, the ionization peaks around 95% at the maximum laser intensity of $\approx 2.2 \times 10^{15}$ W/cm$^2$ present in the waveguide without pulse compression. In contrast, when the waveguide is filled with 4 Torr of argon, the rapid ionization (peaking near 300%, corresponding to fully depleted Ar$^{2+}$) leads to strong spatio-temporal self-compression of the pulse [59] — from 38 fs with no gas present in the
waveguide, to \(<19\) fs when argon is present (Fig. 3.6). A comparison of the spectra of the pulses measured after the waveguide with no gas and with 4 Torr argon is shown in Fig. 3.7. The high level of ionization reduces the throughput of the waveguide from \(\approx 60\%\) with no gas present, to \(\approx 35\%\) after propagating through 4 Torr of argon. Figure 3.8 shows that the primary pulse can be further compressed to 14 fs in 9 Torr argon, but this further decreases the throughput to \(\approx 27\%\).

At pressures of 14 – 15 Torr of argon, self-compression saturates and a secondary trailing pulse grows to a size comparable with the main pulse, similar to what has been seen in self-compression before [59]. It is possible that the radial laser beam size also modulates due to spatio-temporal coupling. The highest harmonics were observed at pressures of 4 – 5 Torr of argon, when the pulse duration was measured to be 17 – 19 fs, corresponding to a peak laser intensity in the waveguide of \(> 2.6 \times 10^{15} \text{ W/cm}^2\).

![Figure 3.6: Comparison of the measured pulse temporal profile and phase measured with the waveguide filled with no gas and with 4 Torr of argon. With 4 Torr of argon in the waveguide the pulse duration is reduced from 38 fs to 19 fs.](image)

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Figure 3.7: Comparison of the measured pulse spectrum with the waveguide filled with no gas and with 4 Torr of argon. With 4 Torr of argon in the waveguide the spectrum is blue shifted and broadened and the transform limited pulse duration is reduced from 24 fs to 18 fs.

Figure 3.8: Measured laser pulse at various pressures showing that as the gas pressure is increased, the pulse duration continues to decrease to $\approx 14$ fs at 9 – 10 Torr. At pressures of 14 – 15 Torr of argon, self-compression saturates and a secondary trailing pulse grows to a size comparable with the main pulse.
3.3.3 High Harmonics from Multiply Ionized Argon

Under optimal conditions of self-compression, the highest photon energies generated in argon extend up to $\approx 543$ eV (see Fig. 3.9(b)), representing an increase of $> 180$ eV from that previously observed in argon [51]. At these high ionization levels, the structure of the HHG spectrum forms a quasi-continuum as expected, and discrete peaks are not visible [9,10]. The spectrum was calibrated using the scandium absorption edge at 400 eV and the titanium edge at 454 eV, and the oxygen edge at 543 eV can also be seen due to oxide layer contamination on the optics and filters. Numerical simulations show that harmonic emission from argon above $\approx 370$ eV must emerge from $\text{Ar}^{2+}$ ions (see below and Fig. 3.9(c)).

![Figure 3.9](image)

Figure 3.9: (a) Transmission curves for an 0.5 $\mu$m scandium filter (green), an 0.4 $\mu$m titanium filter (blue) and two 0.2 $\mu$m chromium filters assuming a 20 nm layer of $\text{Cr}_2\text{O}_3$ at each surface (red). (b) Harmonic emission from a 150 $\mu$m inner diameter, 2 cm long fiber filled with low pressure argon (4 Torr), driven by a self compressed 19 fs pulse. The dashed black line indicates background noise level. The highest edge that can be seen in the data around 543 eV is due to oxide contamination layers formed on both the filters and optics.

For comparison, HHG spectra were taken in helium and neon for the same input laser energy and with the pressure optimized for highest harmonic generation in helium and neon (10 Torr).
Figure 3.10(b) shows that the photon energy cutoff in argon extends $\approx 100$ eV beyond that in helium and $\approx 200$ eV beyond the cutoff in neon. For the helium and argon data shown in Fig. 3.10, integration times of 30 minutes were used because of the weak, non-phase-matched HHG signals.

![Graph showing comparison of spectra in different gases](image)

Figure 3.10: Comparison of spectra taken in 10 Torr helium (black), 4 Torr argon (blue), and 10 Torr neon (red). The spectra for helium and argon compare the same number of shots with the same filters, which provides a direct comparison of brightness. The data taken in neon are a comparison of cutoff photon energies and not of absolute brightness. Filter transmission for the argon data shown above.

The HHG spectra of Fig. 3.9 can be understood by considering ADK ionization given the successive ionization potentials of the three atoms:

<table>
<thead>
<tr>
<th>Species</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>24.6 eV</td>
<td>54.4 eV</td>
<td></td>
</tr>
<tr>
<td>Neon</td>
<td>21.6 eV</td>
<td>41.0 eV</td>
<td>63.5 eV</td>
</tr>
<tr>
<td>Argon</td>
<td>15.8 eV</td>
<td>27.6 eV</td>
<td>40.7 eV</td>
</tr>
</tbody>
</table>

Table 3.1: Ionization potentials of the first three ionization species of helium, neon and argon.
In the case of helium, the ionization is not saturated (95%), and the 450 eV maximum represents the cutoff photon energy for the laser intensity in the absence of pulse compression. The ionization rate depends on both the ionization potential and the charge of the remaining ion. Thus, although the ionization potential of doubly-ionized argon (Ar$^{2+}$ I.P. 40.7 eV) is very close to that of singly-ionized neon (Ne$^+$ I.P. 41.0 eV), the Ar$^{3+}$ is significantly further ionized while the Ne$^+$ is not. According to ADK calculations (see figure 3.11), a peak intensity high enough to fully ionize Ar$^{2+}$ would result in \( \approx 25\% \) ionization of Ne$^+$ even accounting for the experimentally longer (38 fs) pulse in neon. Similar results have been seen in measurements of the ionization products in strong field ionization experiments which found that the peak laser intensity required for Ne$^{2+}$ to appear is 1.5 – 2 times higher than required for the appearance of Ar$^{3+}$ [66].

![Figure 3.11: Fractional populations of Ar$^{3+}$ (black) and Ne$^{2+}$ (red) at the peak of a 20 fs (Ar) and 38 fs (Ne) pulse as a function of peak laser intensity. For each, the BSI corrected rate (solid) is compared with the uncorrected calculation (dashed) as this provides a range around the actual ionization. Despite the similar ionization potentials of Ar$^{2+}$ (40.7 eV) and Ne$^+$ (41.0 eV), Ar$^{3+}$ begins to appear at lower intensities than Ne$^{2+}$ because of the charge state dependence of the ADK rates.](image)

Therefore, the lower HHG cutoff observed in Ne near 280 eV indicates both that neutral Ne is fully depleted (100% ionized) and the laser intensity is too low to ionize Ne$^+$. In addition,
the pulse self-compression mechanism in the multiply-ionizing argon ($\approx 300\%$) enhances the laser peak intensity in argon compared with neon, allowing higher HHG cutoffs of 543 eV to be reached. As discussed below, HHG between 370 eV and 520 eV must emerge only from doubly-ionized Ar$^{2+}$ being further ionized to Ar$^{3+}$. Moreover, for photon energies greater than 380 eV, HHG emission from argon ions is five times brighter than that observed from helium, although helium is significantly more transparent in this photon energy range, and the high levels of ionization in argon significantly reduce the coherence length. Assuming that the coherence length ($L_c$) is dominated by the free electron plasma [67] and that the observed HHG emission in this non-phase-matched regime will be proportional to $(L_c \times (\text{density of emitters}))^2$, we conclude that the effective HHG yield of Ar$^{2+}$ is $\times 45$ times larger than that of helium.

Figure 3.12 plots the ADK [36] argon ion populations as a function of time within the pulse, with the HHG cutoff energy plotted on one of the vertical axes. Significant Ar$^{3+}$ population starts to appear at laser intensities corresponding to a single-atom cutoff of 240 eV. Even taking into account that the ADK rates might over-estimate the ionization levels by $\approx 10\%$ [38], we can nevertheless conclude that harmonic emission between 370 eV and 520 eV must emerge only from doubly-ionized Ar$^{2+}$ being further ionized to Ar$^{3+}$. 
Figure 3.12: (a) Calculated ionization levels in argon for a 19 fs laser pulse at a peak laser intensity of $2.5 \times 10^{15}$ W/cm$^2$, using ADK rates. Laser pulse (black); Ar (blue); Ar$^+$ (green); Ar$^{2+}$ (red); Ar$^{3+}$ (pink); Ar$^{4+}$ (brown). The right axis shows the predicted HHG cutoff energy for a particular laser intensity, calculated from the cutoff rule. (b) Calculated ionization rates of argon ions, under the same conditions.

3.4 Conclusions

In conclusion, by combining laser pulse self-compression with high harmonic generation within a single gas-filled waveguide, we demonstrate for the first time that bright harmonics can be emitted from multiply charged ions, in this case fully depleted Ar$^{2+}$. The cutoff photon energy in argon was significantly extended to a photon energy of 540 eV for the first time, with a higher brightness than that observed in neutral He for the same laser input energy. In the future, high harmonic emission can be extended to very high photon energies using multiply charged ions with high ionization potentials in combination with quasi phase-matching techniques [53, 68].
Chapter 4

Spatial Coherence Measurement of a Table-top Soft X-ray Source

4.1 Introduction

Chapter 3 described how harmonics in the technologically important water window can be generated by using a high peak intensity 800 nm pulse to generate harmonics from ions. These results demonstrated that under the right conditions very high energy harmonics can be generated from argon. However, the flux was ultimately limited by the inability to phase-match the harmonic process in a highly ionized medium. Recently, an alternative approach to generate harmonics in the water window was developed which uses a longer wavelength laser field, in the mid-IR, to drive the harmonics process. This allows full phase-matching in the water window and several orders of magnitude improvement in the brightness [69].

In this chapter, I present the results of the first spatial coherence measurement of a phase-matched high harmonic source at 330 eV. This is an important step towards the development of HHG as a source of bright, coherent soft X-rays usable for applications. Additionally, it demonstrates several important properties of the source. First, it shows that mid-IR phase-matching [12,69] preserves the spatial coherence of the high harmonic process previously demonstrated using an 0.8 \( \mu \)m laser [29,30]. Second, it shows that the brightness of the source is sufficiently high to perform the experiment, which is particularly significant given that the experiment was done on a low repetition rate laser system. Finally, it demonstrates that using IR phase-matching provides a straightforward way to isolate the high energy region of the HHG spectrum.

Section 4.2 briefly describes how infrared phase-matching was used to significantly increase
the flux of ultrafast, X-ray radiation from an HHG source. Then section 4.3 describes the resulting spatial coherence measurements which were enabled by the improved brightness and discuss the results in the context of the two claims described above.

4.2 Infrared Phase-Matching

4.2.1 Introduction to IR Phase-Matching

As described in chapter 2, most applications to date using high harmonic generation as a source of radiation have been limited to \( \approx 150 \text{ eV} \) because this corresponds to the phase-matching cutoff for harmonics driven by a Ti:Sapphire laser. Chapter 3 describes one approach for generating very high energy harmonics with 800 nm light, but in this case, as well as other similar approaches [48, 70], the flux of the harmonics is ultimately limited by the inability to maintain full phase-matching over extended distances. Recently it was demonstrated that full phase-matching at very high photon energies is, in principal, possible by increasing the wavelength of the driving field [12]. After an overview of the theoretical scaling of the phase-matching cutoff with driving wavelength in section 4.2.2, section 4.2.3 discusses the predicted scaling of the efficiency of the phase-matched harmonics with driving wavelength. Section 4.2.4 briefly describes the experimental results from [69], which demonstrated efficient harmonic generation in the water window by phase-matching harmonics generated by a 2 \( \mu \text{m} \) field.

4.2.2 Scaling of the Phase-Matching Cutoff

In order to understand the scaling of the phase-matching cutoff with driving wavelength, it is best to start with the critical ionization, equation 2.20 derived in section 2.3.4:

\[
\eta_c = \left[ 1 + \frac{\lambda_L^2 r_e N_{\text{atm}}}{2 \pi \Delta \delta} \left( 1 - \frac{1}{q^2} \right) \right]^{-1}, \tag{4.1}
\]

which gives the highest ionization fraction that can be phase-matched for a given laser wavelength (assuming \( 1/q^2 \approx 0 \)). In general, the ADK rates must be numerically integrated to calculate the
ionization level during a pulse. However, approximate closed-form solutions to the integrals in equation (2.2) can be calculated [50, 71]. Here we use the standard ADK rates and not the BSI corrected rates because, in general, the critical ionization occurs at a fraction of a percent. The analytic solutions give the ionization fraction at the end of a pulse of width $\tau$ and intensity $I_L$, which can be inverted to write down the peak intensity as a function of the ionization level [71].

The ionization fraction is here assumed to be $\eta = 0.9\eta_c$ to give the high harmonic cutoff near the critical ionization, which we will define as the phase-matching cutoff, $E_{pmc}$ given by the harmonic cutoff at the intensity where the critical ionization is reached. Assuming that as the wavelength is varied, the pulse duration remains $N$ cycles, the phase-matching cutoff is given by [50]:

$$E_{pmc} = I_p + \frac{0.5I_p^{3+a}\lambda_L^2}{\ln\left[0.86(N\lambda_L/c)3^{2n^*-1}G_{lm}C_{n^*+1}^2/(-\ln(1-0.9\eta_c))\right]^2},$$

(4.2)

where $I_p$ is the ionization potential in eV, $\lambda_L$ is the laser wavelength in microns, $a = 0.5$ is a correction factor to the approximations used to perform the integration, $c$ is given in [\mu m/fs]. Figure 4.1 plots the phase-matching cutoff as a function of driving wavelength as derived from equation 4.2 showing that the phase-matching cutoff scales to very high photon energies for longer driving wavelengths. In particular, for a 2 $\mu$m laser wavelength, harmonics can be phase-matched throughout the water window.

To develop some intuition for the $\lambda_L$ scaling of the phase-matching cutoff, it is helpful to recognize that for long wavelength driving lasers and high-energy harmonics $\eta_c \approx \frac{2\pi\delta_l}{\lambda_L^2r_eNa} \ll 1$ so that the nested logarithm can be expanded in a Taylor series (neglecting the relatively small contribution from $I_p$ so that $E_c \approx 3.2U_p$):

$$E_{pmc} \approx \frac{0.5I_p^{3+a}\lambda_L^2}{\ln(b\lambda_L/(0.9\eta_c))^2} \approx \frac{0.5I_p^{3+a}\lambda_L^2}{\ln(b\lambda_L/(0.9\frac{2\pi\delta_l}{\lambda_L^2r_eNa}))^2} = \frac{0.5I_p^{3+a}\lambda_L^2}{\ln(d\lambda_L^3)^2},$$

(4.3)
Figure 4.1: Phase-matching cutoff as a function of driving laser wavelength for helium (red), neon (green), and argon (blue), for 3 cycle (solid) and 8 cycle (dashed) pulses calculated from equation 4.2. At longer wavelengths, the scaling of the phase-matching cutoff is very favorable, showing that harmonics > 1 keV can be phase-matched with an appropriate driving wavelength.

where $b \equiv 0.86(N/c)^{2n^*−1}G_{\text{lin}}C_{n^*l}^2I_p$ and $d \equiv br_eN_a/0.9(2\pi)\delta_L$. From equation 4.3, it is clear that the phase-matching cutoff scales more slowly than the $\lambda_L^2$ scaling of the single atom cutoff. In addition, it provides some insight into why the scaling is reduced. In the equation, there is a term that looks like $\lambda_L^2/(\ln d\lambda_L^2)$. For $n = 0$, the scaling would go as $E_{\text{pmc}} \propto \lambda_L^2$, but instead there are three powers of $\lambda_L$ in the logarithm in the denominator — two of which come from the scaling of the critical ionization, $\eta_c \propto 1/\lambda_L^2$ and the third from the assumed pulse duration dependence on the wavelength. In addition, there is a dependence on the specific atom used in the effective scaling of the cutoff which shows up in the parameter $d$ and is due primarily to the ionization potential of the gas medium used.

4.2.3 Efficiency Scaling of IR Driven Harmonics

The discussion up to now has focused on the scaling of the phase-matching cutoff with the driving wavelength. An analysis from this perspective neglects the question of brightness. As
described in section [40, 41], from a single atom perspective the HHG yield scales as $\lambda^{-5.5}_L - \lambda^{-6.5}_L$, seemingly devastating to the prospect of using IR phase-matching as a source of bright, coherent soft X-rays. Surprisingly, a careful analysis of the full macroscopic description of HHG shows that IR phase-matching can be used to efficiently generate harmonics well into the soft X-ray and potentially extending even into the hard X-ray region of the spectrum. A full description of the scaling of the efficiency for infrared phase-matching is discussed in depth in [12, 72] and will not be discussed in detail here.

The key insight comes from looking at the gas transmission dependence on photon energy. In high harmonic generation, unlike low-order nonlinear optics, the harmonic medium itself strongly reabsorsbs the light that is being generated. Because of this, even for perfect phase-matching, harmonic emission coherently grows over about six absorption lengths of the medium and then saturates [8]. For a medium longer than six absorption lengths, the rate of absorption due to the medium balances the rate of newly generated harmonics and the process saturates. As a result, the absorption length of the harmonic medium is an important parameter in determining the optimized efficiency of a given high harmonic geometry.

Figure 4.2 shows transmission spectra for helium, neon and argon. For argon and neon, the presence of inner shell absorption edges prevent the transmission from significantly increasing and the phase-matching calculations predict that the resulting harmonic emission will decrease at long driving wavelengths as initially expected. Helium, however, has no inner electron shell. As a result, helium gas becomes almost transparent at photon energies approaching 1 keV. A longer absorption length means that the harmonics can be phase-matched in a longer harmonic medium. Detailed calculations in references [12, 72] predict that when the high harmonic process is properly phase-matched over the absorption limited length in helium, the longer harmonic medium can compensate for the poor single atom scaling and maintain and even improve the efficiency of the high harmonic process into the soft and hard X-ray regions of the spectrum as seen in figure 4.3.
Figure 4.2: Transmission spectra for three of the common HHG gas media, argon (black), neon (blue), and helium (red) showing that at photon energies approaching 1 keV, helium becomes increasingly transparent allowing very long absorption limited harmonic generation media, which increases the efficiency of the harmonic process. From ref [11].
Figure 4.3: Calculated phase-matched HHG efficiency in a 1% bandwidth at the phase-matching cutoff as a function of driving laser wavelength and photon energy at the cutoff for helium (red), neon (green) and argon (blue). All are normalized to the optimized efficiency at 800 nm. The results show that the phase-matched intensity from both argon and neon falls off at long driving wavelengths due to the unfavorable single atom scaling. The efficiency for helium, on the other hand, remains flat and even increases at long driving wavelengths due to the high transparency of helium at high photon energies. Figure from ref [12].
4.2.4 Full Phase-Matching Spanning the Water Window

In our experiment, 40 fs pulses at a wavelength of 2 µm (6 cycles FWHM) are generated in a three-stage optical parametric amplifier (OPA) seeded by a white-light continuum. High harmonics are then generated in helium, neon, and argon by focusing up to 2.4 mJ of the 2 µm idler beam into a 200 µm radius, 1 cm long, gas-filled hollow waveguide [12, 69, 73]. The HHG spectrum is then detected using a flat-field imaging X-ray spectrometer and an X-ray CCD camera. Various metal filters are used to eliminate the fundamental laser light and to calibrate the spectrometer, depending on the photon energy range under investigation [e.g., B (K-edge 188 eV), Sc (L-edge 400 eV), Ti (L-edge 454 eV), and Cr (L-edge 575 eV)].

For a complete discussion of the phase-matching results for HHG driven by a 2 µm field, see ref [69]. The resulting, fully phase-matched spectra for helium and neon are shown in figure 4.4. In helium driven by 2 µm light, the phase-matching cutoff extends up to 520 eV, while the harmonic emission peaks around 450 eV, with some harmonic emission extending past the oxygen K-edge at 540 eV. In neon, the phase-matching cutoff extends to 395 eV and peaks at 370 eV at a pressure of 2600 Torr. In helium, an approximate brightness of \( \approx 10^6 \) photons/sec or \( \approx 10^5 \) photons/shot is observed in a 1% bandwidth around 450 eV (at a repetition rate of 10 Hz). A total of 6 \( \times 10^7 \) photons/sec is observed over the entire water window region (284 – 520 eV). These flux levels are \( > 10^3 \) higher than achieved to date at 0.5 keV [70]. Further increases in flux by orders of magnitude can be expected by using driving lasers with better beam quality and higher repetition rates, higher helium pressures, and longer waveguides with better differential pumping. This is, however, a sufficiently high flux for initial experiments using this source, and in particular for a spatial coherence measurement.
Figure 4.4: Phase-matched harmonics from helium (red) and neon (green) driven by a 2 µm fundamental laser field. The carbon K-edge is visible at 284 eV due to carbon contamination in the spectrometer. As predicted, higher harmonic energies are phase-matched in helium. The two spectra are normalized to the peak of the helium spectrum, showing that helium is in fact brighter when driven by 2 µm light because it is more transparent in the water window than neon.

4.3 Spatial Coherence Measurement in the Water Window

The spatial coherence of high harmonics in the EUV has been well established [29,30] and has played an important role in many of the applications [21,22]. To demonstrate that the HHG light driven by a 2 µm laser is spatially coherent [29], we implemented the first coherence measurement in the water window using any compact light source.

The short wavelengths of the water window radiation impose additional constraints on the experimental geometry. In order to measure and resolve the interference pattern, two requirements must be met. The first is a requirement that the detector be in the far field of the object where the diffraction pattern is given by the Fraunhofer approximation. This is satisfied when the Fresnel number \( F ≡ D^2/L\lambda \), is much less than 1, where \( D \) is the slit separation and \( L \) is the distance from the object to the detector. The second is a requirement that at least \( N \) pixels sample each
fringe in order to resolve the fringe from peak to valley to peak. The minimum value for $N$ is 3 pixels per fringe, but in practice this will not be sufficient as each pixel will integrate a large area and artificially reduce the fringe visibility. A more practical requirement would be twice this, or more. Figure 4.5 plots the results of these constraints and shows that for a lab with space for a maximum object to detector propagation distance of around 2 m, the largest slit separation that can be used for a water window diffraction experiment is around 50 $\mu$m.

Figure 4.5: Minimum distance to the CCD detector from a double slit with a given slit separation. The plotted lines indicate the far field requirement (black line) and the fringe visibility requirement for 3 pixels per fringe (blue line) and 6 pixels per fringe (red line). Calculation assumes a central wavelength of 3.8 nm, a pixel size of 25 $\mu$m, and a maximum Fresnel number of 1/4. Because of the short wavelength and the quadratic dependence of $L$ on $D$ in the far field requirement, the minimum separation of the sample and detector grows rapidly with slit separation.

We placed a double slit in the beam $\approx$30 cm after the waveguide, with slit widths of 10 $\mu$m with a center-to-center separation of 20 $\mu$m. An X-ray CCD camera was placed $\approx$1 m after the double slit, as this distance is sufficient to satisfy both the far field requirement and the fringe visibility requirement (see Fig. 4.5). The entire 70 eV FWHM bandwidth HHG from neon centered around 330 eV was used to illuminate the double slit, with a beam waist of 1.7 mm. Two thin metal
filters (Al and Ti) were used to reject low order harmonics and fundamental light. Figure 4.6(a) shows the measured and predicted interference patterns, while Fig. 4.6(b) shows a lineout of the measured diffraction intensity (red) and simulated lineout (black). The broad spectral bandwidth limits the fringe visibility off-center, as expected. The low HHG beam divergence means that the fringes become smaller than the CCD pixels if the slits are further separated, and the diffraction patterns from the pinholes do not overlap. The strong modulations of the measured diffraction pattern, combined with excellent agreement with simulation, demonstrate that the beam center is spatially coherent.

Figure 4.6: (a) Measured and calculated double-slit interference pattern using HHG from Ne at 330 eV. (b) Comparison between the measured (red) and simulated diffraction pattern lineout (black) assuming a central wavelength of 3.8 nm (330 eV). The broad bandwidth ($\Delta E = 60$ eV) limits the number of fringes. One fringe is not visible due to the overlap of the diffraction from a single and double slit.

Notice that in the image, only the 0th, 1st and 3rd fringes are visible. The 2nd fringe is not visible due to overlapping interferences between the single slit and double-slit diffraction patterns. This can be seen by looking at the equation for the diffraction pattern of a double slit:
\[ I_{\text{diff}}(x) = I_{\text{diff}}^0 \text{sinc}^2 \left( \frac{\pi w x}{\lambda L} \right) \cos^2 \left( \frac{\pi D x}{\lambda L} \right), \]

where \( I_{\text{diff}}(x) \) is the intensity of the diffraction pattern at position \( x \), \( I_{\text{diff}}^0 \) is the peak of the diffraction pattern, \( w \) is the slit width, \( \lambda \) is the wavelength of the diffracting light and \( L \) and \( D \) are defined above. The \( \text{sinc}^2 \) term results from the diffraction pattern of a single slit and the \( \cos^2 \) comes from the interference of the two slits. For \( w = 2D \), as is the case for the results shown in figure 4.6, the first zero of the sinc coincides with the peak of the 2nd diffraction fringe. This is why it is not visible in the image.

The predicted diffraction pattern was calculated assuming a harmonic spectrum with a Gaussian profile centered at 326 eV with a 70 eV FWHM and separately propagating each of the different harmonics from the double slit to the CCD according to the measured distance between the two. The good overlap between the predicted lineout and the measured lineout of the diffraction pattern acts as an independent calibration of the central wavelength of the harmonic spectrum exiting the waveguide. This is important for two reasons that will be developed further in the following paragraphs. First, it verifies that the spectrum measured through the spectrometer was properly calibrated. Second, it demonstrates that IR phase-matching is a well suited technique for generating high energy harmonics that can be isolated from the low energy part of the spectrum.

The first idea is relatively straightforward, whenever measuring the high harmonic spectrum, particularly when working in a new regime for high harmonics, a careful calibration of the spectrum is critical. Misalignments of the spectrometer or gratings can easily lead to erroneous and misleading data. While great care was taken in the measurement of the spectra presented in figure 4.4, an independent verification further improves confidence in the results.

The second concept is slightly more subtle and requires some discussion of the high harmonic process. In principal, this process generates every odd order harmonic between the fundamental at 2 \( \mu \text{m} \) and the highest harmonic generated at \( \approx 2.5 \text{ nm} \). This amounts to \( \approx 800 \) harmonic orders, propagating colinearly at the exit of the waveguide. For many applications, such as bio and nano
imaging, it is necessary to take that very broad bandwidth of harmonics and select a single narrow band of the spectrum. In general, this can be a very difficult task.

Consider, the high harmonic generation in the water window, driven by 0.8 μm light as described in chapter 3 as well as other experiments generating very high energy harmonics using intense laser pulses with a central wavelength near 0.8 μm [48,70]. The spectra are all characterized by a similar structure: relatively bright low order harmonics and dimmer harmonics on the high energy side of the spectrum. For this reason, harmonic spectra in this regime are often shown plotted on a log scale. The high photon energy harmonics are visible when spectrally resolved, but an experiment using the direct beam will be dominated by the low order harmonics which are several orders of magnitude brighter. Multilayer mirrors and thin metal filters can be used to help isolate one region of the harmonic spectrum, but it is a difficult problem to find a combination of filters and mirrors that will efficiently reject all wavelengths from the visible and IR down to the soft X-ray region of the spectrum while maintaining a high enough transparency in the soft X-ray to deliver a usable flux to an experiment.

In this experiment, we demonstrated that simply by using two thin metal filters, it is possible, using IR phase-matching, to do an experiment using soft X-ray light generated in the high harmonic process without spectrally resolving the harmonics. There are three major differences between soft X-ray harmonics generated as in refs [48,70,74] and the results presented in this chapter that help to make this possible.

First, the water window harmonics generated by 2 μm light in this chapter are phase-matched allowing a high brightness in the soft X-ray region of the spectrum. In contrast, the non-phase-matched harmonics in [48,70,74] fall off rapidly with harmonic order because the coherence length when Δk ≠ 0 is proportional to 1/q. While quasi-phase matching techniques provide a promising approach to selectively enhance a narrow bandwidth of harmonics in the water window [53,68], to date, selective enhancement of harmonics has only been demonstrated to ≈ 150 eV [52,75].

Second, the very high gas pressure necessary for phase-matching an IR driving field (≈ 3.5 atm in Ne and > 10 atm in He) acts like a filter to significantly reduce the transmission of low
energy harmonics relative to high energy harmonics through the waveguide (see for example, the transmission of helium and neon in figure 4.2).

The third advantage of using IR light to drive the harmonic process is due to the quantum efficiency of the X-ray CCD’s used to detect the soft X-ray light. Figure 4.7 shows quantum efficiencies for Andor X-ray CCD cameras. For the experiments described, a BN camera was used. The quantum efficiency curve shows that the detector is very sensitive to photons in the visible, peaking around 2 eV (≈ 620 nm), with a quantum efficiency around 60%. At longer wavelengths, the quantum efficiency falls off rapidly. At 0.8 µm, the quantum efficiency is around 30-40%, and by 2 µm the quantum efficiency falls to almost 0, meaning the detector is not sensitive to the fundamental wavelength. While it is still important to reduce the flux of fundamental light that reaches the detector in order to prevent damage to the CCD or counts from 2-photon effects, it is not necessary to reject as much of the fundamental light as it is for an 800 nm driving field where the CCD is sensitive. These three effects, which are unique to IR phase-matching, helped to allow this first table-top SXR spatial coherence measurement.

Figure 4.8 shows a comparison of a lineout of a diffraction pattern measured using the harmonics from neon with one using harmonics generated in helium. The measured high harmonic spectrum from helium is blue shifted relative to the spectrum from neon as seen in figure 4.4. The fringe spacing is reduced in figure 4.8 due to the shorter central wavelength. The diffraction pattern from helium harmonics has a reduced fringe visibility because of the broader bandwidth of the harmonics and because the reduced fringe spacing is not well sampled by the detector pixels.
Figure 4.7: Quantum efficiencies for Andor X-ray CCD cameras. The work in this thesis was done on the BN type. Figure from ref [13].

Figure 4.8: Comparison of the experimental diffraction patterns measured using harmonics from $10^4$ Torr helium (red) and 2600 Torr neon (green). The harmonic spectrum from helium is blue shifted relative to that from neon, this results in a more closely spaced diffraction pattern. The fringe visibility of the harmonics from helium is reduced due to the broader bandwidth of the helium spectrum and because the reduced fringe spacing is not well sampled by the detector pixels.
4.4 Refocusing Narrow-Band High Harmonics in the Water Window

One of the important uses of coherent soft X-ray light is in coherent imaging of bio and nano samples. Soft X-ray imaging techniques require monochromatic sources, so it is necessary to select and refocus a narrow window of the spectrum. Our collaborators at the Center for X-Ray Optics (CXRO) at Lawrence Berkeley Lab designed and fabricated a multilayer mirror with a peak reflectivity reaching 22% in the water window, centered at about 400 eV with a fractional bandwidth of $\lambda/\delta\lambda \approx 200$ when the mirror is aligned at 11.5° from normal (see figure 4.9). The multilayer structure was fabricated on a curved substrate with a 1 m radius of curvature. The mirror efficiently selects a narrow bandwidth in the soft X-ray, but also reflects lower photon energies and would reflect low order harmonics and fundamental light.

The wavelength dependence of the diffraction experiment described in section 4.3 demonstrated that two thin metal filters are sufficient to reject the fundamental and low order harmonic light co-propagating with the soft X-ray light at the output of the waveguide. The multilayer was placed after the filters, 1 meter from the waveguide to refocus the beam with one-to-one imaging 1 m away on a CCD detector. The measured beam profile is shown in 4.9 (b). The beam is astigmatic due to the 11.5° off normal reflection. In addition, the CCD was deliberately moved slightly out of the focus in order to resolve more of the beam because in focus the beam width only fills about one pixel in the y-dimension. This measurement is important as it demonstrates that harmonics in the water window can be refocused with a sufficiently narrow bandwidth for coherent imaging. In the future, combining IR phase-matching with higher repetition rate lasers will make it possible to do coherent soft X-ray imaging with high harmonic generation.
Figure 4.9: (a) Reflectivity curve of the soft X-ray multilayer mirror coated and measured at the Center for X-Ray Optics at Lawrence Berkeley Lab. The mirror has a peak reflectivity around 20% at a central photon energy near 400 eV with a bandwidth $\lambda/\delta\lambda \approx 200$. The peak reflectivity is for $11.5^\circ$ from normal incidence. (b) Image (insert) and lineout (blue circles) with gaussian fit (green line) of the high spectral purity, refocused soft X-ray beam.

4.5 Conclusions

In summary, using a recently developed, 2 $\mu$m driven high harmonic source, we implemented spatial coherence measurements in the soft X-ray region for the first time using any compact light source. These advances will enable high-resolution tabletop microscopies of materials, nano- and biological samples with unprecedented combined spatial and temporal resolution.
Chapter 5

Development of Ultrafast, Transient Absorption Spectroscopy Spanning the Water Window: Initial Results and Future Plans

5.1 Introduction

Chapters 3 and 4 described two methods to generate harmonics in the water window region of the spectrum — spanning 284 – 540 eV. This spectral range is important for a number of applications because it overlaps with the inner shell absorption edges for many commonly occurring elements (including carbon, nitrogen, and oxygen). Of the two methods presented in this thesis, mid-infrared phase-matching appears to be the more promising technique to generate bright, coherent, ultrafast radiation in this region of the spectrum. Quasi-phase matching techniques may provide an appealing alternative as they would preserve the high single atom efficiency of harmonics driven by near-infrared fields, but to date, no quasi-phase matching technique has been developed with the generality of the IR phase-matching model presented in [12] and verified in [12, 69, 76]. Based on this assessment, we decided to develop a high repetition rate, mid-IR, high harmonic phase-matching beamline which could be used for initial applications of high harmonics in this region of the spectrum.

5.2 IR Driven High Harmonic Phase-Matching: A Unique Source for Transient Absorption Spectroscopy

Because of the ultrafast time resolution, broad spectrum, and scalability, phase-matched high harmonics driven by mid-IR sources provide a unique tool for many spectroscopic applications.
These ideas are discussed in more detail in the following sections.

5.2.1 Temporal and Spectral Properties of IR Driven Harmonics

With current technology, there are a few technologies for the production of femtosecond scale pulses of extreme ultraviolet and soft X-ray light: 1) third generation synchrotrons with femtosecond slicing [1], 2) free electron lasers (FEL) [77], 3) laser generated plasmas [78] and 4) high harmonic generation. Synchrotrons and FEL’s can each provide bright sources of soft X-ray light with high spectral purities (λ/∆λ ≈ 1000), and synchrotrons are tunable over ranges of 10’s to 100’s of keV. Synchrotrons, FELs and laser generated plasma sources all have temporal resolutions around 100 fs. For high harmonics, 10 fs resolution is regularly achieved, and in principal, sub-femtosecond resolution is possible [27]. Furthermore, the femtosecond slicing technique used at synchrotrons reduces the soft X-ray flux by about three orders of magnitude per shot [1] making some experiments challenging or even impossible. Similar to the synchrotron sources, laser driven plasmas can be highly tunable, but have limited flux [1]. FELs provide the highest brightness of all, but are limited in tunability and repetition rate. To date, most ultrafast, soft X-ray, transient absorption spectroscopy has been performed on synchrotrons because of the flux and energy tunability that they provide but without using femtosecond slicing they are limited to around 10 ps temporal resolution. There is an opportunity for high harmonics to provide a significant contribution to the field because of their compact nature and the high temporal resolution they can provide.

In addition, one of the features of harmonics produced with IR phase-matching is that the harmonic spectrum is very broad. This is a result of the fact that the index of refraction for the noble gases rapidly approaches 1 for harmonics above 100 eV and for harmonics higher than 30, 1/q^2 is below an 0.1% correction to the plasma dispersion and can be neglected. Referring to equation 2.19 in chapter 2, there is almost no harmonic dependence on the phase-matching pressure and a broad range of harmonics are simultaneously phase-matched. On the low energy side, the bandwidth is limited by the reabsorption due to the high gas pressures necessary to phase-match the process. On the high energy side, it is limited by the phase-matching cutoff as discussed in chapter 4. The
very broad bandwidth can cover multiple absorption edges in a single laser shot, which makes it possible to coherently excite or simultaneously monitor different elements in a sample.

An example of where this has proven useful was in a recent study of femtosecond resolved magnetic dynamics in a permalloy sample, using harmonics in the EUV [17,79]. Figure 5.1 shows results where a small ($\approx 60$ fs) delay between the demagnetization response of nickel and iron is visible. In an energy scanning technique, as would be necessary for a synchrotron or FEL, it would be very difficult to identify such an effect as real and not a consequence of drift or noise. As high harmonics allow the full spectrum to be recorded simultaneously, subtle timing differences between different elements in a sample can be meaningfully interpreted.

![Figure 5.1](image)

**Figure 5.1:** (a) EUV harmonic spectrum reflected off of a permalloy sample, containing both nickel and iron, for an external magnetic field pointed up (green) or down (red) and the corresponding asymmetry (blue). The asymmetry, $A = (I_+ - I_-)/(I_+ + I_-)$ where $I_+$ is the spectrum with the magnetic field pointed up and $I_-$ is the spectrum with the field flipped, shows a large response at the Fe edge (55 eV) and the Ni edge (68 eV) which allows the magnetic response of the Ni and Fe in the sample to be independently monitored. (b) Asymmetry as a function of time delay between a laser pump and EUV probe for Fe (red) and Ni (blue). A small, 60 fs, delay is observed between the response of the Fe and the response of the Ni.

### 5.2.2 Scalability of IR Driven Phase-Matched Harmonics

As discussed in chapter 4, one of the primary limitations on the applications of high harmonics was the narrow energy range over which harmonics could be efficiently generated. Infrared phase-
matching, however, is a generalizable technique which has already been demonstrated to > 1 keV photon energies (see figure 5.2) [14, 80], spanning many technologically and scientifically relevant absorption edges. Furthermore, as the driving wavelength is increased, the bandwidth of harmonics becomes increasingly broad — leading to the ability to monitor either many elements at once or two elements with absorption edges that are spaced far apart spectrally.

![Normalized high harmonic spectra from He, driven by 0.8 µm (yellow), 1.3 µm (green), 2.0 µm (blue), and 3.9 µm (purple), showing IR phase-matching from 0.1 keV to 1.6 keV. Positions of some elemental absorption edges are indicated along the bottom of the plot. From ref [14].](image)

The initial IR phase-matching demonstrations were done on low repetition rate (10 – 20 Hz) laser systems, as these systems were able to generate the high peak intensities needed to generate harmonics at long wavelengths. As higher repetition rate sources are developed, applications will open up in the broad range of photon energies that have been demonstrated. From a technological perspective, both at high and low repetition rates, the laser sources capable of producing harmonics are generally easier to develop the closer they are to 0.8 µm. As a result, the demonstrations of full phase-matching of the high harmonic process were done step-by-step at increasing driving wavelengths [12, 69, 81]. In the process of upgrading to kHz sources suitable for high harmonics at these wavelengths, we expect a similar trend. For this reason, we plan to first develop the ultrafast
spectroscopy technique for harmonics driven by 1.3 \( \mu \)m light. In parallel, colleagues are working to develop the laser sources needed to extend kHz phase-matching to > 1 keV so that spectroscopy can be done over the full range of photon energies demonstrated.

### 5.3 Development of a High Repetition Rate, Soft X-Ray Beamline

In this section, the newly developed soft X-ray beam line for transient absorption spectroscopy in gas phase samples is described. Initial plans for a liquid phase spectroscopy are briefly discussed as well.

A schematic of the experimental setup is shown in figure 5.3. A two-stage, cryo-cooled Ti:Sapphire chirped pulse amplifier produces a kHz train of 25 fs pulses centered at 0.8 \( \mu \)m with pulse energies up to 7 mJ. A vacuum spatial filter is used to clean up the beam spatial profile and down-collimate the beam, which then pumps a three-stage optical parametric amplifier (OPA). The OPA generates a 1 mJ signal beam (central wavelength 1.2 – 1.4 \( \mu \)m) with a pulse duration around 35 fs. Co-propagating with the signal beam is an idler beam, centered at 2 \( \mu \)m, and the residual 0.8 \( \mu \)m pump light. In the harmonic beamline, the 1.3 \( \mu \)m light is focused into a high harmonic waveguide, where the soft X-ray light is generated, with a typical spectrum shown on the top left of figure 5.3. The harmonics pass through a hole in a mirror and then the gas cell, which can be filled with the gas sample of interest, before being measured in an X-ray spectrometer. The gas cell is differentially pumped on either side to rapidly reduce the pressure outside of the sample.

At the output of the OPA a dichroic mirror is used to separate the residual 0.8 \( \mu \)m light from the signal beam for use as the pump in the transient absorption experiment. It is recombined collinearly with the harmonic beam on the mirror with the hole and focused into the gas cell. A translation stage in the 0.8 \( \mu \)m beam path varies the relative time delay between the pump and the harmonic probe. A shutter in the pump arm is used to reduce effects of slow drift in the harmonic spectrum. Time overlap between the pump and probe arms was found by overlapping the two beams on a BBO crystal with all of the vacuum components in place but with the chamber at atmospheric pressure. As the time delay is varied between the two, there is a visible, green mixing
product that appears at time overlap.

The data presented in this chapter were taken in the geometry shown in figure 5.3. Some changes to the geometry will be necessary to allow liquid samples. First, for the gas cell, differential pumping is used to rapidly reduce the gas pressure outside of the cell. In contrast, for the liquid cell, windows are necessary to confine the sample, which introduces additional absorption into the beamline. In order to minimize the absorption in the windows, the cell was designed with very thin, 30 nm, silicon nitride (Si$_3$N$_4$) windows, which require small, 25 µm, apertures for mechanical stability. Consequently, the harmonics will be refocused to optimize the transmission through the sample. For refocusing, we will use a single, nickel coated, glancing incidence optic which will allow broadband refocusing up to 800 eV photons with a high (≈ 70 – 80 %) reflectivity.
5.4 Preliminary Results

Recently, we have demonstrated several key steps in the development of this beamline for applications in ultrafast, soft X-ray, transient absorption spectroscopy. Section 5.4.1 describes initial results demonstrating mid-IR phase-matching at kHz repetition rates with photon energies up to 270 eV. These results show that the brightness of the mid-IR driven harmonics can be improved by orders of magnitude by increasing the repetition rate. Furthermore, strategies for extending phase-matched harmonics to > 300 eV in the current beamline will be discussed as this would allow transient absorption experiments at the carbon edge at 284 eV. Section 5.4.2 describes initial results using this mid-IR driven beamline for static, gas phase spectroscopy experiments.

5.4.1 Phase-Matched Harmonics Driven by kHz 1.3 \( \mu \text{m} \) Light

An important first step in the development of a soft X-ray transient absorption spectroscopy beamline is the demonstration of bright soft X-rays at high photon energies at high repetition rates (\( \approx 1 \) kHz). The kHz OPA described in section 5.3 produces 30-40 fs pulses with energies up to 1 mJ with a central wavelength ranging from 1.2 \( \mu \text{m} \) to 1.4 \( \mu \text{m} \). To demonstrate the effectiveness of this source for the generation of high harmonics, we used the 1.3 \( \mu \text{m} \) beam to generate harmonics in argon, neon and helium. Figure 5.4 shows phase-matched harmonic spectra from each of these three gases at kHz repetition rates. Bright, phase-matched harmonics from helium extend to about 270 eV. Harmonic structure is visible in at least a portion of each spectrum (for helium only to about 150 eV). For spectroscopic applications, it is important to note that for all three gases, while there is harmonic structure, the harmonics are closely spaced and the signal does not go to zero between harmonic peaks. Thus, for all three gases, the spectrum can be considered a quasi-continuum.

Along the top of figure 5.4 the position of several elemental absorption edges is indicated, showing that this source can be used to access information on many elements. The element with an edge in this regime with perhaps the most significant applications is carbon, which is just beyond the bright region of the spectrum for helium shown. This is a limitation due to the peak intensity
Figure 5.4: Experimental spectra for kHz, phase-matched harmonics generated from argon (blue), neon (red), and helium (black), driven by pulses with a central wavelength of 1.3 µm. Each spectrum is normalized to its peak. Bright, phase-matched, harmonics from He extend beyond 250 eV to about 270 eV.

of the laser in the gas medium and not a limitation of phase-matching, as the phase-matching cutoff for harmonics driven by a 1.3 µm laser pulse extends beyond the carbon edge to about 310 eV [12]. Extending the cutoff energy high enough to phase-match harmonics beyond the carbon edge would require only a 15 % increase in the peak intensity of the laser in the harmonic medium or an increase of the laser wavelength to 1.4 µm with the same intensity. Either of these could be achieved in future experiments by changing the focusing geometry with the same input laser energy and wavelength or by taking advantage of the tunability of the OPA to increase the central wavelength to 1.4 µm. This result shows that bright harmonics can be generated spanning into the water window at high repetition rates. The following section will focus on the application of this source in spectroscopy. In addition, this source can be used for element specific imaging with spatial resolution approaching 10 nm.
5.4.2 Static Absorption Spectroscopy of Autoionizing States of Xe and Kr

With the beamline in place, we began implementation of the gas-phase, static absorption spectroscopy experiment, which was described in section 5.3. For the first application of the technique we decided to use two of the heavy noble gases (krypton and xenon) as they both have strong absorption resonances with energies in the spectrum of harmonics generated from argon.

Figure 5.5 shows raw data from spectra used to calculate the absorption spectra of krypton both with the gas sample ($I$) and with no gas present ($I_0$) as well as the calculated transmission spectrum, $T$, as a function of photon energy, $h\nu$, where the spectrum is calculated according to

$$T(h\nu) = \frac{I(h\nu)}{I_0(h\nu)}.$$ 

(5.1)

With krypton in the cell, the overall transmission is reduced, but in particular, two strong resonances are visible around 90 eV where there is a sharp drop in the transmission. It is interesting to note that the resonances fall between two harmonics in the spectrum shown. This again demonstrates that the closely spaced harmonics are well suited to spectroscopic applications, as there is still strong signal between the peaks of the harmonic structure.

Figure 5.6 plots the absorbance of both krypton and xenon, where the absorbance, $A$, is defined as:

$$A = -\ln T.$$ 

(5.2)

The sharp peaks that are visible correspond to resonances between electrons in the outermost $d$ electron shell into high energy, unoccupied $p$-shell states. The short lived, highly excited states that result from this process are referred to as autoionizing states because they decay by ejecting the high energy electron into the continuum [82, 83]. For example, the lowest energy transition shown in figure 5.6(a), corresponds to a transition from the ground state of xenon: $[{}^5\text{Kr}]5s^24d^{10}5p^6$ to $[{}^5\text{Kr}]5s^24d^95p^66p^1$, removing an electron from the 4d shell of xenon to the unoccupied 6p shell. Degenerate splitting of the d-shell is also visible in the splitting of the resonance energy between
Figure 5.5: Normalized intensity for harmonics from Ar driven by a 1.3 µm laser pulse after passing through a gas cell filled with no gas (black) or 1.5 Torr of krypton (red). Each spectrum is separately normalized for easy comparison, highlighting the differences between the two. The transmission of the gas cell is calculated as the ratio of the two and shown in blue.

electrons from d\(^{5/2}\) states and electrons from d\(^{3/2}\) states. The notation in the figure, \((n_1d_j)^{-1}n_2p\) corresponds to removing an electron from the \(n_1\) level d-orbital with angular momentum \(j\) and promoting it to the \(n_2\) level p-orbital.

Figure 5.6: (a) Measured absorbance as a function of photon energy for 700 mTorr of xenon in a 2 cm gas cell. The strong peaks correspond to resonances with autoionizing states. (b) Absorbance of 1500 mTorr of krypton in a 2 cm gas cell.
These absorption spectra, in conjunction with the harmonic spectra from section 5.4.1, show that this beamline will soon be available for ultrafast spectroscopy on a broad range of molecules.

5.5 Conclusions and Future Plans

Infrared phase-matching has been demonstrated to 270 eV at high repetition rates. With only minor improvements to the experimental geometry, this can be extended above the carbon edge at 284 eV. Plans are in place to do initial transient absorption experiments in the gas phase on molecules such as carbonyl sulfide (OCS) and sulfur hexafluoride (SF$_6$) where both the sulfur and carbon edges will be accessible. In systems such as this, vibrational modes in the molecule can be impulsively [84, 85] excited with an intense femtosecond laser pulse. As the molecule vibrates, the local electronic structure surrounding the sulfur atom will dynamically change, which will show up as changes in the structure near the sulfur L-edge. Simple systems such as this will enable us to demonstrate that we can monitor and interpret ultrafast changes in the charge density in molecules. We will then build on the understanding we obtain in this process to extend to more complicated molecules dissolved in a solution where we can study charge transfer mechanisms and ultrafast, photo-initiated reactions.


