

Long and Short Wavelength Optical Sources for Attosecond Science

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Author's Statement

Declaration of Originality

Except when otherwise noted, all work contained within this thesis is my own.

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Summary

In this thesis I describe work extending attosecond science into new regimes through the development of novel light sources. Thus far attosecond science has been driven primarily through two technologies: titanium-doped sapphire lasers capable of generating few-cycle femtosecond laser pulses in the near infrared (800 nm) wavelength range, and high harmonic generation driven by these pulses, which creates attosecond pulses in the extreme ultraviolet frequency range (10-150 eV).

We attempt to move into new regimes for attosecond science through the development of light sources at new wavelengths. Through the use of an optical parametric amplifier and hollow-core fibre pulse compression, we have generated 1.3-cycle pulses at a central wavelength of 1750 nm (7.1 fs duration) with excellent spatio-temporal quality and high energies of 750 μ J per pulse at a repetition rate of 1 kHz. Three novel diagnostics were developed in order to characterize the temporal properties of these pulses: a SEA-F-SPIDER, a third harmonic single-shot FROG, and a third harmonic D-scan.

Our short-wavelength infrared laser source has been applied to high harmonic spectroscopy of substituted benzenes. By careful control of macroscopic conditions, we obtain harmonic spectra comparable to theoretical calculations. We find a minimal effect of deuteration upon the few-femtosecond dynamics of benzene.

Using the few-cycle 1750 nm pulses, high harmonic generation has been extended to the soft X-ray regime, and we have generated attosecond pulses at all photon energies across the water window (284-540 eV). Energies of tens of picojoules are generated, with estimated pulse durations of several hundred attoseconds. The spatial properties of the harmonic radiation were also examined, and found to be well described by Gaussian optics. Finally, the soft X-ray harmonic radiation was used to obtain X-ray absorption spectra from a variety of samples to demonstrate the utility of our source.

“Non-perturbative dynamics? Allan, you used to be a rebel.”

- Charlotte Bailey

“At ten to the minus six, Blu Tack is vacuum compatible.”

- Thomas Siegel

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Above all, thank you Paloma. I planned for these years to be all about physics, but they've been all about you.

List of Acronyms

Acronym	Definition
ADK	Ammosov-Delone-Krainov
ATI	Above-threshold Ionization
BBO	Beta Barium Borate
BoPET	Biaxially-oriented Polyethylene Terephthalate
CCD	Charge Coupled Device
CDI	Coherent Diffractive Imaging
CEP	Carrier Envelope Phase
CPA	Chirped Pulse Amplification
D-Scan	Dispersion Scan
DFG	Difference Frequency Generation
EOS	Electro-Optic Sampling
EXAFS	Extended X-ray Absorption Fine Structure
FEL	Free Electron Laser
FME	Forward Maxwell Equation
FROG	Frequency Resolved Optical Gating
FS	Fused Silica
FWHM	Full Width at Half Maximum
GDD	Group Delay Dispersion
HHG	High Harmonic Generation
HHGS	High Harmonic Generation Spectroscopy
HCF	Hollow-Core Fibre
HOMO	Highest Occupied Molecular Orbital
ID	Inner Diameter
IR	Infrared
LUMO	Lowest Unoccupied Molecular Orbital
MCP	Microchannel Plate
NEXAFS	Near Edge X-ray Absorption Fine Structure
OD	Outer Diameter
ODE	Ordinary Differential Equation
OPA	Optical Parametric Amplifier

OPCPA	Optical Parametric Chirped Pulse Amplification
P3HT	Polythiophene
PACER	Probing Attosecond Dynamics by Chirp Encoded Recollision
PCGPA	Principle Components Generalized Projections Algorithm
PDE	Partial Differential Equation
PET	Polyethylene Terephthalate
PID	Position Integral Derivative
PPT	Perelomov-Popov-Terent'ev
RABBIT	Reconstruction of Attosecond Beating By Interference of two-photon Transitions
SAE	Single Active Electron
SFA	Strong Field Approximation
SEA-SPIDER	Spatially Encoded Arrangement SPIDER
SEA-F-SPIDER	SEA Filter-based SPIDER
SHG	Second Harmonic Generation
SPIDER	Spectral Phase Interferometry for Direct Electric-field Reconstruction
SPM	Self Phase Modulation
SPR	Single Particle Response
SWIR	Short-Wavelength Infrared
SWORD	Spectral Wavefront Optical Reconstruction by Diffraction
SXR	Soft X-Ray
TDSE	Time Dependent Schrödinger Equation
THG	Third Harmonic Generation
Ti:sapph	Titanium-doped sapphire
UV	Ultraviolet
VLS	Variable Line Space
VUV	Vacuum Ultraviolet
XANES	X-ray Absorption Near Edge Structure
XPM	Cross-Phase Modulation
XUV	Extreme Ultraviolet
ZAP-SPIDER	Zero Additional Phase SPIDER

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Chapter 1

Introduction

1.1 Introduction

The advancement of scientific research is often closely tied to the development of increasingly precise measurement tools. Since the development of the laser, the advancement of ultrafast science has been intimately connected to the development of improved ultrashort laser pulses, which provide precise temporal measurements. With each breakthrough decreasing the duration of pulses, new timescales could be studied, and new phenomena understood. From the initial nanosecond pulses of the 1960s, ultrafast lasers quickly advanced to the femtosecond domain. Breaking this important barrier allowed for the first real-time measurement of molecular dynamics, which lead to the development of femtochemistry [1]. This was the state of the art in ultrafast science for over a decade, in which molecular dynamics at the femtosecond scale remained the fastest phenomena directly observable in the time domain. It was not until 2001 that the first pulses of attosecond duration were measured [2,3], opening the door to attosecond science and the measurement of the even faster electronic dynamics.

Numerous advances have been made in the first decade and a half of attosecond science. Real time observation of electron motion in atoms [4], tracking charge migration inside organic molecules [5], ultrafast control of the conductivity of solids [6], and measuring time delays in photoemission [7]; these are just a few of the advances enable by attosecond science. Despite these accomplishments, attosecond science today is still performed in much the same way as 2001, as all these experiments begin with a modelocked titanium-doped sapphire (Ti:sapph) laser compressed to a few-femtosecond pulse duration driving high harmonic generation (HHG) to create attosecond pulses in the extreme ultraviolet (XUV). Pump-probe experiments with attosecond resolution are then performed with the strong infrared field and the weak attosecond XUV field. Strong fields are required to ensure the process is field-sensitive, otherwise the attosecond resolution is lost [8].

Since the strong laser field distorts the dynamics in the system under study, a great deal of effort has been placed in improving the conversion efficiency of HHG to allow attosecond-attosecond

pump-probe measurements [9]. Another limitation, less obvious than the flux, is the range of photon energies accessible via HHG driven by near-infrared (NIR) lasers; in general photon energies above 150 eV cannot be reached via HHG driven by Ti:sapph lasers [10]. The XUV region has several drawbacks which limit the applicability of attosecond science. Almost all materials absorb strongly in the XUV, which means experiments must be performed in vacuum and either with very thin samples or examining surface effects; studies of bulk effects in samples are challenging, and samples inside solution are effectively impossible. Furthermore, if we are interested in using inner-shell resonance absorption edges of atomic species as localized structural probes, only a limited number of atomic species have such inner shell resonances inside the XUV spectral region. The powerful techniques of X-ray absorption spectroscopy thus cannot be brought to bear on most problems if we are limited to XUV photon energies.

A route to increasing the range of photon energies accessible by HHG is to break away from the ubiquitous Ti:sapph laser and move to longer driving wavelengths. The maximum photon energy emitted by HHG scales with the square of the wavelength [11], thus we are able to generate soft X-ray (SXR) photons by moving from the NIR to the short-wavelength infrared (SWIR). In particular, by moving to driving wavelengths around $1.75\ \mu\text{m}$, we can generate high harmonics spanning the so called water window (WW), from the carbon K edge at 284 eV to the oxygen K edge at 540 eV [12]. This spectral region is of particular interest because organic molecules, including amino acids, absorb the X-rays strongly while water transmits the radiation; imaging and spectroscopy *in vivo* thus becomes possible. In particular both the carbon and nitrogen K edges are in the water window, meaning X-ray absorption near-edge spectroscopy (XANES) can be applied to a wide variety of systems, including large and complex systems which cannot be addressed using current attosecond techniques. X-ray spectroscopy is powerful because it is sensitive to both electronic and nuclear structural dynamics, but the features manifest in different regions of the absorption spectrum. Thus electronic and nuclear dynamics can be studied independently, and their coupling at the few-femtosecond time scale, a major topic of interest in attosecond science [13], effectively studied.

Another attosecond measurement technique, which does not explicitly rely on attosecond pulses, is high harmonic spectroscopy (HHGS) [14]. As will be shown in section 2.5 and chapter 4, a high harmonic spectrum can be viewed as a few-femtosecond pump-probe experiment with subfemtosecond resolution. HHGS has been used to make measurements of sub-fs nuclear [15] and electronic [16] dynamics, but has been limited to small molecules with large ionization potentials because of the high field strengths ($\geq 10^{13}\ \text{W}/\text{cm}^2$) necessary to drive HHG with NIR laser fields. However, moving to long wavelengths dramatically decreases the intensity required by a factor of the wavelength squared, and increases the time window by a factor of the wavelength. Thus large systems with slower dynamics become accessible to study via HHGS with longer wavelength driving fields.

Longer wavelength driving fields necessitate the use of novel laser technology. Unfortunately there are no appropriate laser schemes for generating few-femtosecond pulses at high energies in the SWIR ($1.3 - 3 \mu\text{m}$); for this reason frequency conversion schemes are necessary. In particular wavelengths of around 1750 nm can be generated from Ti:sapph lasers through optical parametric amplifiers (OPAs) or optical parametric chirped pulse amplifiers (OPCPAs). The multi-cycle pulse output of an OPA can be further compressed through the use of a hollow-core fibre (HCF) in the same manner as 800 nm pulses. The characterization and subsequent optimization of few-cycle pulses in the SWIR require new pulse measurement techniques, as detectors are very limited for SWIR radiation.

The application of SWIR lasers to high energy HHG and HHGS comes with additional challenges related to the phasematching of the HHG process. As will be discussed in section 5.1.2, the efficiency of a single emitter decreases dramatically with the driving wavelength. For this reason careful optimization of the macroscopic conditions is required. For efficient generation at high energies very high gas pressures are required, placing strict requirements on the vacuum system. In HHGS, careful control is required to account for macroscopic effects, in order to produce a signal which can be meaningfully compared with the emission of a single molecule.

This thesis is structured as follows: In chapter 2 I will review the background motivating long wavelength sources for attosecond science. Notational and mathematical conventions will be outlined, followed by descriptions of XANES spectroscopy, tunnel ionization, and the microscopic and macroscopic aspects of high harmonic generation. In chapter 3 I describe the technology for the generation and characterization of few-cycle SWIR laser pulses, along with the system developed at Imperial College. I also present the various pulse measurement devices we have built and the pulse measurement results, showing we generate sub-two-cycle pulses at a central wavelength of $1.75 \mu\text{m}$. In chapter 4 I discuss the macroscopic conditions necessary for performing meaningful HHGS, and present a series of experiments in benzene using our long wavelength source. In chapter 5, the generation of soft X-ray harmonics from our few-cycle SWIR source is presented. I describe the apparatus developed to enable HHG in this new regime, then show carrier-envelope sensitive harmonic spectra extending across the water window. Our results are a significant improvement over current state-of-the-art, boasting higher fluxes and photon energies. In chapter 6 potential applications of the harmonic source are explored. Static XANES measurements are obtained in polymers at photon energies up to the oxygen *K* edge, while a spatial phase measurement shows the potential for application to microscopy.

1.2 Contributions

All work in this thesis was performed collaboratively. The development of the short-wavelength infrared laser source at Imperial College described in section 3.4.1 was contributed to by all

members of the laboratory, but primarily by Dane Austin, Peng Ye, and myself. The SEA-F-SPIDER described in section 3.4.3 was developed primarily by Dane Austin and Tobias Witting. The single shot FROG from section 3.4.4 was designed and constructed by Dane Austin and myself. The few-cycle idler system from section 3.5 at Rutherford Appleton labs was built by Paloma Matia-Hernando and myself; the D-scan was designed by Adam Wyatt and constructed by the three of us. The high harmonic spectroscopy experiments in chapter 4 were performed by a large team with apparatus constructed by Felicity McGrath. I led the technical development for and experiments on soft X-ray harmonic generation detailed in chapter 5, and the subsequent applications to XANES in section 6.1. These experiments were performed by a team, though primarily with David Wood. The XANES measurements of organic solar cells from section 6.1 were performed with samples developed by Lukas Miseikis.

1.3 Publications

A.S. Johnson, L. Miseikis, D.A. Wood, D.R. Austin, C. Brahms, S. Jarosch, C.S. Struber, P. Ye, and J.P. Marangos. *Measurement of sulfur $L_{2,3}$ and carbon K edge XANES in a polythiophene film using a high harmonic supercontinuum*. Structural Dynamics Vol. 3, pp. 062603 (2016). [doi:10.1063/1.4964821](https://doi.org/10.1063/1.4964821)

Dane R. Austin, Felicity McGrath, Lukas Miseikis, David Wood, Peter Hawkins, **Allan S. Johnson**, Morgane Vacher, Zdenek Man, Alex Harvey, Olga Smirnova, and Jon P. Marangos. (2016) *Role of tunnel ionization in high harmonic generation from substituted benzenes*. Faraday Discussions (2016). [doi:10.1039/C6FD00116E](https://doi.org/10.1039/C6FD00116E)

Dane R. Austin, T. Witting, S.J. Weber, Peng Ye, T. Siegel, Paloma Matia, **Allan S. Johnson**, J.W.G. Tisch, J.P. Marangos. *Spatio-temporal characterisation of intense few-cycle $2\mu\text{m}$ pulses*. Optics Express, Vol. 24, Issue 21, pp. 24786-24798 (2016). [doi:10.1364/OE.24.024786](https://doi.org/10.1364/OE.24.024786)

A Sanchez-Gonzalez, TR Barillot, RJ Squibb, P Koloren, M Agaker, V Averbukh, MJ Bearpark, C Bostedt, JD Bozek, S Bruce, S Carron Montero, RN Coffee, B Cooper, JP Cryan, M Dong, JHD Eland, L Fang, H Fukuzawa, M Guehr, M Ilchen, **A S Johnson**, C Liekhus-S, A Marinelli, T Maxwell, K Motomura, M Mucke, A Natan, T Osipov, C stlin, M Pernpointner, VS Petrovic, MA Robb, C Sathe, ER Simpson, JG Underwood, M Vacher, DJ Walke, TJA Wolf, V Zhaunerchyk, JE Rubensson, N Berrah, PH Bucksbaum, K Ueda, R Feifel, LJ Frasinski, JP Marangos. *Auger electron and photoabsorption spectra of glycine in the vicinity of the oxygen K -edge measured with an X-FEL*. Journal of Physics B: Atomic, Molecular and Optical Physics, Vol. 48, Issue 23, pp.234004 (2015). [doi:10.1088/0953-4075/48/23/234004](https://doi.org/10.1088/0953-4075/48/23/234004)

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Allan S. Johnson, Felicity McGrath, Dane Austin, Peter Hawkins, David Wood, Lukas Mis-eikis, Emma Simpson, Ricardo Torres, Susan Parker, Thomas Siegel, and Jon Marangos. (2017) *An apparatus for high-fidelity attosecond spectroscopy in high-pressure vapours*. In preparation.

Chapter 2

Background

In this chapter I review some of the background that motivates our work developing ultrafast sources, as well as the physical concepts underlying the work presented in this thesis. I begin by reviewing the mathematical description of ultrafast laser pulses, introducing several useful representations and ideas. I then discuss the measurement of attosecond dynamics, with emphasis on measurements requiring time-resolved methods, before moving on to a description of X-ray spectroscopy. Finally I present the background necessary to the generation of attosecond pulses and more generally attosecond temporal confinement.

2.1 Ultrafast Laser Pulses

The fundamental tool for attosecond science is the ultrafast laser pulse, here meaning those with durations below 1 ps. Ultrafast lasers are a ubiquitous technology, having been commercially available for several decades and reaching into fields as diverse as precision metrology, super-resolution imaging, and laser machining [17–19]. Here I briefly review the description of ultrafast laser pulses and establish the conventions used throughout this thesis.

Laser propagation is governed by the electromagnetic wave equation,

$$\frac{\partial^2}{\partial z^2} \vec{E}(t, \vec{r}) + \nabla_{\perp}^2 \vec{E}(t, \vec{r}) - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \vec{E}(t, \vec{r}) = \frac{1}{\epsilon_0 c^2} \frac{\partial^2}{\partial t^2} \vec{P}(t, \vec{r}), \quad (2.1.1)$$

where we have assumed a non-magnetic medium with no free currents or charges, and that the variation in the polarization over one wavelength in space is small [20]. In this expression $\vec{E}(t, \vec{r})$ is the electric field as a function of time t and space $\vec{r}$, z denotes the direction of propagation, $\nabla_{\perp}^2$ is the gradient in the transverse directions, and $\vec{P}(t, \vec{r})$ is the polarization response of the medium. The time-dependent polarization response can generally be treated as a function of the incident electric field $\vec{P}(t, \vec{r}) = f[E(t, \vec{r})]$. In vacuum the polarization is zero, while in a linear material it is a linear function of the electric field, $\vec{P}(t, \vec{r}) = \chi^{(1)} \vec{E}(t, \vec{r})$, where $\chi^{(1)}$ is the first order material susceptibility. For non-linear materials, the polarization can be expanded

in powers of the electric field,

$$\vec{P}(t, \vec{r}) = \chi^{(1)} \vec{E}(t, \vec{r}) + \frac{\chi^{(2)}}{2} \vec{E}(t, \vec{r})^2 + \dots \quad (2.1.2)$$

where $\chi^{(n)}$ is the n^{th} order susceptibility; this describes the non-linear optical response and the realm of perturbative non-linear optics. For sufficiently high fields, the polarization cannot be expanded as a series, and must be treated non-perturbatively, as is the case for high harmonic generation and tunnel ionization. Here we will restrict ourselves to the vacuum case, in which the wave equation takes the form

$$\frac{\partial^2}{\partial z^2} \vec{E}(t, \vec{r}) + \nabla_{\perp}^2 \vec{E}(t, \vec{r}) - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \vec{E}(t, \vec{r}) = 0. \quad (2.1.3)$$

Any solution to the wave equation can be written as a superposition of planewaves, and from this property it can be shown that the propagation of the electric field at any plane z is uniquely determined by its value at $z = 0$ [21], with the form

$$\vec{E}(k_x, k_y, z, t) = \vec{E}(k_x, k_y, z = 0, t) e^{ik_z z} \quad (2.1.4)$$

where k_i is the wavevector in the i^{th} spatial direction. The field at any point (x,y,z) can then be determined by Fourier transform. Since $k_z = \sqrt{k^2 - k_x^2 - k_y^2}$, we can thus consider the laser field in two spatial dimensions and one temporal dimension.

If we now assume the laser is linearly polarized, we can drop the vector notation. In an ideal laser pulse the spatio-temporal coupling is minimal, for instance in the output of an oscillator or fibre, and the laser pulse can be factorized as

$$E(x, y, t) \approx E(x, y) E(t).$$

If the pulse exhibits no space-time coupling or we are considering only one point in space, we can express the pulse purely in either the temporal $E(t)$, or spectral $E(\omega)$ domains, which are related to each other via a Fourier transform:

$$E(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E(t) e^{i\omega t} dt \quad (2.1.5)$$

$$E(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E(\omega) e^{-i\omega t} d\omega. \quad (2.1.6)$$

This implies, from the bandwidth theorem, that the duration in the time domain $\Delta\tau$ and the bandwidth in the spectral domain $\Delta\omega$ are related by

$$\Delta\tau \Delta\omega \geq K \quad (2.1.7)$$

where K is a constant related to the pulse shape. This means that generating a short pulse in

the time domain requires a large bandwidth in the spectral domain.

It is often convenient to represent the pulse in the time domain as

$$E(t) = A(t) \cos(\omega_0 t + \phi_0), \quad (2.1.8)$$

where $A(t)$ is a slowly varying function called the envelope, ω_0 is the carrier frequency describing the rapid oscillation in time, and ϕ_0 is the carrier-envelope phase (CEP), the phase between these two components. While the effect of the CEP is generally negligible for many-cycle duration pulses, it strongly affects the field shape of a few-cycle laser pulse; its impact will be discussed further in section 2.4.1. This formulation also allows us to examine slower changes in the pulse shape independent of the fast oscillations of the field.

In the frequency domain, we split $E(\omega)$ into a positive and negative frequency branch as

$$E(\omega) = \frac{1}{2}[\mathcal{E}(\omega) + \mathcal{E}^*(-\omega)] \quad (2.1.9)$$

where $\mathcal{E}(\omega)$ is the *analytic function*, defined only over positive frequencies. Since $E(t)$ is purely real, all information is contained in the positive frequency branch of $E(\omega)$, and since we assume no DC component the partition is exact. We can thus consider only the positive frequency branch $\mathcal{E}(\omega)$, and further partition it as

$$\mathcal{E}(\omega) = |\mathcal{E}(\omega)| e^{i\phi_\omega(\omega)} \quad (2.1.10)$$

where ϕ denotes the phase of the light and ω is the angular frequency. Because direct measurement of $|\mathcal{E}(\omega)|^2$ is possible simply by using a spectrometer¹, the formulation in equation 2.1.10 is useful to describe ultrafast pulses, and measurement of the pulse is reduced to measurement of the spectral phase, as described in section 3.3. Furthermore, within the realm of linear optics material dispersion can be treated as an additive phase in the spectral domain with magnitude $\phi_\omega(\omega) = n(\omega)d$ where $n(\omega)$ is the refractive index and d is the material thickness. Therefore the partition into spectral amplitude and phase is very useful. To examine the phase of a pulse in the spectral domain, we can expand the spectral phase $\phi_\omega(\omega)$ around the central frequency ω_0 as

$$\phi_\omega(\omega) = \phi_0 + \phi_1(\omega_0 - \omega) + \frac{1}{2!}\phi_2(\omega_0 - \omega)^2 + \frac{1}{3!}\phi_3(\omega_0 - \omega)^3 + \dots \quad (2.1.11)$$

where the term $\phi_n = \frac{\partial^n \phi_\omega(\omega)}{\partial \omega^n} \Big|_{\omega_0}$ is referred to as the n^{th} -order phase. The zeroth order phase is the CEP in the time domain, as can be seen from the linearity of the Fourier transform.

¹By definition $\mathcal{E}(\omega)$ is non-zero for only positive frequencies, so $\mathcal{E}(\omega) \times \mathcal{E}^*(-\omega) = 0$, hence $I(\omega) \propto |E(\omega)|^2 = |\mathcal{E}(\omega)|^2 + |\mathcal{E}^*(-\omega)|^2$. Since in the laboratory we measure only positive frequencies, a spectrometer gives $|\mathcal{E}(\omega)|^2$ directly.

The first-order phase ϕ_1 , also known as the group delay, becomes an overall time-delay of the pulse when transformed to the time domain, and thus has no effect on the pulse shape.² This is not true for higher order phases. The second order phase, also known as chirp, results in a different arrival times for the different colours - namely a linear variation of the colour with time. Provided the chirp is sufficiently strong, the variation of frequency with time can be approximated as $\omega(t) \approx \omega_0 + t/\phi_2$ [22]. When second order phase is added by propagation through a material it is known as group delay dispersion (GDD), and is generally the largest contribution to the stretching of pulses by propagation through a material. The third order or cubic phase ϕ_3 results in the generation of pre- and post- pulses, and is often the lowest-order phase which cannot be fully corrected in an ultrafast optical system.

2.2 Ultrafast and Attosecond Dynamics

Practically all quantum systems, such as atoms, molecules, polymers, and solids, are expected to show attosecond dynamics when excited by a sufficiently rapid impulse. The dynamics in such systems are most accurately treated with relativistic quantum mechanics such as the Dirac equation, however most can be described by the time-dependent Schrödinger equation³

$$-i\hbar \frac{\partial |\Psi(\vec{R}, t)\rangle}{\partial t} = [\frac{\vec{p}^2}{2} + V(\vec{R}, t)] |\Psi(\vec{R}, t)\rangle \quad (2.2.1)$$

where $\vec{R}$ is a generalized coordinate for the, in general, multi-particle system, $\vec{p}$ is the momentum operator, V is the potential, and Ψ is the wavefunction. While some systems undergo strong dynamics in which $V(\vec{R}, t)$ is strongly time dependent, in most cases the time-dependence of the Hamiltonian is slow and its effect upon the wavefunction can be treated adiabatically. A notable exception is the case of systems in strong laser fields, which is developed more in sections 2.4 and 2.5 for the cases of tunnel ionization and high harmonic generation. At this point however, we will consider the case where the system Hamiltonian can be treated as primarily time independent. A solution to the Schrödinger equation where $V(\vec{R}, t) \approx V(\vec{R})$ has the form

$$\Psi(\vec{R}, t) = \sum_n^{\infty} c_n \psi_n(\vec{R}) e^{-iE_n t} \quad (2.2.2)$$

²Considering the transform back into the time domain $\int |\mathcal{E}(\omega)| e^{-i(\phi_1+t)\omega} d\omega$ shows the phase acts as a simple temporal shift

³Attosecond dynamics are ubiquitous at relativistic scales because of the high velocities involved, but are beyond the scope of this thesis.

where n is the principle quantum number, an integer, E_n is the corresponding energy, c_n is a weighting coefficient, and $\psi_n(\vec{R})$ is the spatial wavefunction which satisfies

$$E_n \psi_n(\vec{R}) = \left[\frac{\vec{p}^2}{2} + V(\vec{R}) \right] \psi_n(\vec{R}). \quad (2.2.3)$$

Each ψ_n and E_n correspond to a different energy eigenstate of the system, while Ψ is in general a superposition of said eigenstates. The resulting superposition will undergo dynamics comprised of oscillations corresponding the energy gaps $\Delta E = E_n - E_m$ between any two occupied states n and m , with period $2\pi\hbar/\Delta E$. The more occupied states, the more superimposed frequencies, and the more complex the dynamics. A system with an energy gap of just 3 eV, typical of light absorbing systems, will have time dynamics with a period of 1.5 fs, requiring sub-femtosecond sampling to accurately characterize. In general, attosecond dynamics correspond to the energy gaps characteristic of valence electronic states [23].

A system with simple dynamics as described above does not always require attosecond measurement; for instance, a hydrogen atom in a superposition of the ground state and the first-excited state will have charge density oscillating with a period of ≈ 400 as, but this oscillation is perfectly reflected in the frequencies in its emission spectrum. The lifetime of the superposition is further reflected in the linewidth of the emission line. Performing a challenging pump-probe experiment would yield no new information. Spectral domain measurements have, for instance, yielded measurements of rapid motion in water solution of less than 50 attoseconds by assuming a simple time decay structure [24]. Attosecond dynamics necessitate attosecond measurement only when they are complex and not reflected directly in the spectral domain, in much the same fashion as femtosecond measurements. However, before discussing some forms of attosecond dynamics which necessitate attosecond measurement, it is worth noting that measurements of attosecond dynamics can also be of interest for purely practical reasons, even if they could in principle be inferred from the energy spectrum. An analogy to microscopy is useful here - because of the coherence of a light field, it is in principle possible to measure the light scattered from a microscopic particle in the far field and, from the broad features, reconstruct the object. It is however considerably simpler and more transparent to use microscopy, constructing an image of the object with the correct spatial resolution. In the same way the conjugate variables of $\vec{k}$ and $\vec{r}$ can be used for spatial imaging, both E and t can be used to reconstruct temporal dynamics, but the techniques of microscopy and chronoscopy can be significantly easier to model and interpret. This was recognized in the field of femtochemistry, where femtosecond resolution allowed differential measurements of the evolution of transient states that had previously been limited to low resolution continuous measurements which averaged over the initial, intermediate, and final states [1]. Furthermore the fluorescence signal of short lived transients may simply be too weak and too broad to be measured in a realistic experiment with continuous-wave illumination.

Let us examine non-exhaustively some specific observables or channels which can be addressed

by time-resolved spectroscopy, and not through time-independent methods. The most immediately apparent is the potential to track dynamics which proceed to or from dark states and through non-radiative transitions. As an example, DNA and RNA are well known to undergo a variety of internal conversion processes after absorbing UV light, which help prevent genetic damage upon exposure to UV [25]. Considering only the RNA base uracil, many different nonradiative channels can be largely ignored, and a relatively simple reaction diagram can be developed, a cartoon of which is shown in figure 2.1. Apart from the ground S_0 and excited S_2 states, there also exists a dark state S_1 , and the potential for two nonradiative transitions, from S_2 to either S_0 or S_1 , once again disregarding at least five channels which are less energetically favourable [26]. While continuous-wave measurements can yield information on the transition probability to S_2 and the subsequent lifetime in that state, they are blind to whether the system relaxes to the S_0 or S_1 state, and to the lifetime of the dark state. Pump-probe experiments, in which excitation to S_2 by a UV pulse was followed by a strong laser pulse ionizing from both S_2 and S_1 , suggest that most of the population from S_2 decays nonradiatively within 100 fs, with a longer lived trapped portion of the S_2 population decaying radiatively over 2.6 ps, while the S_1 state survives well over 10 ps [26]. Much faster non-radiative relaxation dynamics are thought to occur, with decay times below 100 as possible in some systems [27], which can again only be probed through time-resolved methodologies.

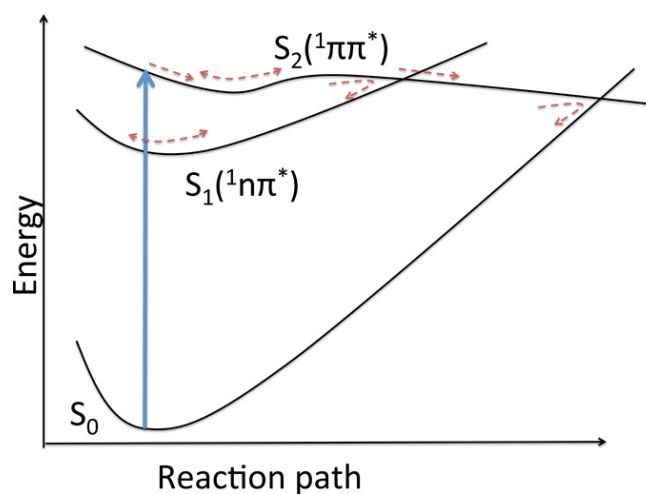


Figure 2.1: Cartoon of the states involved in the reaction following UV absorption by uracil. Two different crossing points are present, allowing for non-radiative decay to either the dark state S_1 or to the ground state S_0 . Reprinted with permission from S. Matsika *et al.*, J. Phys. Chem. A, 2013, 117 (48), pp 12796 - 12801. [26]. Copyright 2013 American Chemical Society.

Another example is the case of overlapping decay channels: if an excited state of a molecule or solid undergoes fluorescent decay, it is usually possible to assign a lifetime to the state by assuming an exponential decay and fitting the decay lifetime to the linewidth of the emission. In more complex systems however, a state may decay through various channels with different lifetimes. This may be due to the intrinsic structure of the molecule or due to environmental broadening [28]. These broadened transitions can overlap if they are sufficiently dense or the decay sufficiently fast, making partitioning of the spectrum difficult. In the time domain these

contributions are clearly separate, and fitting of multiple exponentials to measurements made in the time domain is a common methodology for analyzing decay channels [29–31]. Related to this, but conceptually distinct, is the case of non-exponential decays. In these cases the decay cannot be adequately modelled by an exponential decay at all, and the extraction of lifetimes from the spectral width is not possible. This is illustrated in figure 2.2, where complex dynamics in the time domain (including a decay, partial revival, and oscillations) lead to a complex line-shape in the spectral domain. This is the case when the continuum has a non-uniform density of states; for example, X-ray absorption and decay inside large molecules or clusters exhibits strongly non-exponential decay, and can even demonstrate oscillations in the population [32]. The X-ray decay case is particularly interesting as lifetimes are generally below 10 fs in duration, ranging to sub-femtosecond, and are important in the application of free electron lasers to “diffract before destroy” schemes [33], in which the timescale for damage is set by these relaxation processes.

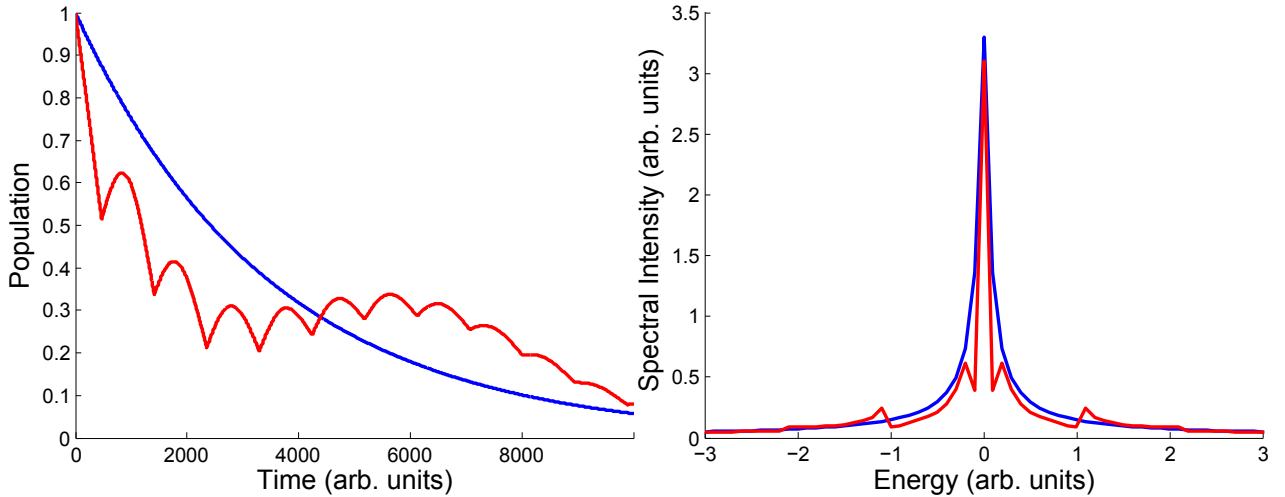


Figure 2.2: *Left:* A simple exponential decay curve (blue) is contrasted with a hypothetical decay curve exhibiting complex dynamics (red). *Right:* Resulting linewidths of the two cases. Extraction of decay time from the complex red curve is ill-defined.

Combining the ideas of dark states, non-radiative decay, and non-exponential decay, interactions with a bath in an open quantum system can also modify dynamics in a fashion not reflected in the spectrum. Extracting dynamical information from such systems has motivated the development of a wide variety of spectroscopic tools, including two-dimensional spectroscopy [34] and quantum process tomography for light harvesting complexes [35, 36].

Another variable not reflected in spectral measurement is the relative phase of the various energy states, which changes depending on the mode of preparation as well as reflecting the intrinsic dynamics of the system. While this does not directly affect dynamics in an open quantum system [37], the relative phase of energy states can yield information about the system and plays an important role in coherent control schemes. Many measurements of attosecond

dynamics thus far have been focused on extracting these phases, and indeed the first attosecond transient absorption measurement returned the phase information of an atom's density matrix [4]. In this seminal experiment, atomic krypton was ionized by a few-cycle laser pulse, and the coherence of the excited wavepackets was probed by transient absorption of an XUV attosecond pulse. Due to the broadband nature of the attosecond pulse, holes created in different states of the krypton ion by tunnel ionization can be projected to the same continuum states and interfere. The time-dependent absorption spectrum thus encodes the relative phases of the different ionic states and their mutual coherence. In reference [4], the degree of coherence between various states was successfully extracted, demonstrating for the first time that strong-field ionization is capable of generating electronic coherences which could potentially be applied in strong field coherent control schemes. In many ways, the application to coherent control schemes is where attosecond science can be predicted to have the largest impact. For a prototypical coherent control scheme [38], attosecond pulses generate highly coherent superpositions of many electronic states, which can subsequently be made to interfere by interaction with another attosecond pulse, and the resulting reaction products controlled by the relative phases (timing). The use of strong fields to control the electronic and optical properties of materials on a sub-femtosecond timescale has also been demonstrated, and has potential applications in ultrafast switching [39, 40].

Putting aside the question of coherent control, and considering only using attosecond science techniques to examine the attosecond response of various systems, there remains an open question - does any of this have anything to do with nature? In a laboratory we first trigger dynamics using attosecond pulses, and the phase imparted between states by our excitation process appears in our measurement of the ensuing dynamics; this is the fundamental basis of coherent control in both the attosecond [41] and femtosecond [38] domains. However nature does not usually produce attosecond pulses, which are broadband, short in time, and highly coherent. Photo-excitation in nature, and in light harvesting technology, involves sources like the sun which are broadband, but weak, continuous, and of very low coherence. Brumer and Shapiro [42] have even called into question the relevance of coherences in light harvesting materials observed in ultrafast laboratories, as sunlight will not excite such coherences, and have shown that the evolution of a system excited with thermal light will not demonstrate any coherence. A simpler question is to ask how excitation with continuous light could create an attosecond response (the idea of excitation being an instantaneous process that occurs at some time within the illumination is not one that withstands a proper quantum treatment). One answer to these arguments is to note that we can discuss separately the coherence of the process, which depends only on the system, and the state, which is prepared by the excitation and then evolves according to the process [43]. In this case one can discuss the attosecond dynamics and coherences of the process independently from the initial state preparation. Attosecond spectroscopy can then yield information about this process even if it does not act on the same highly coherent states in nature. However it is worth noting that an attosecond timescale can

be identified in nature, namely the coherence time of the light. Sunlight is incredibly broadband, with a spectrum reaching beyond our fastest lasers. This translates into an extremely short coherence time of around 600 as [44]. This idea has been spectacularly demonstrated in the femtosecond domain [45], where low-coherence amplified spontaneous emission was used to trigger and track femtosecond dynamics. In the attosecond domain coherent excitation can occur on an ultrafast timescale, dictated by the coherence time; an attosecond decay process then ensures the process is not dephased by subsequent optical interaction. The potential for attosecond dynamics in nature is then clear, as well as the essential role of time-resolved measurements in unraveling them.

2.3 X-ray Absorption Near-Edge Structure Spectroscopy

During our discussion of attosecond dynamics we touched upon how the first transient absorption measurement of attosecond dynamics used an XUV pulse to probe the electronic states of a krypton atom [4]. However, there are several advantages to using attosecond pulses in the soft X-ray (SXR) regime instead, particularly the water window (WW) region from 284 eV to 540 eV, where water is transparent but hydrocarbons absorb strongly. This would allow the probing of samples inside solution, where absorption is prohibitively high in the XUV. SXR attosecond pulses could also allow for time-resolved coherent diffractive imaging (CDI) with few-nanometer resolution [46]. Another highly attractive opportunity is to perform X-ray Absorption Near-Edge Structure (XANES) spectroscopy, as well as Extended X-ray Absorption Fine-Structure (EXAFS) spectroscopy, with attosecond resolution. The development and use of SXR attosecond pulses are a significant topic this thesis, so I will now review the theoretical background of XANES and EXAFS and discuss the unique opportunities they provide for tracking attosecond dynamics. This section aims to be a clear introduction to the topic, but is in no way an exhaustive discussion of the field; interested readers are referred to reference [47] for a more complete overview.

The interpretation of X-ray spectra is strongly linked to the Hartree-Fock picture of multi-electron systems. Electrons are assigned to artificial single electron states with well defined quantum numbers, constructed from a properly diagonalized multi-electron Hamiltonian [48]. These electron states are known as orbitals; one can then speak about whether or not orbitals are occupied, and about the energy of the orbitals, treating multi-electron correlations as a higher order correction. For isolated atoms these orbitals and their symmetries are well known, and correspond to the s , p and d orbitals with orbital angular momentum of $l = 0$, $l = 1$, and $l = 2$, respectively. A diagrammatic representation of state structure is shown in figure 2.3: the lines represent states of different energies, the black dots the electrons occupying the states, and the direction of the arrows the spin. States can only be occupied by up to two electrons with opposite spin according to the Pauli exclusion principle [48]. In general, states are occupied starting from the lowest energy and filled upwards. The outermost electron orbitals

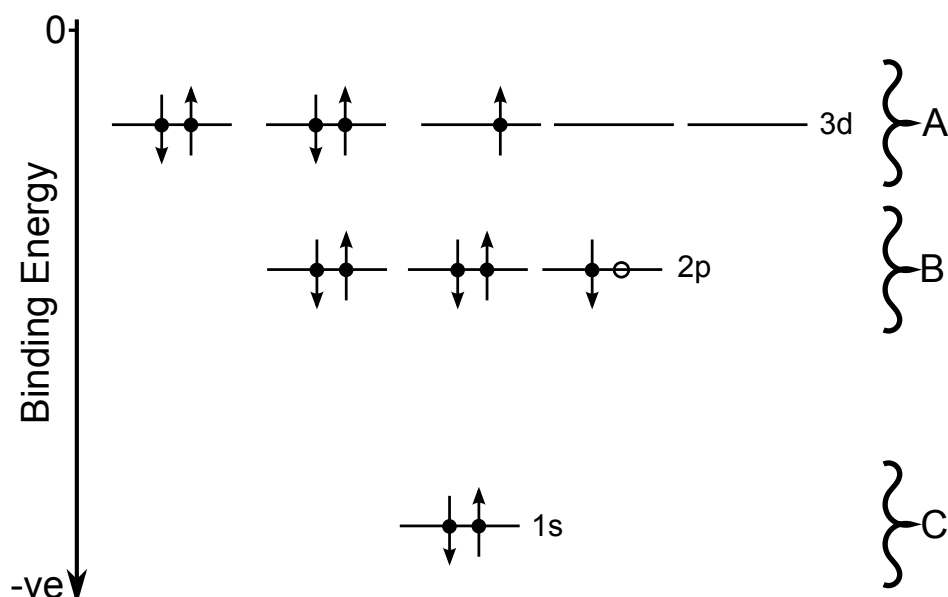


Figure 2.3: Diagram of Hartree-Fock orbital occupations and energies. The orbitals labeled A are valence, those labeled B are inner valence, and the one labeled C is core. The states are arranged by binding energy and labeled by angular momentum, with occupation indicated by the black dots. A ‘hole’ is shown in the $2p$ state, with a partially occupied orbital in the $3d$.

are known as valence states, and are generally considered to be responsible for most chemical properties. Next are inner valence electrons, with ionization energies in the VUV. More tightly bound electrons are known as core-electrons, and it is these that X-rays interact with. Valence electrons may have binding potentials of less than one to around ten eV; core electrons have binding energies of tens to thousands of eV.

X-ray photons can induce transitions between occupied core states and unoccupied ones of the correct parity. As shown in figure 2.4a), a sufficiently high energy photon can cause an electron in the $1s$ orbital to be excited to the hole in the $3p$ orbital, but due to conservation of angular momentum cannot excite it to a d state. In general there are three regions that a transition can take place to: an unoccupied bound state as just described, quasi-bound states, and continuum states. Unoccupied bound states correspond to molecular orbitals or valence states; they are generally well separated in energy and appear as isolated peaks in an X-ray absorption spectrum for lower energy bound states. The higher lying Rydberg states are increasingly closely spaced as the energy approaches the ionization threshold and the individual peaks cannot be resolved. Quasi-bound states are those immediately above the ionization threshold. Electrons have enough energy to escape the system, but due to shape of the system potential can also remain bound for some time before tunneling. In the absorption spectrum these manifest as features following a steep rise in the X-ray absorption at the ionization threshold known as the absorption edge. Because the quasi-bound states result from the shape of the potential, these transitions are also known as shape resonances. XANES deals with the study of these two regions, and treats the continuum resonances as a result of multiple scattering events from

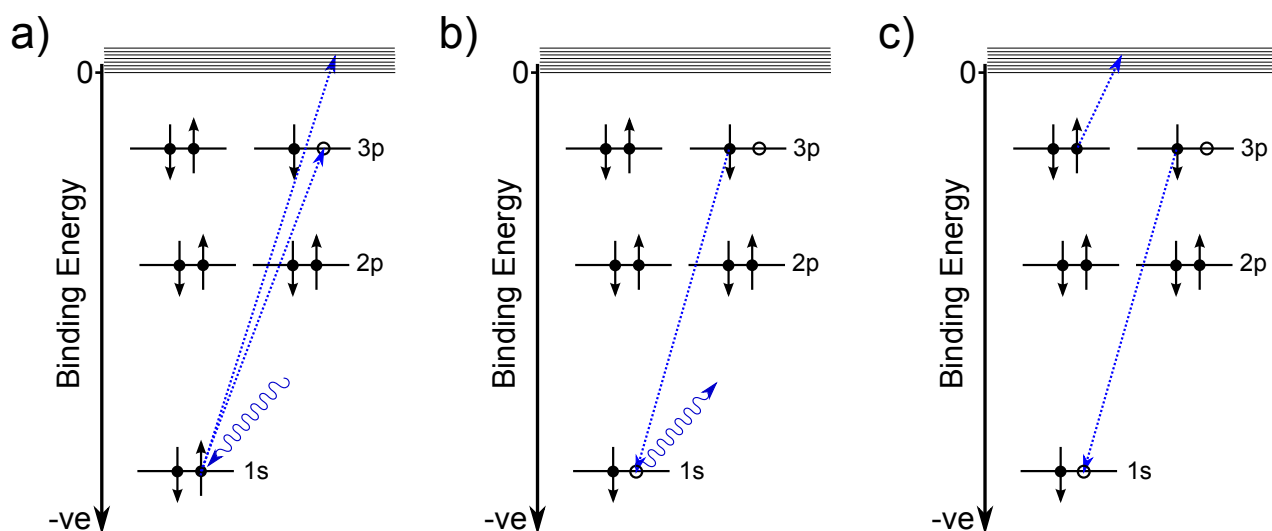


Figure 2.4: Schematic of X-ray absorption and multi-electron effects. a) A core electron can be excited to either a bound hole or a continuum state. Note we have reduced the dimensionality of the orbitals for clarity. b) The created inner hole is filled by an outer-lying electron, releasing a photon via X-ray fluorescence. c) The inner hole is filled by an outer-lying electron, with excess energy carried away by an Auger electron.

nearby neighbors. Finally, significantly beyond the absorption edge (around 50 eV beyond) there is a gradual decrease in the X-ray absorption as the photon energy moves away from the resonance. Electrons absorbing photons of these energies are fully ejected from the atom, but have a chance of scattering from a nearby neighboring atom and returning. The interference of direct and scattered electrons causes slow oscillations in the absorption with photon energy, and can be used to determine the inter-atomic distances and structures. This region well beyond the absorption edge is examined by EXAFS. A diagram of all three regions is shown in figure 2.5, with each region labelled and coloured.

The advantage of XANES or EXAFS over other spectroscopy techniques lies in their highly localized and element specific nature. Even in a large system the initial core electron is extremely tightly confined to a region of one nuclei, in comparison to the delocalized orbitals in the valence region. As atomic X-ray absorption lines are well spaced in energy (hundreds to thousands of eV apart), particular atomic species and their local environment can be selectively probed one at a time. The initial core state is generally only very weakly perturbed by the environment or any dynamics in the outer shells; it forms an excellent reference for tracking dynamics in the higher lying states when projected onto them by the X-ray photon. XANES and EXAFS also return complementary information. Since oscillations in the EXAFS region correspond to interferences between the outgoing electron and scattering from a neighboring atom, the energy (and thus momentum) of the electron at constructive or destructive interferences encodes the distance to the neighboring atoms. Thus EXAFS acts as a probe of lattice or nuclear structure. These interferences appear at free electron energies of hundreds of eV; given the small lattice spacing of typical materials, this gives a sub-fs response time. Thus time-resolved EXAFS can in

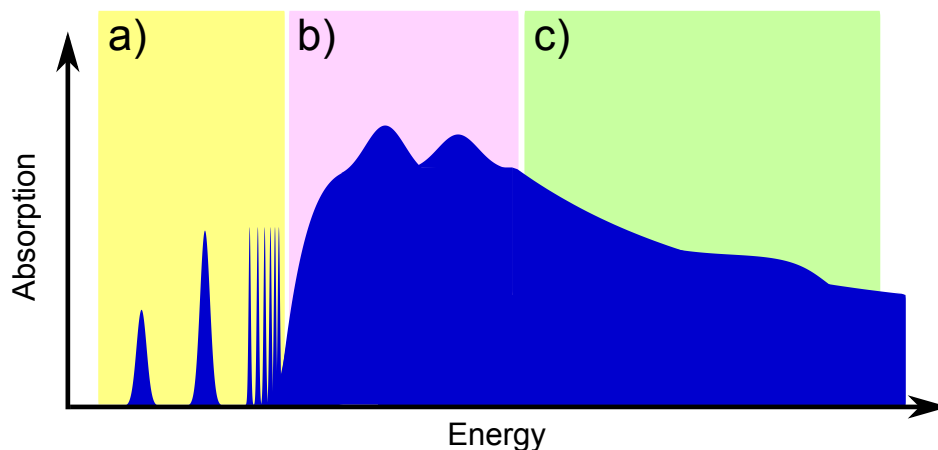


Figure 2.5: Illustration of an SXR absorption spectrum. a) Pre-edge structure in yellow, relates to bound-bound transitions. b) Near-edge structure in pink, corresponds to quasi-bound transitions. c) Post-edge structure in green, from ionized electrons scattering off neighbouring atoms.

principle measure structural dynamics on the sub-fs timescale. Post-edge XANES spectroscopy is complicated by the multiple scatterings, which make analysis complex and time consuming. Furthermore the scattering corresponds to slow free electrons, decreasing the potential temporal resolution to the femtosecond scale. However, the pre-edge region is a relatively clear measure of hole dynamics, where excitation can only occur into partially or fully vacant orbitals in an instantaneous transition. This allows phenomena such as charge migration or transfer to be probed sensitively and locally simply by tracking the amplitudes of pre-edge transition peaks as a function of time [49]. In principle the nuclear states will also be encoded onto these peaks according to the Franck-Condon principle, but in practice these states are only sufficiently well separated to resolve in a few simple systems, most notably N_2 [50].

The simple picture presented thus far of either exciting a core electron into a hole or ionizing it and subsequently scattering is complicated by the impact of multi-electron dynamics. The outgoing electron can collide with another electron in the system as it leaves, either exciting the bound electron or ionizing it completely. Even ignoring this possibility, in general ionizing an electron from an inner shell leaves the system in an energetically unfavorable state. A higher lying electron will relax and fall into the potential well, filling the core-hole vacancy. The energy released by this relaxation can either be emitted as a photon (X-ray fluorescence) or be absorbed by the system, in which case a highly excited state could be produced, or another electron could be ionized completely, as shown in figure 2.4b) and c). This secondary ionization is known as an Auger process. All these decay processes have characteristic lifetimes, generally a few femtoseconds, and calculating how they impact the XANES or NEXAFS spectrum is numerically challenging [51].

Despite the challenges associated with multi-electron effects, XANES has been used successfully to track ultrafast dynamics in a wide variety of systems. Spin state dynamics in iron

(II) complexes have been tracked at the timescale of hundreds of femtoseconds at time-sliced synchrotrons, shedding light on the formation of the quintet state [52], and XANES has been used for measuring femtosecond electron rearrangement in the insulator to metal transition of VO_2 [53]. When used with a broadband pulse, all unoccupied or partially occupied states in a XANES spectrum can be probed simultaneously, tracking population across many states. This allows non-radiative decays and non-exponential decays to be tracked, and even the presence of dark states inferred, which is key for the measurement of non-trivial attosecond dynamics, as described in section 2.2. As sources for performing few-femtosecond and attosecond XANES become more widely available it is safe to anticipate time-resolved XANES will grow to have a much broader impact in the future.

2.4 Sub-cycle Dynamics in Strong Laser Fields

Having discussed attosecond dynamics, we now review the necessary steps towards generating attosecond transients. It is often claimed that the fastest controllable events which we can generate are ultrafast light pulses [54]. The output of a Kerr-lens modelocked oscillator is a train of femtosecond duration pulses at megahertz repetition rate; this constitutes a series of controllable, deterministic events which are orders of magnitude faster than can be achieved with electronics or other technologies [39]. The very shortest pulses generated in this fashion can be below 10 fs in duration [55], and with advanced compression techniques pulses of only a few femtoseconds can be generated using the output of these systems [56]. However, with one notable exception [57], the generation of sub-femtosecond pulses through conventional non-linear optical routes has not been possible, despite promising results from Raman sideband generation [58, 59]. In order to study attosecond dynamics, it has therefore been necessary to utilize *sub-cycle* effects, non-linear optical processes which vary strongly not with the pulse envelope, but rather with the electric field of the laser pulse, and thus within an optical cycle.

While other sub-cycle non-linear effects exist [60], by far the most prominent is *tunnel ionization* [61]. Consider an atom exposed to a laser pulse; if the laser field is very strong, but its period is long compared to the timescale of electron motion, it can be treated as a quasi-static contribution to an electron's potential well. Far from the core this field is stronger than the Coulomb attraction, and so the electron is now trapped in a local minimum of the total potential, and quantum mechanically has a finite probability of tunneling through the barrier, as shown in figure 2.6. An electron with binding energy $E = -I_P$, where I_P is the ionization potential, can be thought of emerging from under the barrier with zero kinetic energy at the point where the field and static potential have a potential energy of $-I_P$. As the distance to the crossing point $V(x) + x \cdot E(x) = -I_P$ scales inversely with the electric field, and the probability of quantum-mechanical tunneling is exponential with the width of the barrier, the probability of tunnel-ionization is exponential with the electric field. This provides very strong temporal confinement to the ionization process [61], so that for a pulse

of moderate intensity ($\approx 10^{14}$ W/cm²) and optical wavelength the ionized electron wavepacket has attosecond duration.

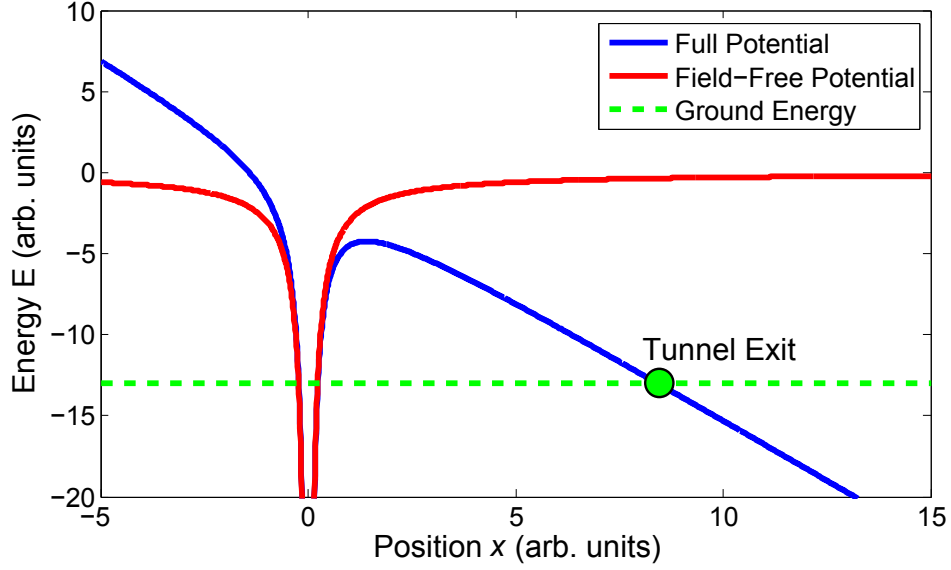


Figure 2.6: Schematic of a Coulomb barrier suppressed by a strong laser field. Bound electrons can tunnel through the suppressed barrier and exit at the zero crossing site.

This quasi-static approach to ionization in strong fields is known as the Keldysh picture [62], after its originator. The validity of the quasi-static tunneling rate is determined by the Keldysh parameter $\gamma = \omega_0 \sqrt{2I_P}/E_0$, where ω_0 is the frequency of the electric field and E_0 is the field strength. The tunneling picture applies when $\gamma \ll 1$, while $\gamma \gg 1$ indicates multi-photon ionization is more accurate. The simple picture of quasi-static tunnel ionization is thus increasingly accurate with stronger fields and longer wavelength lasers. The original Keldysh model has been extensively expanded since, with the Ammosov-Delone-Krainov (ADK) tunneling rate including the structure of hydrogenlike atoms [63], the Perelomov-Popov-Terent'ev (PPT) ionization rate treating the long range Coulomb potential of the atom [64], and the Yudin-Ivanov rate considering sub-cycle non-adiabatic effects [61]. The ADK ionization is given by

$$w_{ADK}(t) = A_{n^*, l^*} B_{l, |m|} I_P \left(\frac{2(2I_P)^{3/2}}{E(t)} \right)^{2n^* - |m| - 1} \times \exp \left(-\frac{2(2I_P)^{3/2}}{3E(t)} \right) \quad (2.4.1)$$

where A and B are functions of the effective principal quantum number n^* , effective angular momentum l^* , actual angular momentum l , and magnetic quantum number m . We can see that the dominant exponential term is universal, not dependent on the structure of the system. The understanding of tunnel ionization, including its temporal nature, has allowed it to be applied as a probe for ultrafast dynamics in a variety of methods, including laser-induced electron diffraction [65], photo-electron holography [66], and atto-clock measurements [67]. Within the scope of this thesis however, tunnel ionization is most important as the first step in high-harmonic generation, and the origin of the temporal confinement which leads to attosecond pulse generation. This aspect will be expanded upon in section 2.5, but first we examine the

impact of the electric field on the generation of attosecond electron bunches.

2.4.1 Carrier-Envelope Phase

When sub-cycle dynamics and effects are driven by fields in which the amplitude varies significantly on a few-cycle timescale, the exact form of that field is extremely important and the CEP becomes important. Recall from equation 2.1.8 that we can factorize a pulse into a slowly varying envelope function and fast oscillating carrier frequency. The phase between these two components is the CEP, and modifies the waveform significantly. Figure 2.7 shows the effect of the CEP on the waveform of a 1.5 cycle pulse, as well as on the ionization rate calculated with the ADK ionization rate. By shifting the CEP by $\pi/2$, the highest power reached by the pulse is different, and ionization is shifted from one strong burst to two equal but weaker bursts. This illustrates clearly the importance of the CEP and the impact it will have on ultrafast measurement.

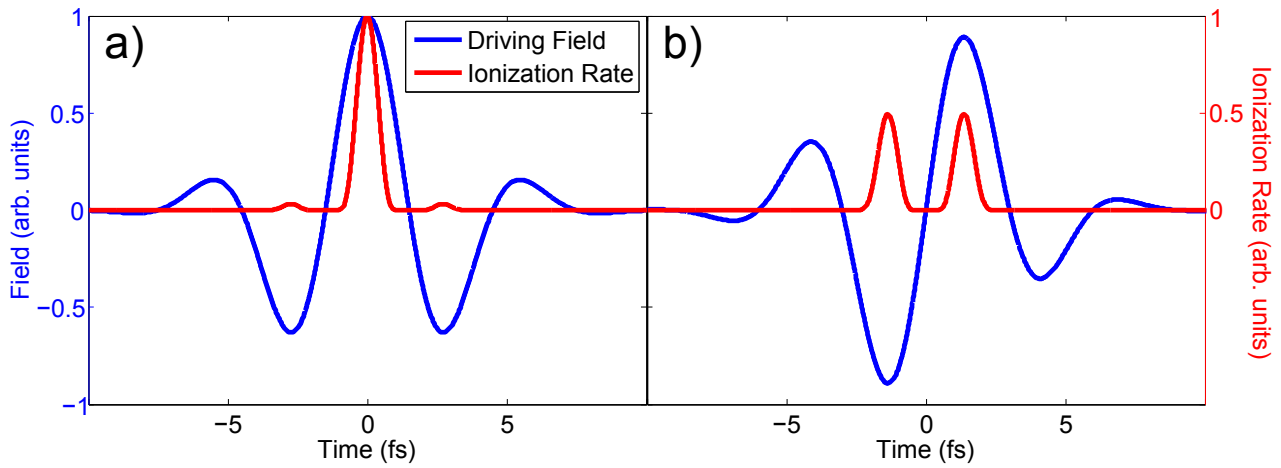


Figure 2.7: Illustrative ionization dynamics for a 7 fs, 1800 nm pulse with peak intensity of 10^{14} W/cm², calculated using the ADK ionization rate. **a)** Ionization rate from a cosine pulse ($\phi_0 = 0$). Electron emission is confined to a single sub-femtosecond burst. **b)** Ionization rate from a sine pulse ($\phi_0 = \pi/2$). Electrons are emitted as two bursts of equal amplitude. The peak of the intensity envelope and period are constant between the two cases.

Unfortunately the CEP of a laser is in general not stable; the difference in phase velocity and group velocity inside a laser cavity causes the CEP to constantly drift as the pulse train travels around the cavity. Stabilizing the CEP is critical to controllable sub-cycle effects. While in the time domain CEP is the offset between the carrier frequency and the intensity envelope, in the frequency domain it appears as the absolute frequency offset [68]. Knowing the absolute frequency allows for extremely precise frequency metrology through the frequency comb structure of a femtosecond oscillator [69]. It is the frequency domain aspect of CEP that has motivated much of the original research in carrier envelope stabilization, and provides us with the methodology required to measure and thus control the CEP offset, *beat-frequency interferometry*. Let us consider the simplest case, $f - 2f$ interferometry. Here an octave-spanning pulse and its second harmonic are interfered; the resulting interferogram encodes the

changes in CEP. In the frequency domain the pulses are given by

$$E_f \propto \sqrt{I_f(\omega)} e^{i[\phi_f(\omega) + \phi_0]}$$

$$E_{2f} \propto \sqrt{I_{2f}(\omega)} e^{i[\phi_{2f}(\omega) + 2\phi_0 + \omega\tau]}$$

where f and $2f$ denote the fundamental and second harmonic, respectively, I is the spectral intensity, $\phi(\omega)$ is the spectral phase, τ is the delay between the two pulses, and ϕ_0 is the CEP. The resulting interferogram has an oscillatory component given by

$$S(\omega) \propto 2\sqrt{I_f(\omega)I_{2f}(\omega)} \cos(\omega\tau - \phi_f(\omega) + \phi_{2f}(\omega) + \phi_0) = 2\sqrt{I_f(\omega)I_{2f}(\omega)} \cos(\Phi(\omega)).$$

Provided the pulse and second harmonic have sufficient bandwidth that there is a spectral region where $I_f(\omega)I_{2f}(\omega)$ is non-zero, i.e. the spectrum is octave spanning, this beat term can be used to extract the CEP [70]. Presuming the time delay and spectral phase vary more slowly with time than the CEP, a condition which is usually satisfied before even considering CEP locking, any change in the phase of these fringes is indicative of an identical change in the CEP, i.e. $\Delta\Phi(\omega) = \Delta\phi_0$. In oscillators, which have predictable but fast changes in CEP, this is used to stabilize the frequency at which the CEP changes, but for low repetition rate, high power systems, this can be used to track changes in CEP on a shot-by-shot basis.

Note that beat frequency interferometry does not determine the value of the CEP unless all other factors are precisely known; in practice this never occurs, and $f - 2f$ interferometers are used exclusively for tracking changes in the CEP, $\Delta\phi_0$. Other methods do exist for measuring CEP exactly, such as stereo above-threshold ionization (stereo-ATI), based on the variation of strong-field ionization with the electric field amplitude [71, 72], or electro-optic sampling (EOS), which uses the vector response of the electro-optic effect [73, 74]. EOS however relies on the existence of an even shorter sampling pulse, and is generally limited to longer wavelength sources (terahertz radiation), while stereo-ATI requires a photoelectron detection system and high intensities, reducing its utility as a live diagnostic. Half-cycle cutoffs in HHG also explicitly encode the CEP via the spectral dependence on trajectories and the strong-field ionization rate [75]. An HHG system has similar drawbacks as stereo-ATI (complexity, high intensity) as a diagnostic, but viewed inversely, CEP control is important for the temporal-spectral control in HHG. For these reasons beat-frequency interferometers continue to be the standard technique for carrier-envelope phase stabilization.

2.5 High Harmonic Generation: The Single Atom Response

In section 2.4 it was shown that strong-field ionization from few-cycle laser pulses can be used to generate electron bunches with extremely strong temporal confinement. The attosecond nature of the electron emission can be used to track attosecond dynamics, but the use of strong-field ionization for ultrafast metrology has numerous drawbacks and is somewhat limited in scope [8]. In this section we describe the phenomenon of *high harmonic generation* (HHG), a process by which atoms or molecules illuminated by strong-laser fields emit highly coherent, high frequency radiation in the form of attosecond pulses. A schematic of an HHG spectrum is shown in figure 2.8; a rapid drop in flux at low orders following the power-law scaling of perturbation theory is seen, followed by a region of almost constant spectral intensity. Finally the harmonics decay rapidly in region known as the cutoff. HHG and the resulting attosecond pulses provide a route towards optical attosecond measurements, and have a deep connection to strong-field ionization. In this section I describe the response of a single atom or molecule to the strong fields used in HHG, and discuss how this results in the emission of high energy attosecond pulses. In section 2.6 the macroscopic phase-matching conditions for high harmonics are described.

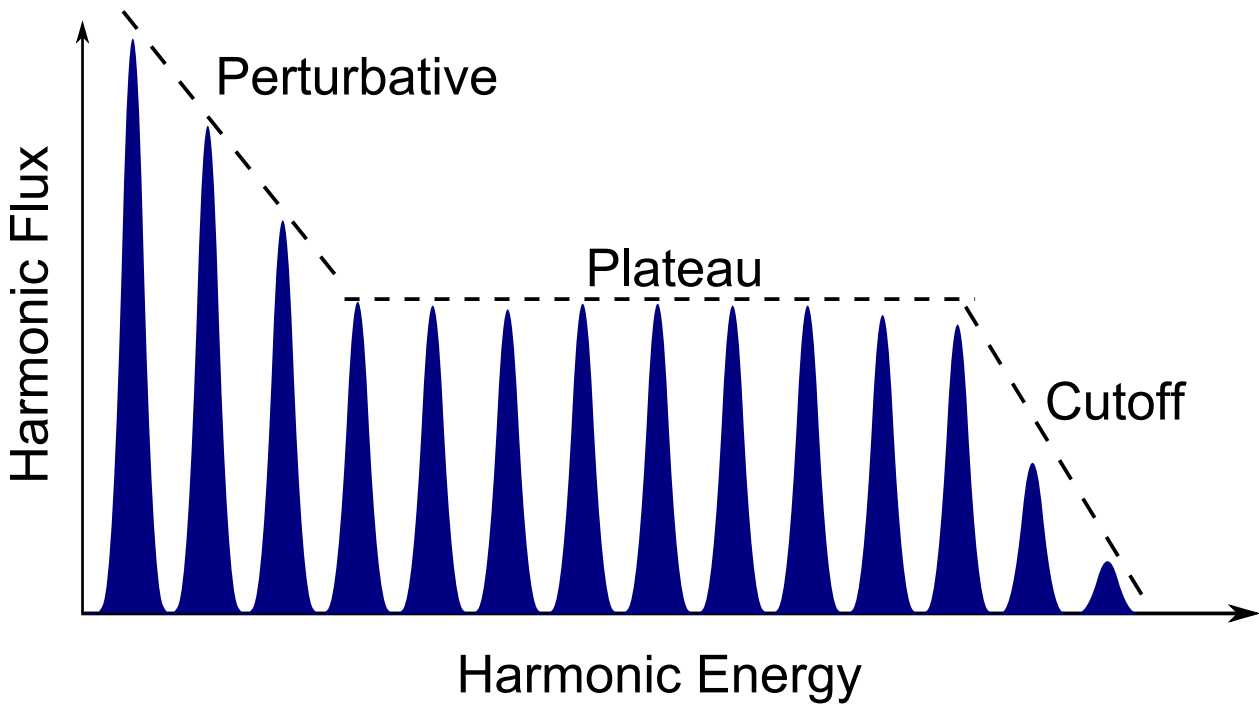


Figure 2.8: Representation of a high harmonic spectrum. At low energies the harmonic flux decreases rapidly according to a perturbative power law, and is then constant over a large energy region known as the plateau. Finally, the harmonics decay rapidly at a region known as the cutoff.

2.5.1 The Three Step Model

In perturbative non-linear optics, the electrons inside a sample respond to the presence of an external driving field and move inside the potential well they are bound in. If the driving field is particularly weak, they are only displaced small amounts from the minimum of the potential well. The potential can be approximated as harmonic, which leads to linear optics.⁴ If the electron is driven more strongly, it experiences the anharmonicity of the potential well, which is reflected in the dipole response of the system and gives rise to perturbative non-linear optics [20]. However, as seen in figure 2.8, the deviation from the power-law at higher harmonics is a clear sign of non-perturbative non-linear optics. In HHG the driving field is so strong that electrons are driven from the potential well entirely. So while perturbative non-linear optics is governed by the bound-bound transition of a system, HHG can be thought of as the non-linear optics of the bound-continuum (unbound) transitions.

HHG is best understood through the semi-classical three step model [11], in which the three steps are:

1. Ionization
2. Propagation
3. Recombination.

The “semi” in “semi-classical” arises from the first step, in which the system ionizes through tunnel ionization, a quantum mechanical process. Once ionized, the electron follows a classical trajectory in the propagation step. For a linearly polarized field $E = E_0 \cos(\omega_0 t)$, where E_0 is the field strength and ω_0 is the field frequency, in a one dimensional model the electron obeys the equation of motion

$$\ddot{x} = -E_0 \cos(\omega_0 t) \quad (2.5.1)$$

with initial conditions $\dot{x}(t_i) = 0$ and $x(t_i) = 0$, where t_i is the time of ionization. Note that more advanced variations of the three step model can place the electron at the zero potential exit of the tunneling barrier, but this is not necessary for this exposition, and can lead to some practical problems at low field strengths [76]. With $x(t_i) = 0$, we obtain

$$\dot{x}(t) = -\frac{E_0}{\omega_0} [\sin(\omega_0 t) - \sin(\omega_0 t_i)] \quad (2.5.2)$$

$$x(t) = \frac{E_0}{\omega_0^2} [\cos(\omega_0 t) - \cos(\omega_0 t_i)] + \frac{E_0}{\omega_0} \sin(\omega_0 t_i)(t - t_i). \quad (2.5.3)$$

The key observation is that, for certain birth times, the electron returns to its initial position and can re-collide with the atom or molecule it came from, provided that the final term, which

⁴This is known as the Lorentz model.

is a uniform drift away from the initial position, does not dominate. Note that we have neglected the influence of the magnetic field entirely, which is to say we ignore the Lorentz force $\vec{B} \times \vec{r}$. This force acts to drive the electron monotonically away from the core as it propagates and reduces the probability of returning to the initial position. However, since $|E| = |B|/c$, this term only becomes relevant when the velocity of the electron approaches the speed of light, which occurs only for longer wavelengths and higher field strengths than considered in this work.

The last step, recombination, occurs when the electron returns to the ion and is recaptured, releasing its kinetic energy as a high energy photon. By numerically finding the roots of equation 2.5.3 the recombination time can be determined, and from equation 2.5.2 the kinetic energy at return can be determined. The photon emitted will then have an energy of $\dot{x}^2(t_r)/2 + I_p$, where t_r is the return time. The three step model predicts that the maximum photon energy emitted is $3.17U_p + I_p$ in agreement with both theory and experiment [11], where $U_p = E_0^2/4\omega_0^2$ is the ponderomotive potential, the mean energy of a free electron in a laser field.

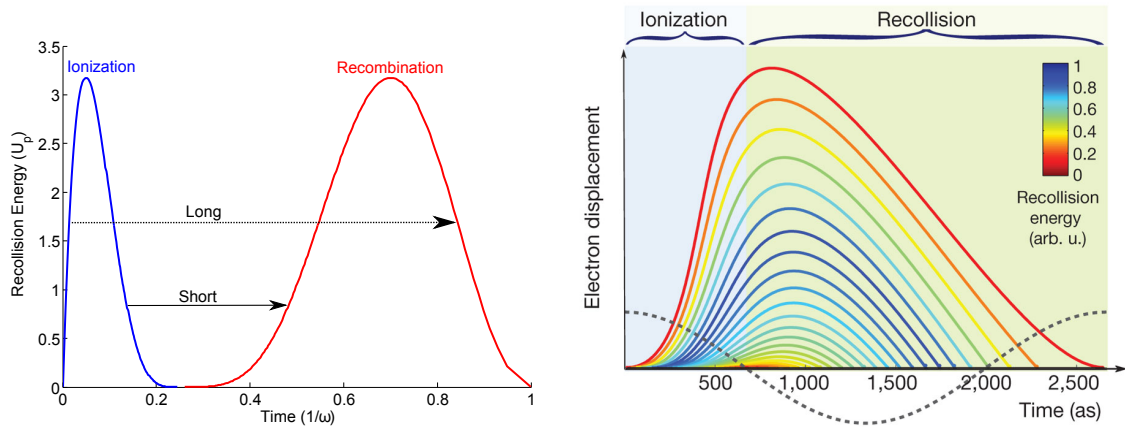


Figure 2.9: *Left:* Classical ionization and recombination times as a function of the recollision energy. Two distinct classes of trajectories are shown, the short and long trajectories, which exhibit opposite chirps. *Right:* Trajectories in real space as a function of time, with colours indicating the energies. The chirp of short and long trajectories can clearly be seen. Reprinted by permission from Macmillan Publishers Ltd: Nature 485, 343-346, copyright 2012 [77].

Figure 2.9 shows the relation between birth times, recollision times, and recollision energies in the classical picture. The first observation is that the emission of the highest energy harmonics is sharply peaked in time. In a multi-cycle pulse this leads to a train of attosecond pulses separated by one half of the laser period, as the recollision process repeats every half cycle. The interference of these pulses leads to the emission of discrete harmonics in the frequency domain, hence the term high harmonic generation. If the driving pulse is sufficiently short that only a few bursts contribute, spectral filtering of the highest energies results in isolated attosecond pulses in a scheme known as amplitude gating; spectral filtering can be achieved by the use of absorptive metal foils [78]. The second observation is that the emission is chirped; that is to say, different energies are emitted at different times in a straightforward increasing or decreas-

ing manner. This chirp negatively impacts the pulse duration of the emitted attosecond pulse, but is extremely important in high harmonic spectroscopy, where it provides an intrinsic link between emission energy and time delay. This aspect is further expanded in chapter 4. Finally, for each energy, there are two distinct trajectories that contribute to it, one short trajectory and one long trajectory, which coalesce at the highest energy harmonics. These two trajectories have different chirps and lag the driving field by different times, i.e. have a different phases of emission.

From the classical trajectory analysis several extremely important scaling laws can be inferred [79]. The first is that the electric field introduces only an overall scaling in equations 2.5.3 and 2.5.2 - thus the electric field does not change the timing of the various trajectories, though it does change the distance travelled in the continuum (scaling $\propto E_0$) and the recollision energy (scaling $\propto E_0^2$). The frequency conversely has more effects. The recollision energy scales $\propto \omega^{-2}$, but perhaps more importantly the wavelength controls the timing of the trajectories, which scales as $\propto \omega^{-1}$. This means the returning electron chirp (gradient of energy with respect to time) decreases linearly with the driving wavelength - longer wavelength driving fields lead to higher photon energies with less chirped emission. This makes longer wavelengths highly promising for driving shorter attosecond pulses at higher energies. However, the electron spends more time in the continuum, and thus off-axis momentum components, ignored in the treatment above, become increasingly important, decreasing the chance of recollision. Increasing the field E_0 similarly increases energy, but causes an almost insurmountable issue in the highly increased ionization rate, leading to ground state depletion and poor phasematching, both of which will be discussed later.

2.5.2 The Strong Field Approximation

While the semiclassical three step model gives a large amount of intuition for HHG, quantitative, and for many features qualitative, predictions of harmonic emission require a quantum mechanical treatment of the light-matter interaction.⁵ This can be done by solving the Schrödinger equation directly, or through an approximate method known as the strong field approximation (SFA). In both cases two approximations are made initially, the *single active electron* (SAE) and the *dipole* approximations. The SAE approximation assumes that, as tunnel ionization is exponentially less likely for more tightly bound electrons, dynamics can be accurately treated by only considering the outermost valence electron, and treating all other electrons as contributing only through an effective potential. The dipole approximation assumes that the external driving field can be treated as uniform across the entire spatial region of interest [80]. This approximation is justified as, even for the highest intensities in HHG, the maximum distance traveled by a free electron in the field away from the atom is still negligibly small compared to the wavelength of the driving laser. In the transverse direction the spatial variation in field

⁵Only first-quantization is necessary, the laser field can be treated classically.

strength is even slower, given by the focal tightness of the driving laser, which is typically an order of magnitude larger than the wavelength.

With these approximations, the Schrödinger equation then reads as

$$\frac{-i\partial|\Psi(t)\rangle}{\partial t} = \left(\frac{\hat{p}^2}{2} + V(\vec{r}) - \vec{E}(t) \cdot \vec{r}\right)|\Psi(t)\rangle \quad (2.5.4)$$

where we have used atomic units. In this form the Schrodinger equation is numerically tractable, and can be solved relatively simply through simple propagation methods such as the split operator [80]. However, it is still numerically time consuming and the results are often difficult to interpret. In many cases, it is better to use the SFA (also known as the Lewenstein model), an approximate method shown to not only allow quantitative predictions, but also to recreate the physical intuition of the three step model [81]. In addition, the Schrödinger equation within the SAE approximation ignores all internal structure and dynamics of the system, which can be included in the SFA through the choice orbitals and dipole matrix elements, as will be seen.

We begin by applying the *strong field approximation*, from which the model derives its name. In the SFA one assumes the system can be accurately treated considering only the ground and continuum states, and that the evolution of the continuum states is dominated by the laser field. The condition for these approximations to be valid is the same as for tunnel ionization, $\gamma \ll 1$. Neglecting the contribution of bound excited states, we write the wavefunction as

$$|\Psi(t)\rangle = e^{iI_p t} [g(t)|g\rangle + \int d^3\vec{p} f(\vec{p}, t)|\vec{p}\rangle] \quad (2.5.5)$$

where $|g\rangle$ denotes the ground state and $|\vec{p}\rangle$ denotes a continuum momentum eigenstate, i.e. $[\frac{\vec{p}^2}{2} + V(r)]|\vec{p}\rangle = \frac{p^2}{2}|\vec{p}\rangle$. These continuum eigenstates are not yet given any specific form, and are expected to generally be complicated near the core. We have additionally factored out the fast oscillations of the ground state from its bound energy; $g(t)$ thus denotes only the field induced population changes of the ground state. This trial solution can be substituted back into the Schrödinger equation. By taking the overlap of the resulting equations with $|g\rangle$ and $|\vec{p}_2\rangle$, we obtain two coupled differential equations:

$$ig'(t) = \langle g|\vec{E}(t) \cdot \vec{r}|g\rangle g(t) + \int d^3\vec{p} f(\vec{p}, t) \langle g|\vec{E}(t) \cdot \vec{r}|\vec{p}\rangle \quad (2.5.6)$$

$$if'(\vec{p}_2, t) = (I_p + \frac{p_2^2}{2})f(\vec{p}_2, t) + \langle \vec{p}_2|\vec{E}(t) \cdot \vec{r}|g\rangle + \int d^3\vec{p} \langle \vec{p}_2|\vec{E}(t) \cdot \vec{r}|\vec{p}\rangle f(\vec{p}, t) \quad (2.5.7)$$

Here we make the second approximation, by setting

$$\langle \vec{p}_2|\vec{r}|\vec{p}\rangle = -i\delta(\vec{p} - \vec{p}_2)\nabla_p + G(\vec{p}, \vec{p}_2) \approx -i\delta(\vec{p} - \vec{p}_2)\nabla_p, \quad (2.5.8)$$

which is to say we formally neglect continuum-continuum transitions (scattering). Here ∇_p is

the gradient in momentum space. Higher order terms of the scattering matrix $G(\vec{p}, \vec{p}_2)$ can be re-introduced as perturbations on the zeroth order solution, if necessary. This is also equivalent to treating the continuum wavefunctions $|\vec{p}\rangle$ as Volkov state plane waves, eigenstates of a free particle in an oscillating electric field.

After making this approximation, equation 2.5.7 becomes a linear partial differential equation, and can be transformed into an ordinary differential equation (ODE) through the method of characteristics [70]. This ODE is simply solved through the application of integrating factors, and yields an equation for the continuum population of

$$f(\vec{p}, t) = -i \int_{-\infty}^t dt_b g(t_b) \vec{E}(t_b) \cdot \vec{d}(\vec{p} + \vec{A}(t_b)) e^{-iS(\vec{p}, t, t_b)} \quad (2.5.9)$$

where $\vec{A}(t)$ is the vector potential of the laser field, $\vec{d}(\vec{p}) = \langle g | \vec{r} | \vec{p} \rangle$ is the dipole moment between the continuum and ground state, and $S(\vec{p}, t, t_b) = \int_{t_b}^t dt' I_p - \frac{1}{2}(\vec{p} + \vec{A}(t'))^2$ is known as the action. It gives the phase accumulated by the electron in the continuum, under the action of the laser field.

From this point we can calculate the dipole response, which will determine the emission of harmonics and act as a source term for macroscopic field propagation methods. The dipole moment is given by

$$\langle \Psi | \vec{r} | \Psi \rangle = -i \int d^3\vec{p} \int_{-\infty}^t dt_b g^*(t) \vec{d}^*(\vec{p} + \vec{A}(t)) g(t_b) \vec{E}(t_b) \cdot \vec{d}(\vec{p} + \vec{A}(t_b)) e^{-iS(\vec{p}, t, t_b)} + c.c. \quad (2.5.10)$$

This form is not significantly easier to deal with than the Schrodinger equation itself. However, we can make a very significant simplification by the principle of stationary action. The integral over momentum has two components, a slow variation of the dipole moment and a fast oscillation in the exponential factor. The fast oscillation of this phase factor means most contributions average out, and we obtain significant contributions to the integral only when the exponential factor is slowly varying, i.e. at points of stationary phase. We can thus reduce the integral to a Gaussian integral over this region of phase. After performing this integration over momentum, the equation reduces to

$$\langle \Psi | \vec{r} | \Psi \rangle = -i \int_{-\infty}^t dt_b \left(\frac{2\pi}{t - t_b} \right)^{3/2} \vec{d}^*(\vec{p}_{st} + \vec{A}(t)) g(t_b) \vec{E}(t_b) \cdot \vec{d}(\vec{p}_{st} + \vec{A}(t_b)) e^{-iS(\vec{p}_{st}, t, t_b)} + c.c. \quad (2.5.11)$$

where $\vec{p}_{st} = \frac{-1}{t - t_b} \int_{t_b}^t dt' \vec{A}(t')$ is the stationary momentum. This is the full strong field approximation or Lewenstein model [81]. The key factor is that there is now only one integral, over time. The stationary momentum and action can be integrated previously. At this point the model is fast calculable numerically, and can be solved analytically for the case of some potentials.

Note that the integral over time can also be solved by the stationary phase method and leads to the so-called quantum orbit picture, as the resulting solutions take the form of complex classical trajectories [82]. The quantum orbit model is confusingly often referred to as the strong field approximation as well. The quantum orbit model has the advantage of offering a great deal of physical insight due to its trajectories picture, but suffers from greatly increased analytical complexity and, while slightly faster to compute numerically, requires a great deal of care to avoid performing the integrations in the complex plane incorrectly [21]. We will only look at the stationary phase points, which are required to draw the connection to the classical three-step model. For this, we need to move to the dipole moment in frequency space by Fourier transforming equation 2.5.11. We re-label the time t as t_r , for reasons which will become clear momentarily, and factor the $e^{i\omega t_r}$ of the Fourier transform into the action $e^{iS(\vec{p}_{st}, t_r, t_b)}$. The action in frequency space then takes the form $S_\omega(\vec{p}, t_r, t_b) = \int_{t_b}^{t_r} \frac{(\vec{p} + \vec{A}(t'))^2}{2} + I_p - \omega t_r$. The three equations for the saddle points over $\vec{p}$, t_r , and t_b are

$$\nabla_{\vec{p}} S_\omega(\vec{p}, t_r, t_b) = \vec{r}(t_r) - \vec{r}(t_b) = 0 \quad (2.5.12)$$

$$\frac{\partial S_\omega(\vec{p}, t_r, t_b)}{\partial t_r} = \frac{p(t_r)^2}{2} + I_p - \omega = 0 \quad (2.5.13)$$

$$\frac{\partial S_\omega(\vec{p}, t_r, t_b)}{\partial t_b} = \frac{p(t_b)^2}{2} + I_p = 0. \quad (2.5.14)$$

The first equation shows the saddle point of momentum occurs when the electron returns to the point at which is born at the time t_r . This allows us to associate t_r to the return time of the trajectory when the free electron recollides. The second stationary phase point says the energy of the photon emitted ω is given by the kinetic energy at the time of return, plus the ionization potential. These two conditions are exactly in keeping with the classical three step model, and justify the trajectory picture. The last term, the saddle point over birth times, contains the quantum character, as it necessitates a negative kinetic energy at birth. This is consistent with the concept of tunneling, as under a tunneling barrier a particle would have to have negative kinetic energy, and thus a complex velocity. This leads to complex orbits in the quantum orbit picture, allowing for interferences and the true quantum nature of HHG to be elucidated [81].

Here we can make some extremely important observations which come from the SFA model but are not readily apparent in the classical picture. In equation 2.5.11, the population of the ground state $g(t)$ occurs at two separate times, ionization (t_b) and observation (t or t_r). From the stationary phase analysis, we know this will be dominated by the contribution at the time of return. If, in a sufficiently strong field, the ground state population is significantly decreased through ionization before the recombination step, HHG is effectively shut off. This provides a hard limit to the intensity which can be used for HHG, providing the strongest motivation for using longer wavelengths to increase the photon energies emitted as opposed to increasing intensity. The second observation is that, as $g(t)$ is purely real in the SFA, all dynamical phase

information is carried in the stationary phase term $S_\omega(\vec{p}_{st}, t_r, t_b)$.⁶ The form of the stationary phase is, to first order,

$$S_\omega(\vec{p}_{st}, t_r, t_b) \approx -\frac{I_0}{4\omega_0}[t_r(\omega) - t_b(\omega)], \quad (2.5.15)$$

where I_0 is the intensity of driving field [84, 85]. Since the birth and recombination times vary only weakly with the intensity, we can treat the phase as $S_\omega(\vec{p}_{st}, t_r, t_b) \approx \alpha_{\omega,i}I$, where $i = s, l$ denotes either the short or long trajectory contribution [85]. This can be understood in an intuitive picture, since in the SFA a given harmonic order is generated by a fixed recollision energy. As the intensity increases, an electron of a fixed return energy spends less time in the continuum - it is born later, and accelerates faster. Thus, the time delay between the emitted radiation and the fundamental is decreased, and the phase relationship changes. It has been shown that the $\alpha_{\omega,i}$ values have only a weak dependence on the harmonic order within the plateau and cutoff regions, but change rapidly between the two. Furthermore they are different for the long and short trajectories, leaving in practice four cases to consider. Since $g(t)$ is purely real, we can use the simple intensity-dependent dipole phase term alone for calculations of phase matching conditions, as will be discussed later.

2.6 High Harmonic Generation: The Macroscopic Response

2.6.1 Laser Field Propagation

The high harmonic response calculated from the Schrödinger equation or the SFA gives the response of a single atom to a strong laser field, but an important asset of HHG is that it is fully coherent. While the response of a single atom or molecule is very weak, the HHG signal can build up coherently as the driving laser pulse propagates through the medium and result in a macroscopically detectable signal [79]. However, the emission can be heavily modified during this propagation. Here the fundamental laser is distorted by dispersion from the medium, the harmonics are absorbed by other atoms, and harmonics emitted at different points and times in the medium sum to generate the observed macroscopic signal. The propagation of the full field is governed by Maxwell's wave equation

$$\frac{\partial^2}{\partial z^2}\vec{E} + \nabla_\perp^2\vec{E} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{E} = \frac{1}{\epsilon_0 c^2}\frac{\partial^2}{\partial t^2}\vec{P} \quad (2.6.1)$$

⁶In principle the ionization dipole matrix element could also introduce dynamic phase shifts, but measurements of the phase of attosecond pulses [83] and analysis of the TDSE [80] show that the semi-classical action does indeed accurately characterize the phase. This would not necessarily hold around a material resonance, where small changes in the momentum $\vec{p}_{st} + \vec{A}(t_b)$ would result in large changes of the dipole moment.

where $\vec{P}$, the medium polarization, includes the dipole moment from the SFA or TDSE which acts as a source term for high harmonics. It is most common at this point to perform two actions, a coordinate transformation and an approximation. The first is to transform to the “co-moving frame”, $\tau = t - z/v_g$ and $\eta = z$, where the frame itself ‘moves’ at the group velocity of the pulse v_g (alternatively this can be viewed as going to the local time frame of the pulse), as for most purposes we are concerned only with evolution of the pulse itself. The approximation is the “slowly evolving wave approximation”, where we discard the term $\frac{\partial^2}{\partial z^2} \vec{E}$ from the differential equation. There is still a $\frac{\partial}{\partial z}$ term that was added during the coordinate transform, so this is not discarding propagation, but rather stating that changes to the waveform take place on a length scale longer than one wavelength, an excellent approximation for all but the most dispersive or highly ionized media. This leaves the wave equation as

$$\frac{\partial}{\partial z} \vec{E} - \frac{v_g}{2} \nabla_{\perp}^2 \int_{-\infty}^{\tau} d\tau \vec{E} = \frac{-2\pi}{v_g} \frac{\partial}{\partial \tau} \vec{P} \quad (2.6.2)$$

which is known by several names, including the Forward Maxwell Equation (FME), as removing the second derivative with respect to z also discards reflections. Finally, it is normal to separate the propagation of the high harmonics from that of the fundamental, where the fundamental acts as a source term for the harmonics but the two fields do not otherwise interact. This ignores the possibility of depletion of the fundamental or recombination of the harmonics, but HHG is generally so inefficient that this is unlikely to become a problem.

When treated separately, each field can be subjected to further approximations. In particular the frequency of the harmonic field is too high to be affected by the generated plasma, and cannot drive non-linearities of its own. In contrast, the fundamental drives and is strongly distorted by plasma generation, and can generate phase gradients through the Kerr effect, but is generally not strongly absorbed or dispersed by the neutral medium. The two waves can then be treated as

$$\frac{\partial}{\partial z} \vec{E}_l - \frac{v_g}{2} \nabla_{\perp}^2 \int_{-\infty}^{\tau} d\tau \vec{E}_l = \frac{-2\pi}{v_g} \frac{\partial}{\partial \tau} \vec{P}_l \quad (2.6.3)$$

$$\frac{\partial}{\partial z} \vec{E}_H - \frac{v_g}{2} \nabla_{\perp}^2 \int_{-\infty}^{\tau} d\tau \vec{E}_H = \frac{-2\pi}{v_g} \frac{\partial}{\partial \tau} \vec{P}_H(E_l) \quad (2.6.4)$$

where E_l is the fundamental laser and E_H are the harmonics, P_l neglects neutral gas dispersion, and P_H neglects plasma dispersion and other non-linearities. These wave equations are quite complicated, and given the inherent relationship between harmonic generation, plasma generation, and fundamental pulse distortion, the macroscopic response of high harmonic generation is necessarily a highly coupled problem. The most obvious approach to dealing with this complexity is to solve the problem numerically. However, numerical solutions generally offer very little in the way of physical insight or scaling laws, and for this reason we turn to a very simple picture of phase matching and harmonic generation.

2.6.2 Phase Matching of High Harmonics

High harmonics are emitted throughout the medium as the fundamental beam propagates through it, adding coherently. In order for macroscopic buildup to occur, the emission must be in phase with the propagating harmonic field i.e. $\phi(\omega, z) = \phi(\omega, z + \Delta z)$. In perturbative harmonic generation this is often expressed in terms of the $\vec{k}$ -vectors for the fundamental and harmonic fields, since the phase is determined by the $\vec{k}$ -vector via $\phi(z + \Delta z) = \phi(z) + k_z(\omega)\Delta z$. Furthermore in a perturbative non-linear optical process the generated signal inherits the phase of generating field, so if the difference in the $\vec{k}$ -vectors of the fundamental and harmonic fields is small then the generated and propagating fields build up coherently [20].

The problem is that the phase of the emitted radiation in HHG is intensity dependent, so the phase imparted by the fundamental field varies throughout the focus. Simple analysis in terms of $\vec{k}$ -vectors does not capture this aspect, and macroscopic buildup may not occur. It was pointed out by Balcou *et al.* that we can assign an *effective* $\vec{k}$ -vector to the intensity-dependent atomic response [84]. The intensity-dependent phase is used to define $\vec{K}_{\omega, \omega_0}(r, z) = \nabla \Phi_{\omega, \omega_0}(I(r, z))$, where Φ_{ω, ω_0} is the single atom phase of emission at frequency ω driven by a field at frequency ω_0 , and $I(r, z)$ is the intensity of the driving field. We can use the atomic dipole phase from equation 2.5.15 to draw a map of $\vec{k}$ -vectors for a Gaussian beam passing through a focus [85]. The same idea of effective $\vec{k}$ -vectors can be applied to the phase shift of a Gaussian beam as it passes through a focus, known as the Gouy phase. Figure 2.10 shows the distribution of $\vec{k}$ -vectors for the generating pulse as it goes through focus, and the effective $\vec{k}$ -vectors of the dipole response from the intensity dependent phase through the same region.

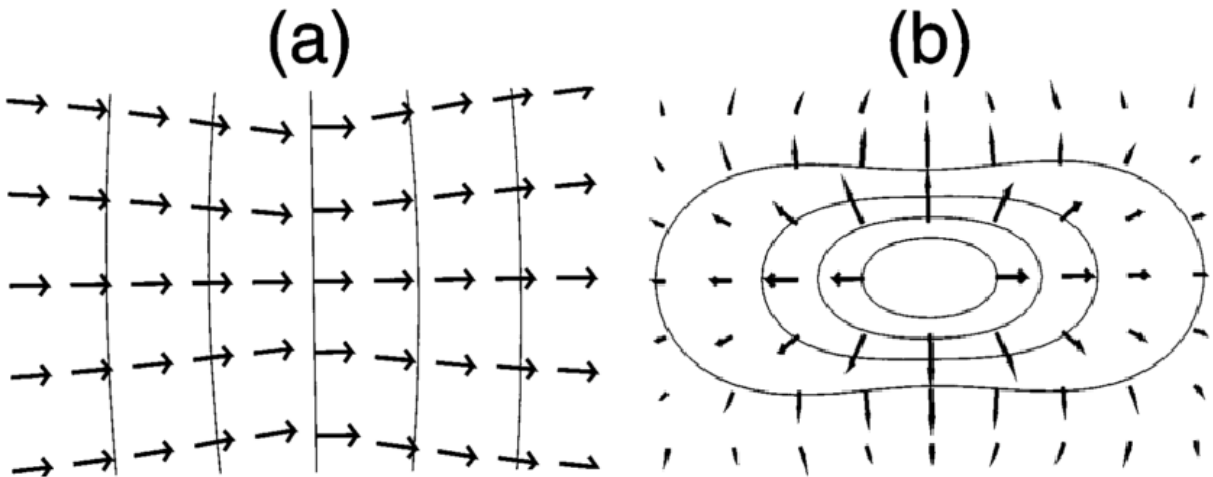


Figure 2.10: a) Spatial distribution of $\vec{k}$ vectors of a Gaussian beam passing through a focus. b) Spatial distribution of atomic $\vec{K}$ vectors arising from the intensity dependent phase of the single atom response in HHG. Reprinted figure with permission from Balcou *et al.*, PRA 55, 3204-3210, 1997 [84]. Copyright 1997 by the American Physical Society.

Balcou *et al.* used these ideas to develop a simple picture of phase matching in HHG, though it is immediately apparent that due to these spatially varying effects phase matching will only be possible at specific points in the beam for any given configuration. We can break the phase matching condition up into a number of constituent terms as follows:

$$\begin{aligned}\Delta\vec{k}(\omega) &= q\vec{k}_{\omega_0} + \vec{k}_{\omega} + \vec{K}_{\omega,\omega_0} \\ &= q(\vec{k}_{\omega_0,g} + \nabla\Phi_{Gouy} + \vec{k}_{\omega_0,p}) - \vec{k}_{\omega,g} + \vec{K}_{\omega,\omega_0}\end{aligned}\quad (2.6.5)$$

where $q = \omega/\omega_0$ is the harmonic order and $\vec{k}_{\omega}$ is its $\vec{k}$ -vector in the medium, $\vec{k}_{\omega_0,g}$ is the $\vec{k}$ -vector of the fundamental in the neutral material, Φ_{Gouy} is the Gouy phase of the fundamental, and $\vec{k}_{\omega_0,p}$ is the $\vec{k}$ -vector of the fundamental due to the free electrons from plasma formation. When $\Delta\vec{k}(\omega) = 0$ the emission is phase matched, which can be achieved by having the harmonic emitted into a direction other than on-axis. Indeed the harmonic emission from the long trajectories is most often emitted completely off-axis, with much greater divergence [84].

Equation 2.6.5 is expressed as a completely static quantity, a picture which will only be accurate when the temporal evolution of the fundamental pulse can be ignored. Given that HHG necessarily involves short pulses with high intensities, which are highly sensitive to dispersion and necessitating strong non-linearities, this can only be satisfied by very short interaction regions where these effects are negligible. The model could be improved through a suitable spatio-temporal dependence of the fundamental and harmonic $\vec{k}$ -vectors [86,87], but this would dramatically increase the complexity and reduce the intuition provided by the model.

The geometric (Gouy) phase and atomic dipole phase change sign through the focus of the pulse, meaning the relative position of the medium and the focus can dramatically affect the phase matching of the harmonics [84]. The neutral material contribution is always positive while the plasma contribution is always negative. Furthermore, as plasma can only be created at the expense of ionizing the neutral medium, these two contributions are intimately linked through the intensity of the laser pulse. The contribution of the neutral gas dispersion is given by

$$\Delta k_g(\omega) = (1 - \eta)P\frac{\omega}{c}[n(\omega) - n(\omega_0)], \quad (2.6.6)$$

where P is the pressure of the gas, η is the ionization fraction, and $n(\omega)$ is the refractive index defined at the appropriate unit of pressure. The ionization contribution is given by

$$\Delta k_p(\omega) = -2\pi c P N_a \eta r_e \left(\frac{\omega}{\omega_0^2} - \frac{1}{\omega} \right) \quad (2.6.7)$$

where N_a is the number density at one unit of pressure and r_e is the classical electron radius [88]. Given that $\omega \gg \omega_0$ for harmonic frequencies, it is customary to drop the $1/\omega$ term and keep only the ω/ω_0^2 term, which correspond to the plasma acting on the harmonic radiation and

the fundamental, respectively. Substituting these expressions back into 2.6.5, we can obtain an expression for the phase matching pressure [89, 90],

$$P_{PM}(\omega) = \frac{-q\nabla\Phi_{Gouy} - \vec{K}_{\omega,\omega_0}}{(1-\eta)\frac{\omega}{c}[n(\omega) - n(\omega_0)] - 2\pi cN_a\eta r_e(\frac{\omega}{\omega_0^2} - \frac{1}{\omega})}. \quad (2.6.8)$$

It was pointed out by the Kapteyn-Murnane group that, in a hollow waveguide, the intensity does not change in the propagation direction. Instead of a spatially varying Gouy phase there is then only a constant geometric phase given by the waveguide [88, 91], so phasematching is determined only by the ionization fraction and the gas pressure. Since phasematching is only possible if the denominator is positive, it is possible to derive a critical phasematching ionization fraction η_c where $\Delta k_p(\omega) = \Delta k_g(\omega)$, where the frequency dependence of the harmonics only appears in the refractive index. They obtained critical ionization fractions for He, Ne and Ar of 0.5%, 1% and 5%, respectively [90]. This is not to say higher ionization levels cannot result in efficient phase matching, but these schemes rely on strongly non-adiabatic pictures of coherent buildup of HHG during the laser pulse which do not lend themselves to intuitive pictures; the interested reader is referred to the following for details: [92–94].

2.6.3 Absorption Limited High Harmonic Generation

One important concept in phase matching HHG is that of absorption limited generation. In general the generating medium in HHG also absorbs the emitted harmonics quite strongly. The obtainable flux then saturates at the limit supported by the absorption length. We can define two length scales, the coherence length $L_{coh} = \pi/\Delta k(\omega)$, the length over which harmonics build up coherently, and the length over which harmonics are absorbed and their intensity decreased by a factor of e , $L_{abs} = 1/(2\alpha)$, where α is the absorption coefficient. The growth of the field is then given by

$$I(\omega) \propto \rho^2 \frac{1 + e^{-2\alpha L} - 2e^{-\alpha L} \cos(\Delta k_z L)}{\alpha^2 + \Delta k_z^2} \quad (2.6.9)$$

where L is the medium length and ρ the density [88]. If perfect phase matching were achieved, then $L \approx 10L_{abs}$ would be sufficient to obtain the maximum photon flux, as shown in figure 2.11. Constant *et al.* examined the conditions for obtaining absorption limited generation when L_{coh} is not infinite, and found that conversion efficiency as high as 50% of the ideal case could be reached by ensuring [95].

$$L > 3L_{abs} \quad (2.6.10)$$

$$L_{coh} > 5L_{abs}. \quad (2.6.11)$$

This rule of thumb is often used when considering how to design an HHG source. At low photon energies (VUV to XUV) L_{abs} can be quite small, but at higher SXR energies noble gases

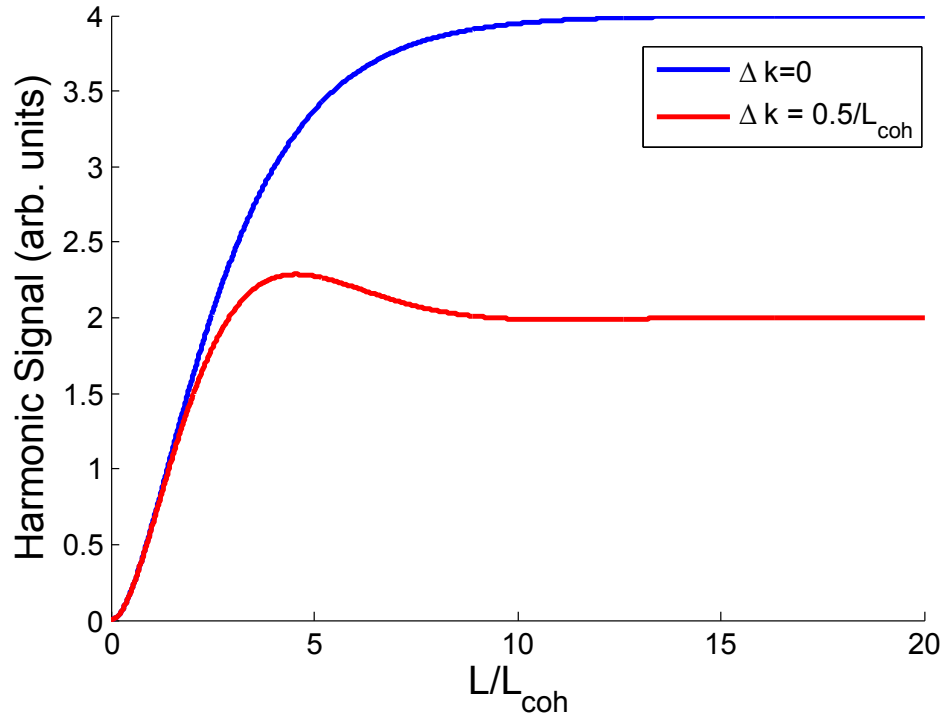


Figure 2.11: Growth of harmonic signal for perfectly phase matched and partially phase matched HHG in the presence of absorption.

become increasingly transparent.

Chapter 3

A High Power, Few-Cycle, SWIR Laser Source

The enabling technology that was developed in the course of my PhD begins with a few-cycle laser source capable of driving high harmonic generation. As discussed in the previous sections, scaling laws and ionization limits mean there are critical advantages for attosecond science by moving the high intensity laser sources to longer wavelengths. In this chapter I will outline the background to the development and characterization of a few-cycle, high power laser source in the short-wavelength infrared (1750 nm), then describe the systems I have participated in building at Imperial College London and the Artemis facility at Rutherford-Appleton Laboratories.

3.1 OPAs and CEP Stability

Traditionally, femtosecond laser technology has been focused around 800 nm wavelengths because this is the central wavelength of titanium-doped sapphire (Ti:sapph), an extraordinary gain medium for modelocked lasers first demonstrated in the late 1980s [96,97]. Titanium sapphire allows for extremely broadband, high power pulse generation, due to its broad gain bandwidth, high thermal conductivity, and weak thermal lensing [98]. While some gain media are capable of broadband lasing at wavelengths in the SWIR, none have thus far been used to generate the high powers necessary to push to the few-cycle limit [99–101].

In order to generate few-cycle SWIR pulses we start from our 8 mJ Ti:sapph laser system, a technology scalable to the joule level [102], and use non-linear optics to generate pulses in the SWIR. The technique we use is optical parametric amplification (OPA), which uses the non-linearity of difference frequency generation (DFG) to amplify a long wavelength beam pumped by a shorter wavelength beam. In difference frequency generation a pump photon is down-converted into two photons of lower energy, named the *signal* and *idler*, where the signal is traditionally the higher energy of the two [20]. The terminology is derived from radio technology, and does not have any special significance. There are two important aspects to

DFG which make it suitable for high power femtosecond amplification. First, DFG can be stimulated, that is to say the presence of a signal or idler photon alongside the pump dramatically increases the probability of the non-linearity occurring, and thus multiple amplification stages can be combined to achieve efficient conversion from pump to signal and idler. Second, DFG is a non-resonant parametric process, and thus can support very large bandwidths (not being dependent upon a material gain-line) and very high energies (as energy is not deposited into the non-linear material). These properties make DFG an ideal process to generate longer wavelengths with high powers [103].

In an OPA, multiple amplifier crystals in which DFG takes place are cascaded to provide amplification. Each is pumped independently by the short wavelength pump (in our case, an 800 nm Ti:sapph) and the signal from each stage is used to seed the subsequent stage. Conversion efficiencies of up to 50% from pump to signal plus idler are possible, and sub-100 fs pulses can be generated at significantly longer wavelengths than the pump, limited primarily by phase-matching inside the non-linear crystals. There is an additional advantage to OPAs for attosecond science, namely passive CEP stabilization. In the case where an OPA is *self-seeded*, that is the initial signal component which is subsequently amplified is generated in some way from the pump itself, the idler produced at the same time is passively CEP stable [104]. The phase of the signal is inherited from the pump while the idler phase is given by

$$\phi_{idler} = -\pi/2 + \phi_{pump} - \phi_{signal} \quad (3.1.1)$$

where ϕ_i denotes the phase of each component. Since the pump and signal phase are locked, and therefore fluctuate together, the phase of the idler is given only by the difference between them, usually set by the path length inside the OPA [104]. This allows us to use a non-CEP-stable Ti:sapph system to generate a CEP stable long wavelength pulse.

It is worth noting now the existence of another implementation of OPAs which is capable of generating even broader bandwidths at higher powers, known as optical parametric chirped pulse amplification (OPCPA). Here a stretched seed pulse is used as in CPA, which can be amplified through DFG in crystals as normal. This allows for much greater amplification over even broader bandwidths than OPAs, as pumping can be done with much longer pulses at much higher fluences [105]. OPCPAs are even capable of generating few-cycle pulses directly, and can be CEP phase stabilized as in OPAs [106, 107]. OPCPAs are a relatively new technology and are not widely commercially available, and thus come at considerable cost, in both funds and time. For this reason, we choose an alternative route of combining conventional OPA technology with HCF pulse compression to create few-cycle SWIR pulses, which is described in section 3.2.

3.2 Hollow-Core Fiber Compression

At present, no commercially available high-power laser systems are capable of producing octave-spanning pulses with the potential for supporting CEP-stable, sub-two-cycle pulses necessary for the generation of isolated attosecond pulses through amplitude gating [108]. In order to generate such extreme bandwidths it is either necessary to use next-generation laser sources (i.e. OPCPA), or to spectrally broaden the output of a conventional high power laser source. Spectral broadening of a conventional source, i.e. our SWIR OPA output, can be performed through the use of a non-linear material response like self phase modulation (SPM) or optical shock formation. This approach is typically implemented in one of two fashions, either by filamentation or by hollow-core fibre (HCF) compression; in both approaches the laser is focused to the high intensities necessary to stimulate non-linear processes and then guided in order to extend the interaction length over which the broadening takes place. In filamentation this is performed by the careful balance of divergence, ionization-induced defocusing, and self-focusing leading to self-confinement [109]. In HCF compression this is performed by coupling the focused beam into the propagating modes of a hollow capillary filled with gas, where it can propagate for long distances at high intensity. While filamentation currently supports the broadening of pulses with the highest energy, HCF compression supports the generation of the shortest pulses and boasts extremely good mode quality in all regimes of interest for us. We have thus opted to implement HCF pulse compression for our SWIR OPA system in order to generate the sub-two cycle pulses necessary for many avenues of attosecond science.

3.2.1 Transmission Through Hollow Fibres

An HCF is a waveguide in which a medium of lower refractive index (typically vacuum or a gas) is surrounded by a medium of higher refractive index, e.g. a glass tube. Unlike in normal fibre optics, the mode is guided not by total internal reflection, but rather by glancing reflections off the inner surface walls. This allows very high intensities to be propagated as the energy density in the high refractive index cladding is zero, unlike in normal fibres where the mode is confined inside a solid material and generally has an exponential intensity tail penetrating into the cladding.

The modes of an HCF, first determined by Marcatili and Schmeltzer in 1964 [110], are quite complicated and in general support complex polarization states. However, coupling in with a linearly polarized laser beam limits coupling to the so-called Electric Hybrid modes EH_{1m} , where m is an integer, which have a transverse, linear electric field, and a small longitudinal magnetic component. The spatial distributions of these modes are known to be Bessel modes truncated at the wall of the fibre, at which point the mode always has a field zero. The intensity

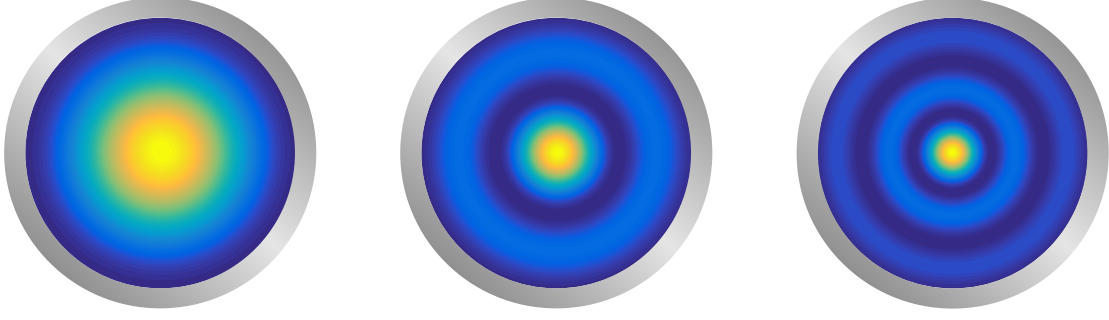


Figure 3.1: *Left to right:* The first, second, and third modes of an HCF, with superimposed fibre wall. Note all three modes have zero energy density at the walls, allowing high intensity throughput.

I of the m^{th} mode is given by

$$\begin{aligned} I_m(r) &= I_m(0) J_0^2\left(\frac{u_{1m}r}{a}\right) & r < a \\ I_m(r) &= 0 & r \geq a \end{aligned} \quad (3.2.1)$$

where r is the radial coordinate, J_0 is the zeroth order Bessel function of the first kind, u_{1m} is the m^{th} solution to $J_0 = 0$, and a is the radius of the hollow core. Examples of the first three fiber modes are shown in figure 3.1; note in particular the zero energy density at the walls, allowing propagation of high-intensity radiation. The coupling of a laser beam into these modes is determined by the overlap of the incident beam mode with the fibre modes, which in the case of a Gaussian laser beam is given by

$$\eta_m = \frac{4[\int_0^a r J_0(u_{1m}r/a) e^{-r^2/w^2} dr]^2}{w^2 \int_0^a r J_0^2(u_{1m}r/a) dr} \quad (3.2.2)$$

where w is the $1/e^2$ beam radius of the beam (approximately 0.85 times the FWHM) [111]. The coupling efficiency for this perfectly aligned, theoretical Gaussian beam into the fibre then depends critically on the beam waist. The coupling for a variety of w/a values into the first three fibre modes is shown in figure 3.2; as can be seen the coupling is predominantly into the lowest order mode, where at the optimal value of $w = 0.64a$, 98% of the incident energy is coupled into the first mode. The coupling efficiency is very stable to fluctuations around the optimal beam waist and position, though it suffers greatly from non-Gaussian incident profiles. For this reason it is vital to couple with a well-shaped laser beam.

The modes of a hollow fibre all undergo exponential loss during propagation given by $I_m(r, z) = I_m(r, 0)e^{-\alpha_m z}$, with the loss coefficient α_m given by

$$\alpha_m = \frac{u_{1m}^2 \lambda^2 (\nu^2 + 1)}{8\pi^2 a^3 \sqrt{\nu^2 - 1}} \quad (3.2.3)$$

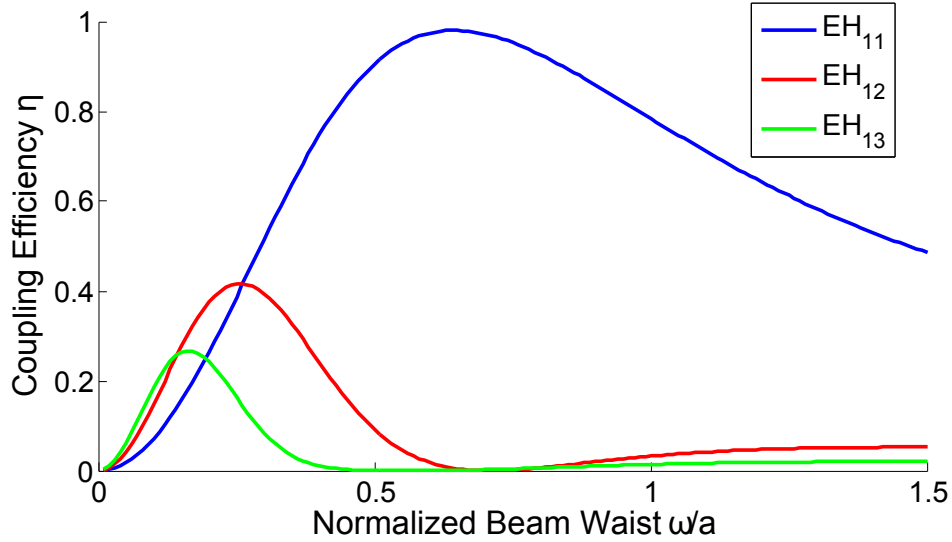


Figure 3.2: Coupling efficiency of a Gaussian beam into the first three modes of an HCF as a function of the beam waist. At the maximum value 98% of the input energy is coupled into the lowest order mode of the fibre.

where λ is the wavelength of the light and ν is the ratio of the refractive index of the cladding to the refractive index of the core [112]. As α is monotonically increasing with m , it is very important to couple into the first order mode in order to maximize transmission through the fibre. This mode-dependent loss also allows the fibre to “clean up” the mode of the beam; provided the input coupling was sufficiently good, the output mode will be essentially comprised of the first order mode, barring unwanted non-linear processes within the fibre itself. Additionally, the propagation constant β_m ($\vec{k}$ -vector) is mode dependent, further motivating strong coupling into the first order mode; otherwise the different excited modes can “slip” temporally and beat. This introduces complications to the non-linearities in the fibre, and upon exiting the fibre, ruins the temporal profile [113].

3.2.2 Fibre Broadening

The intensity of the coupled modes may be sufficiently high to stimulate significant non-linear processes. If so, since the gaseous fill of a fibre exhibits inversion symmetry, the lowest order contributing process will be χ^3 or Kerr non-linearities, which can be treated as a perturbation to the refractive index of the gas. In the absence of non-linearities the electric field inside a fibre factors into a transverse and a longitudinal component $\mathcal{E}(r, \theta, z, \omega) = F(r, \theta)A(z, \omega)e^{i\beta_0 z}$, where β is the propagation constant ($\vec{k}$ -vector) and we have moved to cylindrical coordinates. Substitution into the Maxwell wave equation 2.6.1 shows the solution for the field is separable. By also assuming the *slowly varying envelope approximation*, that the $A(z, \omega)$ term is slowly

varying with z , the propagation equations take the form:

$$\nabla^2 F + (n^2 \beta_0^2 - \beta^2) F = 0 \quad (3.2.4)$$

$$2i\beta_0 \frac{\partial A}{\partial z} + (\beta^2 - \beta_0^2) A = 0, \quad (3.2.5)$$

where β is the propagation constant for the mode and n is the refractive index [114]. Equation 3.2.4 is the Bessel equation, and its solutions lead to the modes described in eq. 3.2.1 when the appropriate boundary conditions are considered.

If a small perturbation is applied to the refractive index, i.e. $n = n_0 + \delta n$, then the modes satisfying equations 3.2.4 are unchanged except for a modification to the propagation constant β . For large intensity-dependent changes in the refractive index, where the change can no longer be treated as a perturbation, the refractive index becomes spatially dependant ($n = n(r, \theta)$) and the analysis becomes much more complicated; these cases are discussed in section 3.2.3. Assuming, however, that this small-perturbation approach is valid, the change in the propagation constant is then given by

$$\delta\beta = \frac{\beta_0 \int \delta n |F(r, \theta)|^2 d\sigma}{\int |F(r, \theta)|^2 d\sigma} \quad (3.2.6)$$

which shows the effect is averaged over the entire spatial distribution of the mode, leading to uniform non-linearities over the entire mode [114]. This limited spatio-temporal coupling is a great advantage of HCF pulse compression over other methods, and can intuitively be understood in the ray picture as each ray sampling the full area of the fibre evenly after many reflections through propagation.

The effect of this perturbation upon the system is best understood through a series of transformations to equation 3.2.5. We set $A(z, \tau) = \sqrt{P} e^{-\alpha z/2} U(z, \tau)$, where P is the peak power and α is the mode attenuation constant. $\tau = \frac{t-z/v_g}{T_0}$ is the time transformed to a reference frame moving at the group velocity v_g and normalized to T_0 , the 1/e half width of the pulse [114]. We will also expand the propagation constant β up to third order. This allows equation 3.2.5 to be re-written as

$$\frac{\partial U}{\partial z} + \frac{i}{2L_D} \frac{\partial^2 U}{\partial \tau^2} - \frac{1}{6L_{D'}} \frac{\partial^3 U}{\partial \tau^3} = i e^{-\alpha z} \left(\frac{1}{L_{SPM}} |U|^2 U + \frac{i}{L_S} \frac{\partial}{\partial \tau} |U|^2 U \right). \quad (3.2.7)$$

This equation requires some unravelling. The terms on the left correspond to normal propagation; the first is simple translation. The second term corresponds to second-order dispersion, with characteristic length $L_D = \frac{T_0^2}{\partial^2 \beta / \partial \omega^2} \Big|_{\omega_0}$, while the third is analogously third-order dispersion, with $L_{D'} = \frac{T_0^3}{\partial^3 \beta / \partial \omega^3} \Big|_{\omega_0}$. L_D and $L_{D'}$ define effective length scales for the dispersion. These dispersive terms depend upon the bandwidth, gas pressure, and gas species. Second-order dispersion generally dominates, but can generally be compensated later using an appropriate

compression scheme (prisms, chirped mirrors, etc.) The terms on the right-hand side correspond to the non-linear contributions. The first corresponds to SPM, with an effective length scale $L_{SPM} \approx \frac{1.5a^2c}{n_2\omega_0 P}$. The second is self-steepening, with a length scale $L_S = \frac{\kappa}{\omega_0 T_0} L_{SPM}^2$, where κ is an $O(1)$ constant that depends on the pulse shape [115]. Both of these non-linear terms induce broadening, but in very different fashions. SPM comes from the variation of the phase with intensity, and for a symmetric input pulse is likewise symmetric, leading to equal broadening in the red and blue. SPM broadening is characterized by introducing an approximately quadratic phase on the spectrum and by the generation of spectral nulls. Conversely, self-steepening comes from variation of the group velocity with intensity, and results in a delay of the peak of the pulse relative to the leading side, and a steepening of the trailing edge. In the frequency domain this manifests as a tail stretching towards short wavelengths. If the steepness of the trailing edge approaches an instantaneous shift this can result in optical shock front formation [116], but this is not important in our system because of the relative strength of the SPM and self-steepening contributions.

3.2.3 Parasitic Processes

If the intensity in a HCF becomes too high, the approximation of uniform intensity breaks down. Spatial variations become significant on the length scale of propagation, and we can no longer view the fibre interior as having a uniform refractive index. This changes the eigenmodes of the fibre system, and the previously orthogonal fibre modes become highly coupled. This change in refractive index can either be caused by the Kerr effect or by plasma formation. The onset of self-focusing (transverse Kerr non-linearity) is given by the well-known expression for the critical power [20]

$$P_{cr} = \frac{0.148\lambda_0^2}{n_0 n_2}. \quad (3.2.8)$$

The fact that self-focusing is to some extent dependent on power, and not intensity, gives a limit to the throughput of an HCF regardless of its geometry [117]. Plasma formation, on the other hand, is a function of the intensity of the beam, and thus places constraints on the size of the fibre for a given peak power. This effect can be included by calculating the contribution of plasma to the refractive index, given by

$$n_p = \frac{\omega_p^2}{2\omega_0^2} \quad (3.2.9)$$

where ω_0 is the angular frequency of the laser and ω_p is the plasma frequency, proportional to the free electron density in the gas. The free electron density can be calculated using the PPT or ADK ionization rates. In order to minimize losses to ionization through defocusing and the energy lost to plasma formation itself, the contribution from the plasma refractive index should be negligible compared to the Kerr index. Vozzi *et al.* found a scaling law for the fibre radius

in order to suppress ionization losses was given by

$$r_{min} = AT_0^{-0.45} E^{0.51} \quad (3.2.10)$$

where A is a gas-dependent constant and E is the energy of the pulse [117]. Higher throughput and the suppression of both self-focusing and plasma formation can be obtained through the use of differential pumping, where the entrance end of the fibre is kept at vacuum and the exit end is statically filled. This allows the beam to couple into the fibre without ionization or self-focusing, and suppresses these effects until a significant amount of propagation has occurred. As the beam is attenuated throughout transmission, but especially at the entrance due to imperfect mode matching, this can suppress ionization and self-focusing very efficiently and result in significant gains [118].

3.2.4 Compression for the SWIR

While the output from the fiber can have a very large octave spanning spectrum, by the nature of SPM it comes out highly chirped. It is thus necessary to temporally compress the pulse before using it for HHG. Normally this is accomplished using chirped mirrors; these are special dielectric coated mirrors such that different wavelengths penetrate to different depths into the coating, imparting a path difference which compensates chirp [119]. For light in the SWIR however, a more elegant and compact solution exists - at these wavelengths, many common bulk materials exhibit anomalous dispersion. We can thus compress the pulse using propagation through optical-grade fused silica [120]; the dispersion is shown in figure 3.3. It is especially advantageous that not only is the second-order dispersion of fused silica (FS) matched to compensate the phase from SPM, but the third-order phase of FS is also matched to compensate the cubic phase imparted by self-steepening for SWIR pulses [120]. This allows us to easily compress pulses to almost their transform limit.

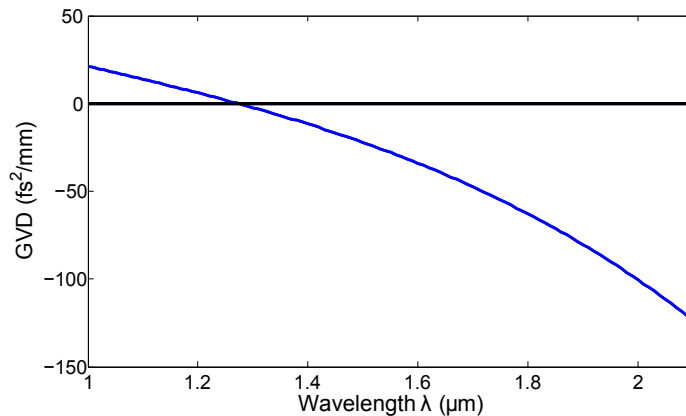


Figure 3.3: Group velocity dispersion of fused silica over the wavelength range of our OPA. At $1.3 \mu\text{m}$ the dispersion changes from normal to anomalous, allowing propagation to compress pulses with wavelengths greater than this.

3.3 Ultrafast Pulse Measurement

It is an unfortunate reality of laser physics that all detectors are slow. This means that for optical frequencies, detectors are not able to resolve oscillations in the light field and can only measure the integrated intensity of a wave over many cycles, and cannot be used to examine the structure of a pulse, particularly for femtosecond pulses where even the duration of the pulse will be completely unresolvable. For this reason, characterization methods of femtosecond pulses are a complex topic of interest - how does one measure an event when they have no faster event to compare it with? For picosecond pulses, electro-optic measurements such as streak cameras, in which the gradient of a microwave field maps the pulse duration to a transverse coordinate, can be used [121], but even these are too slow for femtosecond pulses. Instead, self-referenced techniques must be used, where through various schemes the pulse is used to examine itself.

The simplest self-referenced pulse measurement scheme is *intensity autocorrelation*. When two ultrashort pulses interact in a non-linear medium, they can produce a signal which depends on their overlap, e.g. second harmonic generation, third harmonic generation, etc. If this signal is measured as a function of delay between the two pulses, the signal is called a cross-correlation. In the case of second harmonic generation, this signal is given as

$$A(I_1, I_2, \tau) = \int I_1(t) I_2(t - \tau) dt \quad (3.3.1)$$

where I_i is the intensity profile and τ is the interpulse delay. An intensity autocorrelation is when the two pulses are the same, and the signal contains information about the intensity profile of the pulse. Autocorrelation is a very commonly used method of pulse characterization by virtue of its simplicity, and by assuming a pulse shape (i.e. Gaussian, sinc) it is possible to retrieve a pulse duration from the autocorrelation trace. However, there are significant and unavoidable ambiguities to autocorrelation, and it is not possible to uniquely assign a pulse shape. In other words, autocorrelation, while suggestive, cannot determine the temporal structure of a pulse [122], and does not necessarily provide information on how to improve the pulse duration. More advanced schemes are thus necessary for full and accurate measurement of ultrafast laser pulses.

In this section I will detail the operating principles of three optical methods for fully characterizing ultrashort pulses which have been utilized and developed in this thesis. While other methods exist, two of these three (SPIDER and FROG) comprise the vast majority of pulse characterization systems in use and the third (D-Scan) is increasingly of interest for its ease of use and robustness.

3.3.1 SPIDER

As already discussed, due to the reality of slow detectors it is not possible to directly characterize an ultrashort pulse in the time domain. However, from Fourier theory we know it is equivalent to instead record the amplitude and phase in the spectral domain. Determining the spectral amplitude is quite easy; it can be done simply with an off-the-shelf spectrometer unit. The challenge is in determining the spectral phase, that is the relative phase between adjacent spectral components, which controls the interference between colours that determines the temporal structure of an ultrashort pulse.

Spectral phase interferometry for direct electric-field reconstruction (SPIDER) provides a method for measuring the spectral phase of an ultrashort pulse [123]. It is the spectral analogue of shearing interferometry, a commonly used technique for characterizing wavefronts. In its simplest form, shearing interferometry consists of reflecting a beam of light off of a glass slide at non-normal angle of incidence. The front and back reflections of the slide will be of comparable amplitude, but are laterally displaced by a distance d determined by the thickness of the plate and the angle of incidence, according to simple ray optics. This value d is known as the shear. Provided d is smaller than the original beam size, the two replicas from the front and back surface will overlap and interfere according to the shear. The intensity observed is then

$$I(x, y) = I_0(1 + \cos[\phi(x, y) - \phi(x + d, y)]) \quad (3.3.2)$$

where $\phi(x, y)$ is the phase at (x, y) , I_0 is the intensity of each replica independently, and we have applied the shear in the x direction. Provided the shear is sufficiently small,

$$\phi(x, y) - \phi(x + d, y) \approx \frac{\partial \phi(x, y)}{\partial x} d, \quad (3.3.3)$$

so the fringe pattern encodes the phase derivative across the wavefront. By integrating this value, the spatial phase can be determined up to a constant offset for the pulse wavefront. Note that shear interferometry only finds the phase across one dimension in its simplest form. This will not be a problem in the temporal domain because, as far as we are aware, time is one dimensional.

In order to apply this to the spectral domain, it is necessary to introduce a shear in the spectral domain, i.e. to shift the spectrum of a pulse by a small amount [124]. Spectral shifting can be easily accomplished through the use of acousto-optic or electro-optic modulators, but it is difficult for such devices to span the necessary bandwidth for ultrashort pulse characterization. Shear cannot be directly imparted onto the octave-spanning bandwidths required for few-cycle pulses. This challenge was overcome in SPIDER by the use of sum frequency generation. First, two monochromatic beams with a frequency difference $\Delta\omega$ are prepared, most commonly from the pulse to be measured (though phase stability is perhaps surprisingly not required at this step). Then two upconverted replicas of the original pulse are made by sum frequency

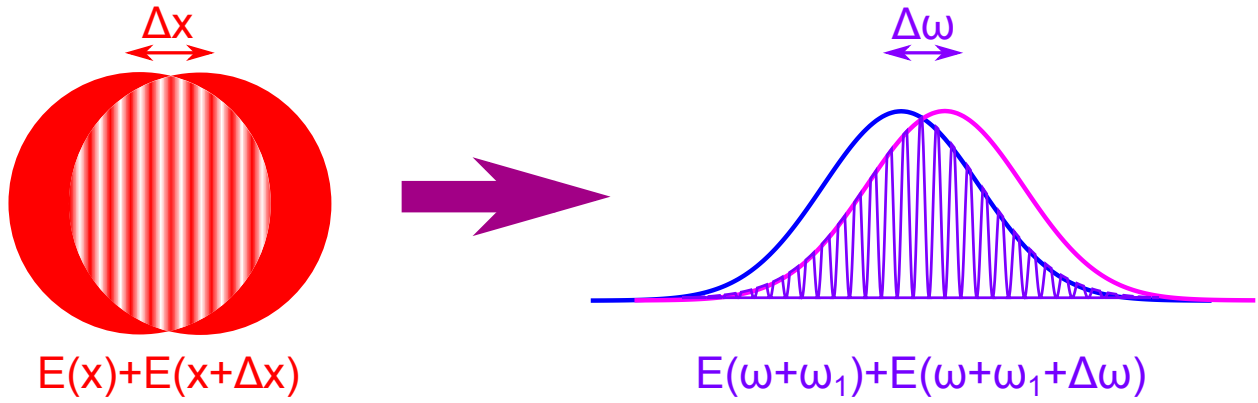


Figure 3.4: Illustration of the correspondence between shearing interferometry in the spatial domain (left) and SPIDER in the spectral domain (right). The phase of the wavefront or spectrum is written onto the resulting varying fringe spacing.

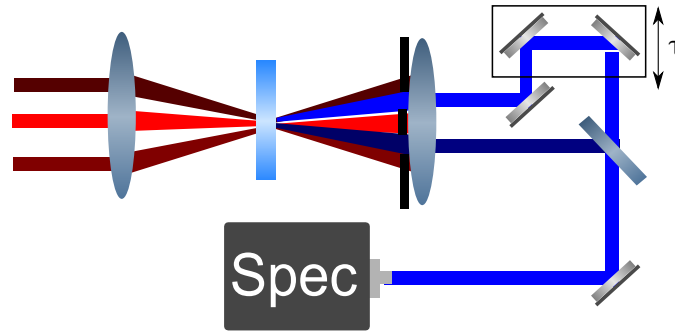


Figure 3.5: Schematic of the ZAP-SPIDER scheme. Three pulses enter the system, a central test pulse and two monochromatic ancillae. Sum frequency in a crystal generates two upconverted copies of the test pulse, which are interfered in a spectrometer with a time delay.

generation between the original pulse and each of the two monochromatic beams [125]. An illustration of the correspondence to shearing interferometry is shown in figure 3.4. Note this scheme is technically a variant known as zero additional phase (ZAP) SPIDER, which is much more common in the measurement of ultrashort pulses; a schematic is shown in figure 3.5. The two upconverted replicas will be identical except for a global phase introduced by the monochromatic beams, and a frequency difference $\Delta\omega$. If the two upconverted pulses are then measured with a spectrometer, the resulting interferogram is of the form

$$S(\omega) = I(\omega) + I(\omega + \Delta\omega) + 2\sqrt{I(\omega)I(\omega + \Delta\omega)} \cos(\phi(\omega) - \phi(\omega + \Delta\omega) - \omega\tau).$$

At this point it can be seen that $\Delta\omega$ acts as a shear in the spectral domain, and can be used to obtain the spectral phase [123]. Using similar Fourier methods as for CEP measurements (section 2.4.1) it is relatively straightforward to isolate the phase component.

Even more so than other methods discussed below, SPIDER depends crucially upon the ex-

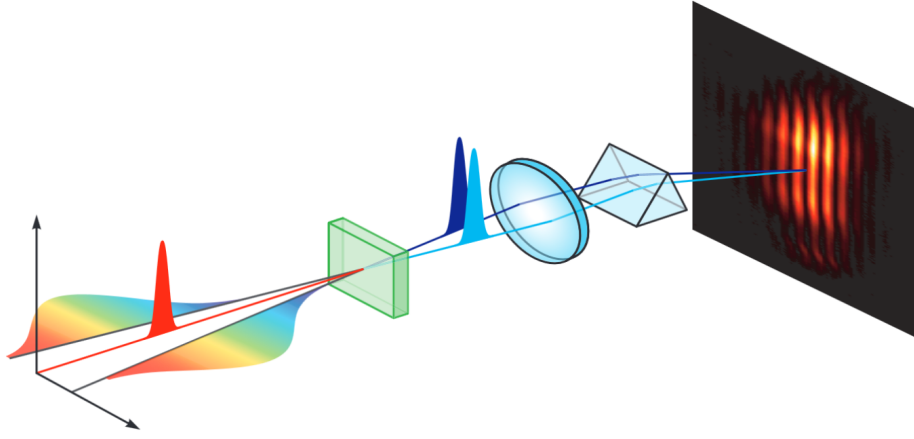


Figure 3.6: Diagram showing the principle of SEA-SPIDER. Until detection the scheme is the same as in ZAP-SPIDER, but the upconverted copies of the test pulse are combined at an angle along the spatial axis into an imaging spectrometer. Figure reproduced from Anderson *et. al.* [124]. ©Astro Ltd. Reproduced by permission of IOP Publishing. All rights reserved.

perimental implementation in order to obtain accurate results. This is because the fringes that characterize the spectral phase are superimposed upon a variety of other fringe patterns, for instance from the delay between the two sheared pulses. A calibration trace taken with zero shear allows for some terms unrelated to the spectral phase of the pulse to be corrected, but the degree of alignment precision and stability required for complex pulse shapes can be prohibitive [122]. However, there exists a particular implementation of SPIDER, the spatially encoded arrangement or SEA-SPIDER, that overcomes these difficulties [126]. A schematic of SEA-SPIDER is shown in figure 3.6, and illustrates the difference between SEA- and ZAP-SPIDER. In ZAP-SPIDER the fringes are written directly onto the spectral domain, while in SEA-SPIDER fringes are written onto the spatial axis in an imaging spectrometer by a crossing angle. Thus the spectral phase fringes superimpose with the transverse spatial fringes, and the spectral phase is not given by the spacing of superimposed fringes, but rather by the tilt of the fringes. This decoupling is extremely valuable, reducing the necessary stability of the interferometer dramatically. SEA-SPIDER additionally reconstructs the phase across the spatial area imaged (a one-dimensional slice) allowing spatio-temporal coupling to be observed.

3.3.2 FROG

Another very popular method of ultrashort pulse characterization is Frequency Resolved Optical Gating (FROG) [127]. Unlike SPIDER, FROG¹ has no simple analogue in linear optics, but can be viewed as a generalization of intensity autocorrelation. As discussed earlier, autocorrelation has unavoidable ambiguities in assigning a pulse shape from an autocorrelation trace, which FROG overcomes by increasing the dimensionality of the trace. This is accomplished by

¹Animal acronyms are an unfortunate tradition in ultrafast optics.

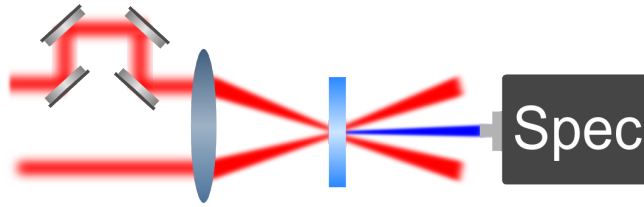


Figure 3.7: Model setup for SHG FROG. Two copies of a pulse are focused into a crystal with a variable time delay between them. The generated second harmonic is spectrally resolved by a normal spectrometer.

measuring the spectrum of the signal at every delay during a normal autocorrelation scan.

For second harmonic generation, the frequency resolved autocorrelation (FROG trace or spectrogram) is given by

$$S_{FROG}(\omega, \tau) = \left| \int E(t)E(t - \tau)e^{i\omega t} dt \right|^2. \quad (3.3.4)$$

This is a specific form of a more general result, where we can break the interaction into the product of a signal $E(t)$ and a gate $g(t)$, here $g(t - \tau) = E(t - \tau)$, with a controllable delay τ . In different versions of FROG, the gate function takes on different forms, but in all versions this transforms the problem of pulse retrieval into a version of the two-dimensional phase retrieval problem [127]. Unlike the one-dimensional phase retrieval problem, which is impossible to invert, the two-dimensional phase retrieval problem has a unique, determinable solution, up to some minor ambiguities (direction of time, CEP) which can be determined with other methods [74].

Figure 3.7 shows the setup for the simplest form of FROG, SHG FROG with a delay line for introducing the variable delay between the signal and gate. While this configuration suffers from problems with stability between arms and temporal blurring from the crossing angle in the crystal, as well as dispersion in the lens, it is a very common setup for the characterization of relatively long pulses (hundreds of femtoseconds). For few-cycle pulses some modifications are necessary [128, 129], which are detailed in section 3.4.4, where we implement a single-shot configuration of FROG suitable for few-cycle pulses.

One of FROG's strengths, apart from its relative ease of implementation, is the sensitivity and speed of the iterative retrieval algorithm used. While different versions of FROG retrieval exist, the most common is the principal components generalized projections algorithm (PCGPA), which has been used to perform real time characterization of laser pulse trains [130]. The PCGPA is an iterative algorithm in which two constraints, the *mathematical* and *experimental* constraints, are subsequently applied to the data. First a pulse shape is assumed, then a full amplitude and phase spectrogram is generated. The amplitude is then corrected using the experimental FROG trace. From this corrected spectrogram, a gate and signal are extracted.

The gate is discarded, and a new gate is generated according to the mathematical form of the FROG trace. Then a new spectrogram is generated, and the process repeats until the error between the generated and measured spectrogram reaches the desired level [131]. This procedure has been applied to reconstruct extremely complex pulse structures very quickly [132].

3.3.3 Dispersion Scan

A third method, more recently developed than FROG or SPIDER, is the dispersion scan or D-scan technique [133]. In a D-scan the pulse to be measured is used to produce some non-linear optical signal, which is then spectrally resolved. This spectrally resolved signal depends on the temporal profile or spectral amplitude and phase of the pulse. If a series of known phase profiles are added to the pulse by increasing or decreasing the amount of propagation through a dispersive medium, a two-dimensional plot of signal spectrum vs. phase shifts can be produced. This two dimensional plot can be used to reconstruct the original pulse through a phase retrieval algorithm, much like in the case of FROG.

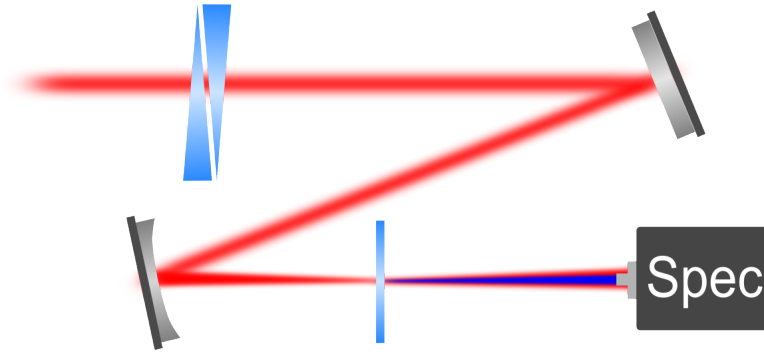


Figure 3.8: Typical setup for a D-scan measurement. Dispersion is introduced by passing through two wedges which can increase or decrease the amount of material traversed. The pulse is then used to generate a non-linear optical signal, which is measured with a spectrometer.

A typical D-scan measurement setup is shown in figure 3.8. The pulse passes through two wedges which can be inserted or removed to control the amount of material traversed, and thus the dispersion. The pulse then generates a non-linear optical signal, typically the second harmonic, and the signal is then measured with a spectrometer. Assuming infinite phase-matching bandwidth, the signal measured, in the case of second harmonic generation, is given by

$$S_D(\omega, z) = \left| \int E(\Omega) E(\omega - \Omega) e^{iz[k(\omega) + k(\omega - \Omega)]} d\Omega \right|^2, \quad (3.3.5)$$

where $E(\omega)$ is the complex spectral amplitude of the pulse, z is the thickness of the glass, and $k(\omega)$ is the k-vector at frequency ω in the dispersive medium [134]. The assumption of achromatic phase matching in the crystal can be corrected by applying a spectral filtering func-

tion, which contains this and other losses. The D-scan algorithm is capable of reconstructing this spectral filter, and so D-scan can recreate pulses even in the presence of truncated phase matching [133].

The D-scan technique has three major advantages over other pulse measurement techniques, two in the setup and one in the reconstruction algorithm [135]. One structural advantage is that the D-scan is in-line, that is to say there is only one beampath, and is thus both extremely stable and very alignment tolerant. The second structural advantage is that in order to use an ultrashort pulse, it needs to be compressed, and this almost invariably involves scanning wedges to tune the dispersion. The D-scan technique thus just involves directing the beam away from the experiment into a crystal and spectrometer setup. Finally, one of the reconstruction algorithms for D-scan has been shown to be highly resilient to the problem of finite phase matching bandwidth in the non-linear medium, which plagues SPIDER and FROG for ultra-broadband pulses [136].

3.4 Source Development at Imperial College

Here I detail the development work we have undertaken at Imperial College London on a few-cycle CEP-stable source in the SWIR. I first outline the development on the source itself, then describe the various diagnostics we have developed for this novel source regime.

3.4.1 Laser and Hollow-Core Fibre

Our system is comprised of a commercial CPA laser system with a commercial OPA front end, followed by an HCF pulse compression station. The CPA laser (KMLabs Red Dragon) consists of a modelocked Ti:sapph oscillator followed by two amplification stages. The oscillator produces sub-30 fs duration pulses at a center wavelength of 800 nm and an 80 MHz repetition rate. These pulses then pass through a grating stretcher which increases their pulse duration to several hundred picoseconds for subsequent amplification. The beam passes through a Pockels cell with sub-10 ns window, which reduces the train to a 1 kHz repetition rate. The beam then passes through the first amplification stage, which consists of 13 passes in a bowtie configuration through a cryogenically cooled, diode pumped Ti:sapph crystal. A second few-ns Pockels cell is used to attenuate amplified spontaneous emission, and we obtain up to 2.6 W of power. The beam then passes through a similar two-pass bowtie amplifier where it is amplified up to 14 W. The pulses are then compressed to around 30 fs with a grating compressor, resulting in a beam of 8 W at 800 nm. We have made several modifications to the original commercial design to improve reliability, including two active stabilization systems for the beam position. Most importantly however we have introduced an active feedback on the chirp of the output pulse - a small fraction of the beam is sent into a SPIDER for live pulse measurements, which controls

an actuator inside the grating compressor. This has proven essential for optimal operation of the subsequent OPA stage.

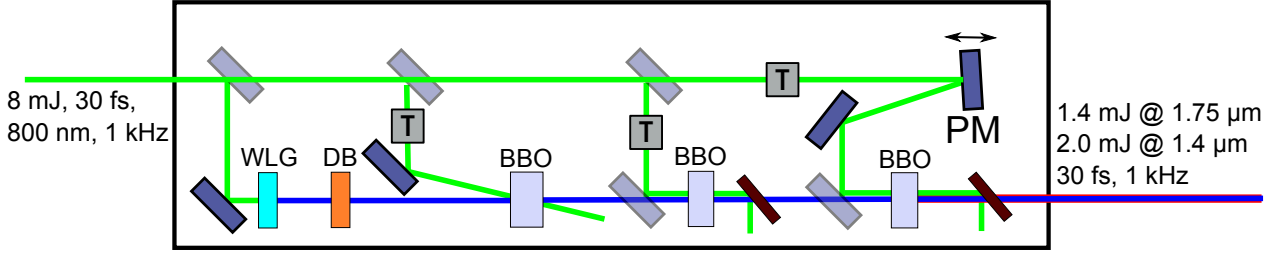


Figure 3.9: Block diagram of our OPA. The CPA input is divided into four stages. The first beam generates white light in a sapphire plate (WLG) and is chirped by a dispersive block (DB). The first pump is delayed in time (block labelled T) and overlapped with the white light in a BBO non-collinearly, amplifying the signal wavelength. The signal is amplified in another BBO collinearly, with the pump afterward removed via dielectric mirrors. The signal undergoes another amplification stage in BBO, with the pump delay finely controlled via a piezo mounted mirror (PM). Another dielectric mirror removes the pump, and the signal and idler exit the system.

The Red Dragon output is passed through a telescope to increase the size of the beam to around $15 \text{ mm } 1/e^2$ diameter and sent into the OPA (Light Conversion HE-TOPAS). The OPA, shown in figure 3.9, consists of seed-generation and three amplification stages. The seed is generated from a small fraction of the pump beam which is focused into a sapphire crystal, where it undergoes massive SPM. The generated supercontinuum is then stretched in time by passing through a highly dispersive glass plate. The seed is then overlapped with another portion of the pump inside a BBO crystal where both the phase matching angle and timing can be adjusted to control the amplified frequency. The amplified signal then undergoes two more amplifications stages inside BBO crystals with increasing power. We have added a piezo-mounted mirror in the pump path of the final amplification stage - this allows for extremely small delays to be introduced between the pump and the signal. This small delay introduces a change to ϕ_{pump} , allowing for CEP control of the idler via the relationship in equation 3.1.1. With 8 W input power, we obtain up to 3.4 W output power in signal plus idler, with the idler at a central wavelength of $1.75 \text{ } \mu\text{m}$.

The full system for pulse compression of the $1.75 \text{ } \mu\text{m}$ pulses is shown in figure 3.10. The idler is separated from the signal via reflective beamsplitters and sent to the HCF setup. In order to obtain the correct mode size for coupling into the fibre we pass through a reflective telescope comprised of an $f = 2 \text{ m}$ convex mirror and a $f = 75 \text{ cm}$ concave mirror. A 1 mm CaF_2 pickoff is used for active stabilization of beam positioning and pointing. We use a HCF of inner diameter (ID) $400 \text{ } \mu\text{m}$ and 1 m length, with each end held inside a hermetically sealed chamber. The entrance and exit windows are 1 mm CaF_2 at Brewster's angle to reduce reflective losses.²

² CaF_2 is weakly birefringent, and ordinarily the glass is cut so the optic axis is perpendicular to the surface. As we pass through the windows with polarization in the plane of reflection this does not impact our final

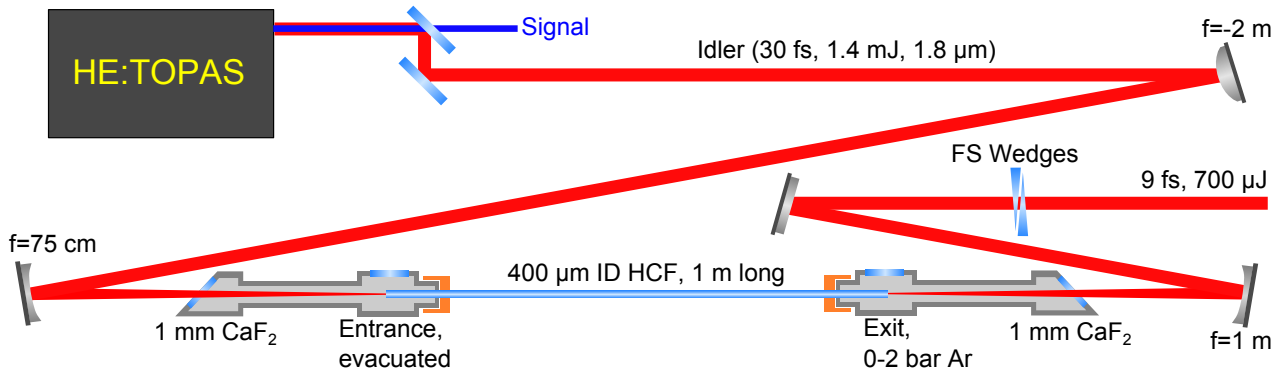


Figure 3.10: HCF setup for SWIR laser pulses. The idler from an HE:TOPAS OPA is separated from the signal by a dichroic beam splitter and coupled into a 400 μm ID HCF. The HCF is differentially pumped, with up to 2 bar of argon at the exit end. The beam is recollimated and compressed with fused silica wedges. Final output is a 7 fs, 750 μJ pulse centred at 1.75 μm at a 1 kHz repetition rate.

We differentially pump the fibre to reduce self-focusing and ionization losses before the fibre; the entrance is held at vacuum while pressures of 0-2 bar of argon are applied at the exit end. The large 400 μm diameter was chosen to minimize losses, due to the λ^2/a^3 scaling of the loss coefficient (equation 3.2.3). The fibre output is collimated with an $f = 1$ m silver mirror. Pulse compression is achieved with a pair of fused silica wedges (Laser Quantum) whose insertion can be tuned for optimal dispersion.

From the OPA we can obtain up to 1.4 mJ pulses in the idler at a center wavelength of 1.75 μm . Remarkably these pulses can be as short as 30 fs - nearly the duration of the pump laser itself, and close to the transform limit of the idler. We have seen that the output of the TOPAS is extremely sensitive to the chirp of the pump, as it strongly affects all three amplification stages as well as disturbing the seed generation. Changes of even 40 fs² can appreciably distort the OPA output; this is why stabilizing the CPA compressor has proved crucial.

A significant challenge to the operation of the HCF is the mode quality of the OPA output. The theoretical transmission of our fibre is $\approx 80\%$, but in practice we achieve transmissions of only 45-55%. While some loss is likely attributable to imperfections in the fibre itself, our online position and focus monitoring for beam stabilization allows us to identify the mode quality as a significant limitation. An example of the mode in and out of our HCF is shown in figure 3.11; clearly significant spatial filtering has taken place. In order to reduce losses we place the compression wedges for the idler at Brewster's angle, allowing us to reach a final output power of up to 800 μJ with a pulse duration of down to 7 fs, less than 1.5 optical cycles.

polarization, but it would have to be considered when using elliptically polarized light, or with polarization at an angle to the plane.

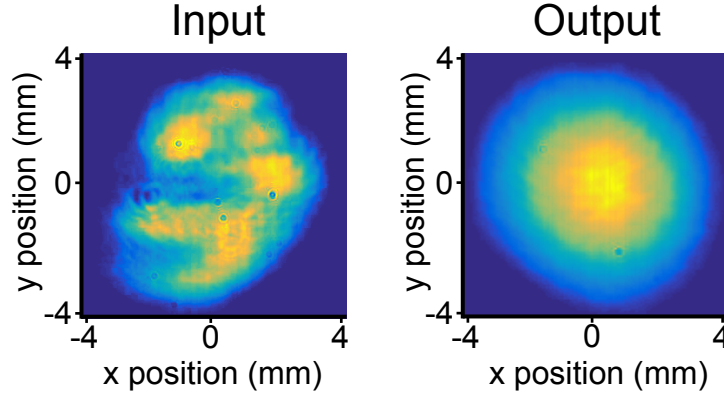


Figure 3.11: *Left*: Far field input mode to HCF. *Right*: output mode far field of the HCF.

3.4.2 Idler CEP stability

In order to control the idler CEP via the pump-seed delay inside the TOPAS it is necessary to have a measure of the CEP drift using a beat-frequency interferometer, as described in section 2.4.1. We use a reflection from our compression wedges to drive a 2f-3f interferometer. It is most common in ultrafast science to use f-2f interferometers to measure CEP; in our HCF however the very high frequency components that would interfere in such an apparatus are generated primarily through self-steepening, and are more sensitive to various input parameters than normal SPM contributions. Furthermore, due to the asymmetric broadening, we often do not generate frequencies at the long wavelength end while still obtaining a few-cycle pulse. The use of a 2f-3f interferometer relaxes the bandwidth requirement from octave spanning to two-thirds octave spanning.

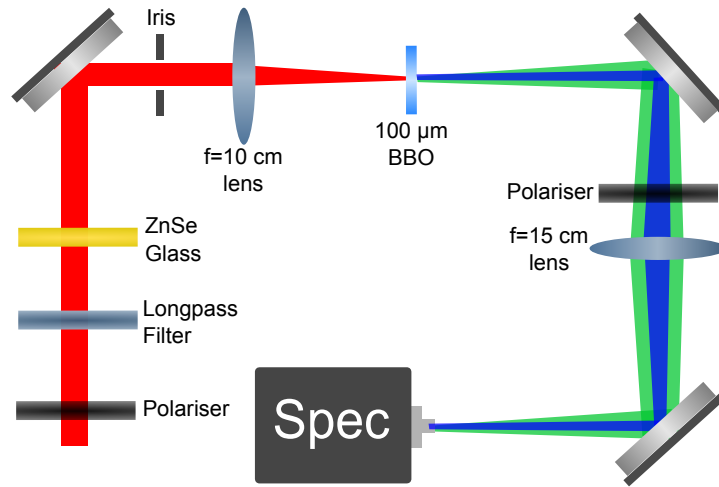


Figure 3.12: 2f-3f interferometer design. The input pulse is filtered and chirped, then focused into a $100\ \mu\text{m}$ thick crystal. The emitted second and third harmonics are focused into a spectrometer and the spectral fringes used to lock the CEP.

Our 2f-3f design is shown in figure 3.12. The first section constitutes the preparation optics. The incoming beam passes through a polarizer (Thorlabs LPNIR), a necessary step since any unwanted light with the perpendicular polarization is preferentially selected by the Brewster reflection. A long-wavelength filter (Thorlabs FEL1100) is used to reject unwanted parasitic visible light from the fibre and OPA, which would produce additional fringes in the spectrum atop the CEP fringes. A 2 mm thick piece of ZnSe is used to chirp the incoming pulse due to its extremely high dispersion in the SWIR. As the 2f contribution from the short wavelength end interferes with the 3f contribution from the long wavelength end, this chirp translates into the time delay between the 2f and 3f components of the signal and thus the time delay in the beat-frequency interferogram. The use of pulse chirp to introduce time delay results in an extremely stable common-path interferometer.

The now appropriately filtered and chirped pulse is focused into a 100 μm thick BBO crystal. By appropriate choice of angle, both the second and third harmonic are efficiently phasematched over an overlapping region of 600-700 nm. The emitted harmonics are then passed through a polarizer to project them to the same polarization axis to allow interference, and imaged into a spectrometer. We observed strong and stable fringes across a large region, and using these as an error signal we have achieved CEP stabilities down to 180 mrad rms across several hours, measured in a single shot mode. This is comparable to state-of-the-art commercial systems, which provide CEP stability of around 100 mrad rms. However, for the experiments described later in this thesis it was necessary to place the 2f-3f interferometer in a more remote location in the laboratory. The extra drift introduced limited us to the CEP stability of around 230 mrad, as shown in figure 3.13.

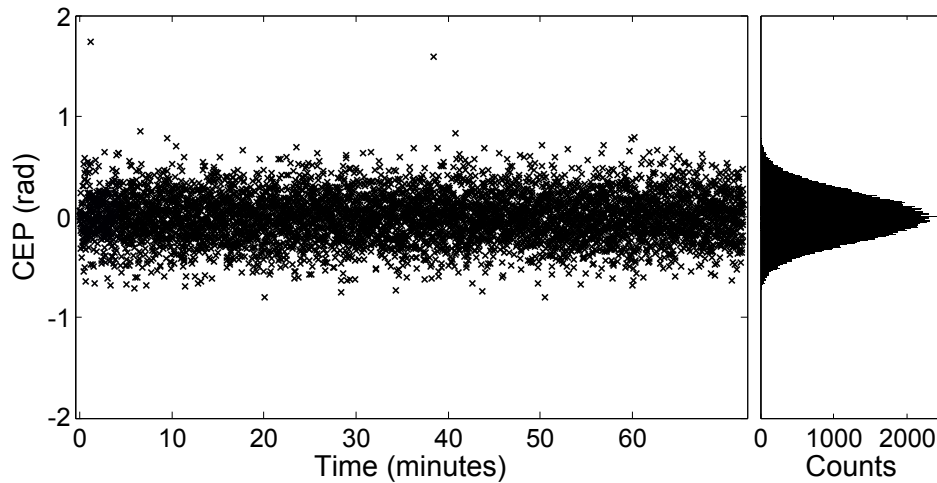


Figure 3.13: Stability of CEP, as measured by our 2f-3f interferometer, over the course of seventy minutes. A stability of 230 mrad rms, single shot, is obtained. Only 1 in every 100 measurements is shown for clarity.

3.4.3 SEA-F-SPIDER

The primary pulse characterization apparatus in our laboratory is a SEA-SPIDER; a schematic is shown in figure 3.14. While our SEA-SPIDER is not conceptually different from the ideal case discussed in section 3.3.1, there are several technical differences between previous implementations of SEA-SPIDER and our own [56, 126]. We use the filter-based arrangement (SEA-F-SPIDER), where ancillae are prepared by passing pulses through narrowband ($\Delta\lambda \approx 2.5$ nm) filters. The few-cycle idler presents three main challenges over other pulses for SPIDER characterization, namely the SWIR wavelength, the fluctuating bandwidth, and the spectral nulls resulting from the SPM broadening. Normally the ancilla pulses are derived from the test pulse in some way. For the short-wavelength infrared, upconversion with a much shorter wavelength than the center wavelength of $1.7 - 2.1 \mu\text{m}$ is desirable, as standard silicon photodetectors are blind to light longer than 1150 nm, and signals nearer the peak efficiency of silicon will have higher signal-to-noise. While we can produce sufficiently short wavelengths from the HCF to ensure that even the longest wavelengths produced (around $2.4 \mu\text{m}$) are upconverted to the high sensitivity region of silicon, a more robust solution that does not sensitively depend on the degree of broadening is desirable. For this reason we derive our ancillae from a portion of the 800 nm CPA light split off before our OPA. This provides a stable ancilla source, and upconverts our pulses into the region from 450 to 600 nm where the absorption of silicon is high. Another advantage of using the CPA output is that the ancillae can be prepared to a very high spatial quality (i.e. spatially filtered) independently of the quality of the pulse under test. This prevents spatial inhomogeneities of the ancillae from affecting the spatial structure of the upconverted pulses, and thus ensures accurate spatio-temporal reconstruction.

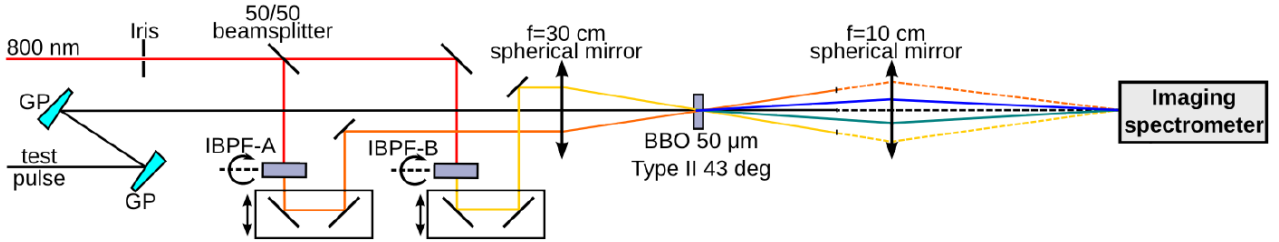


Figure 3.14: SEA-F-SPIDER diagram for use in our laboratory. The ancillae are derived from a fraction of the CPA output taken prior to pumping the OPA and spectrally filtered with interferometric bandpass filters (IBPF). The test beam (HCF output) is attenuated through reflections off glass plates (GP) then upconverted with the CPA ancillae and re-imaged into an imaging spectrometer. Figure courtesy of Dane Austin.

The spectral nulls in the idler spectrum present a different challenge. SPIDER cannot reconstruct the phase across a spectral null unless the frequency shear $\Delta\omega$ is larger than the span of the null; only with this condition fulfilled can the phase on one side be related to the phase on the other. Without a large shear, an arbitrary phase offset between different spectral regions cannot be constrained. However the resolution of the SPIDER measurement depends on the

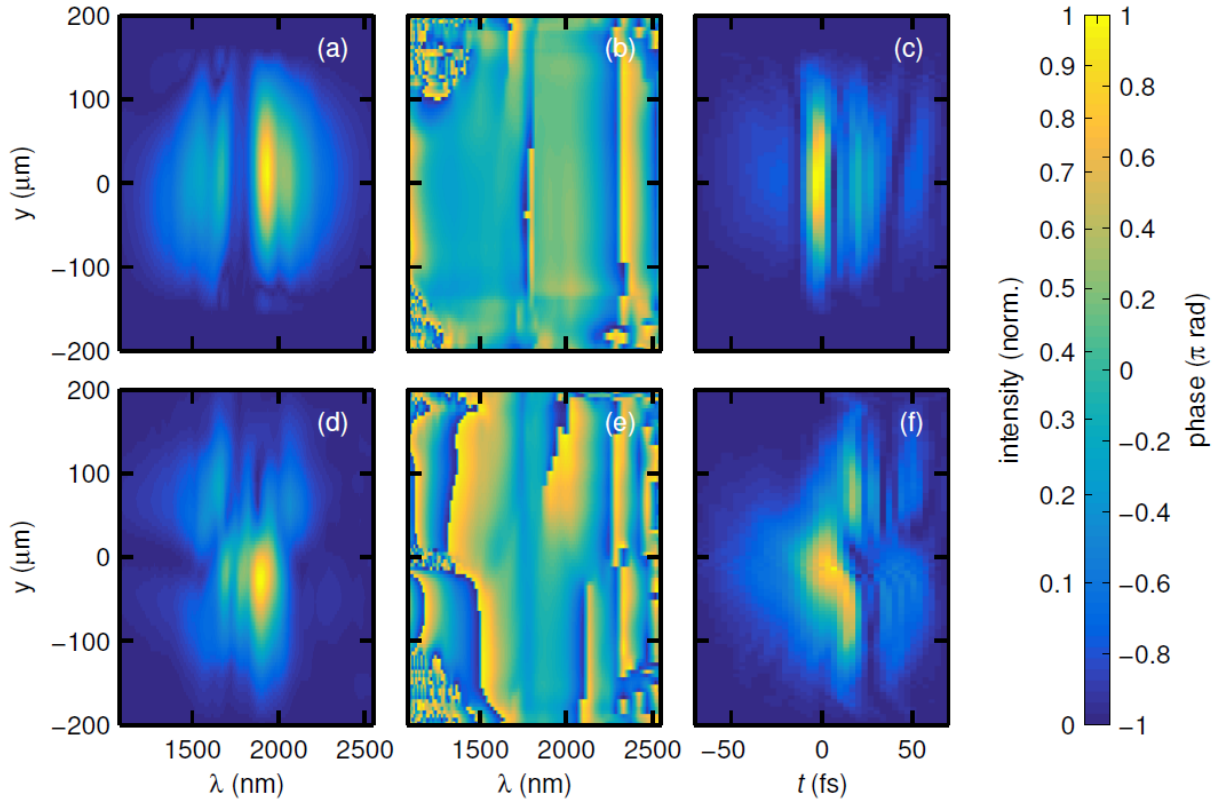


Figure 3.15: SEA-F-SPIDER spatio-temporal reconstructions of 2060 nm pulses when the fibre is well-aligned (a,b,c) and when the input beam is 50 μm away from optimal in the transverse direction (d,e,f). The first column shows the spatio-spectral intensity, the second the spatial-spectral phase, and the third the spatio-temporal intensity. The intensity colormap is non-linear to exaggerate weak features. Reproduced from [113], under the terms of the Creative Commons Attribution 4.0 License.

magnitude of the shear as well, and generally favors a smaller value of $\Delta\omega$. These two conflicting requirements are overcome through the use of a multiple shear algorithm [113], where signals taken with large shears are used to overcome the relative phase ambiguity and signals taken with small shears give the high resolution required to accurately reconstruct a few-cycle pulse. Multiple shears also improve the precision of the reconstruction. The system was calibrated by ensuring the upconverted spectrum agreed well with a measurement of the fundamental spectrum, and that the phase introduced by a known dispersive element (2.4 mm of fused silica) was accurately reproduced.

Figure 3.15 shows full spatio-temporal reconstructions obtained using our SEA-F-SPIDER of 2060 nm pulses broadened in 1.4 bar of argon. Subplots a and d show the spectrum, b and e the spectral phase, and c and f the temporal duration. Subplots a, b, and c correspond to the case where the fibre is optimally aligned while d, e, and f are from a deliberately mis-aligned configuration where the input beam was offset transversely from the center of the hollow-core. In the well-aligned case the pulse has excellent spatio-temporal structure, while the mis-aligned case shows strong spatio-temporal coupling [113].

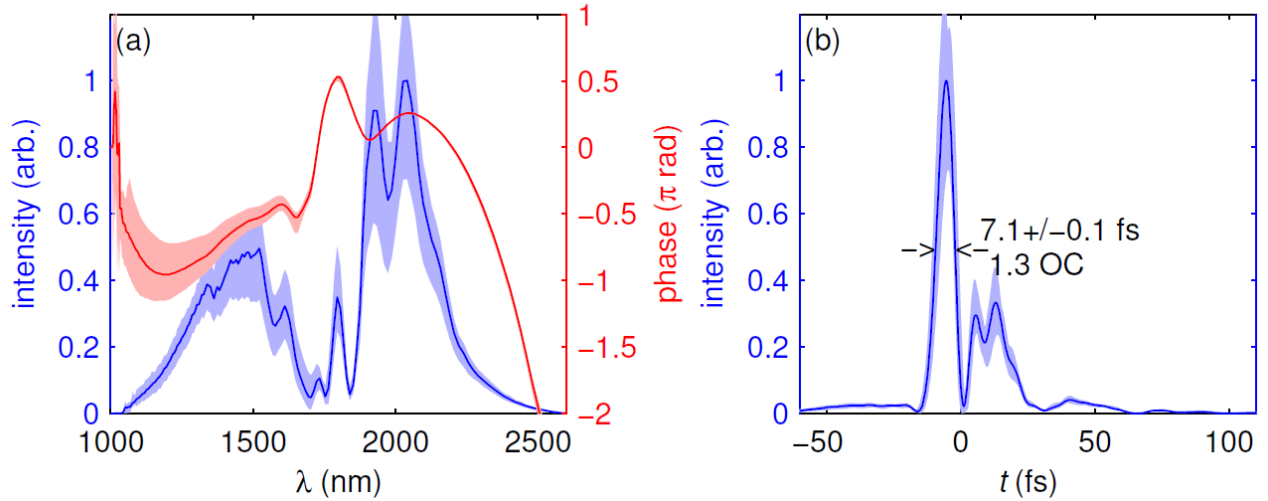


Figure 3.16: a) Idler spectrum and spectral phase of our HCF output centered at 1800 nm measured via SEA-F-SPIDER. b) Corresponding temporal profile. The pulse duration is 1.3 optical cycles. The variation over ten measurements (extrema) are shown by the shaded areas. Reproduced from [113], under the terms of the Creative Commons Attribution 4.0 License.

In the well-aligned case it is reasonable to examine only the temporal profile, integrated over the spatial dimension. Figure 3.16 shows the temporal profile of our pulse under optimal conditions, with 0.75 bar of argon in the fibre and 2.4 mm of FS to compress the pulse to 7.1 fs FWHM. This corresponds to a pulse of 1.3 optical cycles, sufficiently short to support very efficient amplitude gating of HHG. The pulse exhibits some undesirable features from uncompensated higher order phases. There is a large satellite pulse at the 30% intensity point. As SPIDER does not exhibit a direction of time ambiguity as do some forms of FROG, we can identify this as a post-pulse which should not adversely effect HHG because the ionization caused will not degrade the phasematching of the earlier harmonic emission. Additionally, any out of phase harmonics generated will have a cutoff much lower than those from the main pulse and a much lower flux due to the exponential scaling of the tunnel ionization. We also observe very weak pre- and post- pulse tails. At the intensities required for HHG these should have little impact, though they could present problems were the pulse used to perform relativistic physics. In our case they serve only to parasitically remove energy from the main pulse; in the pulse shown, 52% of the energy is contained in the main peak.

This result represents in many ways an ideal generation and measurement. We are able to perform a full spatio-temporal characterization, measuring complex broadband pulses in the SWIR exhibiting strong spatio-temporal coupling. Using this feedback we can eliminate spatio-temporal coupling and robustly generate near single-cycle pulses with good stability, an ideal source for attosecond science experiments. In comparison to other few-cycle SWIR sources previously presented [120], ours produces the shortest pulses, and for pulses with less than two-cycle duration, the highest energies. While SEA-F-SPIDER is capable of providing full information, allowing us to make these unambiguous statements, our system has several draw-

backs. The need to match the path length of the test pulse and the ancillae means any change in the optical path of the test pulse requires significant rebuilding, limiting the flexibility of the arrangement. Careful calibration of the SEA-F-SPIDER is required in order to ensure accurate reconstruction, particularly for spatio-temporal analysis. For this reason we have also examined the use of simpler diagnostic tools.

3.4.4 Single-Shot FROG

While the SEA-F-SPIDER is an extremely powerful diagnostic, the need for a simpler, more routine diagnostic for the output of the HCF became clear in the course of my PhD. For this reason we began to develop a single-shot third-harmonic FROG capable of measuring few-cycle pulses. In a single-shot FROG, the temporal delay is introduced not with a delay scan, but by the crossing angle of the two pulse copies in the non-linear medium. Different positions across the spatial overlap of the beams sample different time-delays; by re-imaging the interaction plane to an imaging spectrometer a FROG trace can be obtained in a single shot [127]. Single-shot FROG is very well suited for measuring ultrashort pulses as the crossing angle, which introduces temporal blurring in a scanning FROG, instead acts as the source of temporal delay. We use a third harmonic FROG in order to relax requirements on the detector in our imaging spectrometer, as the more common second harmonic creates spectral components beyond the 1100 nm cutoff of a silicon CCD. The use of third harmonic changes the form of the FROG spectrogram, but presents no problems for the standard FROG algorithms [137].

Figure 3.17 shows a diagram of our third-harmonic single-shot FROG. In order to avoid introducing additional spectral phase a split mirror acts as the beamsplitter, geometrically cutting the beam into two paths. One beam goes down a delay arm; this delay is used to find temporal overlap and calibrate the temporal axis of the FROG. Then the two arms are focused in the y-plane by a 7.5 cm focal length cylindrical mirror; the beams cross in the x-plane at the focus, which is placed at crystal entrance face. The crossing angle is chosen such that the total time window of the interaction is sufficiently large, around 100 fs, and the temporal resolution is sufficiently small, around 500 as, such that the pulse under study is sufficiently well sampled and not distorted by the temporal window [122]. Four beams exit the crystal; the two fundamental beams E_1 and E_2 , and two third-harmonic signals corresponding to $E_1 E_2^2$ and $E_1^2 E_2$. These are re-imaged by a 20 cm focal length spherical mirror onto the entrance of the spectrometer in a 2f-2f geometry. One focal length after the mirror each of the four beams focuses into a vertical line which allows simple beam blocks to filter the unwanted fundamentals and signal, resulting in a single clean FROG signal [129].

A primary challenge in FROG measurements of few-cycle pulses is the phase-matching bandwidth of the non-linear medium, which is usually a BBO crystal for second harmonic FROG [138]. In our system we have elected instead to utilize the phenomenon of surface third-harmonic generation [139], in which the walk-off between a pulse and its third-harmonic inside a bulk

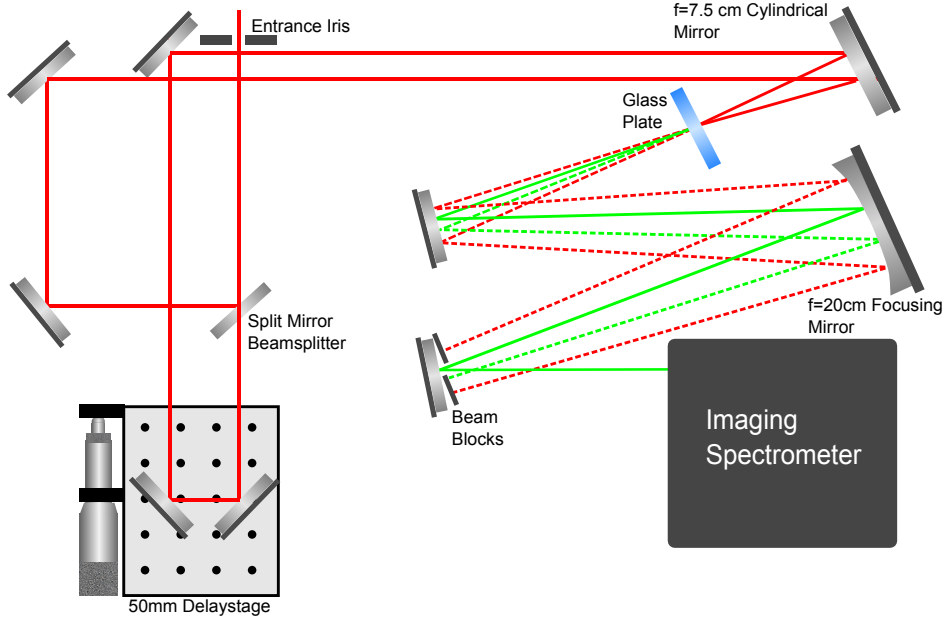


Figure 3.17: Third-harmonic single-shot FROG diagram. The incoming beam is divided by a split mirror and the two beam are recombined by a cylindrical mirror at an angle inside a glass plate. Third harmonic generation produces two copies of the FROG signal. All but one signal beam are blocked prior to an imaging spectrometer which gives the FROG trace.

material strongly confines generation to the surfaces at which the symmetry is broken [140]. This strong longitudinal spatial confinement leads to very broadband phase matching over said region. If harmonic generation is confined to only one surface, this can be used to give a very accurate FROG trace. We achieve such confinement by using a short focal length (7.5 cm) together with a thick medium (5 mm). By focusing on the front plane an accurate FROG signal is generated; at the back plane the intensity has decreased sufficiently to prevent significant third harmonic generation.

In principle any medium can exhibit the surface third-harmonic process. We originally chose to use fused silica, a standard choice for optical glasses given its high damage threshold and high optical quality. However, we had neglected to consider the effect of cross phase modulation (XPM) in our design. XPM between the two fundamental beams causes them to increase in divergence as illustrated in figure 3.18; with sufficiently large XPM, the fundamentals will overlap with the generated third harmonic signal beams and couple into the spectrometer. In a third harmonic FROG, the XPM and THG terms are of the same order in the field, and the problem is further exacerbated in the surface scheme, as signal generation is confined to the surface while XPM can occur throughout. We observed the effect of XPM in our system; as the pulse was spectrally broadened in the HCF, a long wavelength component appeared in the measured signal which was spectrally separate from the main signal, eventually overlapping with the FROG signal as the broadening was increased further.

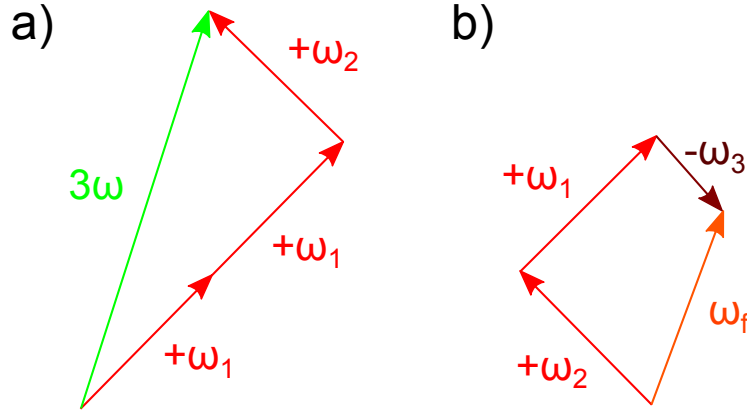


Figure 3.18: Illustration of how XPM increases the spread of the fundamental beams in a single-shot FROG, where ω_1 denotes a contribution from the first pulse, ω_2 and ω_3 originate from the second pulse, and the color and length denote the frequencies. a) Vector summation leading to third harmonic signal. b) Vector summation for broadband XPM. Mixing of different frequencies in the E_2 arm contributing phase leads to a final frequency ω_f emitted into the 3ω direction.

We attempted to overcome this problem through a novel technique, using an absorbing material as the generation medium. Since the THG occurs only at the entrance face, using a medium which absorbs the fundamental frequencies but transmits the upconverted signal would confine XPM to the surface where THG can dominate the response. We identified KG1 Schott Glass as a potential generation medium, as it transmits light from 300 nm up to 800 nm, and very efficiently absorbs light from 1000 nm to 1500 nm. The full transmission data is shown in figure 3.19. While the transmission at 800 nm, corresponding to 2400 nm in the fundamental, is somewhat weak, it should be sufficient to allow accurate measurement of the few-cycle pulse.

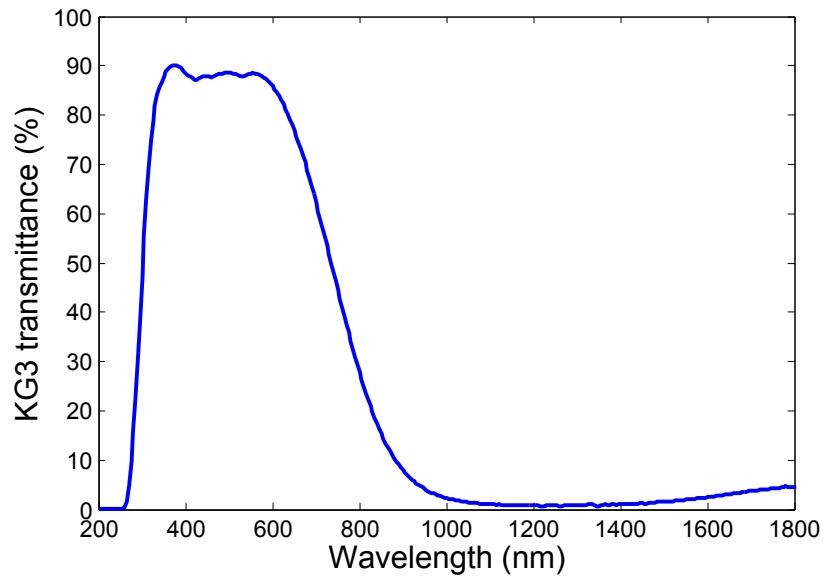


Figure 3.19: Transmission of a 2 mm thick piece of KG1 glass across the third harmonic and fundamental regions of our spectrum. Signal wavelengths (365 nm to 800 nm) are transmitted, while the short wavelength portion of the fundamental is strongly absorbed.

Figure 3.20 shows a FROG trace acquired using KG1 glass as the generation medium. There is no sign of XPM features overlapping with the signal, and indeed a decaying XPM feature (not shown) can be observed at 1100 nm in the imaging spectrometer, well isolated from the main signal. The upconverted bandwidth of the signal spans from around 400 nm to 800 nm, corresponding to upconversion from 1200 nm to 2400 nm, spanning the entire spectrum of our few-cycle SWIR pulse. However, while the use of KG1 glass solved the XPM problem, it introduced a much higher level of scatter than was present in fused silica. Scattering from the glass is re-imaged into the imaging spectrometer, and results in a series of anomalous spectral lines, for instance at -90 fs. In particular, our trace shows scatter originating from the same position in the KG1 as the maximum of our signal, leading to a series of peaks and fringes across the spectrum at the corresponding delay. These features are not representative of the pulse, but will confuse a FROG algorithm, making pulse reconstruction impossible under these conditions. Despite this, the FROG can still be used to optimize pulse compression on a day to day basis. The scattering effects and FROG trace can be easily distinguished by adjusting the time delay, which translates the trace but not the scatter. Because of the intuitive spectrogram nature of FROG, direct optimization of a pulse is in fact possible even without reconstruction. Higher optical quality KG1 glass would be required for true FROG reconstruction, a possibility we are currently exploring.

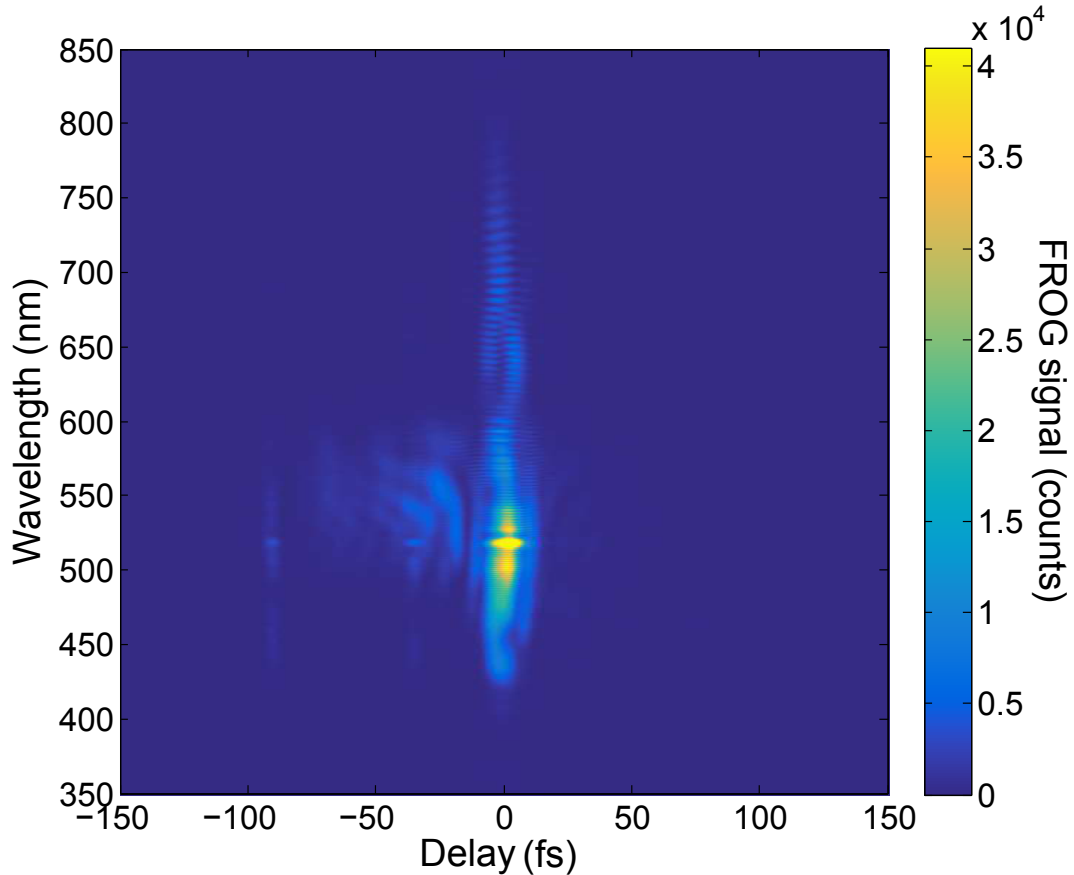


Figure 3.20: SS THG FROG trace of $1.75 \mu\text{m}$ few-cycle pulse. Spectral components from around 400 nm to 800 nm are observed, corresponding to an upconverted bandwidth of 1200 nm to 2400 nm, with no sign of XPM. The signal has several features resulting from scattering in the KG1 glass.

3.5 SWIR Source Development at ARTEMIS

As part of my PhD I had the opportunity to develop a very similar system at the ARTEMIS laboratory of the Central Laser Facility (Rutherford Appleton Laboratory, UK). ARTEMIS is a user facility, where groups from across Europe can submit applications to perform ultrafast experiments. At the beginning of my PhD ARTEMIS already had an HE-TOPAS front end to their CPA laser system. Fellow PhD student Paloma Matía Hernando and I participated in transferring our SWIR HCF pulse compression technology to ARTEMIS in order to increase access for the ultrafast laser user community to longer wavelength sources. The Laser Consortium provided a new differentially pumped HCF chamber and 400 μm inner diameter HCF to ARTEMIS. Paloma and myself performed the necessary characterization of the ARTEMIS idler focus, built the coupling telescope necessary to couple effectively, and characterized the output. As I have already discussed the general principles, I will summarize here to say that the ARTEMIS TOPAS produced 1 mJ pulses at 1800 nm with a 1 kHz repetition rate. Using an autocorrelator (TIPA, Light Conversion) we determined a pulse duration of around 60 fs. We were able to couple 500 μJ of the initial 1 mJ through the fiber, for a transmission of around 50%. The output mode was measured using a Spiricon IR camera and showed very good spatial uniformity. Figure 3.21 shows the output spectrum of the HCF obtained as a function of Ar backing pressure. Good spectral broadening was achieved with significantly higher pressures than at Imperial College, likely due to the decreased input power and increased input pulse duration. Nevertheless, the beam profile remained good and power losses from the increased pressure were minimal.

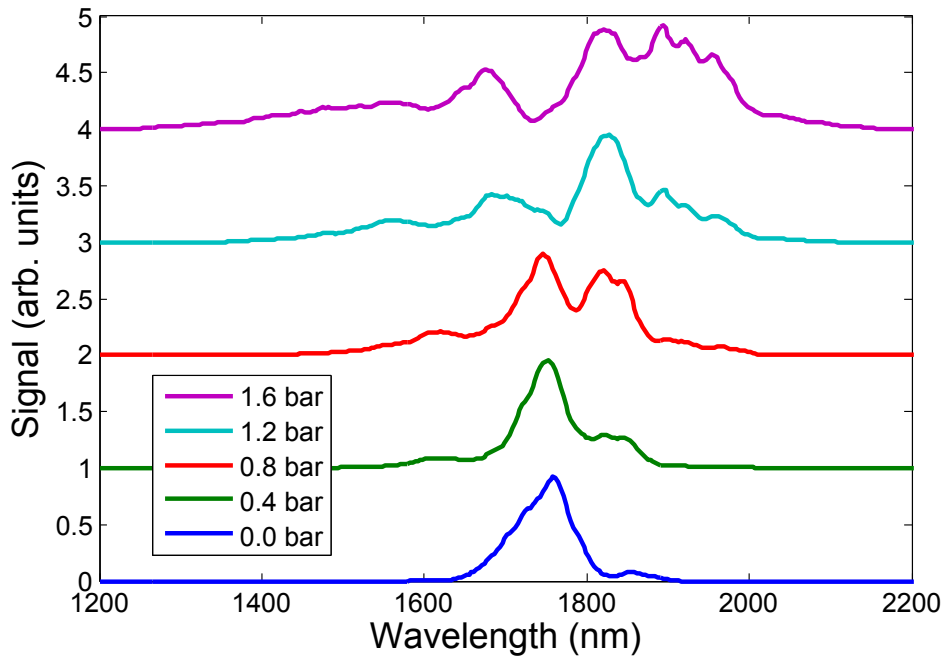


Figure 3.21: Output spectrum from the HCF at RAL as a function of argon backing pressure.

In order to characterize the temporal structure of the generated pulses, we built a single-shot autocorrelator following the design of our single-shot FROG (section 3.4.4). This did not require the use of an imaging spectrometer. Chronologically, this was built before the solution of using an absorptive material as the generation medium was proposed as in section 3.4.4; instead we overcame the difficulty associated with cross phase modulation by simply increasing the angle inside the third harmonic medium, here a piece of fused silica. This sacrificed resolution for simplicity, as the autocorrelator gave a resolution of only a few femtoseconds - rather poor for a pulse which may have a total duration of down to 7 fs. An example autocorrelation is shown in figure 3.22, with a FWHM of 14.5 fs, which corresponds to a duration of 11.9 fs assuming a Gaussian profile [141]. This is a sub-two cycle duration, sufficient for the generation of isolated attosecond pulses; however, the resolution limitations of the measurement are readily apparent in the trace.

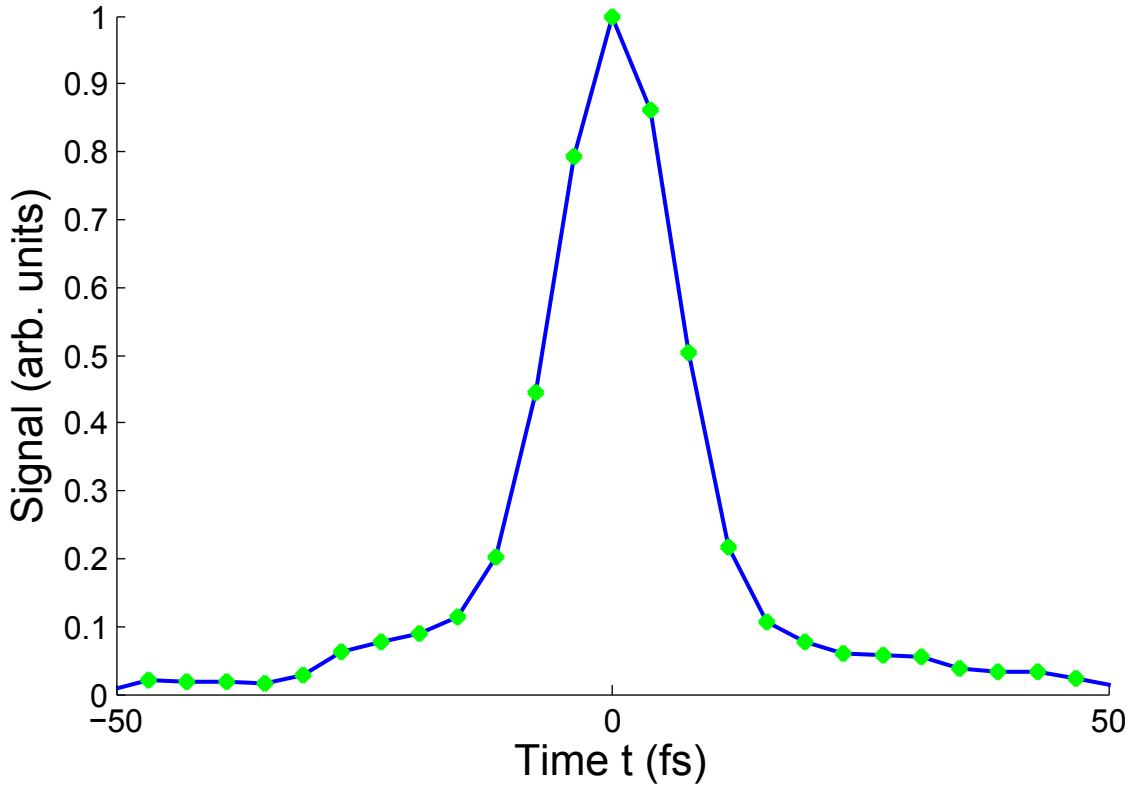


Figure 3.22: Autocorrelation measurement of the HCF output pulse at RAL. The autocorrelation FWHM of 14.5 fs is consistent with a two-cycle pulse, but is poorly sampled.

3.5.1 Dispersion Scan Characterization

In order to perform full pulse characterizations we built, together with Adam Wyatt of RAL, a third harmonic D-scan system for the few-cycle idler. This route was chosen for its increased simplicity over FROG or SPIDER; as the pulse already passes through compression wedges, scanning the dispersion is easily performed simply by scanning their insertion. The use of third harmonic both separates the upconverted signal from the fundamental in spectrum and moves

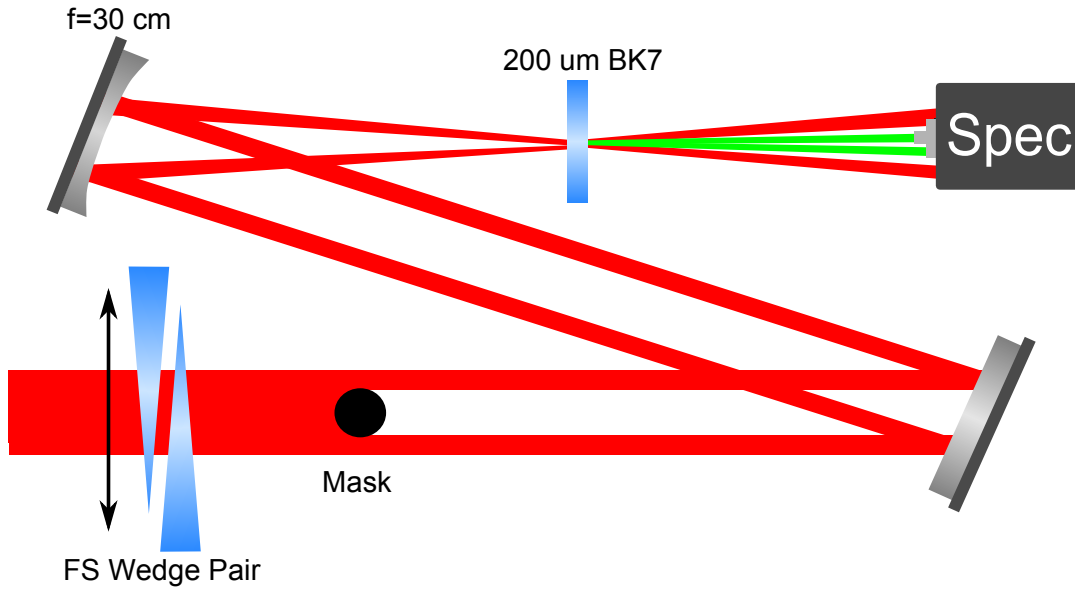


Figure 3.23: Third-harmonic dispersion scan setup at RAL.

the signal fully into the absorption range of silicon detectors in much the same manner as in the single shot FROG. A schematic of the system is shown in figure 3.23, which shows its great simplicity. In brief, the pulse passes through the motorized compression wedges and is focused using an $f = 30$ cm focal length mirror into a piece of BK7 glass $\approx 200 \mu\text{m}$ thick. Unlike in the single shot FROG case, we use a very thin piece of material so that group velocity walk-off is minimized. Thus the generation at the front and back surfaces is in phase, as evidenced by the lack of fringes in the spectrum. The walk-off should only present problems for the broadest of pulses, and this was not observed in any measurement made. The upconverted signal is then sent into a spectrometer (OceanOptics). We use a mask (2 mm hex key) to geometrically split the beam prior to the crystal [134]; this allows us to more easily isolate the signal beam in the spectrometer, which can otherwise be dominated by infrared scatter or parasitic harmonics from the fibre.

Figure 3.24 shows a typical D-scan trace obtained at RAL. The changing spectrum with wedge insertion reflects that the mixing of frequency components is modulated by the different phase relationships between them. We clearly span the regime of ‘shortest pulse’, where the upconversion is broadest. This generally makes the reconstruction more effective, as the signal is more sensitive to phase variation in this region. It would be advantageous to be able to scan an even larger range of dispersion, but we are limited by the available materials and geometry of the wedges. Almost all materials exhibit anomalous dispersion in the SWIR, while those that do not are either very weakly dispersive (N_2) or exhibit large non-linearities (ZnSe).

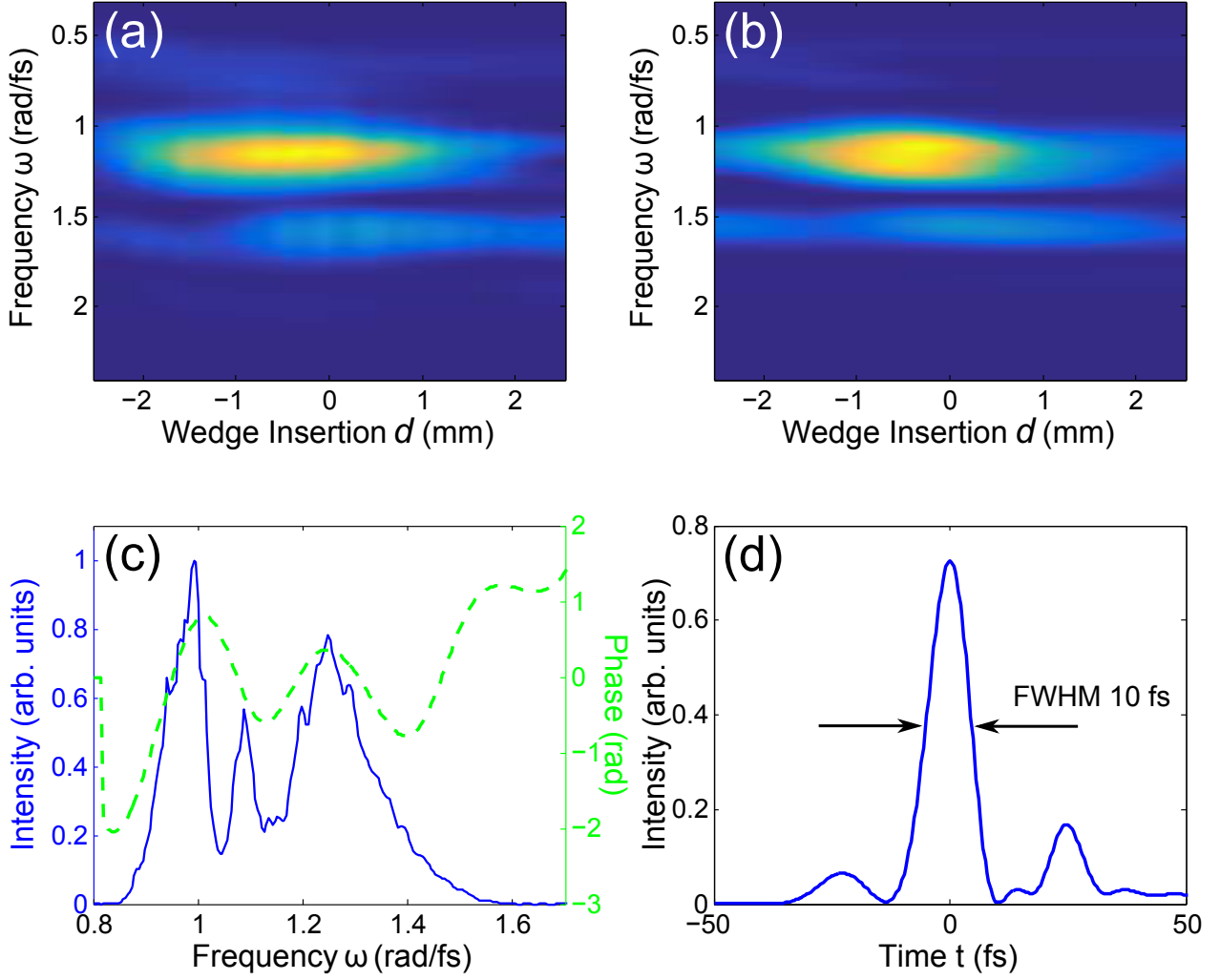


Figure 3.24: Third-harmonic D-scan results from RAL. (a) Experimentally acquired D-scan trace. (b) Retrieved D-scan trace. The agreement is reasonable, with differences attributable to other non-linearities. (c) Retrieved spectral amplitude and phase. (d) Retrieved pulse duration, shown to be 10 fs FWHM duration.

Revealed in the reconstruction is that some features can be associated to other third order non-linearities, namely SPM and XPM. As in the single shot FROG, the long wavelength component is a result of XPM and is difficult to remove. These components complicate the D-scan reconstruction routine significantly, and in fact cannot be treated accurately in the standard implementations. A novel method based on thermal annealing algorithms [142] developed by Adam Wyatt and incorporating these unwanted effects was employed to overcome these difficulties. Using this technique we determined an optimal pulse duration of around 9-10 fs, close to that achieved at Imperial College [143], though further refinement of the reconstruction is ongoing.

Chapter 4

Application of a SWIR Source to High Harmonic Spectroscopy

4.1 High Harmonic Generation Spectroscopy

High harmonic generation spectroscopy (HHGS) is an intriguing application of high harmonic generation to attosecond measurements. The key concept is that the high harmonic process itself can be considered as a type of attosecond pump-probe experiment, in which the ionization step acts as the pump and the recollision step as the probe [15]. Because of the well-defined chirp of the high harmonic process (see section 2.5), each individual harmonic energy can be related to a particular pump-probe time delay, and so a high harmonic spectrum simultaneously encodes an entire pump-probe experiment. The state of the system at the time of return is encoded in the recombination dipole matrix element $\vec{\mu}(t_r)$; as this is dependent on both electronic state and instantaneous nuclear structure, HHGS has been used to study both attosecond electronic [16] and nuclear [15, 144] dynamics. In particular, through its highly sub-cycle nature, HHGS is currently able to provide finer temporal resolution than attosecond pump-probe experiments, down to tens of attoseconds.

HHGS presents significant experimental and theoretical challenges. The presence of the strong laser field distorts the dynamics significantly with respect to the field-free state, and this distortion is difficult to accurately describe with theory. Additionally, correct treatment of the continuum electron and its ionization to better-than-exponential accuracy without use of full TDSE simulations, which are infeasible for more than a few atoms, is demanding. Experimentally, the challenge is to ensure high harmonics can be generated from the sample, and that the intensity, wavelength and ionization potential satisfy the SFA condition $\gamma \ll 1$. Satisfying the SFA condition is essential for the validity of the semi-classical trajectory picture, which enables HHGS to be interpreted as a pump-probe measurement. For small molecules with large I_P this can be accomplished relatively easily at 800 nm, but here the temporal window between ionization and recollision is small, below 2 fs, and so only the fastest dynamics can be studied. For larger molecular systems weaker fields are required to prevent ionization saturation; this

necessitates the use of long wavelengths in order to remain in the quasi-static limit [145]. Moving to longer wavelengths has the additional benefits of increasing the time window between birth and recollision. For a $1.75\ \mu\text{m}$ field, the time window increases to around 4 fs. Hence our SWIR laser source provides a superior driving field for HHGS of larger molecules, allowing us to study significantly slower nuclear dynamics than have been seen before in molecules which previously could not be studied by HHGS at all. We will focus on HHGS from substituted benzene molecules, which have significantly lower I_P (around 9-10 eV) than previously studied molecules such as CO_2 ($I_P = 13.77\ \text{eV}$).

Another challenge for experimental HHGS is the delivery of samples into the gas phase and the isolation of the single-particle response. Benzene and related compounds are normally in the liquid phase, which is common for larger molecules. Optical methods like HHG require higher density-length products than photo-particle schemes, where sufficiently low densities are required that the intrinsic vapour pressure of the sample can be used to introduce sample into the gas phase. We have overcome this difficulty using a heated bath and vapour delivery system, which can back a continuous-flow gas jet with pressures of over 1 bar. In the following sections I will describe how we use this source to overcome a significant and under-discussed experimental challenge in HHGS, the isolation of the single particle response. Most HHGS theory calculations are done for a single molecule or atom, but it is well known that macroscopic effects, such as focal plane averaging and phasematching, can significantly alter the observed signal. Here I will discuss both theoretical and experimental work performed to isolate a macroscopic signal easily comparable to the single particle response. I introduce the concept of *fidelity of an HHGS measurement*, before concluding with an experiment comparing the nuclear dynamics of benzene and deuterated benzene.

4.2 Isolating the Single Particle Response: Theory

It is illustrative to compare phasematching in HHG to phasematching in SHG to understand the problem in HHGS. To efficiently upconvert light in a non-linear crystal, it is necessary to take advantage of the L^2 scaling of the SHG response for phasematched light [20]. This is why frequency doubling crystals inside monochromatic pump lasers are often several centimeters thick. However, there is a trade-off between the efficiency and the bandwidth of the upconversion; this necessitates the use of thin crystals in D-scan and FROG to mitigate the effects of phasematching [128] and isolate a signal which can be compared to the fundamental expression for single emitter SHG which is used in the reconstruction algorithm. A similar concept applies in HHG; optimization of the system for harmonic flux will strongly distort the spectral response as compared to a single emitter. Because we are interested in the faithful reproduction of the microscopic signal in our macroscopic signal, I refer to this quality as *fidelity*, a term from signal processing referring to the degree of exactness with which a signal can be reproduced. I will show that in HHGS it is also necessary to use low conversion efficiency conditions, namely thin

targets, in order to produce a high fidelity measurement.

Let us begin with some general observations to gain further insight into the necessary experimental conditions. Within the strong field approximation, the HHG signal is dominated by the phase accumulated by the electron in the continuum and the interference of multiple trajectories. This means the dipole is exponentially dependent on the driving field and ionization potential, which has allowed many features of HHG to be explained while ignoring the impact of the bound potential completely. Given the dominance of the laser field, it is thus extremely important in HHGS that the driving field remain undistorted throughout the sample. Significant distortion of the driving field will result in changes to the HHG signal that mask the single particle response. This means ionization, self-phase modulation, self-focusing, and dispersion all need to be limited or accounted for. These four effects are linked only by their dependence on the propagation density-length product. The first three are also linked by their dependence on intensity, which cannot be made arbitrarily low due to the dependence of HHG on ionization. Thus, the use of a short density-length product is already strongly suggested without even considering phasematching.

The need to maintain a constant driving field naturally suggests the use of the quasi-static approximation for HHG phasematching. We use the Balcou expression for high harmonic phase matching, equation 2.6.5, which gives the phase-matching length for each colour in the high harmonic spectrum. We set the requirement $L < \min(\pi/\Delta k(\Omega))$, where L is the medium length and Ω is the set of all frequencies in the single particle response. By having a medium shorter than the shortest coherence length, all harmonics will scale in the same L^2 fashion and preserve their relative amplitudes. Equivalently, all frequencies should be within their first Maker fringe [20]. We will return to this condition later.

To rephrase equation 2.6.5 in a manner appropriate here, the vector mismatch Δk between a harmonic of frequency ω and the fundamental driving field can be expressed as

$$\Delta \vec{k}(\omega) = \Delta \vec{k}_p + \Delta \vec{k}_n + \Delta \vec{k}_g + \Delta \vec{K} \quad (4.2.1)$$

where $\Delta \vec{K}$ is the effective $\vec{k}$ -vector mismatch of the single particle response, $\Delta \vec{k}_p$ is the mismatch arising from plasma dispersion, $\Delta \vec{k}_n$ refers to the neutral gas dispersion, and $\Delta \vec{k}_g$ is the geometric phase mismatch, either the Gouy phase shift of the fundamental or the mode dependent dispersion of a waveguide. Let us consider the frequency dependence of the single particle phase. As we saw in section 2.5.2 the phase of a harmonic order at emission scales as $\Phi_{q,i} \propto \alpha_{q,i} I(r, z)$ where $\alpha_{q,i}$ is a constant depending on q , the harmonic order, and i , denoting either long or short trajectory. Since $I(r, z)$ is independent of the harmonics, the spectral dependence enters through the $\alpha_{q,i}$ factors, which are related to the time the electron spends in the continuum between birth and recollision, together with the energy the electron has during those times. It has been shown that across the plateau and cutoff regions of the harmonics

these factors are approximately constant but different for the two regions ($\frac{\partial \alpha_{q,i}}{\partial \omega} \approx 0$), and again are different for the long and short trajectories [85]. Note this does not mean the harmonics are emitted in phase, but rather that their dependence on the intensity of the driving field is the same. Also note that this linear relationship of phase on intensity only holds across a range of intensities, and thus achromaticity can be enhanced by restricting the range of intensities over which HHG is performed inside the sample.

If we differentiate the quasi-static phasematching condition equation 2.6.5 with respect to the frequency, we find

$$\frac{\partial \Delta \vec{k}(\omega)}{\partial \omega} = \frac{\partial \Delta \vec{k}_n}{\partial \omega} + \frac{\Delta \vec{k}_p}{\partial \omega} + \frac{\Delta \vec{K}}{\partial \omega} + \frac{\Delta \vec{k}_g}{\partial \omega} \quad (4.2.2)$$

$$= \frac{(1-\eta)P}{c} [n(\omega) - n(\omega_0)] + \frac{(1-\eta)P\omega}{c} \frac{\partial n(\omega)}{\partial \omega} - 2\pi c P N_a \eta r_e \frac{1}{\omega_0^2} + \pi c P N_a \eta r_e \frac{1}{\omega^2} + \frac{1}{\omega_0} \nabla \Phi_{Gouy}. \quad (4.2.3)$$

If propagation takes place not in a free-space focusing geometry but instead in a waveguide, the geometric phase term $\nabla \Phi_{Gouy}$ is replaced by the waveguide propagation vector of the fundamental field $\frac{u_{1m}^2 \lambda_0}{4\pi a^2}$. The waveguiding of the harmonics will be negligible due to their smaller mode area and divergence. To obtain broadband phasematching we need $\frac{\partial \Delta \vec{k}(\omega)}{\partial \omega} = 0$ around the harmonic frequencies. We discard the $1/\omega^2$ plasma term as high harmonics are necessarily at high frequencies ($\omega \gg \omega_0$), and furthermore we require the ionization fraction η to be small for the quasistatic approximation to hold. The other strongly frequency-dependent contribution is $\omega \frac{\partial n(\omega)}{\partial \omega}$; provided we are far from an absorption resonance, the variation of the refractive index with frequency (and indeed the refractive index itself) is extremely small in the XUV, and this term can be discarded. If this is not the case, then we can expect strong variation of the phase-matching length with wavelength, and unless very sensitive detection allows one to measure signal when L is made very small, HHGS will likely be untenable. This is of course consistent with the fact that the SFA formulation of HHG is only valid at energies far above the I_P , and furthermore assumes planewave continuum states, meaning that even if good phasematching were achieved, the HHGS signal could not be interpreted as a pump-probe measurement.

Let us assume that we are far from a resonance and that $n(\omega) \approx 1$, but allow $n(\omega_0)$ to be non-zero. We are left with the following expression for broadband phasematching:

$$\frac{(1-\eta)P}{c} [1 - n(\omega_0)] - 2\pi c P N_a \eta r_e \frac{1}{\omega_0^2} + \frac{1}{\omega_0} \nabla \Phi_{Gouy} = 0. \quad (4.2.4)$$

This condition is achromatic; if we can achieve broadband phasematching, it will apply at all frequencies. The Gouy phase term can be made arbitrarily small through the use of loose focusing, in which the beam is approximately a planewave across the interaction region. However, in this case we are left with η as the only free parameter. Since we require that the

ionization fraction is small, broadband phasematching cannot be achieved. Instead, we need a contribution from the geometric phase to counteract the material and plasma dispersion to achieve achromatic phasematching at small η . Note that this contribution is still small, since the refractive index of a dilute gas is generally close to one even at longer wavelengths, so the contributions requiring balancing are small. We see that, for a fixed ionization fraction, as we increase the pressure we will require tighter focusing to induce a large shift in $\nabla\Phi_{Gouy}$. However, because we want to minimize $\Delta\vec{k}(\omega)$ as well as $\frac{\partial\Delta\vec{k}}{\partial\omega}$, we will want to use the loose focusing condition with lower pressure. As can be seen by satisfying equation 4.2.4 and substituting it into 2.6.5, the atomic dipole phase is left unconstrained by this argument. However, it can be made small by the use of loose focusing which makes the gradient of the intensity small; hence we conclude the ideal geometry for achromatic phasematching in HHGS is loose focusing into a dilute gas.

Note phasematching in a waveguide can also satisfy equation 4.2.4 where the Gouy phase is replaced with the waveguide propagation vector but, because the waveguide dispersion is much larger than a typical Gouy phase shift, it would require much higher pressures. While the atomic dipole phase contribution is small in waveguides [88], this leads to problems with reshaping of the fundamental. Increasing the core diameter of the fibre will reduce this problem, but only at the point where the guiding is relatively marginal, defeating the purpose of a waveguide.

Let us return to factors other than phasematching which can distort the macroscopic HHG spectrum as compared to the microscopic HHG spectrum and thus reduce the fidelity of the measurement. Intensity averaging is one such effect and is in general unavoidable, as any laser beam will necessarily contain a range of intensities. This averaging can be reduced through the use of spatial and temporal laser sculpting to generate flat-top beams [146, 147], but in many cases intensity averaging can be surmounted in the analysis step, where a simulation is reproduced for many intensities and summed. Another effect is reabsorption of the harmonics, which can reshape the spectrum through the frequency-dependent absorption cross-section σ . Provided we are far from a resonance this should be relatively achromatic, but it can also be reduced through the use of a low density-length product.

Having now identified loose focusing into a low-density gas as necessary for phase matching, as well as minimization of re-absorption and non-linear propagation, it is now tempting to consider the use of a long medium target [148], in order to maximize the harmonic flux. In the case of perfectly achromatic phasematching and absorption, the absorption-limited macroscopic signal directly reflects the single-emitter amplitude, but in the presence of even slight differences in L_{abs} or L_{coh} this will result in large differences in the observed signal. Figure 4.1 shows the effect of small variations in Δk and L_{abs} for signals of identical single particle strength, calculated using equation 2.6.9. At large L there are large differences in the signal levels; only for small $L < \{L_{coh}, L_{abs}\}$ do the signals agree well, even without considering that in a real sample L_{coh}

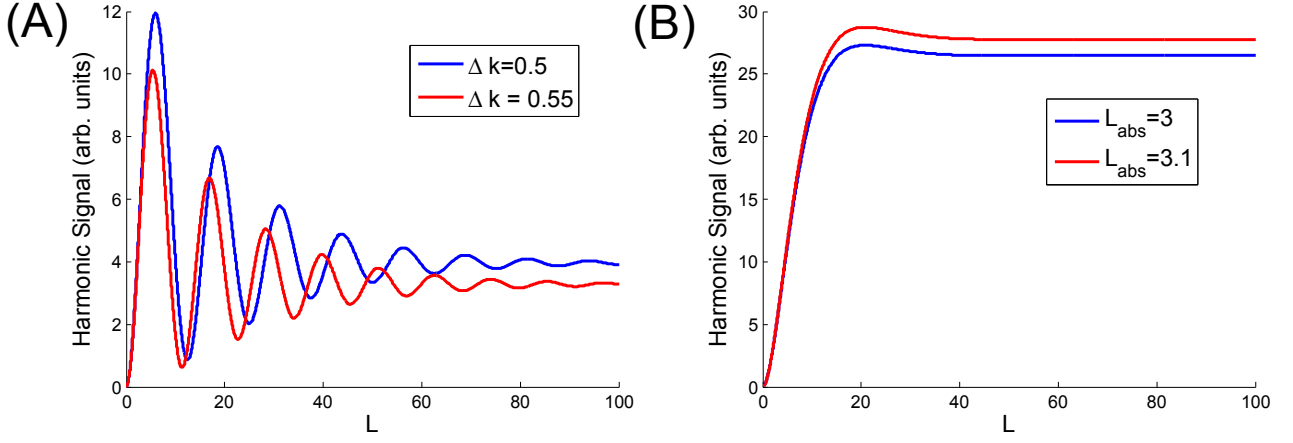


Figure 4.1: Effect of varying phasematching length and absorption length as a function of length on signals of identical single particle strength. (A) The red and blue curves exhibit the final signal level for signals with phasematching lengths of $\pi/0.5$ and $\pi/0.55$, with an absorption length of 10 units. (B) The red and blue curves show the final signal for signals with identical coherence lengths of $\pi/0.1$ and absorptions lengths of 3 and 3.1.

will itself vary throughout the sample for each harmonic order. For this reason it is essential to use not only a sample with low density-length product, but additionally a short propagation length. Only in this condition can the macroscopic harmonic spectrum be taken to represent the single particle response with high fidelity. This geometry can be satisfied by using a gas jet, where the spatial extent of the sample can be limited to hundreds of microns or less.

4.3 Isolating the Single Particle Response: Experiment

With a view towards performing sub-fs pump-probe experiments in benzene and substituted benzenes, I'll now discuss the system we developed for performing high harmonic spectroscopy of these samples and how we experimentally ensure the fidelity of the HHGS signal. Our source is the output of an evacuated HCF at $1.8 \mu\text{m}$; using a long pulse significantly improves the stability of the output. Using a second-harmonic scanning FROG we measured a pulse duration of 30 fs and a pulse energy of $600 \mu\text{J}$. The resulting beam is focused into a $200 \mu\text{m}$ diameter gas jet using an anti-reflection coated 50 cm focal length CaF_2 lens. This results in a focal spot size of around $130 \mu\text{m}$ FWHM with a Rayleigh range of 2.25 cm, much longer than the length of the target, and so suited for HHGS measurements. We automate our scans by having a motorized iris and focus position (Thorlabs stages), while the reflection off a 1 mm CaF_2 glass plate is sent to a camera to record the focal size and fluctuations in pulse energy.

Benzene and substituted benzenes are in the liquid phase at room temperature and pressure, but for HHGS we need them to be in the gas phase with a pressure of order 1 bar in order to back the gas jet. This is accomplished by placing the samples in evacuated sample flasks which are immersed in a hot liquid bath, either water or silicon oil depending on the temperature range required (0-100 °C or 0-150 °C, respectively). The vapour pressure can then

be controlled through the backing temperature without requiring mechanical regulators, which are prone to failing with volatile materials. The vapour is carried to the gas jet via stainless steel lines heated to 175 °C to prevent condensation, and the backing pressure recorded with a capacitance manometer. Finally the gas passes through the jet, which is heated to 200 °C in order to prevent condensation blocking the small aperture. We can achieve backing pressures in excess of 2 bar, which as we will see is more than sufficient for HHGS. The emitted harmonics propagate onto a variable-line-space flat-field grating (Hitachi 001-0437), and are detected by a MgF coated MCP and phosphor screen assembly (Photonis). Metallic foil filters can be optionally inserted prior to the grating for calibration purposes. The screen is imaged with an objective lens (25 mm FL, f/0.95) to a low noise CCD (PCO Pixelfly) and the spectrum recorded. The complete system is shown in figure 4.2.

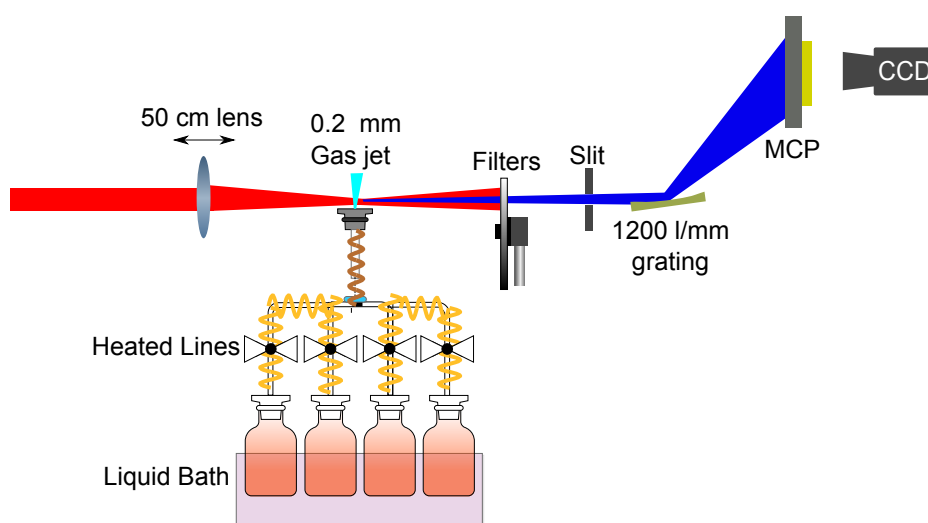


Figure 4.2: System for HHGS in benzenes. The beam is focused into a gas jet backed by high temperature vapour of the normally liquid phase created in a heated bath. The emitted harmonics are detected by a standard XUV grating and MCP spectrometer.

First of all, it is necessary to demonstrate that high-quality harmonics can be generated. Spectra from benzene, toluene, m-xylene and p-xylene are shown in figure 4.3, though we have also obtained harmonics from deuterated-benzene, o-xylene, and chlorine, iodine, and bromene substituted benzenes. Both shown and unshown spectra have well separated and resolved harmonics, good signal to noise, low divergence, and good spatial uniformity. Notably absent, however, are the long trajectory contributions, which are usually observed off-axis [85]. As quantum diffusion increases with the time in the continuum, it is possible these contributions are just too weak to resolve; thus far, no experiment has resolved long-trajectory contributions at long wavelengths in either molecules or atomic species. In order to verify the fidelity of our spectra, we have scanned a range of parameters which influence the macroscopic signal (pressure, focal position, intensity) to find a region in which the influence of macroscopic parameters is minimized. We have identified such a region, but it spans only a very small range of parameters. In particular we find backing pressures of less than 0.3 bar, a target length less

than 20% of the Rayleigh range, and intensities of 3×10^{13} W/cm² or less are required. In contrast, harmonics can be generated across a much broader range of parameters.

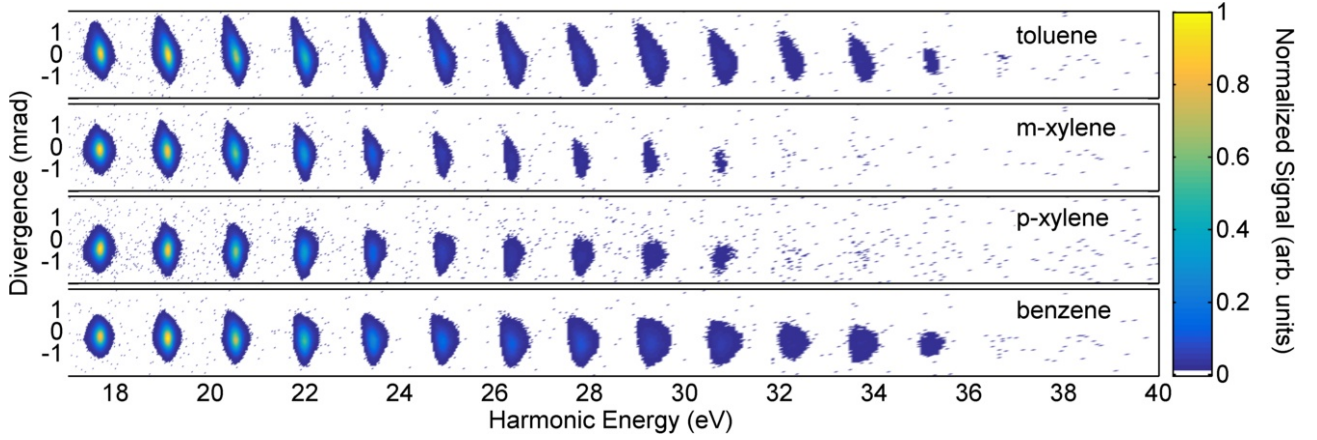


Figure 4.3: Harmonic spectra generated in benzene, toluene, m-xylene and p-xylene. All show good signal to noise, spatial quality, and resolution.

Let us first look at the role of the intensity. Too much intensity can lead to a variety of undesirable effects, including poor phasematching, distortion of the fundamental, saturation of the single emitter, and deviation from the SFA picture necessary for interpreting the experiments. We have scanned the intensity of the driving laser to ensure such effects are not significant. While determining the effect on phasematching is very difficult since the intensity changes the frequency-chirp relationship, and thus the single emitter response, the other factors can be controlled by examining the variation of the cutoff harmonic energy to the semi-classical scaling law $E_{max} \propto 3.17U_p + I_p$. Since we are using a multi-cycle laser field, the highest energy harmonics will be generated after several laser cycles. If plasma stretches the fundamental and decreases the peak power, or if the single molecule emission is clamped by ionization, we will see a lower cutoff than would otherwise be expected. This is exactly what we see in our scans, an example of which is shown in figure 4.4.¹ We normalized the spectra to the total harmonic yield, and plot it as a function of the peak intensity. The peak intensity is measured by the camera image of the focal spot size and the energy; we calibrated this measurement using the high harmonic cutoff in xenon. Up until an intensity of around 30 TW/cm² we see good agreement with the semi-classical cutoff law, but at higher intensities the distribution shifts to lower photon energies. Interestingly we do not observe a blue shift in the harmonic energy from the generation of plasma [149], suggesting deviation from the semi-classical cutoff law is a more sensitive probe of ionization effects than the plasma blue-shift.

As was emphasized in section 4.2 the pressure has a large influence on the phasematching of the harmonics and is quite complex. However, since we hope to be in the achromatic phase

¹If this were simply a reflection of the single particle response, we would expect either a flat spectral cutoff or a slower rate of increase.

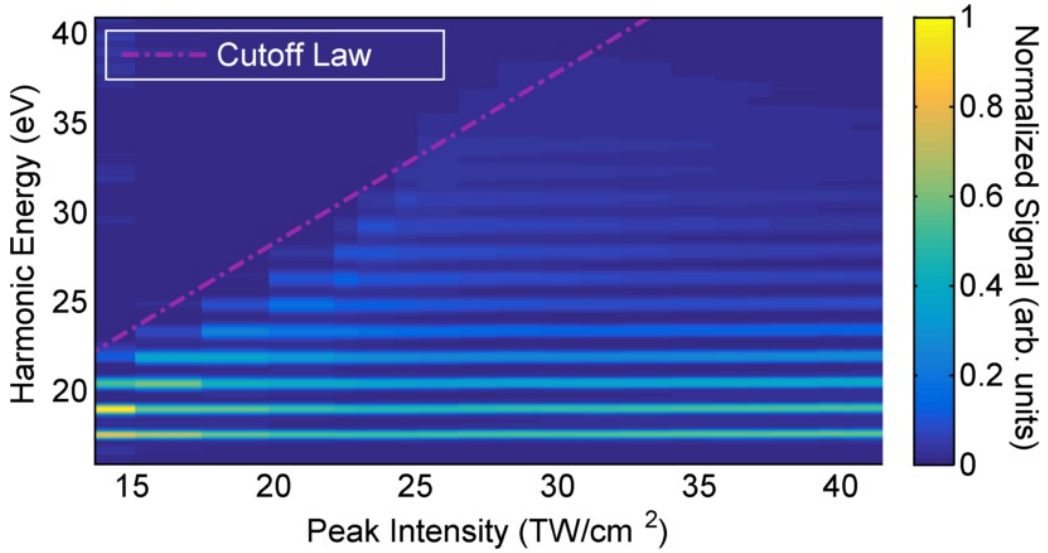
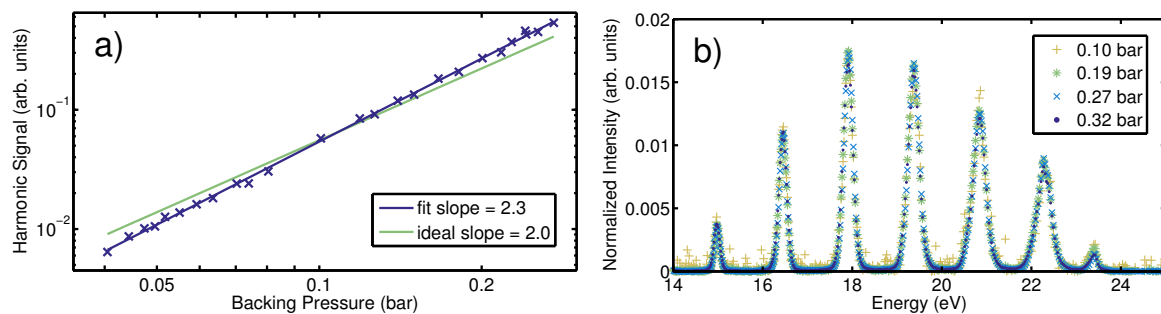


Figure 4.4: High harmonics generated from benzene as a function of driving laser intensity, with spectra normalized at each intensity to total harmonic yield. At lower powers the harmonics follow the semi-classical cutoff well, but deviate at higher intensities.

matching regime and with $L \ll L_{coh}$, the influence on the phasematching length should be minimal. If this condition is satisfied then the primary impact of increasing the pressure should be increasing the density-length product ρL , which for ideal phase matching causes the signal to grow as $(\rho L)^2$. We scanned the backing pressure in benzene from 0.025 to 0.3 bar and examined the growth of the harmonic signal. In figure 4.5a we compare the change in the signal level of harmonic 15 as compared to the ideal growth in signal assuming that $P \propto \rho L$, which would give P^2 growth in signal level. We observed a slightly super-quadratic scaling with backing pressure, with exponent 2.3. As phasematching effects can only decrease the growth in signal, we attribute this super-quadratic scaling to non-trivial gas dynamics in the jet [150], which lead to a non-trivial dependence of ρL on the backing pressure. Nevertheless, this is an encouraging result, as if L was of order L_{coh} we would expect to see saturation or possibly even Maker fringes as the pressure was varied [151]. Because of the gas jet dynamics, we chose to examine the “self-similarity” of the spectrum as the pressure is varied; if we are in effect within the first Maker fringe and achieving achromatic phase matching, changing the pressure should only change the absolute signal level and not distort the spectrum. Figure 4.5b shows the benzene spectra at four different backing pressures, each normalized to the total harmonic yield. The agreement between the four spectra is excellent, and deviations are within the shot-to-shot noise. If we increase the pressure beyond 0.3 bar distortions in the spectrum begin to become apparent; in order to obtain the best signal-to-noise while maintaining good fidelity, we thus identify 0.3 bar as the ideal pressure for HHGS in our system.

Our last free macroscopic parameter is the focus position relative to the gas jet, which affects the $\nabla\Phi_{Gouy}$ and $\vec{K}$ terms in the phasematching. Surprisingly, despite the fact our Rayleigh length is two orders of magnitude larger than L , we still find small changes in the relative position cause significant changes in the harmonic spectrum. Since there is no absolute reference for



(a) Harmonic 15 signal growth compared with ideal P^2 scaling. (b) Self-similarity of the spectra as a function of backing pressure.

Figure 4.5: Effect of backing pressure on the high harmonic spectrum of benzene.

the correct choice of focus position, this would seem to suggest HHGS requires full simulation of the generation region to return useful information, a computationally unfeasible challenge at present. It is tempting to ascribe this variation to changes in the divergence, which are known to accompany changes in the focal position [84], since we have a finite aperture on our spectrometer. This would suggest a route to correcting the harmonic signal by the relative divergence of each harmonics in order to obtain a measure comparable to single particle calculations. However, a more robust route is to instead perform comparisons between different molecules under the same generating conditions and use the ratios between them as the observable. Indeed we find that ratios are indeed independent of the focus position, either between harmonic spectra taken at different intensities or between harmonic spectra from different molecules. Thus HHGS using reference atoms [152] or molecules [15], or alternatively scanning parameters such as intensity or ellipticity [153] can be expected to yield valuable information, while attempts to derive information directly from the harmonic spectrum are significantly more complex.

4.4 Few-femtosecond Dynamics in Benzene

While we have performed comparisons of many different molecules at a variety of intensities, I will present only our results obtained from benzene and deuterated benzene. The results in other molecules can be analyzed in a similar way as will be presented, but the theoretical understanding of those spectra is beyond the scope of this thesis and so they are not addressed here. Comparison of benzene and deuterated benzene is performed in keeping with the original scheme for using HHGS as a pump-probe measurement as described by Lein [154] and performed by Baker *et al.* [15], where a sample and its deuterated equivalent are considered to have identical electronic contributions to the dipole moment. Therefore any differences in the high harmonic spectrum are attributable to the nuclear dynamics, which because of the intrinsic chirp can be robustly extracted.

We follow the analysis procedure of Baker *et al.* and calculate the ratio of the deuterated to protenated sample for each harmonic order; the results are presented in figure 4.6. We perform

the experiment at different intensities because changing the intensity modifies the time-energy relationship of the high harmonic spectrum [154], allowing us to further disentangle static dipole moment effects that depend only on the harmonic energy, from dynamics which will vary with intensity. In sharp contrast to earlier results in methane [15], we see no dynamic or static differences between the harmonics of benzene and deuterated benzene over the approximately 4 fs measurement time. We attribute this difference to the fact that the molecular structure of benzene relevant to HHG is dominated by much slower C-C bonds instead of the C-H bonds in methane. In particular the doubly degenerate HOMO is strongly localized around the C-C bonded ring, and has little density across the faster moving C-H bonds. However, we note this result is in direct contradiction to some calculations which predict a strong clamping of harmonic emission in protenated molecules when compared to the deuterated case [155], though other calculations predict long lifetimes for the nuclear autocorrelation [156, 157]. It may be that the effect of molecular dynamics in this system could be observed by moving to even longer driving wavelengths than the current $1.8\ \mu\text{m}$. Alternatively, similar analysis could be performed on systems with either significantly faster nuclear motion or more strongly differentiated electronic dynamics.

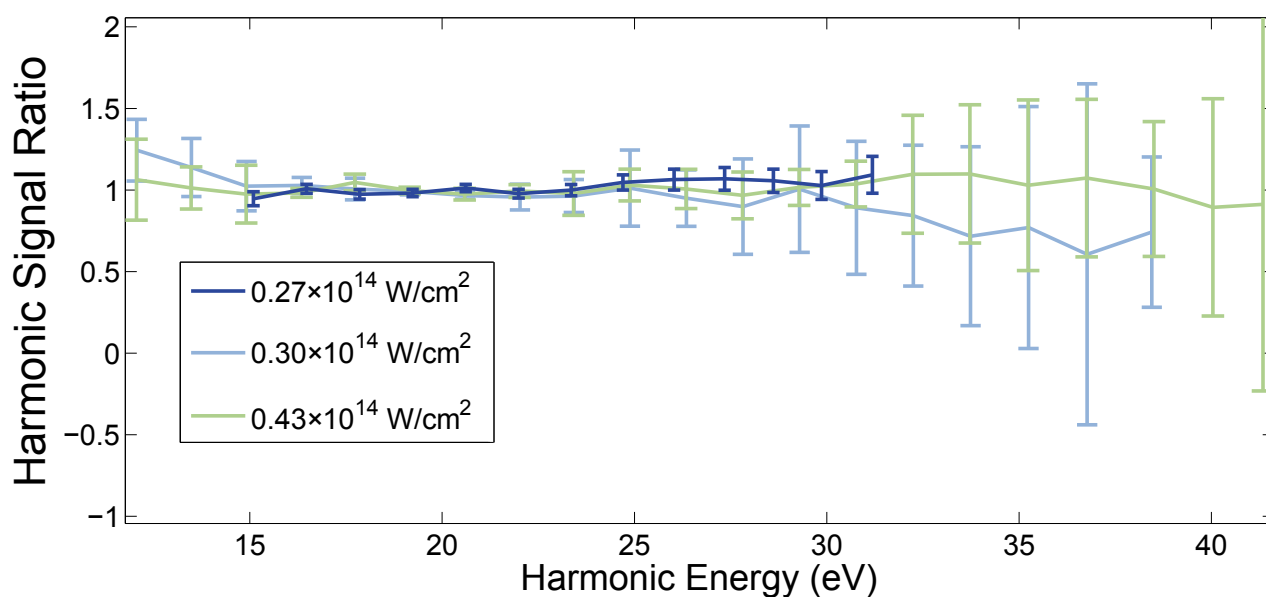


Figure 4.6: Ratio of deuterated benzene harmonic signal to protenated benzene harmonic signal at various intensities. Within error we see no differences, suggesting nuclear dynamics do not impact the HHG in this timescale.

We have also obtained HHG spectra from toluene, p-xylene, m-xylene, chloro-benzene, iodo-benzene, and fluoro-benzene for comparison with benzene. In these cases there are significant variations between the electronic structure of the different molecules as well as the nuclear dynamics, and so the analysis is significantly more complex. Recent work by Dane Austin *et al.* [158] has made significant progress on treating the strong-field approximation component of the problem by implementing accurate ionization and recombination dipole matrix elements for the various molecules, and including multiple electronic states. Figure 4.7 shows experimental

benzene spectra, theoretical spectra assuming no internal dynamics, and theoretical spectra in which a temporal Gaussian autocorrelation of $\tau_{ac} = 1.7$ fs ($1/e$ intensity) has been included by hand, all normalized to the peak harmonic. This temporal autocorrelation mimics the impact of nuclear dynamics by assuming that at short time delays, any nuclear autocorrelation is approximately Gaussian [155]. As can be seen, assuming the dynamics are governed entirely by the static dipole matrix elements and continuum trajectory dynamics leads to significant deviations between theory and experiment at higher energies, while the *ad-hoc* inclusion of an autocorrelation improves agreement at two different intensities. The high energies correspond to longer trajectories, where the impact of nuclear motion is to be expected. The agreement at two different intensities is essential, and suggests the deviation is due to dynamics and not due to uncontrolled factors, such as spectrometer response or, crucially, phasematching conditions. While further work is necessary to compare the fitted autocorrelation time to realistic models of nuclear motion [155–157], the agreement of a single time-constant for different intensities is an important step, and shows the power of the experimental approach.

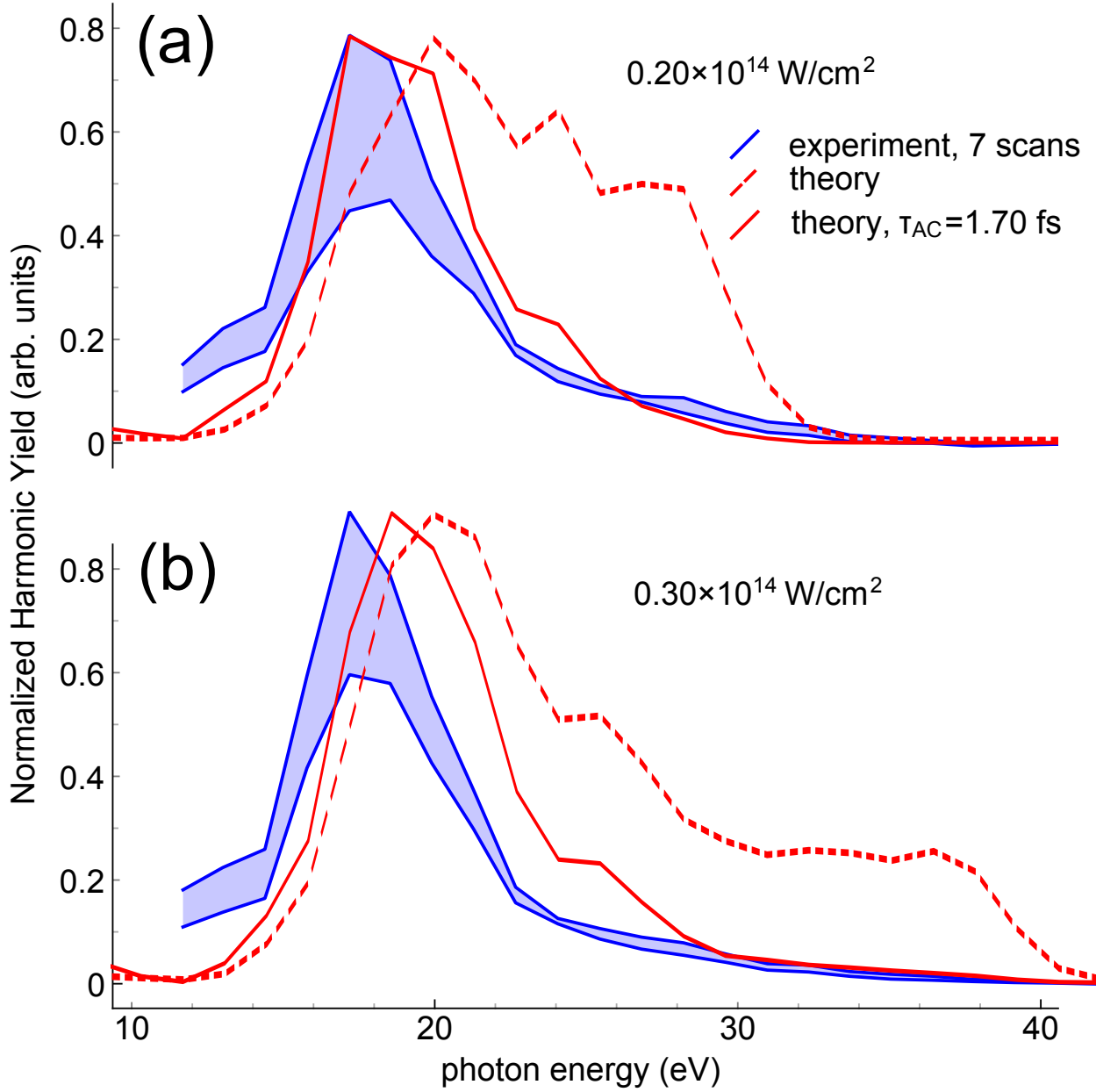


Figure 4.7: Experimental and theoretical harmonic spectra from benzene at (a) $I = 0.2 \times 10^{14} \text{ W/cm}^2$ and (b) $I = 0.3 \times 10^{14} \text{ W/cm}^2$, normalized to the peak harmonic amplitude. Experimental data is shown as the maximum and minimum of seven scans. Theoretical calculations are performed using the SFA, with realistic ionization and recombination matrix elements, and including multiple electronic states. Theoretical spectra are shown for which all dynamics are assumed to be well described by the continuum trajectories, and including an *ad-hoc* Gaussian autocorrelation of $\tau_{ac} = 1.7 \text{ fs}$. Inclusion of nuclear autocorrelation improves the agreement at high energies considerably.

Chapter 5

A Soft X-ray High Harmonic Source

With our SWIR source now well characterized and utilized for HHG spectroscopy of small organic molecules, we turn to the generation of short wavelength (high energy) harmonics, in order to bring the techniques of attosecond science together with those of X-ray science. While the harmonic cutoff law $E_{max} = 3.17U_p + I_p$ indicates that we will be able to produce harmonics deep into the water window, the efficiency of generating harmonics rapidly decreases with driving wavelength [10,159]. For this reason, it is necessary to develop a generating scheme which maximizes the conversion efficiency. This can conceptually be thought of in two ways, which turn out to be strongly coupled: by optimizing the phase matching between the emitted harmonics and the driving field, and by increasing the target gas pressure to increase the number of contributing emitters. As we shall see in our discussion of phase matching, the pressure used in the target can strongly impact the phase matching of the process, and in fact increasing the pressure, and thus the number of emitters, results in significant gains in harmonic flux. We then consider the measurement of our HHG source, and present our generation results.

5.1 Theory of Soft X-ray High Harmonics

The three step model predicts that the cutoff energy of high harmonics scales as $E_{max} = 3.17U_p + I_p$. The highest I_p of any neutral medium is found in helium, with an I_p of 24.6 eV, so the vast majority of the energy in HHG comes from the recollision energy of the electron, $3.17U_p \propto I\lambda_0^2$. As was seen in sections 2.5.2 and 2.6.2, there are strict limits to the intensity that can be used in HHG due to the effects of ionization. Ionization leads to both ground state depletion, which shuts off HHG completely, and to strong phase-mismatch between the fundamental and the harmonics. For this reason, HHG driven by 800 nm lasers has been mostly limited to energies below 150 eV, though harmonics have been generated into the water window with an extremely low flux [160]. The alternative route is to use longer wavelength driving fields, an approach which was first shown to extended the high harmonic cutoff in 2001 [161] and has been exploited successfully to generate high harmonics into water window [12] and beyond [162] with considerably higher flux.

5.1.1 Single Atom Wavelength Scaling

While the photon energy scaling with driving wavelength is simple and given by semi-classical analysis, let us examine the efficiency of HHG when driven with longer wavelength sources. Unfortunately classical models will not prove sufficient here, and we have to turn to the SFA and the TDSE. The first question that needs to be addressed is how to quantify the efficiency, since changing the wavelength changes many facets of the generation. A fixed harmonic order will change in absolute energy, energies measured relative to U_p change in absolute energy, and the cutoff extends to orders and energies not otherwise reached. Furthermore, what laser parameters to hold constant while varying the wavelength are not obvious. Holding the number of cycles and peak intensity constant while changing the wavelength changes the pulse energy; in general, only two of these three factors can be held constant. Discrepancies in definition lead to large variations in the estimate of harmonic conversion efficiency, by at least a factor of λ_0^2 [159, 163]. Here I will consider harmonic efficiency scaling at an absolute photon energy, e.g. emission at 350 eV or 500 eV. Since in the lab we measured conversion efficiencies as total-energy-in to total-energy-out, we consider also a fixed pulse energy, and somewhat arbitrarily, fixed intensity.¹

There are several factors that influence the scaling of HHG efficiency with wavelength. As the wavelength increases, electrons spend longer in the continuum, allowing the wavepacket to spread in the transverse direction - this results in a decreased probability of recolliding with the parent ion [81]. In the longitudinal direction, increased wavepacket spreading results in any given electron kinetic energy being less probable than at shorter wavelengths [23]. More photons need to be absorbed to reach a given harmonic photon energy as the wavelength is increased [164]. Most importantly, the timing of birth and recombination varies quite strongly with wavelength, with long trajectories born closer to the peak and short trajectories born closer to the zero of the field as the wavelength increases [159]. This can be seen by examining figure 2.9, where the timing of harmonic emission is shown to be invariant with respect to wavelength for a fixed fraction of U_p ; since U_p is strongly wavelength dependent, however, trajectories for a fixed energy move down the curve. This decreases the impact of wavepacket spreading on the short trajectories, but increases it for the long trajectories. This is somewhat counteracted by the movement of birth time towards the peak of the field, which increases the chance of tunneling in the first case for the long trajectories, and vice versa for the short trajectories. Using this approach, Austin and Biegert derived a wavelength scaling of $\lambda_0^{-4.1}$ for the long trajectories and $\lambda_0^{-8.5}$ for the short trajectories, where the change in tunneling rate dominates the short trajectory scaling [159]. With the correct definition of efficiency in place [163] this agrees reasonably well with previous TDSE simulations and experiments [164–166].

¹ Conversion to efficiency for a pulse with a fixed number of cycles and intensity is just multiplication by a factor of λ_0 , since that is the scaling for the energy of a pulse with a fixed number of cycles.

An alternative viewpoint is to assume that because of the poor wavelength scaling, one will never use a longer wavelength driving field than is required to reach a particular harmonic order. Thus it is the scaling not of a fixed energy E , but rather the scaling of the highest harmonic energy $3.17U_p + I_P$ which is of interest. The corresponding trajectory has a fixed timing relative to the driving field, being born $\approx 0.1\pi$ after the peak of the field. This fixes the ionization rate, so we see only a weak λ_0 dependence in the birth amplitude through $\vec{d}(\vec{p})$, and none in the overall rate. The electron recollision time is also fixed, occurring at the zero-crossing $\approx 1.4\pi$ after birth. The propagation step is thus fixed. When considering propagation under these conditions, the wavepacket spreading gives a λ_0^{-3} contribution to the efficiency, as the electron spends a factor λ_0 longer in the continuum, giving a λ_0^{-1} factor for spreading in each dimension [81, 159]. The only factor thusfar not considered is the recombination step, which depends on the dipole matrix element evaluated at the momentum of the returning electron. The scaling of this recombination matrix element with momentum (and thus with wavelength of the driving field) may be complicated depending on the species under study, but it has been noted that at high momenta it scales as p^{-1} , thus giving another λ_0^{-2} [159, 167], for a total of λ_0^{-5} . However, we must consider how we wish to measure the HHG spectrum - the single atom response enters Maxwell's equations as the acceleration of the dipole matrix element, but it has been shown that the velocity of the dipole matrix element better reflects the actual macroscopic emission [168]. Depending on which form is used, we need to add additional wavelength scaling factors; Austin and Biegert thus quote a total scaling of λ_0^{-9} for the efficiency of the cutoff harmonic energy, for the dipole velocity, while others give factors of λ_0^{-7} - λ_0^{-8} [163].

If we consider generation at 1750 nm compared to the ubiquitous 800 nm, we can see there will be between a two and three order of magnitude drop in amplitude of the single atom emission. For this reason, careful optimization of the macroscopic generation is even more critical at long wavelengths than for typical 800 nm HHG experiments.

5.1.2 Phasematching Soft X-ray Harmonics

As the single atom response with long wavelength drivers will be weak, careful optimization of macroscopic parameters will be essential for efficient high harmonic generation in the soft X-ray. We revisit here equation 2.6.8 for the phasematching pressure:

$$P_{PM}(\omega) = \frac{-q\nabla\Phi_{Gouy} - \vec{K}_{\omega,\omega_0}}{(1-\eta)\frac{\omega}{c}[n(\omega) - n(\omega_0)] - 2\pi cN_a\eta r_e(\frac{\omega}{\omega_0^2} - \frac{1}{\omega})}.$$

Let us consider just the plane at the focus of a Gaussian pulse [89]. Here $\vec{K} = 0$ and $\nabla\Phi_{Gouy} = 1/z_R$, where z_R is the Rayleigh length. Then we obtain

$$P_{PM}(\omega, z=0) = \frac{-2c\omega}{w_0^2\omega_0^2} \frac{1}{(1-\eta)\frac{\omega}{c}[n(\omega) - n(\omega_0)] - 2\pi cN_a\eta r_e(\frac{\omega}{\omega_0^2} - \frac{1}{\omega})} \quad (5.1.1)$$

where w_0 is the beam waist of the fundamental. If we further discard the $1/\omega$ term coming from the ionization, which for high energies will be negligible, this simplifies to

$$P_{PM}(\omega, z = 0) = \frac{-2c}{w_0^2 \omega_0^2 (1 - \eta)^{\frac{1}{c}} [n(\omega) - n(\omega_0)] - 2\pi c N_a \eta r_e \frac{1}{\omega_0^2}}. \quad (5.1.2)$$

Since the refractive index generally varies slowly with ω_0 , the plasma term in the denominator becomes more important as the frequency ω_0 decreases, requiring higher pressures to phase-match. In addition, there is an overall ω_0^{-2} scaling, so we can expect dramatic increases in the phasematching pressure as the fundamental wavelength is increased. This is actually extremely fortuitous, as higher pressure means a larger number of emitters, which somewhat counteracts the large drop in single atom efficiency.

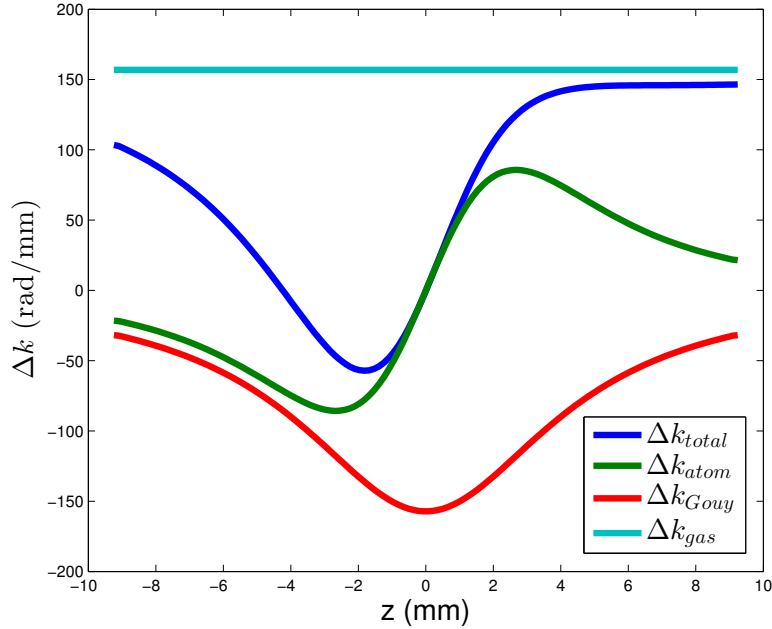


Figure 5.1: Phase matching contributions for focusing a $1.75 \mu\text{m}$ pulse into helium. Phase matching at the focus is achieved with approximately 1.8 bar of helium, but phase matching better than 1 rad/mm is only achieved over a range of $100 \mu\text{m}$.

Exact values for the phasematching pressure can be calculated for particular ionization fractions, but due to the exponential nature of tunnel ionization this fraction can vary strongly through a sample, and even within a laser pulse. Instead we will perform some simple phase-matching calculations assuming the ideal case, neglecting ionization completely. As can be seen in the above discussion, including ionization serves to increase the phasematching pressure, hence this calculation can be taken to represent a lower bound to the pressure. We'll consider a focused Gaussian beam from our HCF as the fundamental, with a beam waist of $50 \mu\text{m}$, a peak intensity of $5 \times 10^{14} \text{ W/cm}^2$, and a central wavelength of $1.7 \mu\text{m}$. We consider phase matching between the fundamental and harmonic emission of 530 eV in energy, simulated by considering only the phase of the harmonic as given from the SFA, Gouy phase, and the

neutral gas dispersion. The results can be seen in figure 5.1. The neutral gas dispersion line can be shifted up and down by raising and lowering the pressure, respectively. In order to obtain phase matching at the focus, a gas pressure of 1.8 bar is required. This is a very large pressure for HHG, and it presents new experimental challenges outlined in the next section. However, the region over which the generation is phase matched is incredibly small; we can expect a coherent build up over only a range of micrometers.

A dramatic increase in the coherence length can be obtained by considering instead a linear gradient in the gas pressure, as shown in figure 5.2. Here good phase matching is obtained over a range of 3 mm, by decreasing the pressure from approximately 2 bar to 1 bar over the phase matched portion. Engineering such a gradient is extremely difficult, but various forms of pressure gradients arise natural from common gas geometries (see section 5.2.1), and thus improvements over the static fill case can be expected to occur. We note again that these pressures are in some sense lower bounds, and significantly higher pressures may well be required in experiment due to ionization effects and non-adiabatic phasematching. In order to satisfy these conditions, significant engineering work must be undertaken.

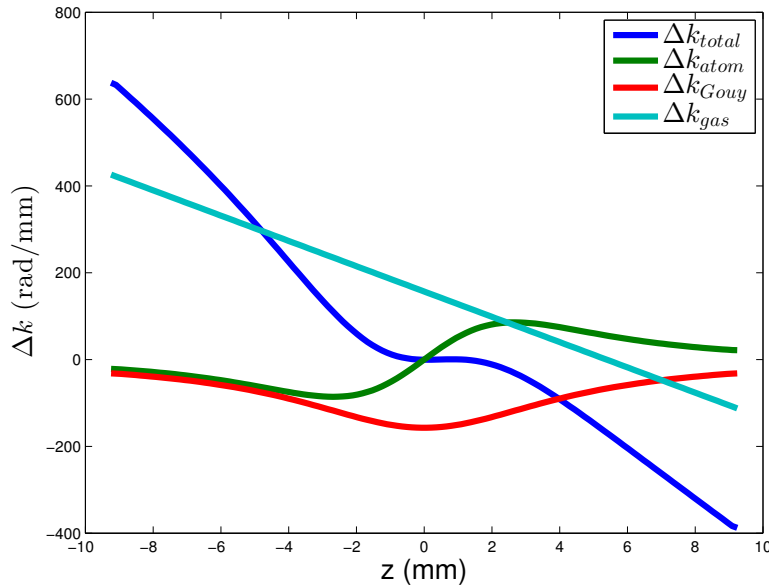


Figure 5.2: Phase matching contributions for focusing a $1.75 \mu\text{m}$ pulse into helium with a linear pressure ramp. Phase matching at the focus is achieved both before and after the focus due to compensation of the single atom response by the neutral medium variation. Pressure decreases by ≈ 1 bar over the range of the phase matched portion.

It is worth considering as well the problem of re-absorption of harmonic radiation. As we saw in section 2.6.3, even for the case of perfect phase-matching, HHG will be limited by the re-absorption of the radiation. This is a “hard” limit, and absorption limited generation has been observed in the XUV where re-absorption of harmonics by the noble gases is strong [169]. In the SXR range however, re-absorption can be quite weak. Figure 5.3 shows the logarithm of the X-ray absorption cross sections of He, Ne and Ar as a function of X-ray energy [170].

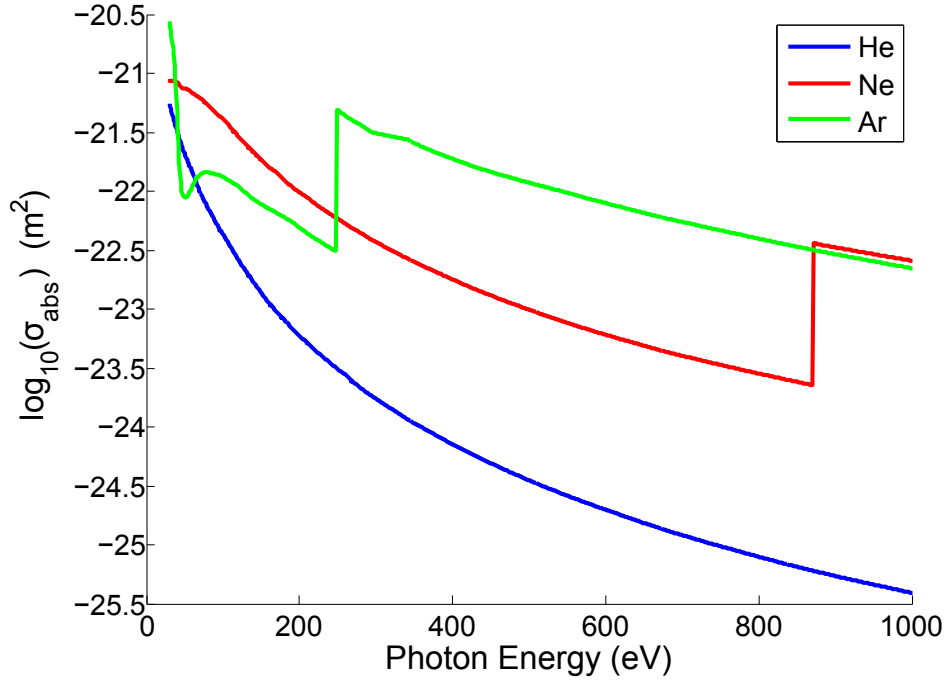


Figure 5.3: Logarithm of the X-ray absorption cross section σ_{abs} for the three “hardest” noble gases as a function of X-ray energy. There is a dramatic decrease of the cross section with increasing photon energy.

The re-absorption in He decreases by four orders of magnitude from 30 eV to 1 keV, with similar trends observed in the other gases. For the highest photon energies, and in particular in helium, re-absorption is thus expected to be negligible and harmonic generation will be limited by phase-matching and propagation of the driving laser field.

5.2 Apparatus for Soft X-ray Generation

Moving HHG from the XUV to the SXR comes with a number of challenges. High pressures are required to phase match the high harmonic emission, requiring novel vacuum engineering, but there are also significant challenges with the characterization and utilization of X-ray emission. In this section I describe the work done on designing the gas target and differential pumping for efficient SXR HHG generation, as well as the design of a new soft X-ray spectrometer.

5.2.1 Gas Target Design

As explained in the previous section, at the high energies we hope to achieve phase matching requires multi-atmospheric gas pressures. As soft X-rays are strongly absorbed by most materials, and as some forms of X-ray detectors can only be operated at high vacuum ($< 5 \times 10^{-6}$ mbar), it is necessary that these experiments be performed in vacuum. However, as the harmonics are absorbed by any material, and the high intensity pulse necessary for generating them is

capable of destroying any solid material, the high density generating region desired cannot be separated from the vacuum chamber by any solid windows. For this reason, reaching the high pressure required in the generating medium while maintaining a low pressure elsewhere is a critical challenge. We are interested in the geometry of either a gas jet or a gas cell. While the very highest energy harmonics have been generated through the use of a capillary [162], thusfar no demonstration of isolated attosecond pulses from this geometry has been shown, and so we will not consider it further at this time.

In a gas jet, gas is leaked into the chamber through a small aperture, which due to the supersonic expansion into vacuum forms a jet [150]. Provided the backing pressure on the nozzle is low, a piezoelectric shutter can be used to synchronize release of the gas with the arrival of the laser pulse, greatly decreasing gas flow into the vacuum. However, at high pressures the piezoelectric shutter either cannot open against the force differential, or quickly fails due to the extreme stress of slamming closed. Solenoid valves may also be used, but operation at 1 kHz is extremely challenging to realize experimentally², and in the regime of interest may lead to cluster formation. This necessitates the use of a continuous flow effusive jet, which increases the gas flow load in the chamber. An alternative approach is that of a gas cell, in which the laser passes through an aperture into a region of high gas density and leaves through another aperture. We will now consider the fluid dynamic considerations of the two schemes, and seek to maximize pressure at the generating point while minimizing gas flow into the chamber.

The basic object in both the gas jet and cell is a short tube connecting a high pressure reservoir to a low pressure evacuated region; I'll discuss the equilibrium conditions for fluid flow in such a system. Both experimental and numerical work on the problem of fluid flow through short tubes has been ongoing for several decades [172, 173], and work is generally scaled to the ratio of the tube length to aperture, L/R , and the dimensionless rarefaction number:

$$\delta = \frac{\sqrt{\pi}R}{2\Lambda_0}. \quad (5.2.1)$$

In the above, Λ_0 denotes the mean free path length in the gas, defined as

$$\Lambda_0 = \frac{\mu(T_0)}{P_0} \sqrt{\frac{\pi k_B T_0}{2m}} \quad (5.2.2)$$

where μ is the viscosity of the gas, P_0 and T_0 are the reservoir pressure and temperature respectively, k_B is the Boltzmann constant, and m is the mass of the gaseous particle. In the literature, rates are usually quoted relative to the mass flow rate in the free molecular regime

²This condition can be satisfied by an Even-Lavie valve [171], but these are expensive, difficult to source, and were not available to us.

$\dot{M}_0$, given by

$$\dot{M}_0 = R^2 P_0 \sqrt{\frac{\pi m}{2k_B T_0}}. \quad (5.2.3)$$

The free molecular flow regime ($\delta = 0$) corresponds to high vacuum, where particles move in effectively uninterrupted straight lines, and represents the slowest flow through an aperture. As a general rule, flow rates increase when the system has a high rarefaction number; as such, we can decrease flow rates by using smaller apertures, heavier gases, decreasing the pressure, or lowering the temperature. In practice our choice of gas is determined by the high harmonic generation process, and the apertures and pressures are chosen to be as small as possible [174]. Decreasing the temperature is a viable, but complicated, method for decreasing the flow without compromising generation. We will see in the course of this thesis that such measures are not necessary.

Let us consider some realistic parameters. For a reservoir of helium at 10 bar and 300 K, connected to the vacuum through an aperture of radius 100 μm , we obtain $\delta = 4710$, well into the viscous flow regime. I chose this value for the radius as it is representative of both typical nozzles for gas jets, which are typically between 50 – 150 μm in radii, and the necessary aperture size for a gas cell, as the beam waist for our focused laser beam is on the order 50 – 100 μm . This rarefaction parameter is outside that usually considered by the literature, but as results asymptotically approach the viscous limit [175], they can be taken as representative.

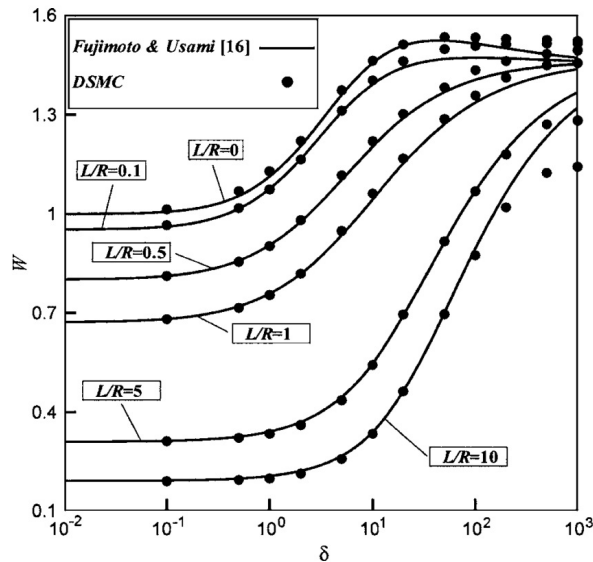
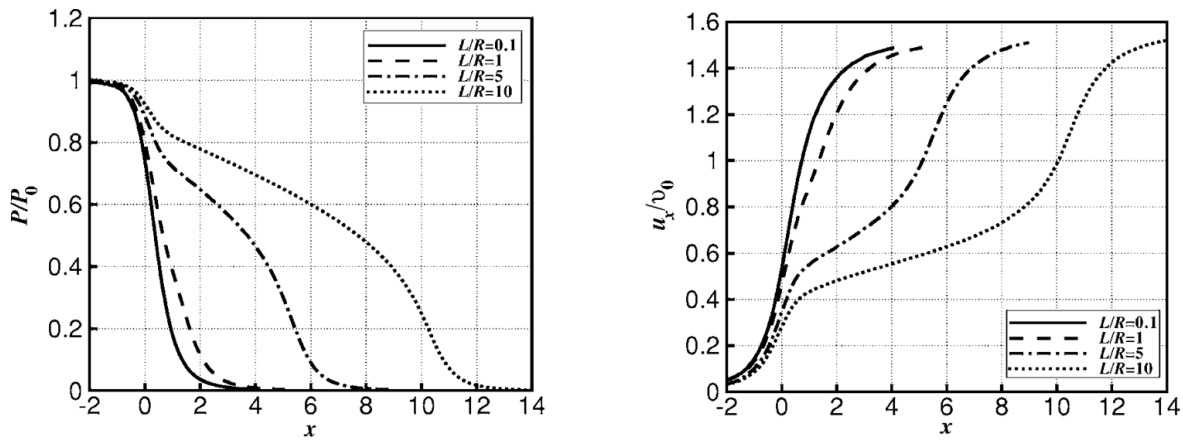


Figure 5.4: Plot of gas flow rates relative to the effusive limit W vs. rarefaction parameter δ for short tubes of varying length-radius ratio. The solid lines are an empirical formula from Fujimoto and Usami, while the dots are a result from a kinematic Monte-Carlo simulation. Reprinted with permission from Varoutis *et al.*, JVSTA Vol. 26, Num. 228, pp. 228-238 (2008). Copyright 2008, American Vacuum Society [173].

Varoutis *et al.* have performed Monte-Carlo simulations of gas flow through tubes in exactly the manner of interest for HHG, and examined the flow rate as a function of geometry. Figure 5.4 shows the pressure drop across a tube as a function of the longitudinal distance x in units of the aperture radius which illustrates that, for $\delta \geq 10^2$, increasing the length of a tube has very little effect on the flow rate, introducing less than a factor of two reduction in flow rate over the whole range simulated and fitted to experiment [173]. Only in the limit of an infinite tube (i.e. a capillary) can we expect a significant decrease in flow based on lengthening the tube; in a gas cell, wall thickness will only have a marginal impact on the achievable backing pressure.



(a) Pressure drop across a tube for $\delta = 100$. Tube begins at 0 and runs until indicated distance. In all cases, the pressure drops to less than 20% of the reservoir value one radius away from the exit.

(b) Axial gas flow speed across a tube for $\delta = 100$. Tube begins at 0 and runs until indicated distance. In all cases the gas accelerates rapidly and forms a jet moving at more than 1.6 times the mean gas speed v_0 .

Figure 5.5: Pressure drop and speed increase of gas flow through a tube. Reprinted with permission from Varoutis *et al.*, JVSTA Vol. 26, Num. 228, pp. 228-238 (2008). Copyright 2008, American Vacuum Society [173].

Figures 5.5a and 5.5b illustrate the other important results obtained from their simulations, which demonstrate potential problems with both the gas jet and gas cell approach. In figure 5.5a we can see the pressure drop across an aperture or tube. The gas pressure at any significant distance away from the aperture, even one aperture radius, is marginal compared to that of the reservoir pressure. For this reason, in order to have a high pressure interaction region in the jet geometry, it would be necessary to have an extremely high backing pressure, at least 5 – 10 times that of the desired interaction pressure. This means the gas flow in the gas jet geometry will be significantly higher than in the gas cell case, for the same interaction pressure. Figure 5.5b illustrates a potential problem with the gas cell geometry, that in the hydrodynamic limit ($\delta \geq 100$) the gas forms a high speed jet emission at the outlet [173]. As stated earlier, the nature of the laser interaction means no windows can be placed in its beam path, and thus this jet must be free to propagate along with the beam through any differential pumping stages used, as in the gas cell the apertures are necessarily aligned along the beam direction. This could result in a dramatic decrease in the effectiveness of differential pumping for such targets.

However, as the pressure only one nozzle radius inside the inlet is effectively the reservoir pressure, a gas cell should provide very precise control of the gas pressure inside the interaction region.

5.2.2 Differential Pumping

The second component to achieving very high pressures, after identifying the correct target geometry, is differential pumping. I have designed a double-stage differential pumping jacket to allow pressures of over 10 bar to be reached in the interaction region. A schematic of the system is shown in figure 5.6; in brief the harmonic target, either gas cell or jet, is placed inside two stages of differential pumping separated by windows with a central clear aperture for laser transmission; windows are used in order to simplify alignment. The inner chamber is connected directly to a large screw pump (Leybold Leyvac LV 80) in order to handle the relatively high gas throughput in this stage, maintaining a mbar level vacuum. The second stage, the enclosing chamber, is pumped by a small turbopump (Varian V-81) capable of handling relatively high pressures, operating up to 5×10^{-1} mbar. Outside the first two stages is a larger chamber containing all focusing and steering optics for the beam. This chamber is separated from the spectrometer chamber by a narrow differentially pumped tube through which the laser passes. Since the spectrometer can be configured with an MCP detector, this chamber must be kept at $\approx 10^{-6}$ mbar. As the beam forms a direct line from target to spectrometer, the jet-like emission from a gas cell decreases the effectiveness of the differential pumping, but it has been found that the limiting factor in our system is the pumping in the main generation chamber.

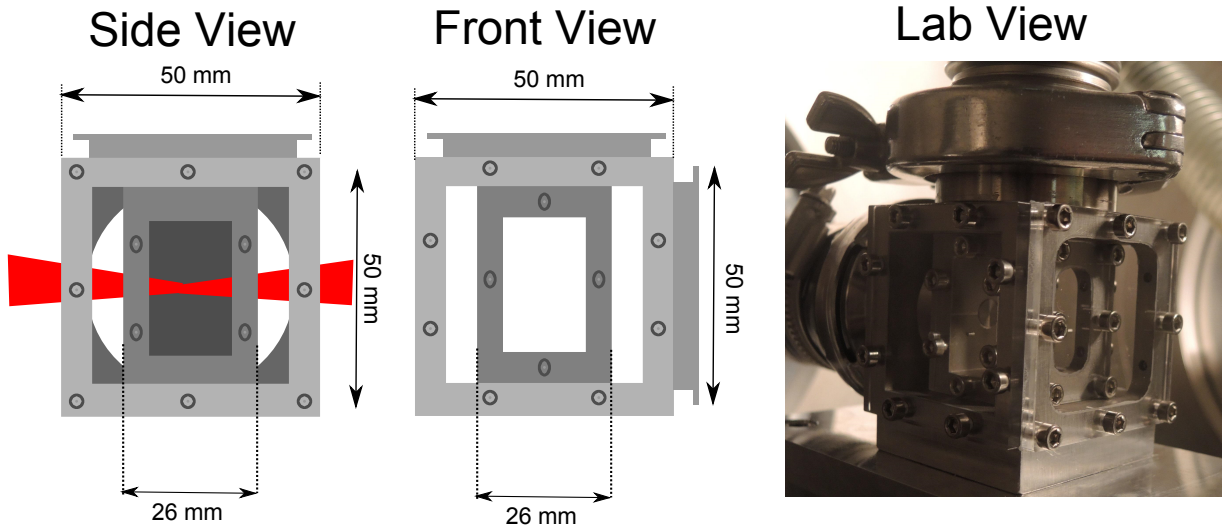


Figure 5.6: *Left:* Diagram of the two-stage differential pumping chamber for high pressure gas targets from two views. Two concentric chambers are present, connected to differential pumping through the top and side by KF40 half nipples. The open spaces are closed with transparent windows for alignment, while the laser (shown on left) passes through pre-drilled holes. The target is placed in the center. *Right:* Final chamber as manufactured.

I have given careful consideration to the design of the differential pumping jacket. A previous

design suffered from a series of problems, especially choking of the pumps by the long thin bellows connecting them to the chambers, and difficulty of use. The final design was machined entirely from a single piece of stainless steel to improve its strength; this allowed two sides to be almost entirely taken up by connections to KF40 bellows leading to the pumps. As pumping rates scale with the area cubed, this presents a massive improvement in pumping speed over the previous version, which could only support KF16 bellows before breaking under the tension.

The dimensions of the chambers have also been carefully considered, as there are two factors in the gas transmission affected by this property. The transmission through an aperture of fixed size will decrease as the chambers become larger, as the hole is further from the expanding jet. On the other hand, as the holes in the windows need to transmit a focused laser beam, the further they are from the focus the larger they need to be. In order to examine this trade-off, I have performed simple calculations comparing the beam waist of a Gaussian beam to the gas leak rate through an aperture at different distances. In order to calculate the percentage of a gaseous beam incident on an aperture at different distances I use simple analytic models for the expansion profile of atomic beams in both the molecular and fluid flow regimes [150]. While these models do not accurately predict absolute flow rates, they are known to be accurate representations of the geometry for jets a few source radii away from the source and beyond. That is to say “free jets are, to first order, independent of source geometry” [150]; this also means we can treat the jet as a point source. By comparing the two limiting cases we can bound the flow for our intermediate case.

I estimate the necessary hole diameter a Gaussian beam requires to pass through as $2w(z)$, where $w(z) = w_0\sqrt{1 + (\frac{z}{z_R})^2}$ is the Gaussian beam waist and, w_0 is the beam waist at focus, and z_R is the Rayleigh range. We have previously measured a spot size of $60\text{ }\mu\text{m}$ FWHM at $1.75\text{ }\mu\text{m}$ wavelength, which fully determines the beam waist at all z . From [150] we know that the expanding jet has a density profile of

$$P(r, \theta) \propto \frac{1}{r^2} \cos^4 \theta \quad (5.2.4)$$

$$P(r, \theta) \propto \frac{1}{r^2} \cos^2 \theta \quad (5.2.5)$$

for the fluid like and effusive flow regimes, respectively. This can be transformed into the same cylindrical coordinate frame as the Gaussian beam to determine flow through the apertures as a function of distance from the focus by integrating the density across the aperture. We can also include an offset for position of the gas source and laser focus, but this proves to be largely negligible in our situation. In general the system is dominated by the linearly increasing hole size further from focus (since far from focus the Gaussian beam behaves in a ray-like manner) and the quadratic decrease in on-axis pressure.

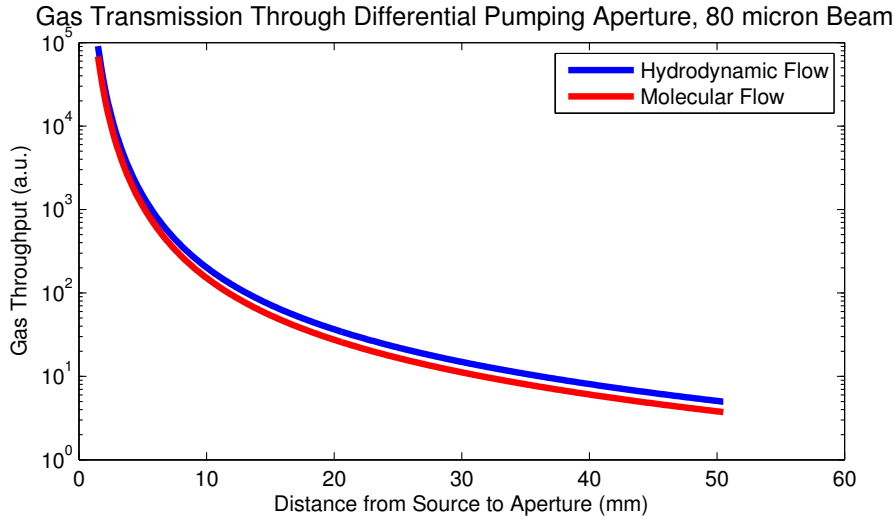


Figure 5.7: Gas transmission through a differential pumping aperture whose size is determined by the beam size of a focused Gaussian beam at 1.75 micron wavelength with an 80 micron FWHM focus. The transmission is a monotonically decreasing function of the distance between the source and the aperture.

Figure 5.7 shows the gas flow through an aperture as a function of the source to aperture distance for the parameters discussed above. The transmission is a monotonically decreasing function of source to window distance, and is very similar for the two limiting cases. We do not simulate the transmission closer than a few source apertures away from the source, as the $1/r^2$ dependence is completely inaccurate there. Given the monotonic behaviour of the flow, it is somewhat arbitrary what source to aperture distance should be chosen for our system. I decided on 12.5 mm to obtain an approximately three order of magnitude drop in pressure between source and aperture. This ensures that for a 10 bar fill pressure inside a tube, which corresponds approximately to 1 bar pressure at the exit of the laser drilled hole, there will be around a 1 mbar pressure at the exit. This means that the second stage can be pumped by a small turbo pump after expansion. The size of this second stage is more arbitrary; I selected a total jacket size of 50 mm so that DN40 bellows could be attached directly while minimizing the footprint inside the larger chamber. Performance of this final design is discussed in section 5.2.4.

5.2.3 A soft X-ray spectrometer

In order to measure the HHG signal and to perform transient absorption studies, it is necessary to have a spectrometer operating in the SXR with sufficient spectral resolution to measure XANES spectra. Since most HHG experiments use XUV photons and measure discrete harmonics, leading to low spectral resolution requirements, this marks a significant departure from the previous technology. We aim for a spectral resolution of ≈ 1 eV, sufficient for resolving harmonic structure and suitable for many XANES measurements. I have performed ray tracing calculations to design a suitable spectrometer which can measure an entire SXR spectrum simultaneously from below 200 eV to above 700 eV, with 1 eV or less resolution. The basic

elements in any spectrometer are a slit to act as a source, a dispersive element such as a grating or prism, and a detector for the spatially separated spectral elements.³ In order to improve the spectral resolution it is most common to re-image the slit onto the detector. In the soft X-ray regime new challenges emerge in spectrometer design, as all materials begin to absorb very strongly at non-grazing incidence, detector options become increasingly limited, and vacuum conditions must be maintained inside the spectrometer. This means that the spectrometer must consist solely of grazing incidence components and be as simple to operate as possible in order to reduce the number of vacuum actuators required.

The dispersive element in an SXR spectrometer is necessarily a diffraction grating operated at grazing incidence, since the refractive index of all materials becomes increasingly spectrally homogeneous and absorptive at X-ray wavelengths, precluding the use of prisms. Diffractive crystals could be used, but these give a monochromatic beam and preclude measurement of an entire spectrum simultaneously. An SXR spectrometer can be designed around a plane diffraction grating combined with grazing incidence X-ray mirrors (for instance gold parabolic, hyperbolic, or elliptical mirrors) to construct a spectrometer in the usual optical fashion. However, these optics are generally very expensive, large, difficult to align, and due to their necessarily weak focusing power, lead to extremely large spectrometers. For this reason, it is advantageous in all but the most demanding applications to make use of a spherical grating, where the diffraction grating is written onto a spherical substrate of radius R . This allows diffraction and imaging from a single optical device, allowing for a very compact, very stable spectrometer design. Each colour (and every diffracted order thereof) comes to focus at a point on the sphere of radius of R known as the Rowland circle [176]. However, because X-ray detectors such as X-ray CCDs or microchannel plates (MCP) are generally flat devices, we ideally want the focal plane of our grating to be not a sphere but a plane. For this reason *variable line space* (VLS) gratings were developed [177]. Here, the line density of the diffraction grating varies over the spatial extent of the grating, modifying the dispersion relationship for rays at different points on the spherical substrate, and shifting the focal point for different frequencies. If the line density function is properly engineered, it is possible to achieve good imaging over a broad spectral range onto a plane rather than the Rowland circle [178].⁴ VLS gratings allow for the design of so called flat-field spectrometers [179], which consist very simply of an entrance slit, a VLS grating imaging the slit, and a detector in the flat field of the grating. There is only one optical component to align, and only three degrees of freedom: object distance, image distance, and grating angle.

Previously in place for high harmonic spectroscopic studies of aromatic organic molecules (chap-

³Spectrometers can also be designed around entirely different modes of operation, such as those depending on fibre optical techniques, which are not considered here.

⁴While the spherical substrate still focuses in the transverse direction, it's focusing power is weak compared to the longitudinal grating direction and can be ignored.

ter 4) was a flat-field spectrometer based around a 1200 l/mm VLS grating. This spectrometer featured slitless operation, which increases signal at the expense of resolution, and a movable flange with an MCP detector for scanning the MCP across the dispersed harmonics. Preliminary spectra obtained from HHG in argon indicated that the maximum observable energy with this spectrometer was around 160 eV; it was thus decided replace the 1200 l/mm grating with a higher density 2400 l/mm grating (Shimadzu 30-003), and to add a slit to improve the resolution. In order to determine the focusing conditions attainable with the new configuration, I performed a series of ray tracing calculations. The line density function for the grating was measured and found to be

$$d(x) = \frac{d_0}{1 + 2b_2x/R + 3b_3x^2/R^2 + 4b_4x^3/R^3} \quad (5.2.6)$$

with $d_0 = 2400$, $b_2 = -52.496$, $b_3 = 2.941e3$, $b_4 = -2.123e5$, and $R = 13165$, where R is the radius of curvature in mm. This fit was performed to match the form given in reference [178] for flat-field gratings. I traced rays sampled from a normal distribution of $\vec{k}$ -vectors and positions for a given divergence and spot size. Energies were explicitly selected to match various harmonics of a 1600 nm field (0.77 eV), and each harmonic was given a normally distributed bandwidth of 0.5 times the harmonic spacing. 100000 rays were traced per harmonic, and examined the effect of grating angle, slit aperture, and all distances to determine the optimal focusing conditions.

A surprising result is that the focusing condition of the grating is different for the case of highly diffuse, incoherent emission and for the highly collimation harmonic rays. Diffuse illumination was found to recreate manufacturer specifications, while collimated illumination shifted the flat field considerable. I proceeded by fixing the source parameters to some realistic values and examining the ideal geometry there. For this reason I fixed a spot size of 15 microns and a divergence of 2 mrad, based on our preliminary experiments. I first scanned the angle until I found a point where the focal plane was both flat between 200 and 550 eV and perpendicular to the laser axis. This occurred at an incidence angle of 1.7 degrees, only slightly differing from the manufacturer specification of 1.4 degrees, though the difference is significant in the focusing observed.

Having fixed the grating angle, I scanned the distances and slit width to find the optimal choices for all other free parameters, as well as to estimate the stability of the solution. I found an optimal solution with a source-to-slit distance of 650 mm, a slit width of 150 μm , a slit to grating distance of 236.7 mm, grating angle of 1.7 degrees, and a grating to detector distance of 220 mm. Figure 5.8 shows simulated images of the detector and corresponding lineouts in the spectral direction at four different energy ranges using there parameters. A detector resolution of 13 microns is assumed; this is the resolution offered by X-ray CCDs. It can be seen at 576.73 eV that the harmonics are just resolved and any decrease in detector resolution will blur out the harmonics. For this reason, I chose to replace the imaging MCP with an X-ray CCD

(Andor iKon-M SO) to obtain the highest resolution possible.

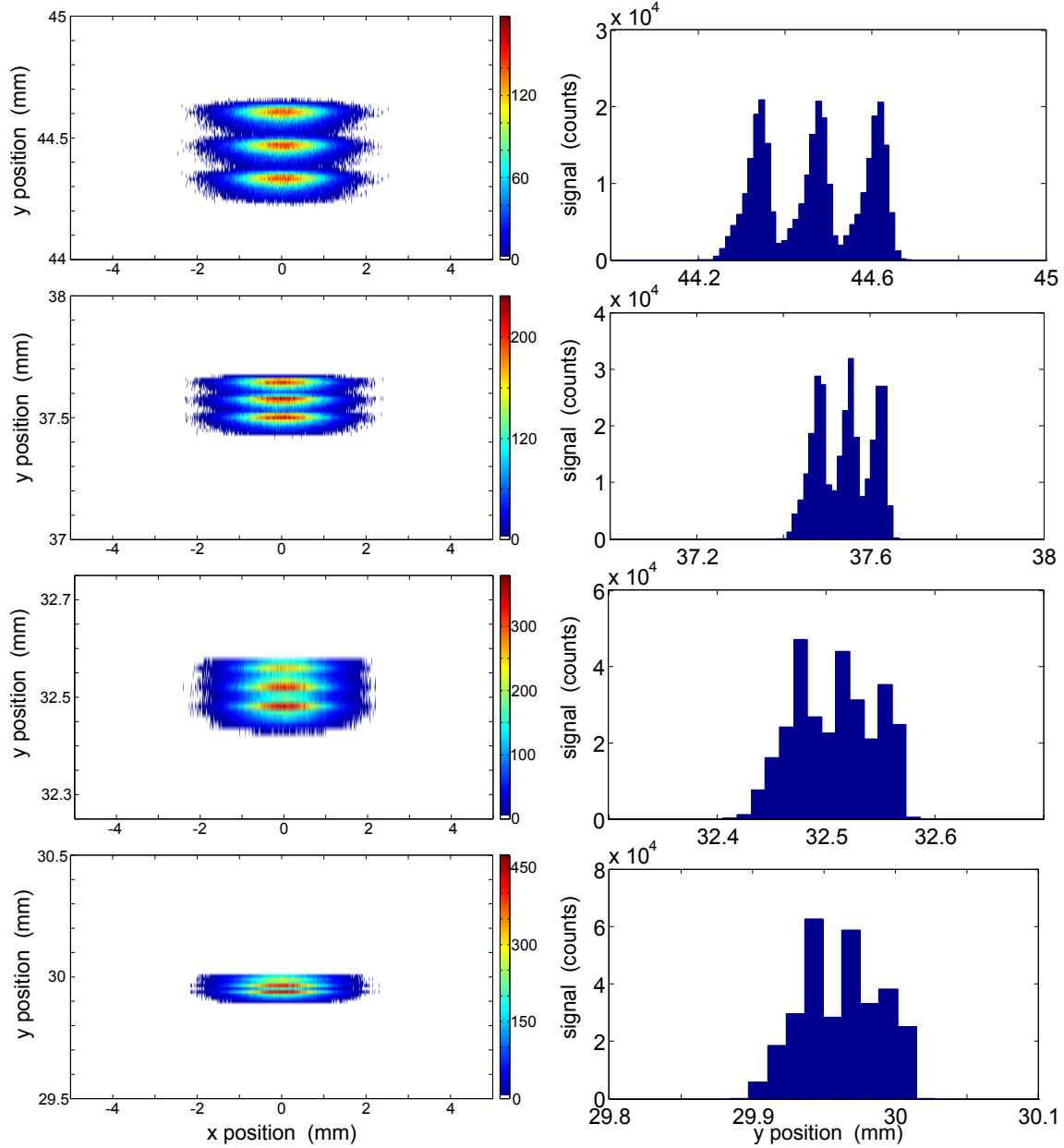


Figure 5.8: *Left:* Detector images for different harmonic energies with 13 micron pixels. *Right:* integrated lineouts of detector images showing harmonic resolution. From top to bottom, harmonics are centred at 211.75 eV, 319.55 eV, 462.77 eV, and 576.73 eV. The pixel size of the detector is readily apparent in the lineouts, showing our resolution is pixel rather than optically limited at the highest photon energies.

Using an X-ray camera also introduces an additional advantage over microchannel plate detection, the potential of photon flux determination. Unlike in an MCP, the quantum efficiency and response of an XUV CCD is well known. In particular, the final counts measured by the

detector are given by

$$C(N_E, E) = \frac{N_E G}{n(E)QE(E)} \quad (5.2.7)$$

where N_E is the number of photons of energy E , G is the gain of the camera (conversion factor of electrons generated by photons to digital counts), $n(E)$ is the number of electrons generated by one photon of energy E , and $QE(E)$ is the probability of absorbing a photon of energy E . In our camera we set $G = 1$ for all experiments. $QE(E)$ and $n(E)$ are both provided by the CCD manufacturer, and can be corrected for, leading to a simple relationship between the number of incident photons and the camera counts.

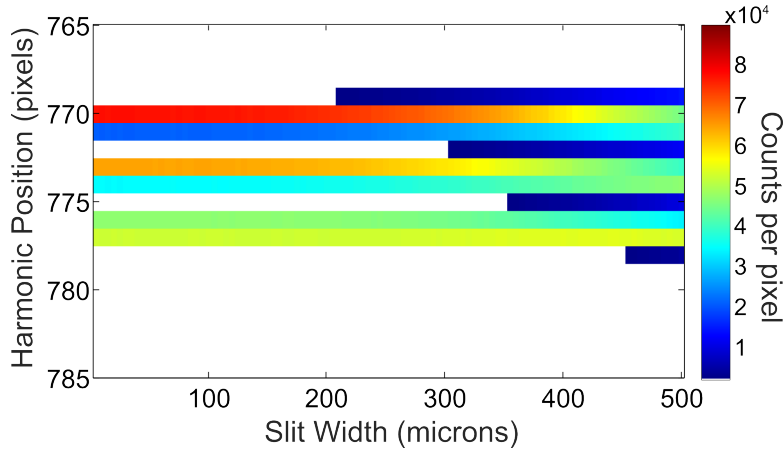


Figure 5.9: Harmonic resolution vs. slit width for harmonics at 462.77 eV. Resolution is fairly constant until slit passes 200 microns in width. Based off this result we set the slit width at 150 microns. Position of slit is held at 236.7 mm.

Assuming the XUV camera spatial resolution as above, we find the spectrometer spectral resolution is very sensitive to some parameters but only very weakly to others. For instance there is very little dependence on the source-slit distance; unless the source is brought significantly closer to the grating than is possible in our chamber, no change in resolution is observed. This does assume a ray picture of the harmonic propagation, which may not be valid for extremely high energy harmonics in which the Rayleigh range may be comparable to our system dimensions, but to go beyond the ray picture is outside of our capabilities. While I scanned all parameters, here I will present just two, slit width and detector position. They are indicative respectively of robust parameters and sensitive parameters. Figure 5.9 shows the spectrum (displayed as pixels) obtained for three harmonics centred around 462.77 eV as a function of the slit width. It is seen that for a large range of slit widths the resolution is not degraded and only at 200 μm does signal “bleed” into adjacent pixels become relevant; similar results are seen for the slit to grating distance. We are then relatively insensitive to these parameters. On the other hand figure 5.10 shows the resolution as a function of the distance between the detector and grating. A shift of 4 mm around the optimal value already causes signal degradation, and a shift of 10% causes the resolution of the individual harmonics to be lost completely. We are

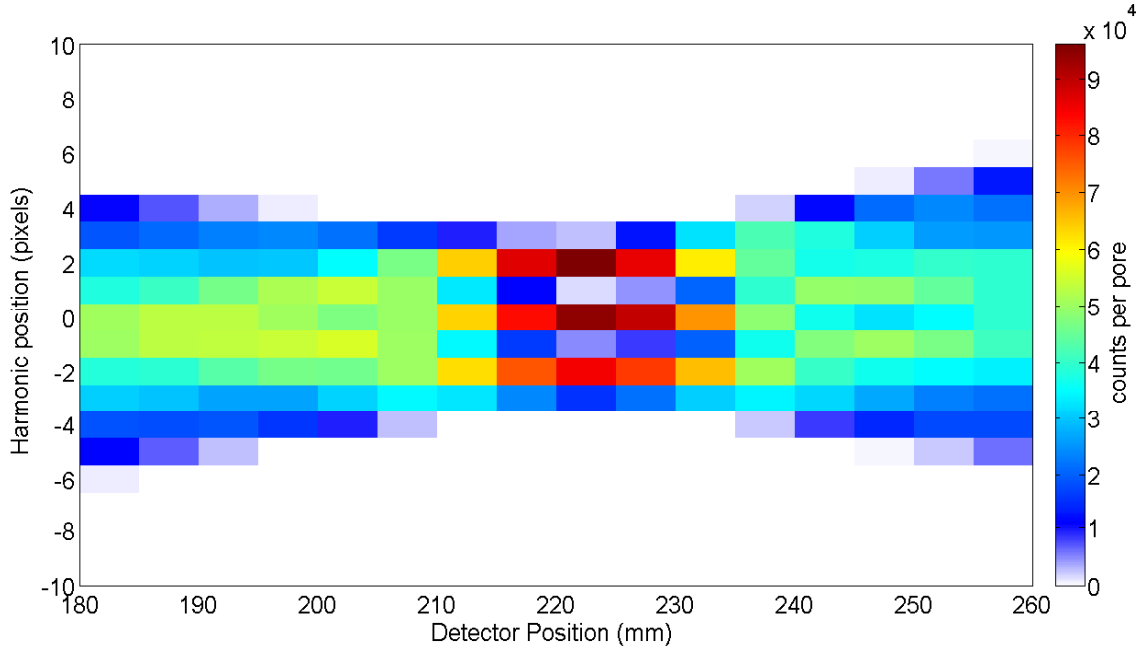


Figure 5.10: Harmonic resolution vs. distance between grating and detector for harmonics at 576.73 eV. Resolution is stable for a range of ± 4 mm around 220 mm, but degrades outside of this range. Stability improves around this point at lower harmonic orders.

similarly sensitive to the grating angle, which has a tolerance of ± 0.2 degrees.

5.2.4 System Performance and Calibration

Figure 5.11 shows the complete system used for our SXR harmonic generation experiments. The compressed idler pulse enters the vacuum through a 1 mm thick Brewster angled CaF_2 window. The beam was reflected off a fold mirror onto a 30 cm focal length focusing mirror (configuration A) or off two fold mirrors then through a 20 cm focal length CaF_2 lens (configuration B). All optics were mounted on a translation stage (OWIS) to allow the focus to be translated in the beam propagation direction. Scans of the relative position of the laser focus and gas jet along the propagation axis (z-scans) are often performed by moving the gas target rather than the laser, but this was not feasible given our differential pumping requirements. Moving the focus instead of the generating medium also has the advantage of fixing the source position. Our target was a gas cell comprised of an 800 μm OD, 720 μm ID needle with laser drilled holes. As we laser drill our target, it was essential that the stage be aligned perfectly so that the transverse position of the focus did not move when scanned. This was characterized with a HeNe laser, which showed a motion of less than half a beam radius at the focus and less than a tenth of beam radius in the far-field over the full 11 cm range of travel of the stage. The target was laser-drilled at atmospheric pressure in order to restrict the motion of metal particulates generated from the drilling process; even with this precaution focusing optics were gradually coated in a thin layer of metal and metal oxides. Drilling at atmospheric pressure has

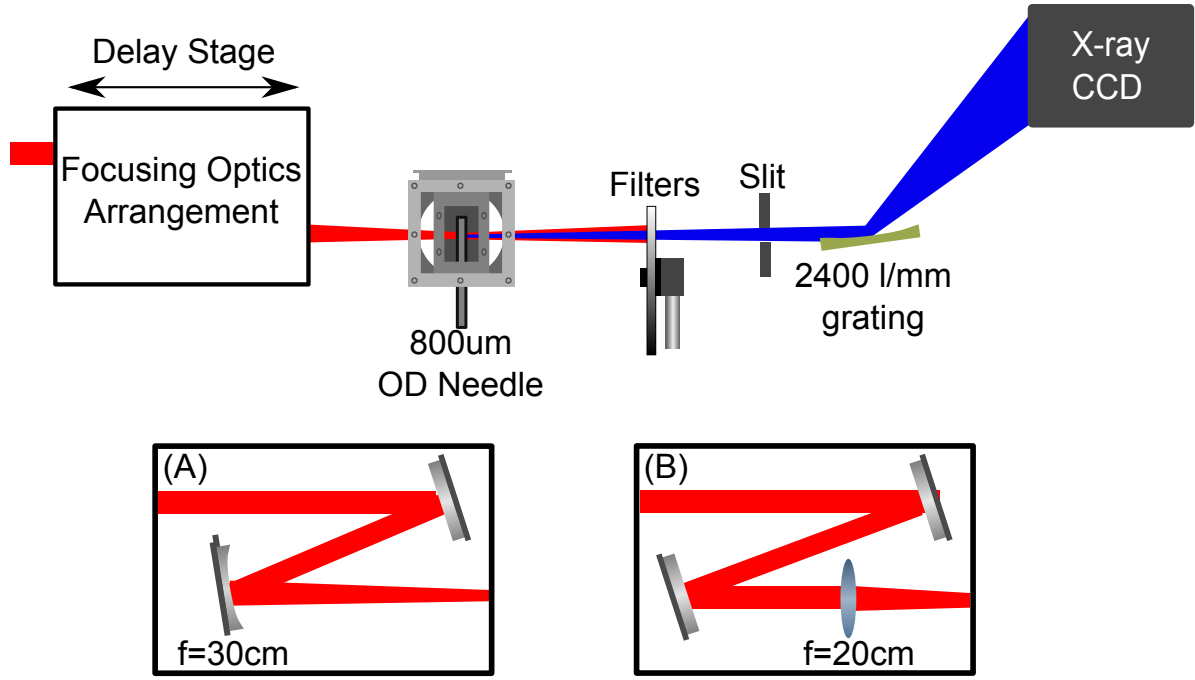


Figure 5.11: System for water window high harmonic generation. The beam enters vacuum through a 1 mm CaF_2 Brewster window; the entirety of the setup shown here is under high vacuum. Not shown are the vacuum chambers and the differential pumping stage between them, nor any details of the pumping.

the potential to create an incorrectly sized aperture due to strong self-focusing and ionization defocusing effects; during HHG, the chamber will be evacuated, and these non-linear effects will be suppressed. To surmount this difficulty we scanned the full range of the translation stage during each drilling to ensure the hole was large enough to transmit the whole beam; this suggests improvements in the drilling process could further reduce gas load on the chamber by using a smaller hole. We also drilled the differential pumping apertures in a similar fashion, using a temporarily inserted layer of burn paper to create a nucleation point for melting in the otherwise transparent material.

The beam then passed through a thin adjustable differential aperture (set to $1 \times 4 \text{ mm}^2$) and into the spectrometer chamber. Light baffling enclosed the beam to prevent scatter until the beam passed through a filter wheel containing thin metallic filters such as aluminium, titanium, and zirconium which removed the visible and IR light; since the XUV CCD is sensitive to lower order harmonics of the idler, a metallic filter is necessary to block this background. The filters also provided us with the absorption edges required to calibrate the spectrometer. The filtered X-rays then passed through a home-built motorized slit 1 cm long, which in the vertical direction (width) can be adjusted from 6 mm wide to closed. After the slit was the 2400 l/mm VLS grating, mounted on a motorized stage allowing for controlled height, angle, and grating-to-detector distance. Harmonics were dispersed by the grating towards a movable

flange holding our X-ray CCD camera. The camera is cooled to $-100\text{ }^{\circ}\text{C}$ by a Peltier cooler stack, which is in turn held at $16\text{ }^{\circ}\text{C}$ by an external chiller. The chamber is kept at 10^{-6} mbar , and in order to prevent any remaining vacuum contaminants sticking to the cooled CCD a liquid nitrogen filled cold trap is operated on the spectrometer chamber.

The performance of our differential pumping apparatus can be benchmarked by a simple pressure scan, recording the pressure reached in each of the separate chambers. The results of one such pressure scan are shown in figure 5.12, where the pressure in the innermost layer of the differential pumping, inside the generation chamber, and inside the spectrometer chamber are plotted as a function of the backing pressure. We immediately see that backing pressures of up to 16 bar of helium present the system with no trouble; even at these extreme conditions it would be possible to run an MCP in the spectrometer chamber. In particular, we observed an over ten order of magnitude drop in pressure between generation and detection of the harmonics. Re-absorption outside of the target is thus expected to be minimal.

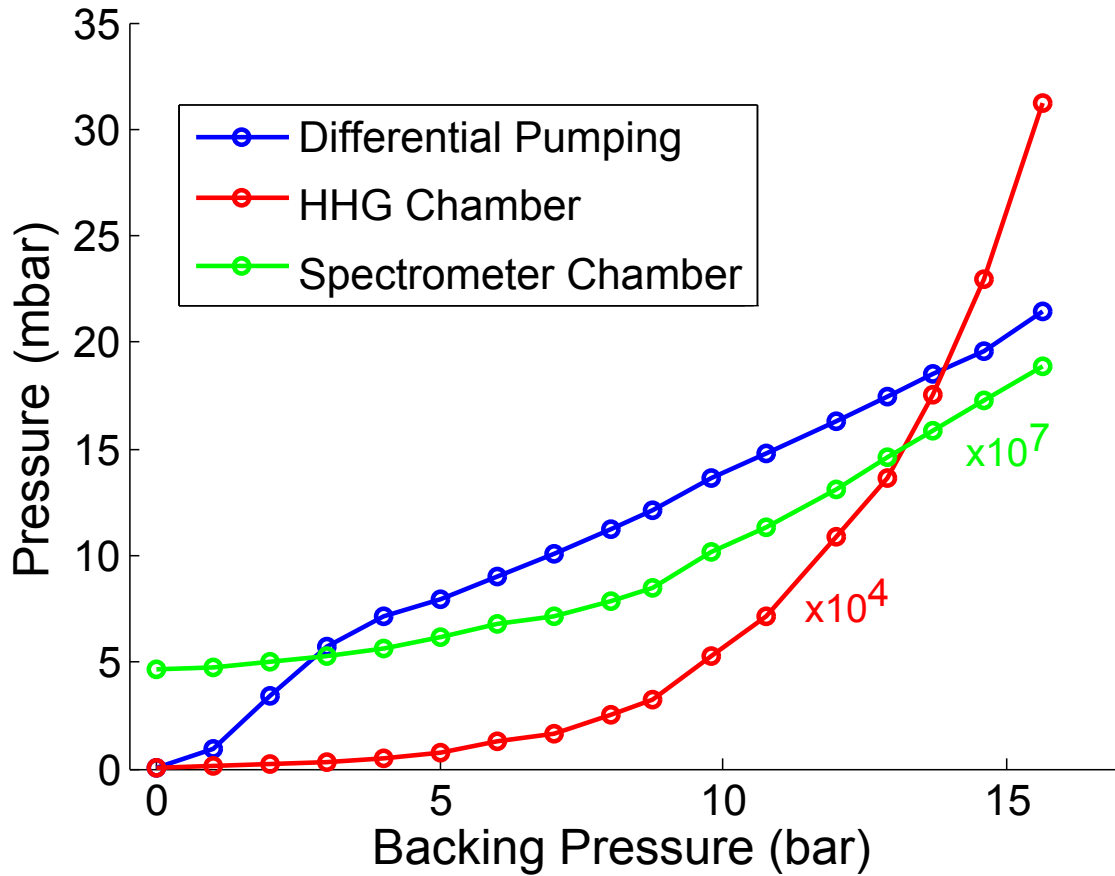


Figure 5.12: Pressure in the various sub-chambers of our vacuum system as a function of the He backing pressure. Pressures of up to 16 bar do not approach any limits for the pumps or detectors.

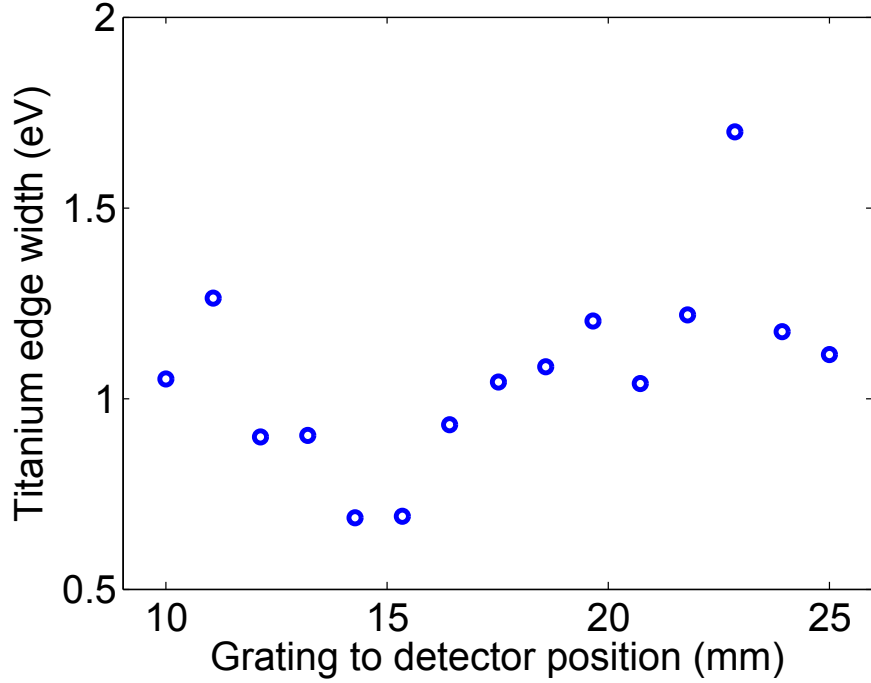


Figure 5.13: Fitted width of the Ti edge as a function of the change in grating-detector distance. The sharpness of the transmission is optimized at around 14.5 mm.

Optimization of the spectrometer resolution was performed by generating harmonics past the titanium edge at 456 eV (detailed in section 5.3.2). The titanium edge is expected to be extremely sharp (less than 4 eV) [180] and optimizing the “sharpness” of this drop is expected to be a good metric for the spectrometer resolution. We fix the grating angle externally to 1.7 degrees and perform scans of the grating-detector distance at different slit widths. We fit the titanium edge with a convolution of the error function, modelling the edge, and a linear function to model the harmonic amplitude. By minimizing the width of the error function fit we identify the region of highest resolution. Higher accuracy could be obtained by performing a full transmission measurement at each point, but the dividing necessary in such an operation requires much higher signal-to-noise, making the integration times required infeasible; two minute integrations at each position are required in the fitting procedure. Furthermore, sufficiently thin filters to perform absorption measurements of titanium are difficult to obtain and handle. Figure 5.13 shows the result of the fitting procedure applied to titanium edge spectra as a function of grating stage position, taken over an hour. There is an unknown offset between the stage position shown and the grating to detector position. A minimum in the fit width is observed around 14.5 mm, and it is at this point we performed our measurements. The width is notably smaller than 4 eV; this is due to the thickness of the titanium filter (250 nm) leading to complete absorption well before the peak of the absorption, effectively narrowing the absorption edge. Calibration of the spectrometer was performed using the titanium edge and carbon contamination at 284 eV. Transmission measurements indicate a resolution of less than 1 eV at 284 eV.

5.3 X-ray HHG Results

SXR harmonics were generated by sending our few-cycle SWIR source detailed in chapter 3 into the apparatus described in section 5.2. The fused silica compression wedges were moved close (1 m away) to the HHG chamber to ensure minimal propagation of the short pulse through material, thus decreasing non-linear effects. The pulse then passed through a 1 mm thick piece of CaF_2 glass at Brewster's angle into the vacuum chamber, at which point it entered the system described in figure 5.11 and chapter 5.2. The weak reflections from the Brewster's angle oriented compression wedges were used for various diagnostics, including the 2f-3f interferometer for CEP stabilization, a SWIR photodiode for power measurements, a camera for pointing stability and power measurements, and a spectrometer. We found the spectrometer served as an excellent measure of system stability and performance, being sensitive to all aspects of the system upstream of the fibre. By maintaining a stable fibre output spectrum we were able to ensure identical generating conditions over several consecutive days. This allowed us to fully characterize the CEP dependent HHG generation as a function of backing pressure and focal position, even when acquisitions of a single harmonic spectrum may take several minutes.

The air path and material dispersion between the fibre output and the HHG gas cell was different compared to the path to our SEA-F-SPIDER diagnostic, so optimization of the pulse duration was performed by examining the CEP dependent HHG spectrum of He at very low backing pressures, approximately 1 bar, which was the lowest at which HHG emission could be observed. Low pressures were used to minimize phasematching effects. The fibre pressure and wedge insertion were then tuned until the HHG showed both the highest cutoff and largest dependence on the CEP, which are both expected to coincide with the shortest driving pulse. Interestingly we found the optimal pulse duration was much longer than the minimum that can be generated from the fibre, and for HHG we used a fibre pressure of 0.4 bar of argon together with a wedge insertion of around 2.2 mm of FS. Measurements with the SEA-F-SPIDER combined with a virtual propagation showed a pulse duration of around 12 fs or two-cycles at the focus under such conditions. Using nominally shorter pulses was observed to both decrease the flux of the harmonic emission and dramatically increase the visible background in the detector. We attribute this discrepancy to complicated phase accumulated during propagation in air not accounted for in the virtual propagation, in particular to overtones from water vapour absorption. In this case increased broadening from the fibre would increase the influence of the overtone centred around 1400 nm. Another possible discrepancy is that the SEA-F-SPIDER is not sensitive to weak components of the pulse, which may parasitically remove energy from the main peak. In this case a shorter pulse may still coincide with a decrease of the peak intensity. The increase in background in the spectrometer is consistent with a broader spectrum in the driving laser field resulting in more generation of visible wavelengths.

Once the optimized on-target pulse duration was found, scans of the emitted harmonic spectra as a function of CEP were obtained from neon and helium, varying the focal position and

backing pressure. These experiments were performed using two different focal length optics of 20 cm and 30 cm, corresponding to focal spot sizes of 40 μm and 60 μm FWHM, respectively. The nominal peak intensities considering the input pulse duration and energies are of order 10^{15} W/cm², leading to a nominal single atom cutoff of over 1 keV. However, as we will see, harmonic emission is clamped well below this point, which we attribute to ionization and phasematching effects.

5.3.1 X-ray HHG in Neon

Using the 30 cm focusing mirror, 860 μJ pulses were sent into the gas cell filled with neon, and harmonics extending to 450 eV were generated, with integration times of 2 s for most measurements. Good spatial characteristics were observed as well in the imaging dimension of our spectrometer. Figure 5.14 shows a pressure scan of the HHG signal from neon taken with the focus of the laser at the gas cell ($z = 15.5$ mm). The spectra are presented as flux at detector, as this measure does not depend on any assumptions of spectral efficiency of the spectrometer or on the integration time. As can be seen, there is a trade-off between the highest flux and the highest cutoff, with the highest cutoff occurring at the lowest pressures and flux peaking at slightly higher pressures of around 1-1.5 bar, before reducing at higher pressures still. The extremely sharp drop at 284 eV is caused by carbon contamination on the optical components, and is equivalent to transmission through a 100-150 nm thick layer of the material.

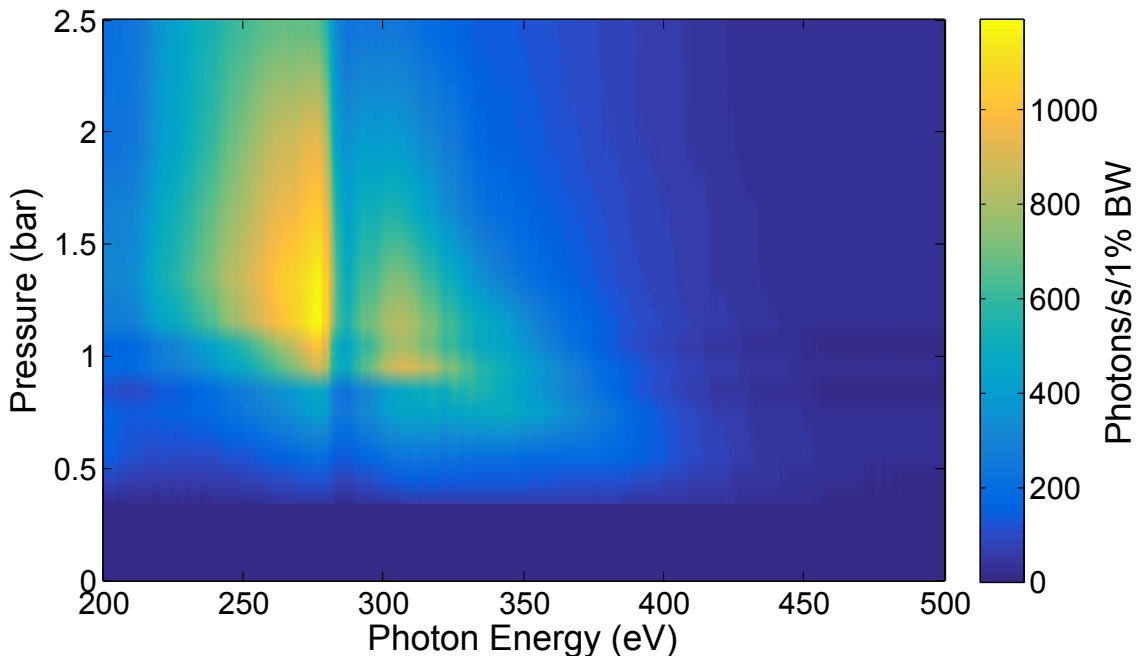


Figure 5.14: High harmonic spectrum of neon vs. backing pressure generated using a 30 cm focal length mirror and a 1.75 μm pulse two-cycles in duration with a pulse energy of 860 μJ . The focus was placed in the center of the gas cell.

Scanning the focal position results in similar changes in flux and harmonic cutoff, as shown in

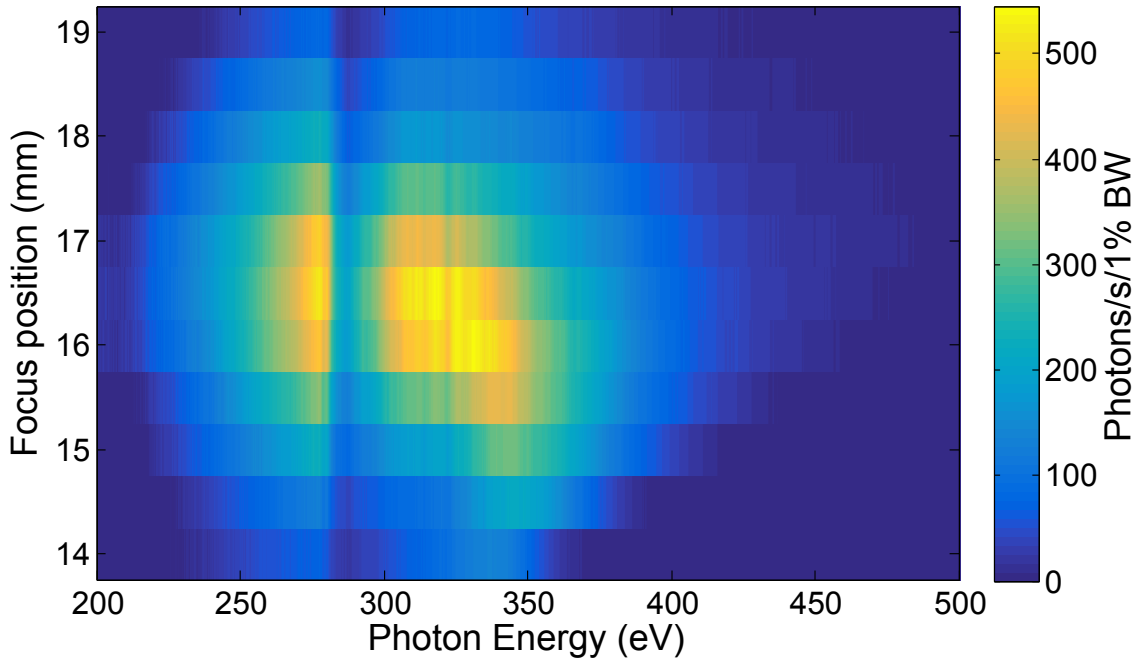


Figure 5.15: High harmonic spectrum of neon vs. focus position generated using a 30 cm focal length mirror and a $1.75\ \mu\text{m}$ pulse two-cycles in duration with a pulse energy of $860\ \mu\text{J}$. The backing pressure was held at 1.75 bar.

figure 5.15, where the harmonic spectrum as a function of focal position is scanned with a fixed backing pressure of 0.9 bar. We note there is once again a trade-off between highest cutoff and highest flux. Harmonics can be generated out well beyond the titanium $L_{2,3}$ edge at 456 eV; this represents the highest energy harmonics ever generated from neon [181, 182].

The results obtained using a 20 cm focusing geometry are qualitatively similar. Here pulses of $750\ \mu\text{J}$ were used due to decreased laser performance, though this still results in nominally higher on target intensities. Figure 5.16 shows the harmonic spectrum as a function of backing pressure. Compared to the results with 30 cm focusing, the flux is higher while the cutoff remains at a similar energy. Considerably higher backing pressures are required to optimize generation in the shorter focal length case, consistent with dimensional arguments from the quasi-static phasematching picture.

Figure 5.17 shows a focal position scan of the neon HHG at a fixed pressure of 1.75 bar. The dependence on the focal position does not show a trade-off between flux and cutoff, unlike in the longer focal case, and both are optimized when the laser beam is focused onto the gas jet at 33 mm.

The clear superiority of HHG with a 20 cm lens instead of a 30 cm mirror, even with a decreased power, is intriguing. Conventional wisdom in HHG is that flux is maximized by using a longer focal length, as this increases the focal volume contributing and decreases the phase-mismatch

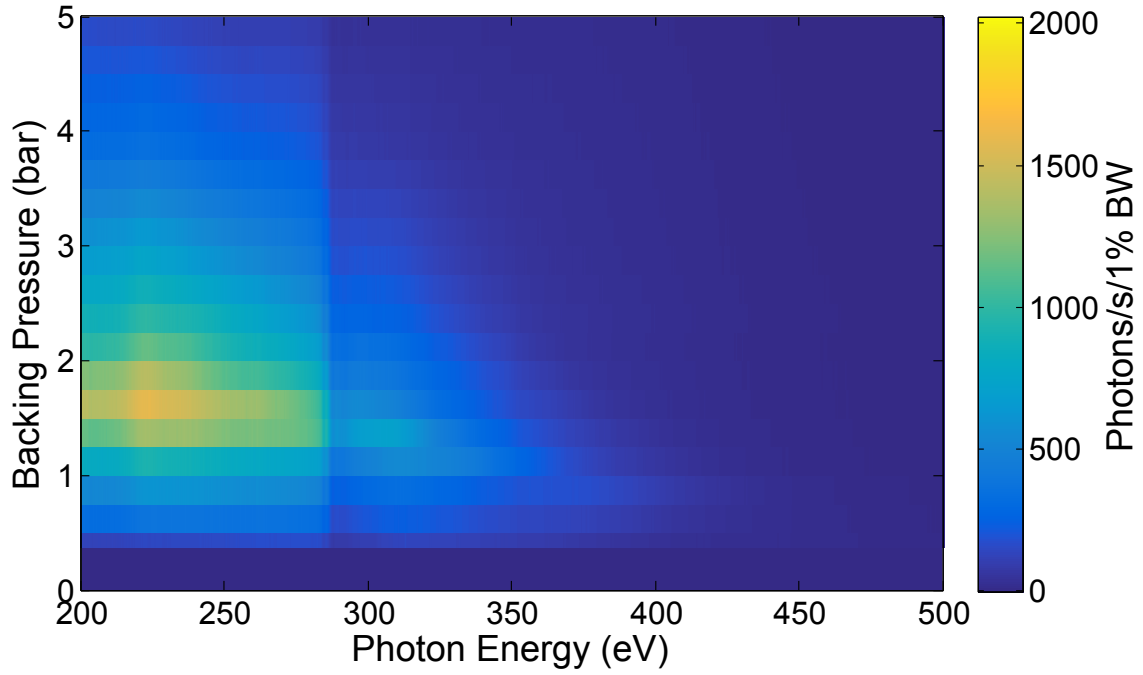


Figure 5.16: High harmonic spectrum of neon vs. backing pressure generated using a 20 cm focal length mirror and a $1.75\ \mu\text{m}$ pulse two-cycles in duration with a pulse energy of $750\ \mu\text{J}$. The focus was placed in the center of the gas cell.

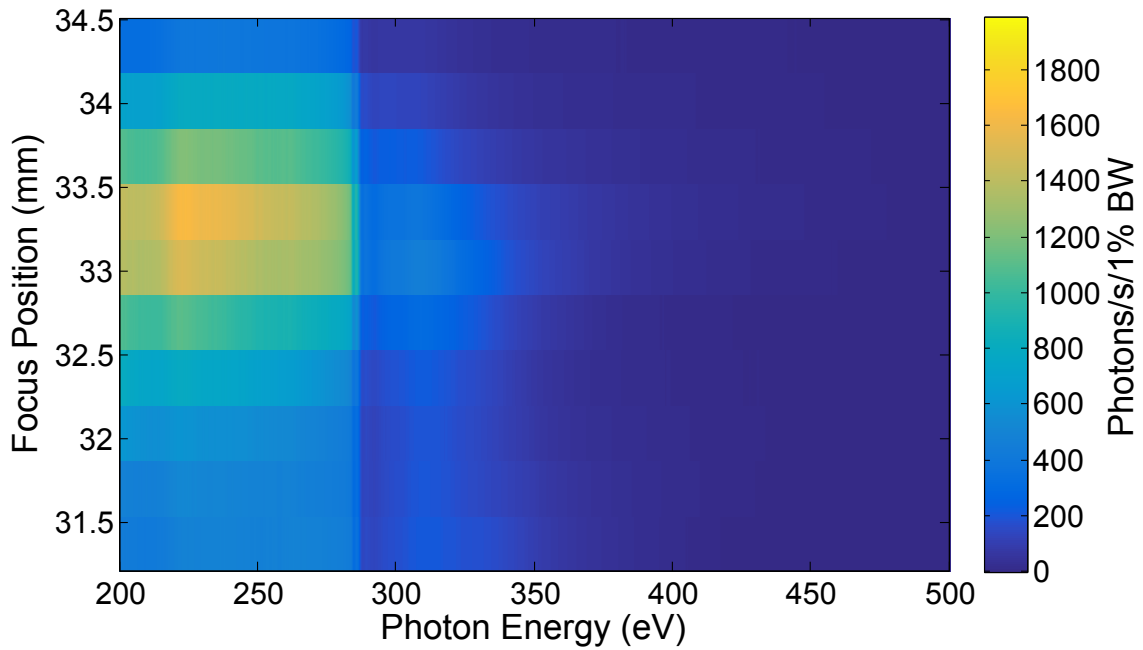


Figure 5.17: High harmonic spectrum of neon vs. focus position generated using a 20 cm focal length mirror and a $1.75\ \mu\text{m}$ pulse two-cycles in duration with a pulse energy of $750\ \mu\text{J}$.

contributions from the intensity dependent dipole phase and geometric phase. There are two potential, and not mutually exclusive, reasons for this somewhat surprising effect. One is that the generation is strongly ionization limited, that is to say the rate-limiting contribution is the initial tunnel ionization in the HHG process. In that case increasing the on-target intensity would result in a growth in the harmonic signal. The other is that the macroscopic phasematching conditions strongly favour the high intensity and steep gradients imposed by the tighter focusing. Full dimensional simulations of the entire pulse propagation and harmonic build-up are necessary to answer this question. We are currently beginning such simulations.

A vital question for the application of SXR harmonics to the time-resolved study of dynamics in matter is whether or not the harmonic emission takes the form of a single attosecond burst or as an attosecond train. Measurement of an attosecond pulse or attosecond pulse train can be performed through an attosecond streaking [2] or reconstruction of attosecond beating by interference of two-photon transitions (RABBIT) measurement [3]. In these schemes the attosecond pulse or train first photoionizes an atom, then the free electron interacts with a strong IR field which imprints sub-cycle timing information onto the photoelectron spectrum. Attosecond streaking is required for measuring isolated attosecond pulses, and relies on the gradient of the IR field. Because long wavelength driving fields have a much smaller gradient than shorter wavelength fields, streaking measurements become significantly more difficult; the first streaking measurement with a SWIR source has only recently been performed [183]. Combined with the low flux of water window harmonics and the small SXR cross-sections of noble gas atoms, attosecond streaking of water window harmonics is a challenging prospect. We do not have the necessary apparatus to perform such a measurement at this time, though commissioning of the necessary electron spectrometer and attosecond beamline is currently under way.

An alternative method which can show the existence of an isolated emission, at the expense of not returning the pulse duration, is to perform CEP scans [75]. The variation in the spectral cutoff with CEP allows one to determine whether an isolated burst is present and what spectral region it covers [181]. An example of a CEP scan taken in neon under 20 cm focusing conditions at 1.25 bar backing pressure is shown in figure 5.18. The harmonic cutoff varies dramatically as the CEP is varied, from a maximum around 350 eV to below the carbon edge. When the CEP is at 1.25π the harmonic emission takes the form of a single crest spanning from around 250 eV to 330 eV. while at 0.75π there are two distinct contributions, one above the carbon edge and below. In the former case an isolated pulse covering the carbon edge is expected, while in the latter only the higher energies correspond to a single attosecond pulses. The CEP scan shows we can generate isolated pulses with bandwidths of order 100 eV, with a pulse duration implicitly below 1 fs.

In order to give an estimate of the pulse duration we perform a comparison to an SFA cal-

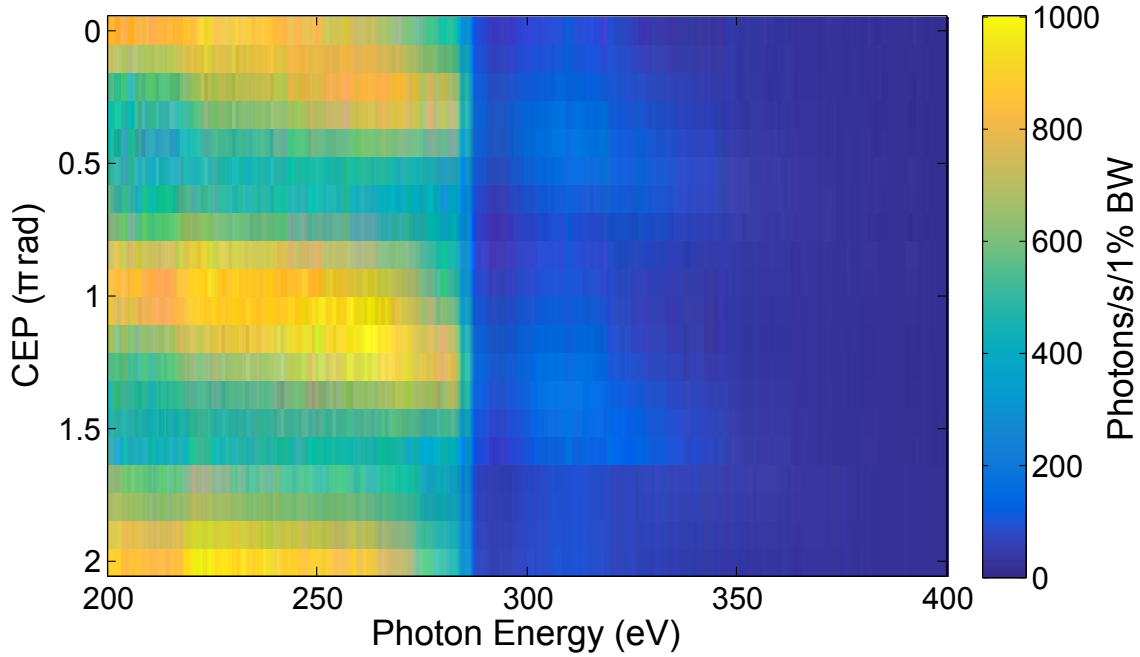


Figure 5.18: High harmonic spectrum of neon vs. CEP generated using a 20 cm focal length lens and a $1.75 \mu\text{m}$ pulse two cycles in duration with a pulse energy of $750 \mu\text{J}$. The backing pressure was 1.25 bar and the focus placed at 34 mm, 1 mm upstream of the target.

culation. Figure 5.19 shows a CEP scan showing motion of the harmonic cutoffs. Red lines indicate a fit of classical trajectories to the half-cycle motion, from which we determine a field amplitude and duration. We can then perform an SFA calculation using these parameters and examine the time-energy spectrogram of the harmonic emission. We extract an 11 fs pulse duration and a peak intensity of $3.6 \times 10^{14} \text{ W/cm}^2$ using this method, in good agreement with our SPIDER measurements. Figure 5.20(a) shows the corresponding SFA calculation; deviation around the carbon K edge is attributed to phasematching effects as the periodicity is incorrect to apply to another half-cycle cutoff. Figure 5.20(b) shows the time-energy spectrogram of the SFA calculation at $\phi_0 = 0.75\pi$. Emission above 280 eV is strongly temporally confined, and filtering only this region gives a pulse duration of around 300 as FWHM. Since the SFA does not include propagation effects, this value can thus only be taken as a lower bound to the true pulse duration. Nevertheless, this is a strong indication that we generate isolated harmonic emissions at our highest photon energies, with pulse duration of hundreds of femtoseconds [184].

We have additionally measured CEP dependent spectra for a wide range of backing pressures and focus positions. Smooth CEP dependence of the harmonic emission corresponding to isolated pulses is observed under all conditions with only weakly varying bandwidth. As can be seen from the pressure scan in figure 5.16, this means isolated pulses anywhere from the carbon K edge up to a photon energy of 450 eV can be generated. This suggests our source can produce, from neon, isolated attosecond pulses capable of probing any absorption edge of interest up to and including the nitrogen K edge, and measure the entire near-edge absorption spectrum simultaneously. This capability makes our SXR HHG source ideal for future attosecond

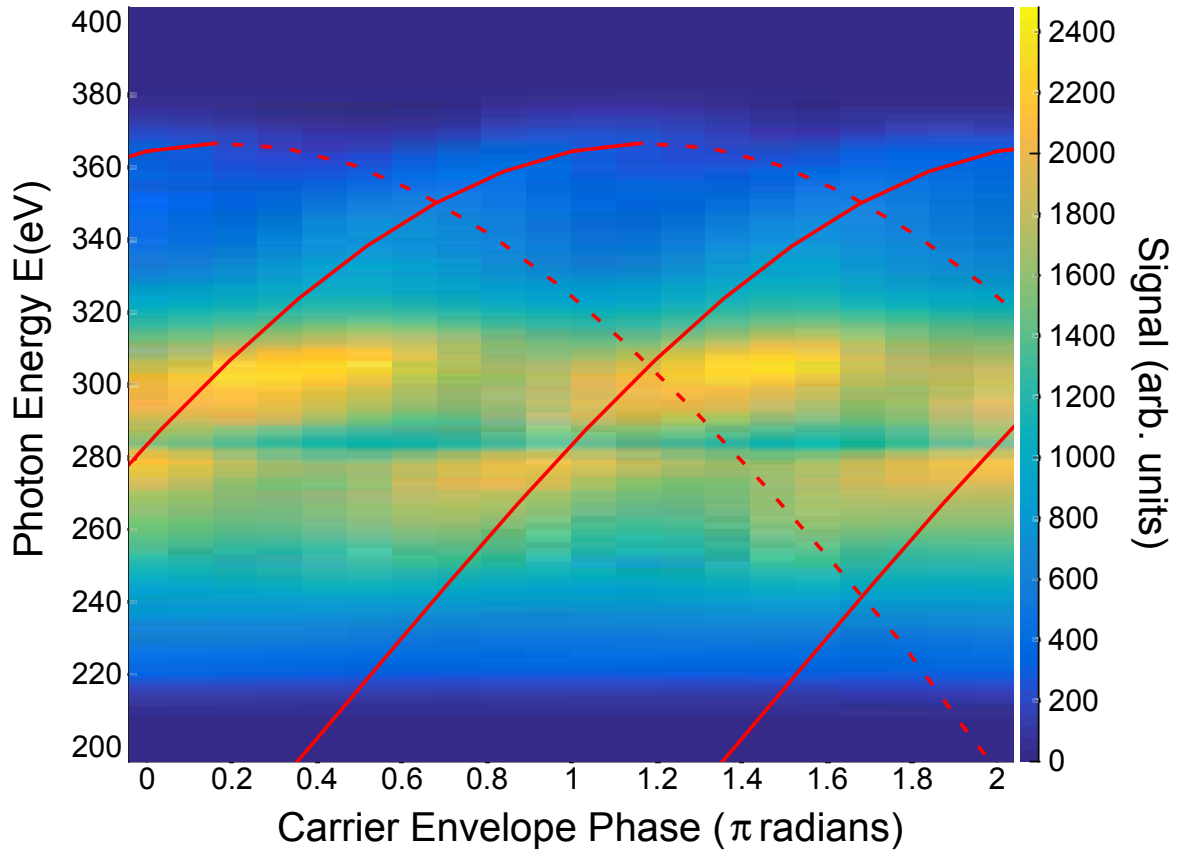


Figure 5.19: High harmonic spectrum of neon vs. CEP generated using a 30 cm focal length mirror and a $1.75 \mu\text{m}$ pulses. The red lines follow classical trajectory fits to the half-cycle cutoffs. The dashed lines correspond to trajectories born more than a half cycle before the field maximum; these trajectories have negligible amplitude. Reproduced from [184] under the terms of the Creative Commons Attribution 4.0 License.

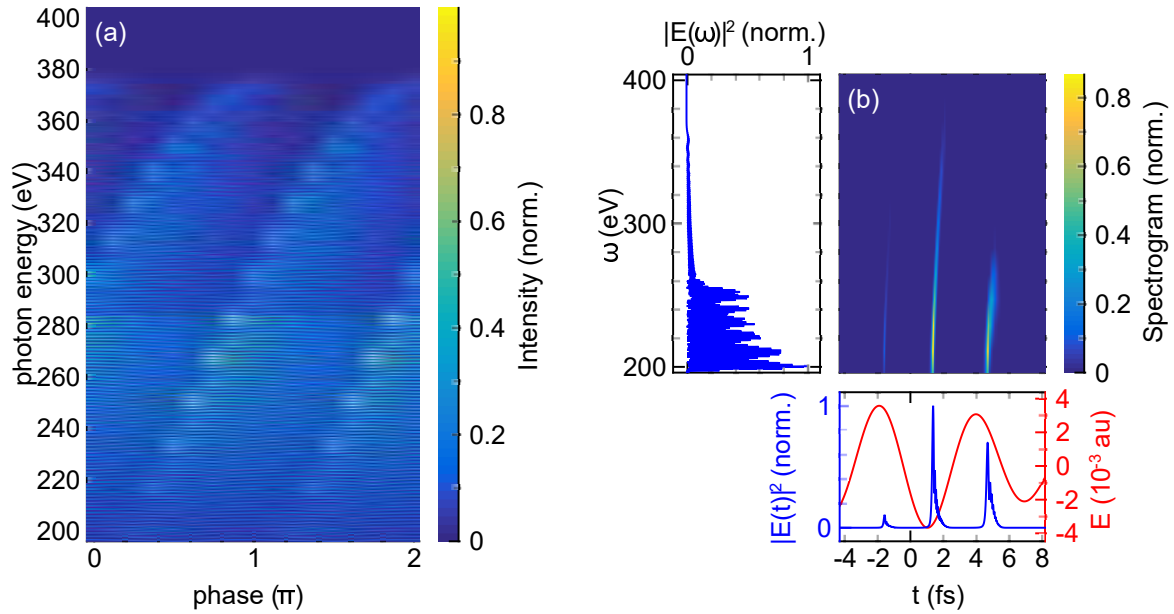


Figure 5.20: (a) Theoretical CEP scan calculated using the SFA and transverse phase matching for pulse parameters matching those extracted from figure 5.19. (b) Corresponding time-energy spectrogram of the harmonic emission, showing strong temporal isolation of harmonics above the carbon K edge. Reproduced from [184] under the terms of the Creative Commons Attribution 4.0 License.

transient absorption experiments.

5.3.2 X-ray HHG in Helium

Using the 30 cm focusing mirror and 860 μJ pulses, harmonics are generated in helium which extend beyond the titanium $L_{2,3}$ edge. A spectrum acquired with a backing pressure of 2.6 bar of He and the focus at the center of the gas cell is shown in figure 5.21; this acquisition was with a 20 s integration time. The most notable feature is a significant drop in the flux compared to neon, approximately one order of magnitude. This also results in much higher noise. Unlike in neon, harmonics can only be observed when the gas target is exactly at the focus, suggesting we are strongly ionization limited and the delivery of the highest intensity is necessary for harmonic generation. Harmonics of reasonable flux were observed from 2 bar to above 5 bar, along with good CEP dependence. However, given the small cutoff extension of around 20 eV compared to neon, and the much lower flux, there is little reason to use HHG in helium under these generating conditions. For this reason we move directly to the 20 cm case, where much higher intensities are possible.

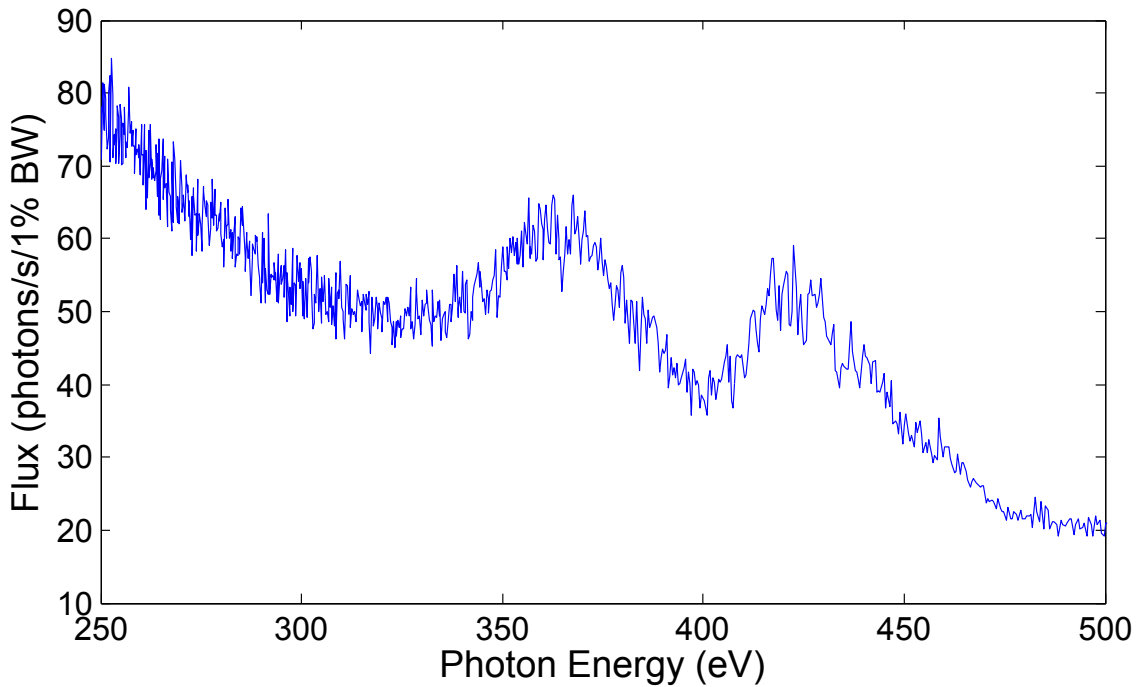


Figure 5.21: High harmonic spectrum of helium generated using a 30 cm focal length mirror and a 1.75 μm pulse two cycles in duration with a pulse energy of 860 μJ . The backing pressure was 2.6 bar and the focus placed in the center of the target.

Figure 5.22 shows a pressure scan of the harmonics generated in helium with a 20 cm lens and 750 μJ pulses, with the focus in the center of the gas target. The flux inside the water window is approximately double the case of the 30 cm focusing optic. Though difficult to observe, there is a motion of the cutoff downward with increasing backing pressure, but the cost in terms of

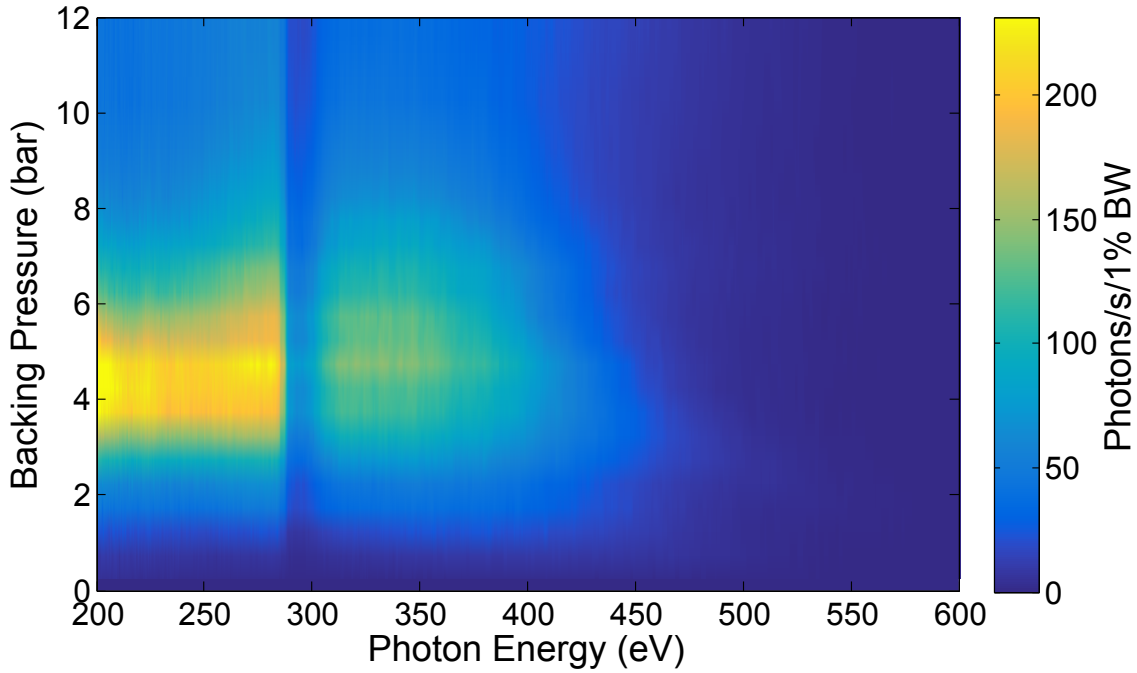


Figure 5.22: High harmonic spectrum of helium vs. backing pressure, generated using a 20 cm focal length lens and a $1.75\ \mu\text{m}$ pulse two cycles in duration with a pulse energy of $750\ \mu\text{J}$. The focus was placed in the center of the target.

flux at low pressures is much stronger than with neon, and so it is difficult to observe the true cutoff at pressures below 2 bar.

Figure 5.23 shows a scan of the focus position. The target and focus overlap at 32.85 mm. Away from focus the flux and cutoff both decrease simultaneously. As in the case of neon, we see the cutoff energy can be tuned by the focus position and backing pressure. Importantly, we see the cutoff from helium harmonics can be tuned to below the maximum cutoff of the neon harmonics, meaning there are no spectral gaps that cannot be addressed by tuning these macroscopic parameters.

The exact location of the cutoff in He is a topic of great interest, as there are several edges of interest above 500 eV such as the oxygen *K* edge (540 eV) and the vanadium *L* edge (520 eV) [53]. Figure 5.24 shows the spectrum from 2 bar of He with the focus in the center of the gas jet over the range 450 eV to 650 eV. The flux begins to decrease around 470 eV, but extends well beyond the oxygen *K* edge at 540 eV to around 600 eV. There is a roughly 50% drop at the oxygen *K* edge itself, which we attribute to oxygen contained in the hydrocarbon contamination seen at the carbon *K* edge. The flux at the detector is very small, but is interestingly high enough to perform XANES measurements at the oxygen *K* edge, as will be shown in section 6.1. Note that the flux delivered to the detector could be dramatically increased by simple modifications to the system; as will be discussed in 5.3.3, the collection efficiency of our system is rather poor. Regular *in situ* cleaning of the optics with UV and ozone to remove contamination [185],

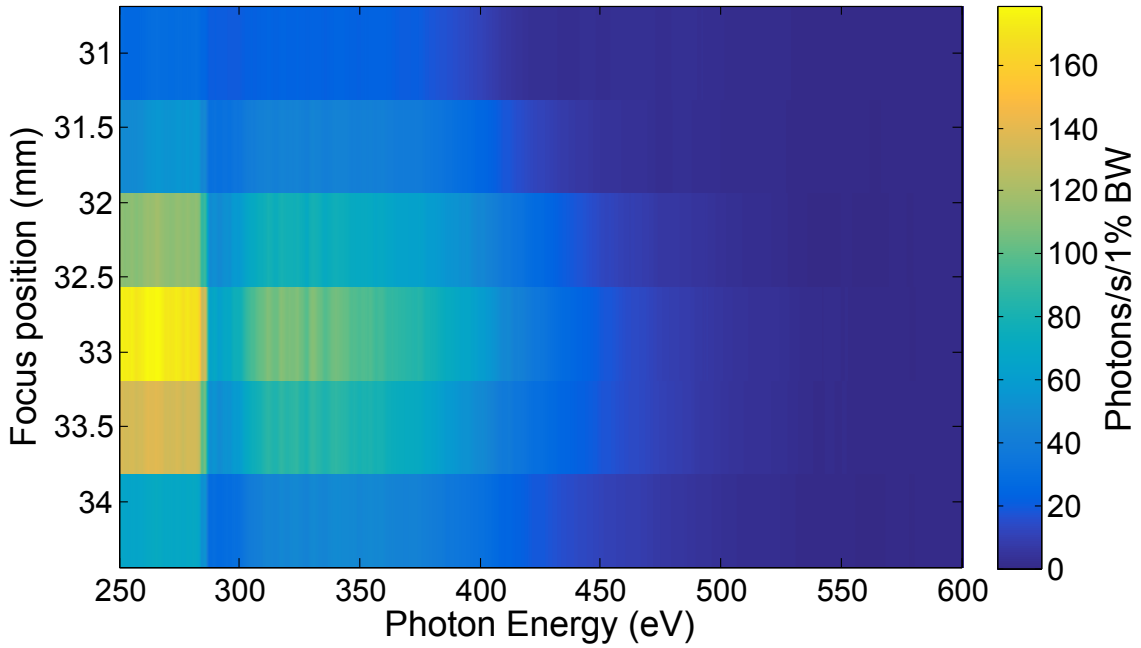


Figure 5.23: High harmonic spectrum of helium vs. focal position generated using a 20 cm focal length lens and a $1.75\ \mu\text{m}$ pulse two cycles in duration with a pulse energy of $750\ \mu\text{J}$. The backing pressure was held at 4 bar.

the use of thinner pinhole-less filters, and a collection optic to increase the angular acceptance could increase the at-detector flux by orders of magnitude.

Finally, figure 5.25 shows a CEP scan of the harmonics at the oxygen K edge. The decrease in flux at the oxygen K edge is visible, and precludes proper observation of CEP dependence beyond the edge. However, clear CEP modulation of the harmonic signal can be seen up to the edge, and from the physics of HHG we know this means that modulation beyond the edge must be occurring as well. Thus we are capable of producing isolated harmonic pulses beyond the oxygen K edge, and by our earlier scans of macroscopic conditions, at any edge of interest inside the water window.

5.3.3 Flux at Generation

For comparison to previously published results, it is useful to estimate the flux at generation instead of at the detector. There are several factors to account for here. The quantum efficiency of the XUV CCD (equation 5.2.7) has already been taken into account for the at-detector flux, but the filter transmission, carbon contamination, grating reflectivity, and spectrometer acceptance angle must all be carefully accounted for. An effective thickness for the carbon contamination can be determined by fitting the absorption of atomic carbon to the drop at the carbon edge, an example is shown in figure 5.26. This contribution can then be divided out; the metallic filter, for which the thickness is previously known, can also be divided out in

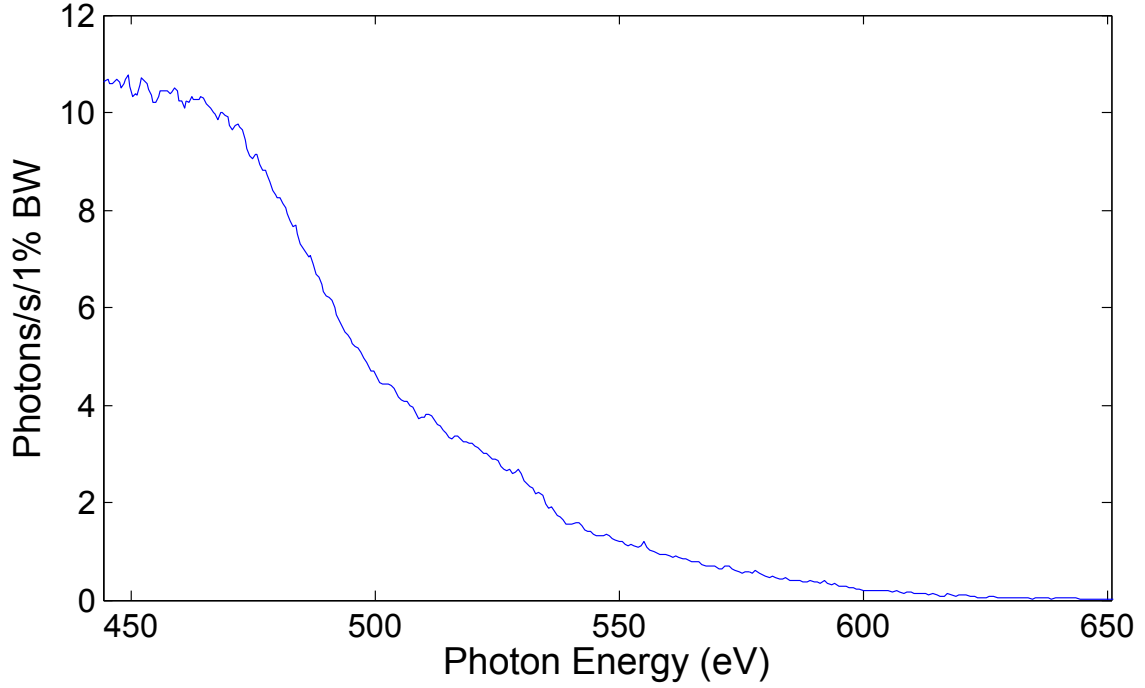


Figure 5.24: High harmonic cutoff of helium generated using a 20 cm focal length lens and a $1.75 \mu\text{m}$ pulse two cycles in duration with a pulse energy of $750 \mu\text{J}$. The backing pressure was 2 bar and the focus was in the center of the gas jet.

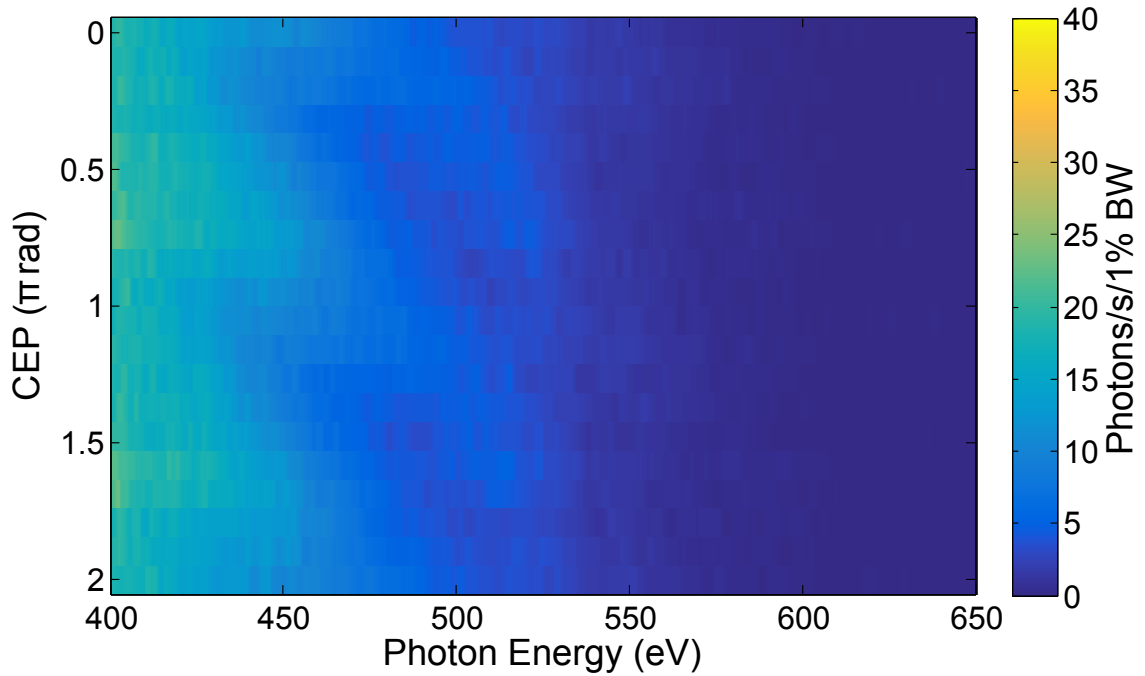


Figure 5.25: High harmonic spectrum generated vs. CEP using a 20 cm focal length lens and a $1.75 \mu\text{m}$ pulse two-cycles in duration with a pulse energy of $750 \mu\text{J}$. The backing pressure was 2 bar and the focus was in the center of the gas jet.

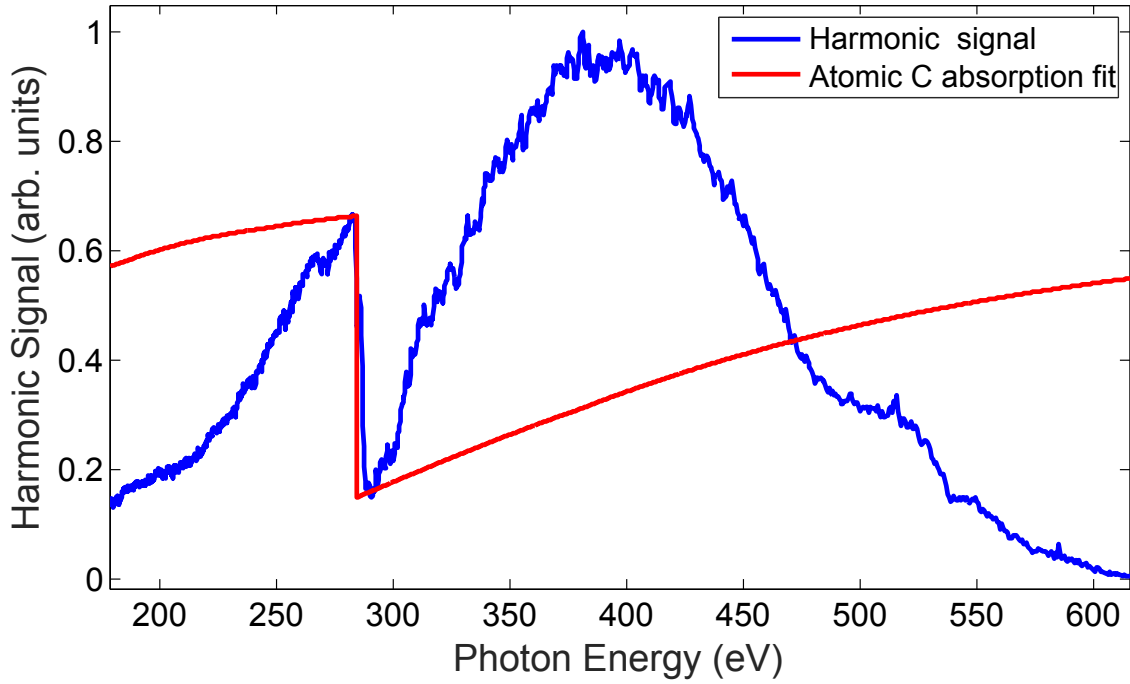


Figure 5.26: Normalized harmonic spectrum from helium, showing carbon contamination. A fit to absorption by atomic carbon is shown in red. The effect of oxygen absorption at 540 eV is also visible, but we do not correct for this.

the same way. Around the carbon edge itself the neglect of near-edge structure will result in artifacts in the signal, but away from this resonance the correction should be accurate.

Correction for the aperture of the spectrometer can be done since we have an imaging spectrometer. Our system exhibits cylindrical symmetry, and so we can reasonably assume a cylindrically symmetric beam profile. We fit a Gaussian to the spatial direction of our signal and estimate the loss on the entrance slit, which is known to have a width of 600 μm . This can be done for different spectral regions of the pulse and for each measurement independently, controlling for variation in the divergence. Since our harmonics typically have a waist around 3 mm at the detector, we find that on average 80-90% of our signal is clipped on the entrance slit. In order to improve signal-to-noise and acquisition times in future measurements it would thus be extremely advantageous to use a re-imaging optic such as a grazing-incidence toroidal mirror to refocus the harmonics onto the spectrometer slit. Grazing incidence optics can have efficiencies above 90%, which would increase our signal levels by over a factor of four compared to our current system. Correction for the grating efficiency provides the greatest challenge to our flux estimation, as the efficiency of the Shimadzu 30-003 grating is, to the best of our knowledge, not publicly available. However quantitative comparisons of the relative efficiency of the Hitachi 001-0471 2400 l/mm grating and the Shimadzu 30-003 are available in the literature [186]. Using the tabulated efficiency of the Hitachi 001-0471 we derive an efficiency for the Shimadzu 30-003, which varies from 2% to 3.2% across the water window.

Table 5.1: Comparison of flux generated at various edges and integrated across the water window. Flux is quoted as photons/s/1% BW for the edges, and as either photons/s or energy per pulse for the total water window. Flux is measured at 300 eV as a proxy for the carbon K edge to avoid possible artifacts from contamination.

Gas Species	300 eV	N K Edge	O K Edge	Total WW Flux
Ne	3×10^6	5.6×10^4	0	71 pJ, 1.4×10^9 photons/s
He	1.6×10^5	4.5×10^4	1.1×10^3	7.7 pJ, 1.44×10^8 photons/s
Previous results (short pulse)	2.3×10^5 [89]	1.5×10^4 [89]	0	2.9 pJ [181]
Previous results (long pulse)	—	—	—	6×10^7 photons/s [188]

Our optimal results are shown in table 5.1, where we show the flux in photons/s per 1% bandwidth at 300 eV and the nitrogen and oxygen K edges, along with the total energy per pulse in the water window spectral region, for neon and helium HHG. With the exception of the oxygen K edge, which requires lower backing pressure (2 bar instead of 4 bar), optimized flux at the edges coincides with maximum flux across the water window. We also for comparison show the highest energies published in the literature for short pulse driving lasers (implicitly attosecond pulse supporting), and long pulse lasers. Long pulse lasers have been used to generate fluxes of up to 2×10^7 photons/s with free space targets [89,187] or 6×10^7 photons/s with capillaries [188]. As can be seen, our source outperforms previous results at all spectral regions and for total flux.

Chapter 6

Towards the Application of Soft X-ray Harmonics

Having generated a high flux source of soft X-ray harmonic radiation, it behoves us to demonstrate its utility for more complex experiments. In this section I present an example application of our SXR harmonic source and a measurement showing its wider potential. First, I show static XANES measurements we obtained from an organic solar cell and a polymer film at the sulfur $L_{2,3}$, carbon K , and oxygen K edges. Secondly, we perform a SWORD characterization of the harmonics to measure the spatial wavefront, which indicates potential as a source for coherent diffractive imaging and X-ray microscopy.

6.1 HHG XANES Measurements

Measuring the near-edge X-ray spectrum of matter can be performed by X-ray transmission, photoelectron yield, scattered electron energy loss, or X-ray fluorescence. Of these, photoelectron yield and electron energy loss spectroscopy are highly sensitive to surface effects, while X-ray transmission and fluorescence return information on the bulk response. X-ray transmission spectroscopy is superior to fluorescence measurements as it avoids the problems of self-absorption in the sample and can measure post-edge structure. In some respects it is superior to electron methods as well, as it allows one to resolve bound state transitions which cannot be seen through photoelectron methods, though it requires higher fluxes given the much lower detection efficiency of X-ray detectors as compared to photoelectron detectors. For our purposes, X-ray transmission is both experimentally simpler, and a more stringent test of the source. Currently X-ray transmission XANES measurements are performed almost exclusively at synchrotrons, though they are possible through plasma sources and at X-ray free-electron lasers (XFELs). Performing an X-ray transmission XANES measurement with a high harmonic source is both a demonstration of its utility, and a necessary step towards performing time-resolved attosecond XANES spectroscopy.

6.1.1 Demonstration of XANES Spectroscopy

We have performed a variety of XANES measurements with our SXR source, determining the near-edge structure of N_2 at the nitrogen K edge (400 eV) and the near-edge of a biaxially-oriented polyethylene terephthalate (BoPET) film at the carbon and oxygen K edges (284 eV and 536 eV). N_2 is the most challenging test of resolution, given its resolvable vibronic progression and multiple electronic states, while BoPET has the highest energy edge.

Measurements in N_2 and BoPET were performed using He as the generating medium. For the BoPET film the sample was placed behind a 200 nm Al filter for measurement of carbon and oxygen K edges. A second copy of the metallic filter was used to obtain sample-free reference measurements. The two configurations (with and without sample) were cycled in order to obtain multiple absorption measurements, which were averaged to produce the final XANES spectrum. For the N_2 measurement, references were taken prior to introducing N_2 into the spectrometer chamber for the transmission data. Because of the super-continuum nature of the harmonic radiation, the entire XANES spectrum can be acquired simultaneously. In principle the measurement could be performed in only two shots, signal and reference, though in practice our flux is prohibitively low for this. The measured transmission (signal) spectrum I_T is related to the sample and source by the equation $I_T = e^{-\alpha d} I_0$ where d is the sample thickness, I_0 is the incident (reference) spectrum, and α is the attenuation coefficient of the sample. The quantity α can thus be obtained by dividing the measured transmitted spectrum by the measured reference, taking the natural logarithm, and dividing by the sample thickness, if known. If the thickness is not known, as in the case of N_2 , α is determined up to a scaling factor. As is normal in XANES analysis, we subtracted a linear fit to the pre-edge structure to isolate the effect of the absorption edge. However, other standard XANES techniques like normalization to the edge amplitude and flattening to the post-edge exponential have not been performed in order to allow for quantitative comparisons.

The BoPET used was purchased from the Lebow company, and consisted of a free-standing, 1 μm thick film. BoPET is an ideal material for demonstration of oxygen K -edge XANES because, as a foil, it is significantly easier to handle than gas, and has a very high proportion of oxygen atoms ($\text{C}_{10}\text{H}_8\text{O}_4$). Ideally a thinner sample would be used as the transmission at the carbon edge is very close to zero, around 1%. A pressure of 2 bar of He was used to extend the cutoff to around 600 eV, and integrations of 5 min were taken with and without the BoPET film. The total measurement time was around 3 hours, which is likely to be prohibitively long for a pump-probe measurement. However, the source was found to be extremely stable over this time frame, with no significant change in spectrum. The resulting oxygen K edge absorption spectrum is shown in figure 6.1, together with a XANES spectrum of a polyethylene terephthalate (PET) film from reference [189]. Because the flux was very limited at the highest energies, we had to open the spectrometer slit, restricting the resolution. Despite the resolution limits, we can resolve the pre-edge structures, as well as the post-edge peak. The difference

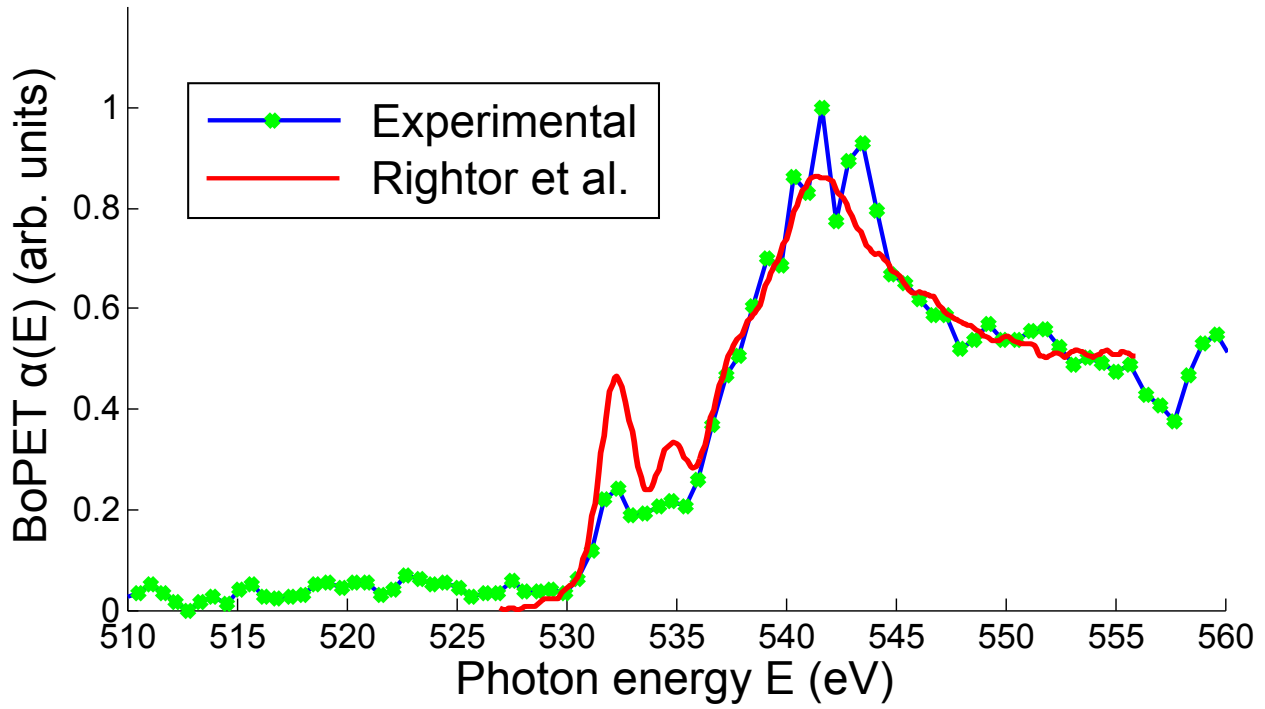


Figure 6.1: Measured BoPET oxygen K edge absorption spectrum normalized to the peak value. The red curve shows a synchrotron measurement in PET from reference [189].

in pre-edge peak weights between the measurement and reference can be attributed to the different mesoscopic structure of the polymers. The noise increases significantly after the edge, attributable to the lower signal levels from oxygen contamination in the spectrometer. Figure 6.2 shows the measured carbon K edge structure of BoPET. Due to the thickness of the sample the transmitted signal near the absorption peak was very low, resulting in a noisy transmission spectrum. Despite this, the two pre-edge peaks are well resolved.

The XANES spectrum of N_2 is another interesting test case to examine, as N_2 is one of the few system in which the vibronic progression has been resolved at X-ray wavelengths. Furthermore, it shows a rich electronic structure as well. As we did not have a gas cell for transmission measurements in our system, we instead took a single 5 min integration of the spectrum from 2 bar of He, then filled the spectrometer chamber with 1.6 mbar of N_2 and took an additional 5 min acquisition for the transmission measurement. The entire measurement took 10 minutes. Figure 6.3 shows the result of the absorption measurement, together with a reference measurement obtained from the literature [50], smoothed to remove the vibrational progression, which is much below our resolution. While the overall peak structure shows reasonable agreement, we see large disagreement in the peaks between 405 eV and 415 eV, the origin of which is not clear at this time.

Our XANES measurements, including the first at the oxygen K edge with a harmonic source and among the first performed in the water window, illustrate the potential of our source for time-resolved studies. Different pre-edge features, corresponding to excitation from lower lying

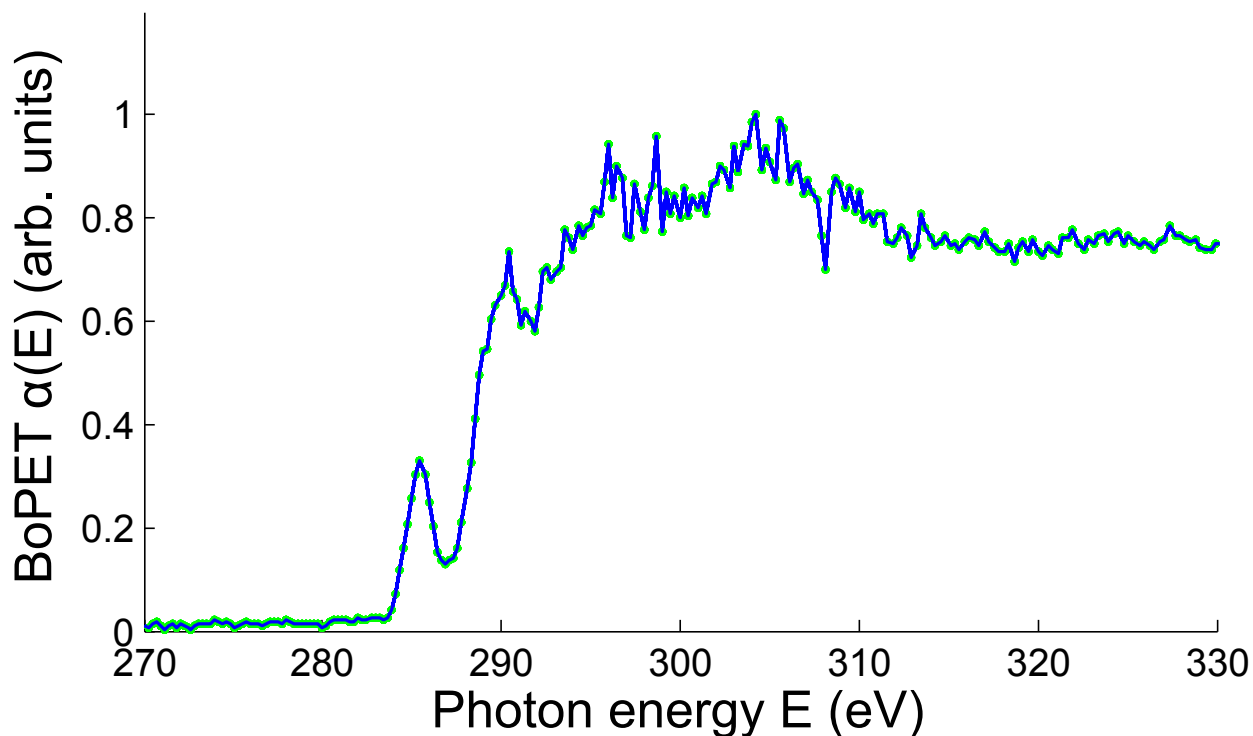


Figure 6.2: Measured BoPET carbon K edge absorption spectrum normalized to the peak value.

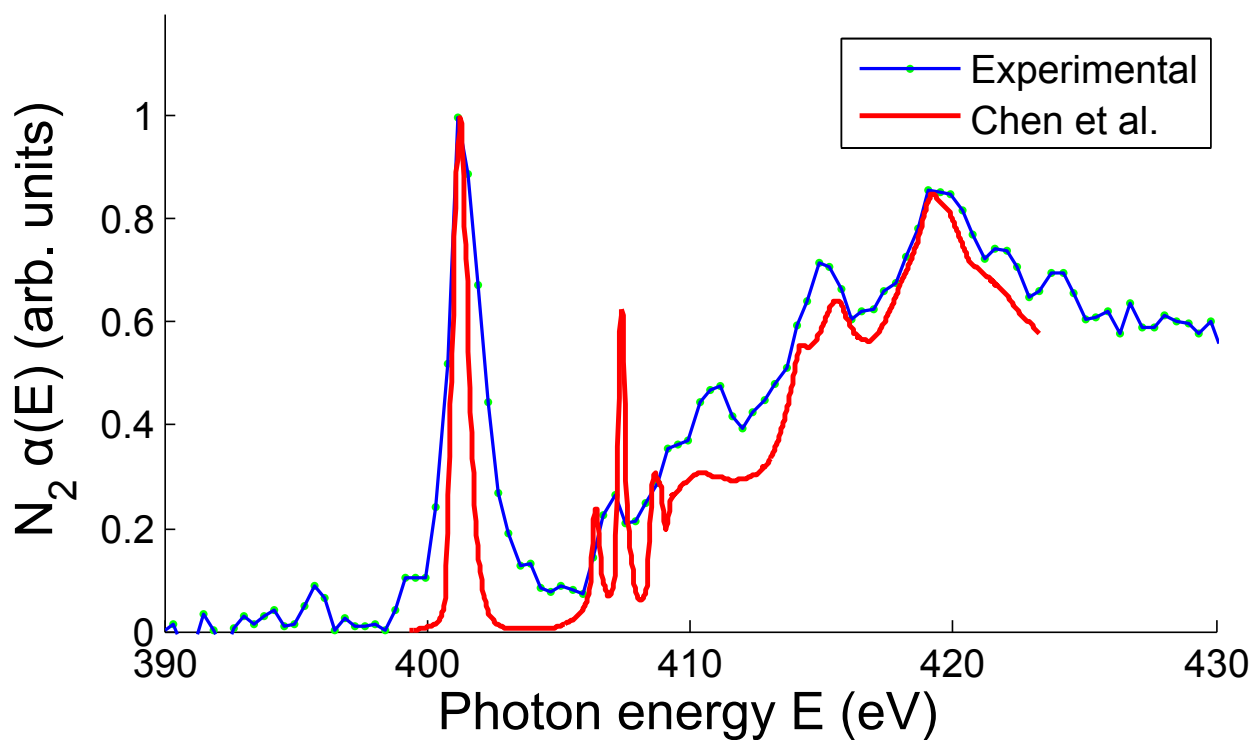


Figure 6.3: Measured N_2 nitrogen K edge absorption spectrum normalized to the peak value. The red curve shows a synchrotron measurement in N_2 from reference [50], smoothed to remove the vibrational progression.

s and p states into valence holes, are clearly resolved and could be used to track changing populations. The improvements to the detection scheme suggested in section 5.3.2, namely pinhole-less filters, carbon decontamination, and a collection optic for the spectrometer, would result in further decreases in acquisition time together with higher resolution.

6.1.2 XANES Spectroscopy of P3HT

The motivation for using HHG as a source for SXR radiation is the possibility of performing attosecond XANES spectroscopy. There are many potential systems of interest that could be studied using atto-XANES; here we demonstrate the first step towards an attosecond pump-probe measurement by measuring the XANES spectrum of Poly(3-hexylthiophene) (P3HT), an organic solar cell. P3HT is a polymer often used in organic solar cells and plastic electronics, with an extremely broad absorption in the visible region. Its unit cell is a thiophene “head” attached to a carbon “tail” - with sulfur present only in the head, it forms an ideal local probe of electron structure. We measure the near-edge structure at both of the sulfur $L_{2,3}$ and carbon K edges (165 eV and 284 eV), using harmonics generated in neon. An identical measurement procedure was applied as in the case of the BoPET film, but using instead a 250 nm Zr filter for measurement of the sulfur $L_{2,3}$ edge. This means that the two edges could not be measured simultaneously, but a future experiment utilizing indium filters would be able to do so. An identical analysis procedure was applied to the experimental data as described in the previous section.

Measurements were made using 200 nm thick films manufactured by my fellow PhD student Lukas Miseikis. The sample thickness was measured using a profilometer. Integrations of 1 min at each configuration were taken before switching, with measurements at the sulfur and carbon edges taken separately due to the different filter requirements, over a time period of 2 hours each. We used a backing pressure of 1.4 bar of neon to generate harmonics at the carbon K edge. The flux was optimized at the carbon K edge, and the measurement there is significantly less noisy than at the sulfur $L_{2,3}$ edge. The carbon K edge spectrum of P3HT we measured is shown in figure 6.4. All four known transitions of P3HT at this edge are clearly resolved and labelled. The agreement to literature measurements is excellent; in particular, by assuming a density of 1.16 g/cm² in agreement with reference [190], we obtain an absolute cross section in agreement with previous synchrotron measurements of P3HT [191]. While our measurement presented in figure 6.4 was obtained in two hours, we are actually able to resolve all the features in just two minutes.

Figure 6.5 shows the measured spectrum of P3HT at the sulfur $L_{2,3}$ edge. The spectrum is quite noisy due to the decreased flux, as well as the significantly poorer laser performance at the time of the measurement. Three peaks are clearly identified and labelled. Due to the near degeneracy of the p_{+1} and p_{-1} states, the three peaks actually correspond to four transitions.

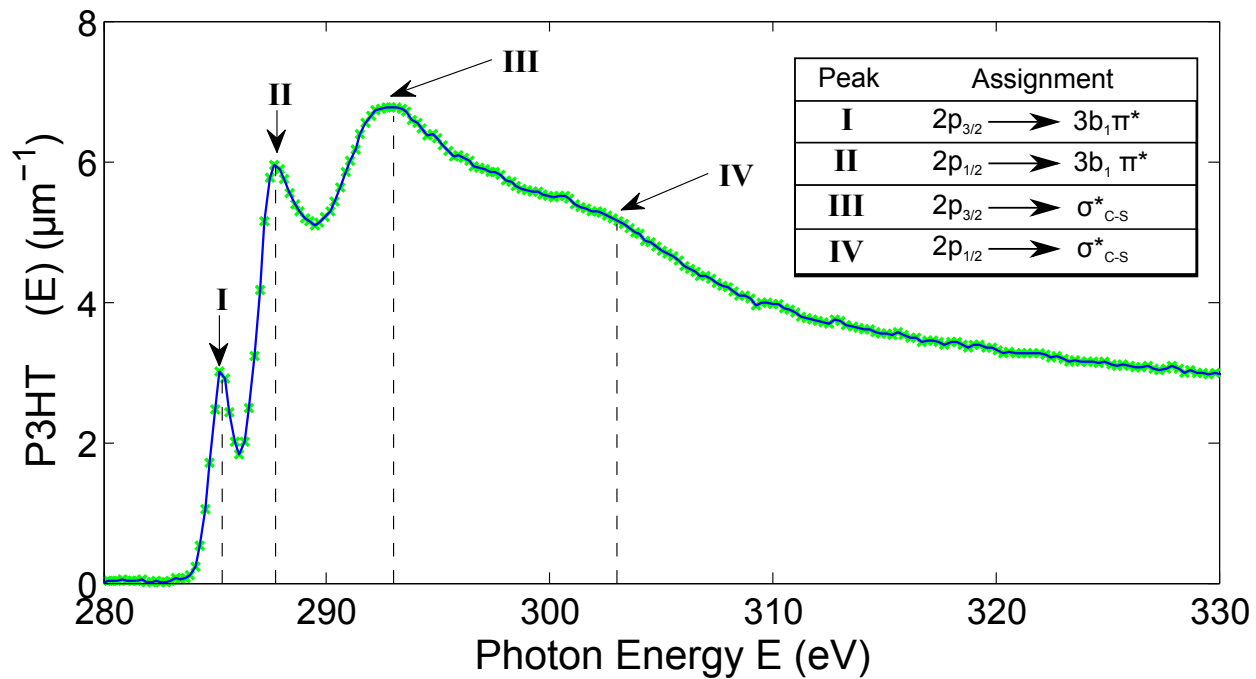


Figure 6.4: Measured P3HT carbon K edge absorption spectrum with labelled transitions. Reproduced from [184] under the terms of the Creative Commons Attribution 4.0 License.

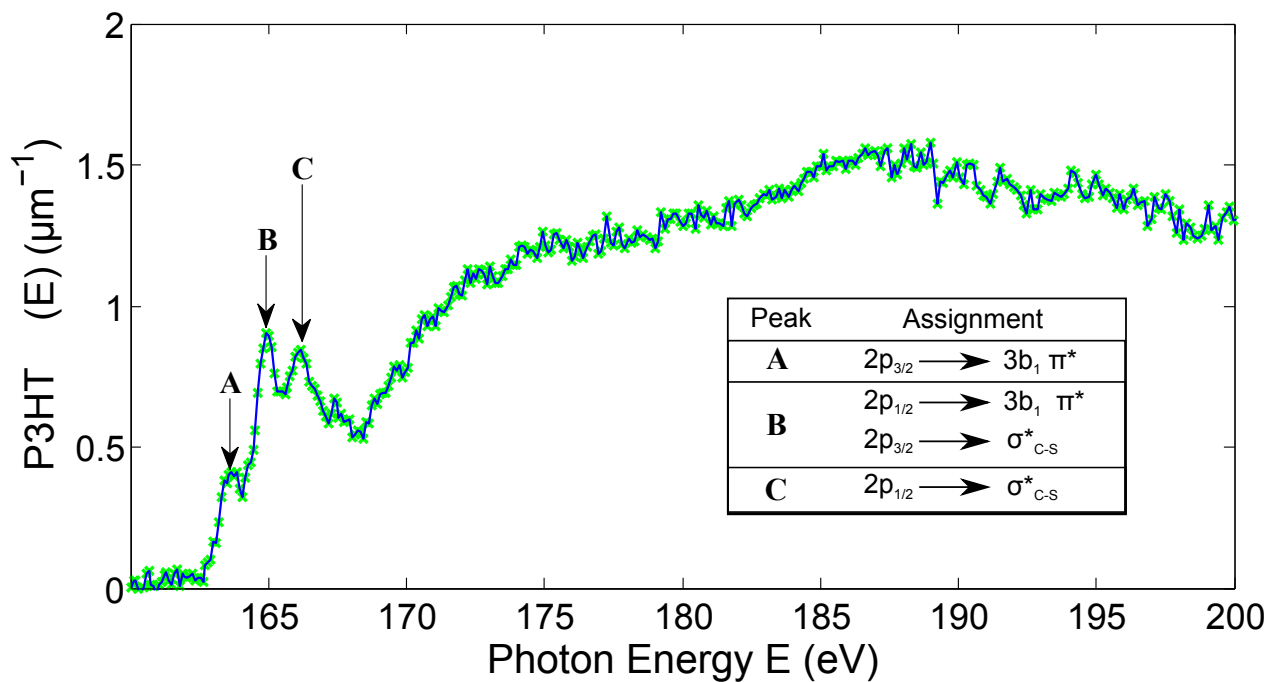


Figure 6.5: Measured P3HT sulfur $L_{2,3}$ edge absorption spectrum with labelled transitions. Reproduced from [184] under the terms of the Creative Commons Attribution 4.0 License.

Unfortunately the noisy spectrum precludes identification of any above-edge features, though we note that recent research suggests the pre-edge may capture the most interesting dynamics in any future pump-probe experiment [49]. We also are able to identify the sulfur L_1 edge (230 eV) in our data, but as it occurs at a region of extremely low filter transmission we are not able to resolve any features.

The high resolution, rapid acquisition of XANES spectra is a necessary prerequisite for any future pump-probe experiment in P3HT. We are clearly able to resolve all features of interest, and an acquisition time of just two minutes is highly encouraging for time-resolved applications. This suggests a full pump-probe scan could be performed on the order of an hour, well within the laser stability time seen in our oxygen K edge measurements. Future steps involve the development of a suitable pump pulse based off the third harmonic of the SWIR pulses at 600 nm, and integration into our pre-existing attosecond beamline.

6.2 SWORD Characterization of SXR HHG

As HHG pushes to ever higher photon energies, there is increasing concern about the spatial properties of the macroscopic emission. Spatial coherence is essential for CDI and is necessary to ensure good spatio-temporal characteristics in pump-probe experiments, but can be degraded through excessive ionization. With long wavelength sources driving HHG in high pressure gases, the possibility of the continuum electron interacting with neighbouring atoms and dephasing from the driving field becomes possible. Connected to this issue, the wavefront of the harmonic emission could become strongly distorted in SXR emission by these same mechanisms, degrading the spatio-temporal quality of the emission and its usability in experiment. SXR HHG in waveguides has been shown to produce harmonics with good spatial coherence, as measured with double slit interferometry [192], but no measurement of harmonic wavefront in the soft X-ray has yet been reported. To that effect, we have measured the spectrally resolved wavefront of harmonics across the water window generated in both neon and helium, using a spectral wavefront optical reconstruction by diffraction (SWORD) measurement [193]. A SWORD measurement is an analogue of a Shack-Hartmann sensor, in which the role of the lens array is played by a diffractive aperture. A slit is placed in the beam in the near field, and the spectrally resolved diffracted orders (approximately a sinc squared distribution, the Fourier transform of the slit) are measured in the far field; the diffraction pattern centroid follows the direction of the phasefront of the beam at the position of the slit, as illustrated in figure 6.6. By scanning the slit, the wavefront curvature is mapped out.

In the Fraunhofer diffraction limit, the spatial phase can be reconstructed as

$$\phi(x_i) = \frac{2\pi}{\lambda} \sum_{i=0}^n \frac{s_i - x_i}{d} \Delta s \quad (6.2.1)$$

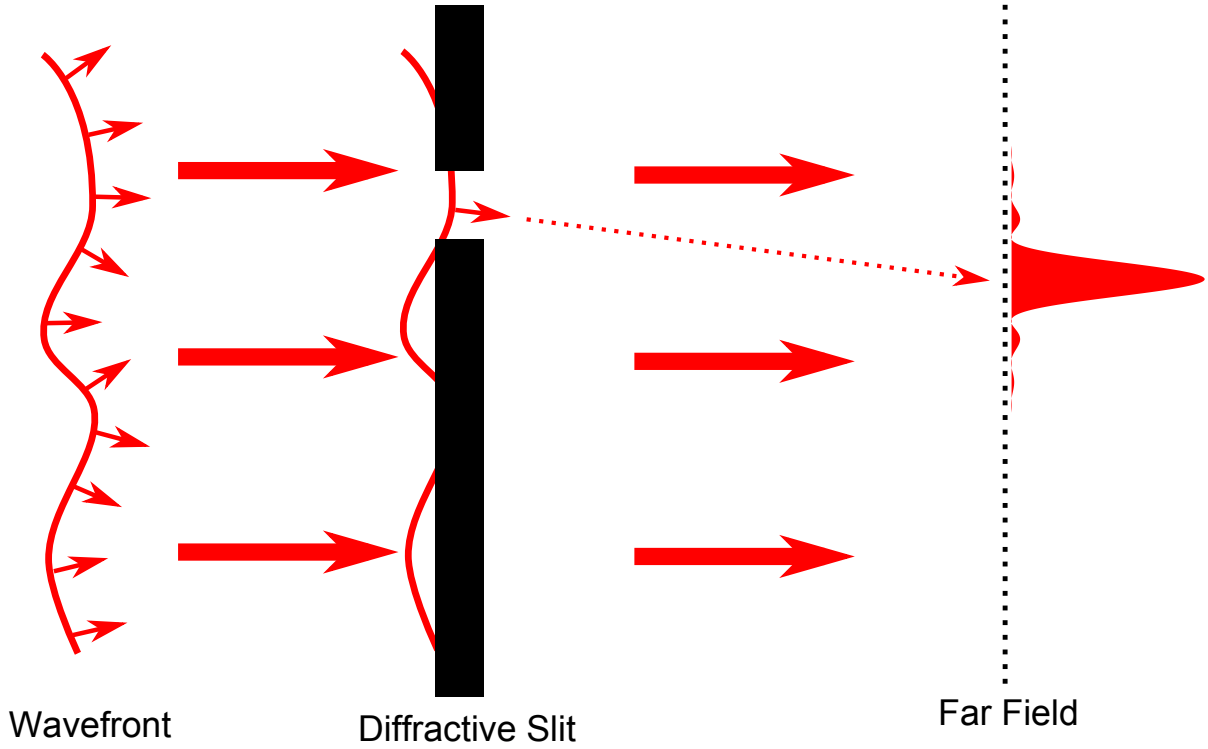


Figure 6.6: Illustration of the SWORD scheme. The local wavefront of the beam is sampled by a slit and diffraction maps the local curvature to the far field position.

where λ is the wavelength, s_i is the location of the diffraction pattern centroid in the far field, x_i is the slit position in the far field, Δs is the sample spacing of the slit, and d is the distance between the detector and the slit. In our system, d is constrained to one meter or less depending on the placement of the slit. At $d = 1$ m, a slit of $40 \mu\text{m}$ could be used while still remaining in the Fraunhofer limit for 2 nm wavelength light; however we opt for using a $10 \mu\text{m}$ slit in order to ensure that the $m = \pm 1$ diffraction orders are resolved on our detector, as an independent verification of the regime. We have performed scans on harmonics generated in helium and neon, with the slit placed one meter from the detector such that the diffraction occurs in the spatially resolved direction of our spectrometer. The slit is approximately 128.5 mm from the target itself. We measure the diffraction at 12 points across the beam, taken $\approx 70 \mu\text{m}$ apart.

We observe well defined peaks in the far field when our slit is in place. I fit sinc^2 distributions to the spatial direction for different spectral regions, taking a bandwidth of $\pm 5 \text{ eV}$ at each value. The fit determines the peak position and amplitude, as well as the width (unused in our current analysis). The amplitudes can be used to measure the intensity distribution in the plane of the slit, while the positions are used to perform the SWORD analysis of the phasefront. Figure 6.7 shows the peak position in the far field as a function of the slit position for lineouts around the carbon K edge, nitrogen K edge, and titanium $L_{2,3}$ edge, taken for harmonics generated in 4 bar of helium. A nearly perfectly linear trend is observed, with all three spectral regions

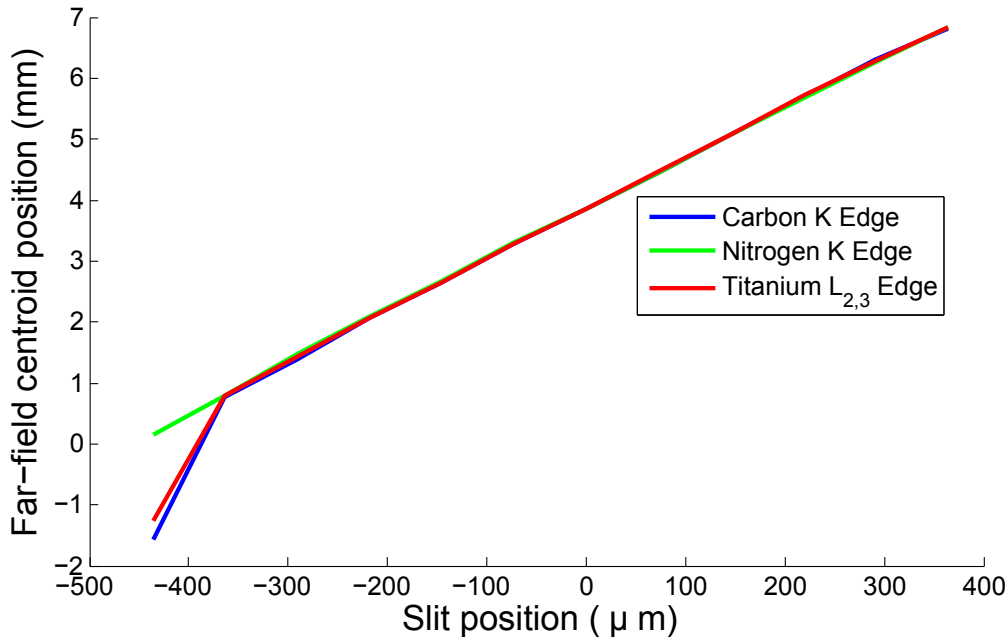


Figure 6.7: Position of diffraction pattern peak on the X-ray CCD vs. slit position for harmonics generated from 4 bar of He. Behaviour at the carbon K , nitrogen K , and titanium $L_{2,3}$ edges are shown; all are linear, with deviation where the diffraction pattern reaches the edge of the detector.

showing nearly identical behaviour; the deviation seen as the position approaches zero is the signal moving off the detector causing the fitting algorithm to fail, since we were not able to center the beam perfectly on the detector. The excellent quality of the linear fit is demonstrated in figure 6.8, which shows the residuals after subtraction of a linear fit to the nitrogen K edge line. The residuals are small, and are largely achromatic. Given the quality of the linear fit, we can attempt to analyze our results directly, without performing a phase reconstruction, via ray optics. The slope of this curve will give us the divergence, and since we know the distance between the SWORD slit and the detector, we can trace the rays backwards and attempt to find the location of the source. We have performed exactly this analysis and found that the harmonics originate from a virtual source before the gas cell. Note this does not mean the harmonics are actually generated in the gas before the target, but rather they are imparted radial phase via the intensity dependent dipole phase $\vec{K}$ which gives them a diverging wavefront. For generation in 2 bar of He we find a virtual source 8 ± 0.4 mm before the gas target, while in 4 bar of He the virtual source is 10 ± 1.0 mm before the gas target. To within our precision, we do not observe any difference in the virtual source position for the three spectral regions, at either of the pressures examined.

If we apply equation 6.2.1 to our data, we reconstruct the wavefront at the slit plane. Figure 6.9 shows the reconstructed phase for harmonics from 4 bar of He. The phase is dominated by a simple quadratic shape, the characteristic wavefront of a diverging beam. Almost no evidence of higher order phases is apparent, and our beam will behave in a nearly perfect Gaussian beam-like manner; in particular it means spatial-spectral coupling will be minimal in the focus.

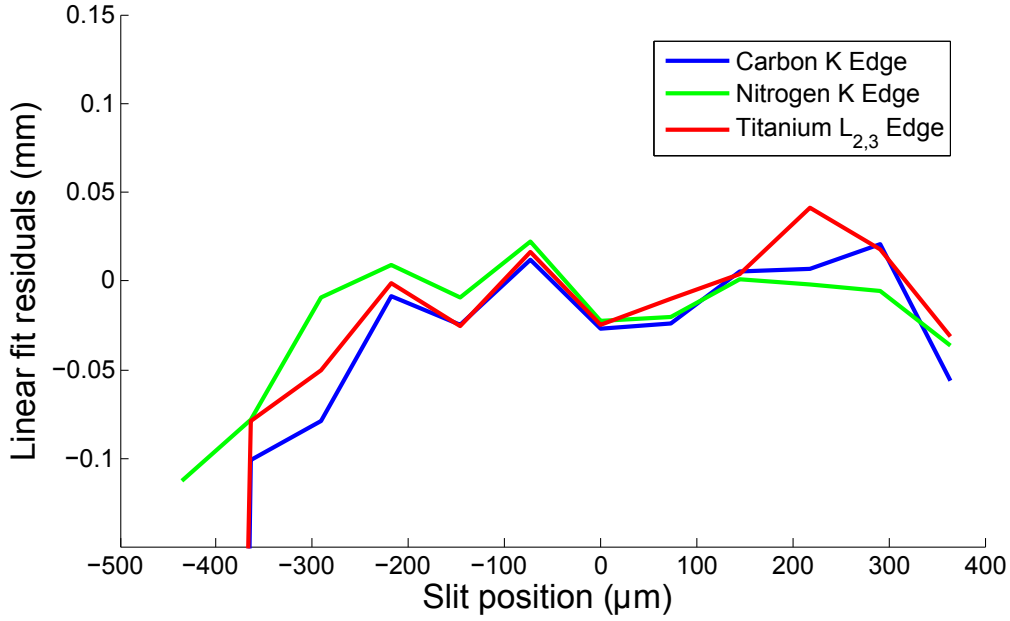


Figure 6.8: Residuals of diffraction pattern peak positions on the X-ray CCD after subtraction of a linear fit.

Due to the extremely broad bandwidths required in attosecond pulses, even small amounts of spatial-spectral coupling can degrade the quality of a focus to such a degree that attosecond pulses cannot be delivered to a target, even if the spectral phase is appropriate [194]. My analysis demonstrate that our source will not suffer from such effects, and that the beam could also be used for imaging applications.

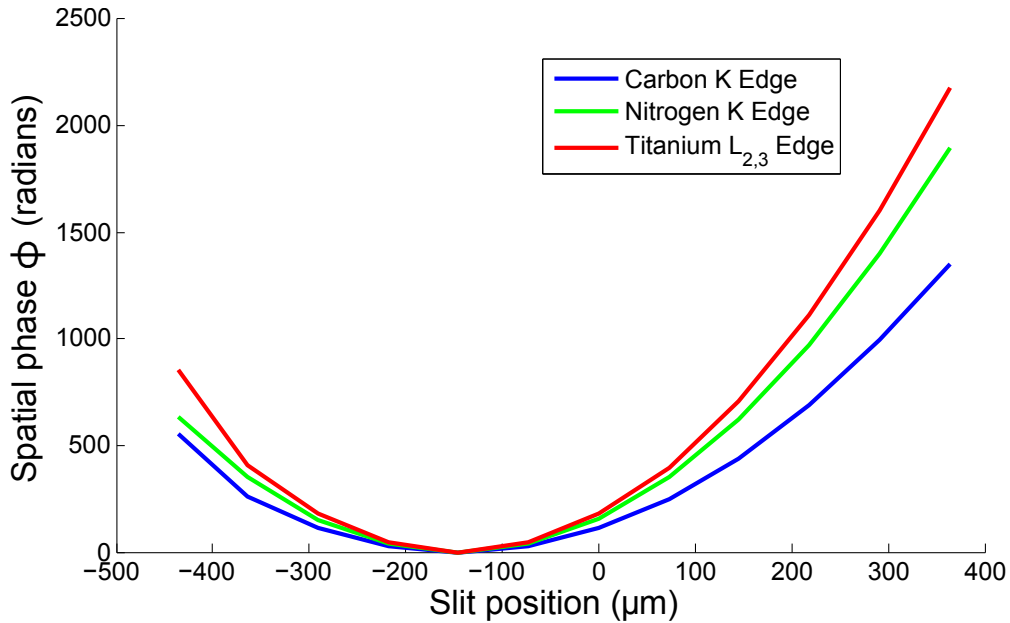


Figure 6.9: Reconstructed phase profile of harmonics generated in 4 bar of He at the carbon K , nitrogen K , and titanium $L_{2,3}$ edges. The phase is nearly perfectly quadratic, showing a high quality diverging beam.

Finally we estimate the spatial-spectral structure of our beam at the virtual focus. Because the phasefront is so well described by purely quadratic phase, we can use the principles of Fraunhofer diffraction to analyze the focus simply by removing the quadratic phase and Fourier transforming. Unfortunately the phase of the harmonics, as seen in figure 6.9, spans over one thousand radians across the beam. This means even small fractional errors in the measurement manifest as extremely large (multiple π) phase variations across the beam, leading to an extremely noisy reconstruction of the focus. SWORD is not suited to such a precise measurement and alternative, more technically demanding, techniques such as lateral shearing interferometry are necessary to resolve finer features [195]. To remove the effect of high frequency noise, I perform a fourth-order fit to the harmonic phase and reconstruct the phase at the focus discarding higher order effects; simulations show the intensity-dependent phase $\vec{K}$ should be well described by including up to fourth order. I use a separately measured spatial-spectral distribution at the detector without the SWORD slit in place, as the amplitude derived from SWORD is much less reliable than the phase curvature. Using this, I find a virtual source size of $1.2 \mu\text{m}$ FWHM. The approximately micron size of our virtual source is very encouraging for future applications. In a realistic experiment, one would re-image not the generating medium but the virtual source of the harmonics into the interaction region. This means even for 1:1 imaging with an ellipsoidal mirror very small spot sizes could be delivered, without recourse to multiple extremely expensive and large X-ray optics to build telescopes. This is obviously powerful for imaging, since the statement applies to all the frequencies in our beam, but is also important for pump-probe measurements. One particularly powerful illustration is that if we assume a pulse duration of 500 attoseconds for the pulse, 50 pJ of energy, and a $1 \mu\text{m}$ spot size, the intensity deliverable by our X-ray source is of order 10^{13} W/cm^2 ; this is approaching the regime where X-ray non-linear optics becomes feasible [196, 197]. Thus next-generation HHG sources may be able to compete with XFELs for X-ray pump-probe measurements in the SXR.

Chapter 7

Conclusion and Outlook

In this thesis I have presented work on the generation of new light sources for attosecond science, namely a few-cycle, high power SWIR laser source, and an SXR attosecond high harmonic source.

In chapter 3 I described the development of our SWIR source. In order to scale the ponderomotive potential of our laser, we use a commercial OPA to generate 1.4 mJ pulses at a central wavelength of 1750 nm from our Ti:sapph CPA system. Compared to the ubiquitous 800 nm wavelength of Ti:sapph lasers, we can expect over a factor of four increase in the ponderomotive potential by moving to the longer wavelength. We compress our approximately 30 fs duration SWIR pulses through the use of self-phase modulation in a HCF, followed by dispersion compensation in bulk fused silica. Due to the poor mode quality of the OPA output, we are limited in transmission to around 50%, giving us pulses of around 750 μJ . However, our compression is shown to be very efficient, and we were able to generate pulses 7.1 fs (1.3 optical cycles) in duration at a 1 kHz repetition rate, with excellent spatio-temporal quality. CEP stability of around 250 mrad was achieved using a feedback loop with a 2f-3f interferometer. We also transferred our technology to the ARTEMIS facility at Rutherford-Appleton laboratories, where two-cycle pulses of around 500 μJ were generated without CEP stabilization.

In order to temporally characterize our pulses we have developed three different pulse measurement techniques: a SEA-F-SPIDER, a single-shot third-harmonic FROG, and a third-harmonic D-scan (at ARTEMIS). Each of these systems was chosen for a balance of completeness and complexity, with the SEA-F-SPIDER capable of full spatio-temporal characterization but suffering from complexity, while the FROG and D-scan exhibit great simplicity.

In our implementation of SEA-F-SPIDER for broadband, SWIR pulses exhibiting spectral nulls, we used pulses generated from residual CPA light around 800 nm as the ancillae. This placed the upconverted, frequency sheared copies near the maximum frequency response of silicon CCDs. A variable shear, independent of the pulse under study, was used to enable reconstruction even in the presence of spectral nulls. Full spatial-temporal reconstructions were

obtained and show nearly perfect decoupling of the spatial and temporal degrees of freedom. Our single-shot, third-harmonic FROG used spatial division of the test pulse in order to avoid material dispersion, and two copies were cylindrically focused into a piece of KG1 Schott glass. Super-achromatic phase matching was achieved by limiting THG to the front surface only, via large group-delay mismatch, while the material absorption suppresses XPM. The use of THG ensures the upconverted signal is near the peak absorption of silicon detectors and that the whole bandwidth of the test pulse can be effectively measured. Currently complete characterization is inhibited by the quality of the KG1 glass, which scatters the beam strongly, but surface polishing should reduce this effect. Finally, the third-harmonic D-scan measured the spectrum created from a thin piece of FS as a function of compression wedge insertion. Using a novel “annealing” algorithm and accounting for the effects of SPM and XPM inside the gain material allowed for the reconstruction of the pulses, even with the limited dispersion range allowed by the wedges.

We found the generation of few-cycle SWIR pulses of high energy to be a simple and robust process. Generation of around 9 fs duration pulses could be done largely independently of the parameters of the input pulse by tuning the gas pressure. The use of bulk material to compress the pulse greatly simplifies alignment compared to the 800 nm case, and reduces the risk of damage to expensive optics. Over four years of operation, no optics involved in the HCF suffered any burns or laser related damage. HCF pulse compression thus seems to be even more simple and robust at 1750 nm than at shorter wavelengths, despite more than two decades of development at 800 nm. The recent availability of low dispersion, high reflectivity mirrors covering the spectral range of the compressed pulse will widen the performance gap even more. CEP stabilization is also considerably simpler, as only a slow loop is required for the output of an OPA. The decrease in the cost of apparatus required to CEP lock an OPA compared to a CPA system is comparable to the cost of the OPA itself, and is much simpler and more robust. The primary challenge of the SWIR is coupling into the HCF, which is sensitive to the mode of the OPA, which was difficult to keep stable. In general these fluctuations could be traced back to the CPA laser system, which exhibited large drifts over time. In order to obtain sufficiently stable operation, we were forced to undertake significant development work on all stages of the CPA system. Current generation commercial CPA systems are capable of generating the flux required to drive a similar commercial OPA without the same stability problems, thus I expect this technology will become increasingly widespread.

Characterization of the SWIR pulses is more challenging than at 800 nm due to the limited availability of detectors which detect the wavelength of the second harmonic. This is counteracted by the fact that broadband phasematching is significantly simpler at long wavelengths, so phasematching is much less of a challenge than at 800 nm. In SPIDER, the necessity of using ancilla pulses of a secondary, shorter wavelength to reach the spectral range of silicon CCDs may prove to be a limit towards the broader application of the SEA-F-SPIDER technique in

the SWIR, though the precision of the technique for examining spatio-temporal coupling is currently unmatched in the SWIR for few-cycle pulses. The use of third harmonic generation as the non-linearity for techniques such as SPIDER and FROG presents additional challenges, in both the power requirements and the complication of Kerr non-linearities. While an absorptive medium overcame the Kerr non-linearity challenge in our FROG, finding appropriate materials limits the generality of the technique. Robust characterization of broadband, few-cycle pulses in the SWIR cannot really be considered a settled problem, and considerable effort should be exerted towards the development of simpler, more general solutions.

In chapter 4 I presented an application of our SWIR source to HHGS of substituted benzenes. High stability of the system was necessary in order to perform comparative scans between different molecules over several hours. In order to isolate an experimental signal which can be compared to single molecule calculations, careful control of the macroscopic conditions was necessary. By adjusting the gas pressure, focus position, and laser power, we isolated a range of parameters where the ratio of harmonics between different molecular species is independent of macroscopic conditions and can be compared to single molecule calculations. Further analysis of spectra obtained under these conditions for a variety of substituted benzenes is currently under way. As a first result we have shown that the influence of deuteration upon the harmonic spectrum of benzene is negligible, suggesting little additional influence of the nuclear motion upon the HHG spectrum between the two species. We speculate this may be due to the strong localization of electronic density around the carbon-carbon bonds. Preliminary analysis comparing benzene spectra obtained at different intensities suggests we will be able to extract nuclear dynamics from the HHG spectra, but further analysis and theoretical effort is necessary.

Our experiments attempt to address a seriously under-considered problem in high harmonic spectroscopy, the isolation of the single emitter response. To the best of my knowledge, our experiments represent the most robust examination of the effect of macroscopic parameters on an HHGS spectrum. The great variation in spectra that we can introduce using such external factors is a cause of concern for the analysis of HHGS, and should exhibit to all practitioners in the field that extreme care is necessary in performing such experiments. Further work on developing robust metrics for the change in harmonic spectrum with regard to focus-target position would remove the final unconstrained parameter in our system, and should be seriously considered in advancing the field of HHGS. Our extraction of nuclear autocorrelation times does show that HHGS retains its power in examining molecular dynamics when these additional precautions are taken; the impact upon the understanding of nuclear dynamics and their coupling to electronic motion is yet to be seen.

The main result in this thesis is the development of a short-wavelength (high photon energy) harmonic source, presented in chapter 5. By focusing our few-cycle SWIR source into a custom designed high pressure gas cell, harmonics spanning the WW spectral range were generated.

A novel differential pumping jacket was designed to maintain good vacuum outside of the generation region; pressures of over 16 bar could be supported in the gas cell while maintaining sub-mbar pressure elsewhere. I remodelled an XUV spectrometer to operate in the SXR, optimizing it for WW harmonic generation and enabling flux measurements. We optimized harmonic generation with respect to focusing geometry, gas pressure, and target species while holding the driving pulse duration fixed at 12 fs. Shorter pulses could not be effectively delivered due to dispersion in air and signal-to-noise considerations; future improvements would include vacuum propagation between the fibre output and the high harmonic generation setup, as well as the use of “pinhole-less” filters to remove visible background light.

By controlling gas pressure, gas species, and focusing geometry, we were able to generate CEP-dependent harmonic half-cycle cutoffs at any energy within the water window, meaning attosecond pulses can be generated at any absorption edge of interest. The highest photon energies were generated from He, easily extending beyond the titanium $L_{2,3}$ edge, and with appropriate focusing and pressure, beyond the oxygen K edge, to a maximum photon energy of 600 eV. This is the highest photon energy generated in a kilohertz harmonic source and the first CEP-dependent (isolated pulse supporting) harmonic radiation extending across the oxygen K edge. The highest photon energy does not correspond to the highest flux; optimizing generation in He for flux, we lower the cutoff to just below the oxygen K edge, and produce a total flux across the water window of ≈ 8 pJ, approximately ten times higher than previously reported from helium and three times higher than from neon [181]. In neon we are limited to photon energies below 500 eV, but significantly higher fluxes are possible. We produce a total flux in the water window of 77 pJ or 1.4×10^9 photons/s, 25 times higher than previously reported from either few-cycle or multi-cycle drivers [181, 188]. This flux is very favourably comparable to other ultrafast sources such as time-sliced synchrotrons.

Compared to harmonic generation at lower photon energies with shorter wavelength driving fields, long wavelength driven SXR HHG is a considerable challenge. Because of the low harmonic divergence and low photon flux, precise alignment procedures and long integration times are required to see any signal. The efficiency of available optics is also much lower in the SXR, further limiting options. Despite this, after careful optimization of the system and the development of procedures to ensure repeatability, generation of harmonics spanning the water window became a routine task by the end of my PhD. Harmonics could be generated within an hour or two of turning on the laser system, with harmonics varying little over the period of a few weeks. We have generally observed a continuous increase in harmonic flux and cutoff with increasing laser power; even higher power laser systems could simplify the generation of water window harmonics considerably. Other improvements which would simplify water window HHG considerably are the harmonic collection efficiency, which may be improved by several orders of magnitude at the carbon K edge. These improvements include the use of a re-imaging mirror to decrease losses from the spectrometer slit, and removal of carbon contamination through ozone

treatment of the optical elements.

The CEP dependence of the harmonics, and the implied generation of isolated attosecond pulses, does not significantly complicate the harmonic generation, a strength inherited from the robustness of the OPA plus HCF scheme. While ensuring good CEP stability occasionally required pausing the rest of the experiments in the laboratory, this is not intrinsic to the method but rather to the peculiarities of our setup; configured differently we obtain sub-200 mrad stability routinely, and no compromises with harmonic flux or cutoff are required to observe strong CEP dependence of the spectra.

There is still an open question with regards to the exact pulse duration of the harmonic source, though it is expected to be hundreds of attoseconds in duration. The pulse duration can be measured through attosecond streaking, but this was not possible to perform with our setup, which does not feature a second interaction region or an electron time-of-flight spectrometer. Streaking measurements with longer wavelength driving fields also present significant experimental challenges which have only begun to be overcome. Because of the very strong macroscopic effects involved in water window HHG, other *in situ* methods of characterizing attosecond pulses are not appropriate.

In chapter 6 I showed the application of our harmonic source to XANES spectroscopy, and a spatial characterization measurement demonstrating its potential for imaging applications and non-linear optics. We performed transmission XANES measurements of a thin film of P3HT using Ne harmonics, and measurements of a Bo:PET thin film and N₂ gas using He harmonics. Our measurements accurately recorded the fine structure at the sulfur $L_{2,3}$, carbon K , nitrogen K , and oxygen K edges, for each system with the appropriate atomic constituents. A measurement at the carbon K edge could be made in as little as two minutes, while measurements at the oxygen K edge took several hours.

HHG is strongly linked to attosecond science, but our results suggest that the broadest impact of HHG based science might actually lie in the femtosecond domain, by providing convenient, table top sources of soft X-rays. With improved collection efficiency it should be possible to obtain a full XANES spectrum at the carbon or nitrogen K edge in a matter of seconds, faster than can be performed at synchrotrons or XFELs, with sub- or few-femtosecond temporal resolution. While flux is a valuable metric for many applications, signal-to-noise and acquisition time set the real limits to performing any linear process such as absorption spectroscopy. Our results clearly show that even with the low flux of HHG, using SXR HHG as a probe for att-XANES measurements should be straightforward. This is not to say time-resolved XANES measurements do not represent a significant challenge, but rather that the challenges are not introduced by the HHG step. Indeed using SXR HHG as the probe automatically ensures sub-fs synchronization between the pump and probe, a major challenge for other femtosecond X-ray

sources. Of course the application to attosecond measurements is currently only possible with HHG based sources, though this may change with the next generation of XFELs.

By performing a SWORD measurement of the harmonic radiation, we were able to reconstruct the spatial wavefront of the X-rays. Our measurement shows a nearly perfect parabolic wavefront for the harmonic radiation. We show the harmonics appear to radiate from a small $\approx 1.2 \mu\text{m}$, virtual source around 10 mm before the gas target. The small spatial extent of the virtual source, together with the lack of higher order phase features in the wavefront, suggest our source would be ideal for imaging applications as well as spectroscopy, and for a sufficiently thin liquid sample could be used as the illumination in an X-ray microscope. Furthermore the virtual spot is sufficiently small that if re-imaged into an interaction region, assuming a modest pulse duration of 500 as and a pulse energy of only 50 pJ, intensities of 10^{13} W/cm^2 could be delivered; this is approaching the regime for X-ray non-linearities, and thus performing X-ray non-linear optics with harmonic radiation can begin to be considered.

As attosecond science uses increasingly high power and long wavelength driving fields, the spatial properties of the emitted radiation needs to be considered more carefully. Our result is the first measurement of the spatial wavefront of HHG outside of either 800 nm driving fields or gas jet geometry, and shows that HHG is a truly scalable approach to generating SXR photons. Unfortunately the precision of the SWORD technique is not sufficient to resolve fine structures on top of the large parabolic wavefront of a diverging beam. Alternative techniques like shearing interferometry, which effectively discard the quadratic term, could reveal the fine structures which limit the spatio-temporal quality of the harmonics. Imaging applications of HHG are expected to be limited by attainable X-ray optics, with the exception of coherent-diffractive (lensless) imaging, where photon flux will be the limiting factor.

The modest flux of HHG has often limited its applications, and though our XANES measurements show this will not limit the utility of SXR HHG as a probe in time-resolved studies, true attosecond-attosecond pulse measurements require much higher intensities capable of driving significant non-linear optical signals. A great deal of effort has gone into improving the conversion efficiency of HHG, or into developing ever more large and complex high power lasers in a “brute force” approach to improving the flux. However, as obtaining non-linear effects is primarily a function of the intensity, using shorter attosecond pulses and tighter focusing is another route towards attosecond-attosecond measurements. Compared to XUV HHG, our harmonics originate from a spot size an order of magnitude smaller, giving a two order of magnitude increase to the intensity, and theoretically a less chirped pulse as well. With next generation SWIR sources offering an order of magnitude increase or more in peak power, and with further gains in conversion efficiency possible using shorter driving pulses, it is reasonable to assume that up to nanojoule energy level harmonics in the water window will be available within the next decade. Combined with a simple reducing telescope or magnifying mirror to

reduce the focus size to a few hundred nanometers, still far from diffraction limited, could deliver pulses with intensities over 10^{17} W/cm², comparable to first generation XFELs. While such scaling has not been demonstrated yet, and indeed non-linear effects are difficult to drive even with longer wavelength, higher pulse energy harmonics, this shows a tentative roadmap to X-ray non-linear optics at the laboratory.

Future work will primarily be in the application of our SXR high harmonic source to time-resolved XANES measurements of optical induced dynamics. As we have already demonstrated the ability to perform XANES measurements with short acquisition times, the integration of our source into a pump-probe scheme is relatively simple. P3HT, for which we have already acquired static XANES spectra, forms an ideal test case. As a constituent of organic solar cells it is of broad interest, and exhibits strong absorption in the visible. A suitable pump-pulse can be generated through THG with the few-cycle idler, and our laboratory already holds an attosecond beamline capable of combining THG with HHG in two arms of a Mach-Zehnder interferometer. Tracking charge migration through the P3HT chain via XANES spectroscopy following resonant single-photon absorption will demonstrate the utility of our source and widen the scope of attosecond science to new condensed phase systems.

The work presented in this thesis presents new few-cycle laser sources at long wavelengths and short wavelength harmonic sources for attosecond science. These sources have already opened new avenues in HHGS and enabled XANES measurements in the water window using harmonic sources, but the largest impact will be felt through future attosecond time-resolved XANES measurements. The simplicity, robustness, and cost of OPA and HCF based few-cycle sources in the SWIR are all strong motivators for a mass movement in attosecond science towards long wavelength driving fields, though further developments in pulse characterization are necessary. The generation of water window high harmonics also involves only marginal investments, namely higher line density gratings and differential pumping, when compared to a standard high harmonic generation apparatus. Given the significant advantages of SXR radiation over the XUV, a greater emphasis on attosecond science at X-ray energies can also be expected in the future, now that it has been shown to be attainable with largely commercial technology. The future of attosecond science may even see next generation laser sources and advanced X-ray optics driving non-linear optics in the soft X-ray regime, along with applications in X-ray microscopy.

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Item 5: Figures 5.4, 5.5a and 5.5b

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